

**Thermodynamical Behaviour of 1-1 Strong
Electrolytes In Water, Dimethyl Sulfoxide And Water-
Dimethyl Sulfoxide Mixtures.**

By

**Talat Zamir
M.Sc (Chemistry.), M.Phil
University of Balochistan
Pakistan**

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Department of Chemistry
University of Balochistan
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Dedicated to All Mighty

ALLAH

“Most Gracious, Most Merciful”

**‘He who taught (the use of) the Pen’
‘Taught man that which he knew not’**

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ABSTRACT

The densities, viscosities and relative viscosities of solutions of several univalent electrolytes Lithium bromide (LiBr), Sodium bromide (NaBr), Potassium bromide (KBr), Rubidium bromide (RbBr) Cesium bromide (CsBr) and reference salts tetra butyl ammonium tetra phenyl borate (BU_4NBPh_4), tetra butyl ammonium bromide (BU_4NBr) and potassium chloride (KCl) were measured over the entire range of concentration at 25 °C to 45°C in pure DMSO, pure water and DMSO- H_2O binary mixtures.

Data was analysed by Jones-Dole equation to determine ion –ion interactions (the *A*- coefficients), ion- solvent interaction, (the *B*- coefficients) for alkali metal bromides in pure DMSO, pure water and DMSO- H_2O binary mixtures. The values of *A*- coefficients were small and almost positive in all the cases. The values of *B*- coefficients were large and almost positive of all the salts in DMSO and DMSO- H_2O mixtures, which showed the structure making abilities of the salts in DMSO- H_2O mixtures at all the five temperatures.

The values of viscosity *B*- coefficients were found negative for KBr, RbBr and CsBr in pure water at all the five temperatures, which showed the structure breaking abilities of the salts while the values of viscosity *B*- coefficients of LiBr and NaBr in water at all the five temperatures were found positive and behave as structure makers.

The viscosity B - coefficient data was further splitted into ionic B - coefficient for non-aqueous solvents by using Gill and Sharma's convention and Gurney's convention into ionic B - coefficients for aqueous solvent systems.

From ionic B - coefficient data it was observed that in pure DMSO all the alkali metals have strong structure making abilities. It was also observed that these structure making abilities were decreased with the increase in ionic radii or temperature. While in aqueous solvents (DMSO- H_2O) mixtures the structure forming capabilities were weakened and structure breaking abilities were appeared at all temperatures.

In pure water except Li^+ and Na^+ all the ions showed the structure breaking properties, which increased with the increase in temperature. The data obtained during this study was found in good agreement with those values which were already available in literature.

The Transition state parameters such as free energies and energies of activation for viscous flow have been calculated for the whole solvent system. From the present study it is concluded that the energy of activation of viscous flow is influenced by the concentration and the size of the solute particles. So the energy of activation of viscous flow for CsBr is greater than for RbBr, KBr, NaBr and LiBr in DMSO and DMSO- H_2O mixtures.

It is also observed that the energy of activation of viscous flow are greater for alkali metal bromides in water than in DMSO due to the presence of a network of hydrogen bonds in water. For the free energy of activation for viscous flow, it is observed that the free energy of activation for viscous flow increases with temperature.

**SYMBOLS FOR PHYSICAL QUANTITIES
USED IN PRESENT WORK**

SYMBOLS	NAME
Bu ₄ NBPh ₄	Tetra-butyl ammonium tetra-phenyl borate
Bu ₄ N ⁺	Tetra-butyl ammonium ion
BPh ₄ ⁻	Tetra--phenyl borate
Et ₄ N ⁺	Tetra-ethyl ammonium ion
I ⁻	Iodide
DMSO	Dimethyl sulfoxide
TMS	Sulfolane
HMPT	Hexa methyl phosphoric tri-amide
Ec	Ethylene carbonate
R ₄ NBr	Tetra-alkyl ammonium bromide
	Di-isopropanol amine
	Sodium carboxylate
	Sodium acetate
	Sodium propionate
	Sodium n-butyrate
	Sodium n-pentanoate
	Tri chloroacetate
Bu ₄ NI	Tetrabutyl ammonium iodide
Bu ₄ NBr	Tetrabutyl ammonium bromide
Bu ₄ NCl	Tetrabutyl ammonium chloride
R ₄ N ⁺	Tetra alkyl ammonium ion
	1-butanol
	1-Propanol
	2-Propanol
	Glycerol
R ₄ NI	Tetra alkyl ammonium iodide
Pr ₄ NI	

Me ₄ NI	
DMF	N-N-dimethyl formamide
Ph ₄ P ⁺	Tetra phenyl phosphonium ion
	Nitrobenzene
	Nitromethane
TABBph ₄	
iAm ₃ Bu ₄ NBPh ₄	Triisobutyl ammonium iodide
NaBPh ₄	Sodium tetraphenyl borate
HMPT	Hexamethyl phosphotriamide
HMPA	Hexamethyl phosphoamide
Bu ₄ NCIO ₄	Tetra butyl ammonium perchlorate
CuClO ₄	Copper perchlorate
Py	Pyridine
Bu ₄ NNO ₃	Tetra butyl ammonium nitrate
Ac	Acetone
3HPN	3-hydroxypropanitrile
PN	Propionitrile
AN	Acetonitrile
Pr ₄ NBr	Tetrapropylammoniumbromide dioxane
ME	2 Methoxyethanol

Related Publications

1. Talat Zamir, T.I. Quickenden. 2003. Viscosity of Alkali-Metal Iodides in Propionitrile and Acetonitrile Mixtures at 25 °C. *Journal of Solution Chemistry* 32: (5) 463-472.
2. Talat Zamir, T.I. Quickenden. 2001. Measurements of the *B* Coefficient of Viscosity for Alkali-Metal Bromides in 3- Hydroxypropionitrile- Acetonitrile Mixtures at 298.15K: *Journal of Solution Chemistry*: 30 (10) 937-947.
3. Dip Singh Gill., Jasbir Singh., Rohitash Singh., Talat Zamir and Terry I. Quickenden 1999. Solvation of Copper (1) perchlorate in propionitrile- acetonitrile and 3-hydroxypropionitrile-acetonitrile mixtures studied by viscosity, conductance and ^{63}Cu NMR measurements. *Indian Journal of Chemistry*. 38A: 913-920.

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CHAPTER 1

1.1. General Introduction

From 1920 to 1950, the majority of research workers in the electrochemical field were occupied with determining, activity coefficients of salts in dilute aqueous solutions, the electrical conductance of molten salts or electrostatic effects on the dissociation constants of acids or bases in aqueous solution. Since the late 1960's, less attention in electrochemistry has been given to the fields concerned with ions in the solution but much work is still required to present a clear picture of ionic solutions.

An ionic solution is always formed by kinetic entities called the mobile ions in the proposed solvents. In general the choice of the solvent or the mixture of solvents usually is directed by the circumstances and the nature of the mobile ions of the electrolyte. It is obvious that in the solid state, inter-ionic forces are so strong that the ions can only vibrate and rotate. The question arises as to how these forces are overcome when the solid ionic lattice dissolves in a solvent to produce a medium of mobile ions? There are, however many ways of overcoming the inter-ionic forces in ionic crystal and producing mobile ions. One of the most important ways in electrochemistry is with the aid of the solvent. In this method ion-solvent interactions overcome the ion-ion interactions of the ionic crystals. To understand this one must know about the chemistry of the solvent.

1.2. Solvent system

The important role played by the solvents in chemistry has long been recognized. After the first quantitative description of solvent effects on chemical reactions, much work has been allocated to solvent effects on rates and equilibrium processes [1]. In the solvation process, changes in energy of reacting states are of critical importance both in proton-transfer and electron transfer reaction. In order to analyze ion-solvent interactions, great interest has been paid to the behavior of solutions of electrolytes in pure solvents and in binary solvent mixtures [2, 3]. The pure solvents can be classified as Protic and Aprotic solvents. Protic solvents contain protons, which they can dissociate e.g. water, alcohols, inorganic acids etc, while aprotic solvents may contain protons, which they are unable to dissociate, but which can accept protons. Acetonitrile, propylene carbonate and dimethylsulfoxide are some examples of aprotic solvents.

1.3. Structure of Water

Liquid water has distinct structural features, such as a high dielectric constant, a maximum density at 4 °C, thermal conductivity, viscosity, critical temperature and analogy to ice. Structural research has shown that liquid water can be described as a somewhat broken-down and slightly expanded form of the ice lattice but this statement must not be taken to mean that there is no association of water molecules in water (Table 1).

Table 1.1 The Structure of ice and liquid water [4]

	Ice	Liquid Water
Mean O-O distance	2.76Å	2.92Å
Number of oxygen nearest neighbors	4	4.4-4.6

X-rays and other techniques indicate that in water, there is a considerable degree of short- range order, characteristic of the tetrahedral bonding in ice. Thus, liquid water partly retains the tetrahedral bonding and resulting network structure characteristic of the crystalline structure of ice. The amount of ice likeness can be altered by altering in temperature, pressure, and also by the presence of ionic solutions. This means that the structural changes can also be studied by examining thermodynamic and kinetic properties of the ionic solutions.

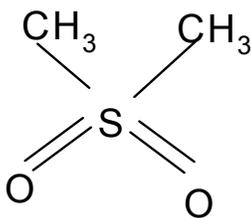
1.4. Structure of Dimethyl sulfoxide (DMSO)

More than 100 years ago, Alexander Saytezeff first synthesized Dimethyl sulfoxide (DMSO) by the oxidation of dimethyl sulfide with nitric acid [5]. In the late 1950's, DMSO was commercially available due to its versatile and valuable properties as a solvent. In 1960's, many scientists became interested in the inorganic and organic applications of DMSO. It is an odorless, hygroscopic liquid with a bitter taste. In 1964 Jacob *et al.*, [6] reported a number of medical uses of DMSO in addition to its proven use in low temperature preservations of living tissues and organisms; these were local analgesic agent, anti- inflammatory adjunct, bacteriostatic agent, diuretic and tranquilizer.

Physical properties suggest that DMSO is highly associated in both the liquid and solid states. It is considered as a good solvent for the alkali metal halides, nitrates, thiocynates and perchlorates and has strong solvating properties for transition metal ions such as Fe^{3+} and Ni^{2+} etc.

Transport parameters of electrolyte solutions such as ionic conductance and viscosity can provide information regarding the nature of the kinetic entities

from which the ion- solvent interaction can be inferred. Label and Goring [7] and Cowries and Toporowski [8] have determined viscosities over the complete range of water- DMSO ratios at 25° and found that in 0.65 mole fraction of water i.e. approximately in 2:1 water: the plots of viscosity versus composition had a maximum.



Structure of Dimethylsulfoxide

Table: 1. 2. Physical Properties of Water and Dimethylsulfoxide. [9].

	Abbreviation	M. Weight	Density ^a	Dielectric ^b Constant	Viscosity ^c	Dipole ^d Moment
Water	H2O	18.02	0.9971	78.30	0.8903	1.85
Dimethylsulfoxide	DMSO	78.13	1.0958	46.70	1.96	3.96

Footnotes: values refer to 25°C unless otherwise stated

a g cm⁻³ b relative permittivity (ϵ_r) c centi-poise (1cP \equiv 10⁻³ Nm⁻² s) d Debye units
(1D=10⁻¹⁸ e.s.u. cm \equiv 3.33564 x 10⁻³ Cm)

1.5. Structure of Water near an ion.

When ions enter to a solvent like water, what happens to the structure of water? The central consideration is that ions orient dipoles. The spherically symmetrical electrical field of the ions may tear water dipoles out of the water lattice and make them point with the appropriate charged end towards the central

ion. Hence, viewing the ion as a point charge and the solvent molecules as electric dipoles, one comes out with a picture of ion-dipole forces as the principal basis of ion-solvent interactions.

Due to the ion-dipole forces, a certain number of water molecules in the immediate vicinity of an ion may be trapped and oriented in the ionic field. Such water molecules may also associate with other water molecules. In other words the ion and its water sheath form a single kinetic entity in which the sheath of immobilized water molecules moves with the ions as shown in Figure 2.1.

At a sufficient distance away from the ion, the influence of the ion is negligible because the ionic fields have virtually reached zero. The normal structure of the water is then undisturbed and is that of the bulk water. There is another region between the solvent sheath and the bulk water that is neither completely oriented nor disoriented. These water molecules are not close to the ion to become oriented perfectly around it, and neither are they sufficiently far away from the ion to be part of the structure of the bulk water. Thus this intermediate region the water structure is partly broken down.

A picture of liquid water interacting with ions.

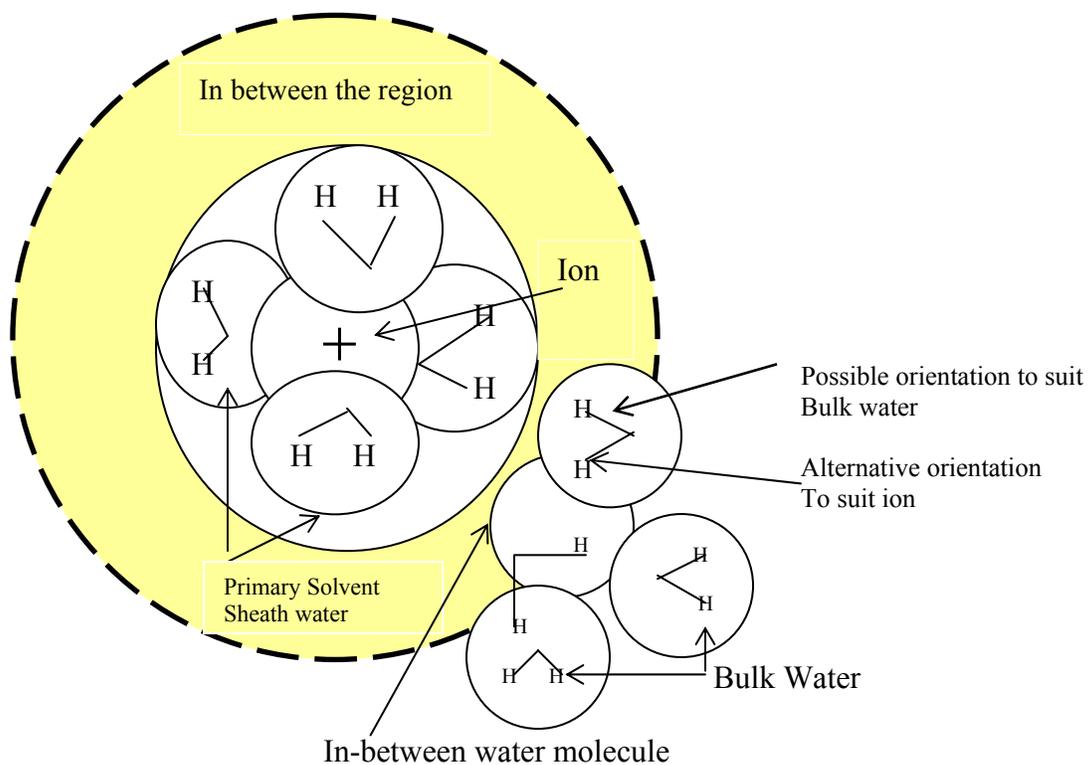


Fig. 1.1. Schematic diagram to indicate that in the (hatched) region between the primary solvated ion and bulk water, the in-between water molecules must compromise between an orientation which suits the ion (oxygen-facing ion) and an orientation which suits the bulk water (hydrogen-facing ion).

Source: John O.M. Bockris and Amulya K. N. Reddy. Modern Electrochemistry, Plenum Press. N.Y. 1977

Fig 1.1 and 1.2, shows the above three regions. In the primary or structure enhanced region next to the ion, the water molecules move as and where the ion moves. In the secondary or structure broken region in which the normal bulk structure of water is broken down to varying degrees, the water molecules do not generally move with the ions. Finally at sufficient distance from the ion, the water structure is unaffected by the ion and display the tetrahedrally bonded networks characteristic of bulk water.

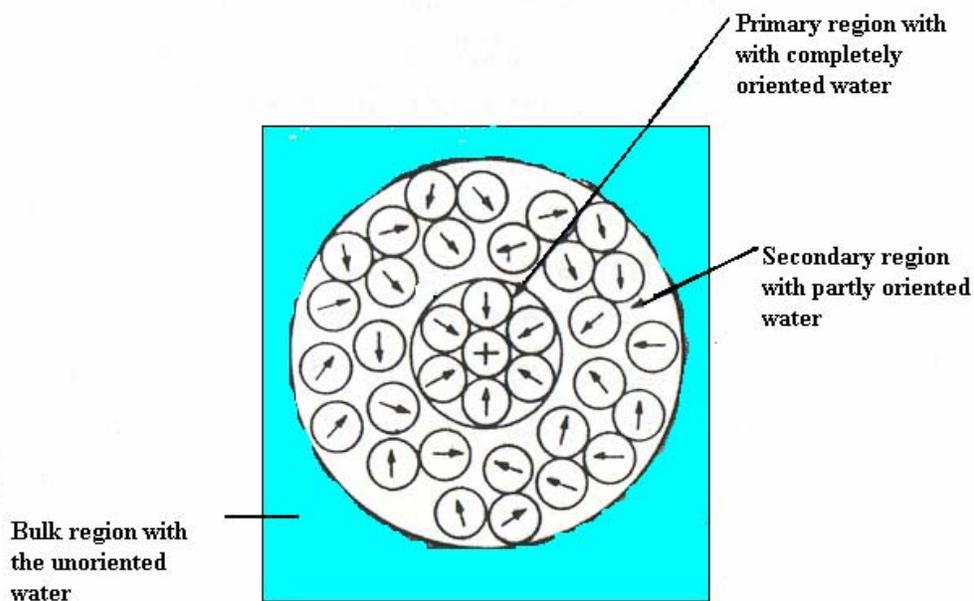


Fig 1.2. The neighborhood of an ion may be considered to consist of 3 regions with differing solvent structures. 1). the primary or structure forming region 2). The secondary or structure breaking region and 3). The bulk region.

These water molecules do not move with the ion, but may be pushed aside by hydrated ions as they diffuse through the solution. The interaction of ions with primary and secondary water molecules generally referred to as solvation (or as hydration when water is the solvent). The term solvation and the term ion – solvent interactions are used synonymously although the former is the structural result of the later. An appropriate way to appraise the solvation of an electrolyte in any solvent is with the help of viscosity data or conductance data.

1.6. Viscosity (η),

A liquid is deformed, when it is subjected to a tensile or shear stress, τ . Under shear, the rate of deformation (or shear rate) γ is proportional to the shearing stress. Newton originally proposed that the ratio of the stress to the shear rate is a constant and is defined as the viscosity. Viscosity is also defined as the resistance that one part of liquid offers to the rate of the flow of another part of fluid or in other words the viscosity is the resistance to flow. The older units of viscosity are dynes sec. cm^{-2} which is also called the poise.

$$1 \text{ Centipoise} = 10^{-3} \text{ N m}^{-2} \text{ s}$$

Accurate measurements of viscosity are very useful in gaining an insight in to the structure of electrolyte solutions [5].

1.7. The dynamic viscosity (η)

The dynamic viscosity of a liquid is equal to the gradient of the shear stress.

$$\eta = d\tau / d\gamma$$

The ratio $\tau / \dot{\gamma}$ are the absolute viscosity for a Newtonian liquid.

1.8. The kinematic viscosity (ν)

The kinematic viscosity (ν), of a liquid is the viscosity coefficient divided by the density of the liquid, ρ ;

$$\nu = \eta / \rho$$

1.9. Relative Viscosity

Relative viscosity is the ratio of solution viscosity and solvent viscosity i.e.

$$\eta_{\text{rel}} = \eta / \eta_0$$

1.10. Specific Viscosity

Specific viscosity is the ratio of the difference between the solution viscosity (η) and the solvent viscosity (η_0) to the solvent viscosity.

$$\eta_{\text{sp}} = \frac{\eta - \eta_0}{\eta_0}$$

$$\eta_{\text{sp}} = \frac{\eta}{\eta_0} - 1$$

$$\eta_{\text{sp}} = \eta_{\text{rel}} - 1$$

1.11. The state of the solutes in electrolyte solutions

It is found that the addition of some salts to solvents causes a change in viscosity. The principal effect of dissolved salts on viscosity is proportional to their concentrations. So it is clear that the electrical forces between ions in adjacent layers of an electrolyte solution will increase the viscosity. The increase in the viscosity takes the view that the ions tend to build and maintain a space lattice structure in the solution, and any influence tending to disturb this space lattice arrangement (whether by thermal motion of the solvent molecules, the electrostatic force from charged electrodes in the solution, or by any relative motion of parts of the liquid) will be opposed by the inter ionic forces. The forces, which tend to maintain a space lattice structure for the ions, therefore tend to stiffen the solution or in other words increase its viscosity [10]. A simple model for the structural modification produced by a small ion is shown in Fig 1.3.

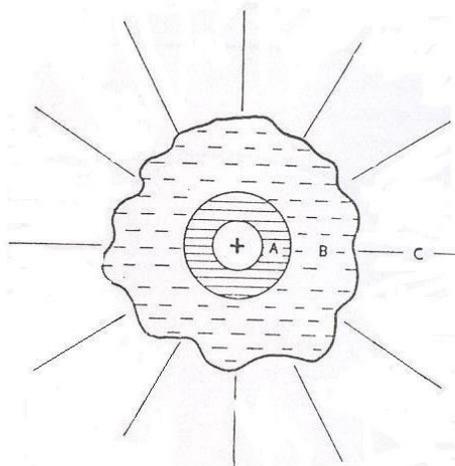


Fig. 1. 3. A simple model for the structure modification produced by a small ion. A., the region of immobilization of water molecules, B., the region of structure breaking, C., the structurally “normal” water.

Frank and Evans [11] imagined that region A is composed of water and that an ion which was small, or multiply charged, or both (for example Li^+ , F^- , Mg^{2+}) might induce additional structure or entropy loss, which tends towards the

net structure making influence. Such influence is also observed in region B. They also observed that the orientation of like poles in region A should always produce at least some disorder in region B. So large singly charged ions (I^- , Cs^+) tend towards a net structure breaking- influence. The influence was discussed by another scientist Gurney [12] that at any rate, it is possible to make entropy data the basis for assigning an orderly gradation of net structure-altering influence to a considerable number of ions. According to this, cations smaller in size and more highly charged are net structure formers. In alkali metals Li^+ , Na^+ are net structure formers. K^+ is slightly structure breaker, and this tendency increases through Rb^+ to Cs^+ . F^- is a structure former, and other halide anions are structure breakers. NO_3^- and ClO_4^- are strongly structure breaking and OH^- seems to be a structure former [11].

1.12. Ion-solvent interaction

Ion-solvent interaction can be defined by starting with solid ionic crystal and reducing the forces, which hold the ions together. A stage is reached when the inter-ionic forces are so weakened that the ions, which could vibrate in the solid, acquire a new degree of freedom, which produces the mobile ion due to freedom of transnational motion. All this is possible with the addition of a solvent which influences the interionic force of the crystal and other types of interaction (ion-solvent interactions are produced).

To understand ion-solvent interactions one must understand the structure of the solvent and the microscopic view of the ion inside the solvent. The spherically symmetrical electric field of the ion may tear water dipoles (considering water as solvent) out of the water lattice and make them point with

the appropriate charged end towards the central ion. Hence viewing the ion as a point charge and the solvent molecules as electric dipoles, the ion-dipole forces act as the principal basis of ion-solvent interactions. So the ion-solvent interactions can be measured with the help of the Jones-Dole expression for viscosities

1.13. The Jones-Dole expression for viscosities of electrolytic solutions

An important way to measure the ion-solvent interaction of different ions in different solvent systems is with the help of Jones-Dole equation, which expresses the relative viscosity η/η_o , as a function of the molar concentration

$$\eta/\eta_o = 1 + AC^{1/2} + BC \text{ -----}1$$

η is the viscosity of the solution and η_o is the viscosities of the pure solvent. C is the molar concentration of the salt. In this equation A and B are constants specific to a particular solvent/salt combination. The A parameter accounts for ion-ion interaction and the B coefficient is a function of ion-solvent interaction. Jones and Dole in their paper on the viscosity of aqueous solutions of strong electrolytes [13] mentioned that Poiseulle [14] was the first scientist who noticed in 1847 that some salts increase the viscosity of water whereas other decrease it. In their attempt to interpret their own and others viscosity data for dilute aqueous solutions of electrolytes, Jones and Dole rejected several expressions suggested earlier e.g. that of Arrhenius [15] $\eta/\eta_o = A^C$, where A was a solute and temperature dependent constant. They noted that electrostatic forces, which tend to maintain a quasilattice of the ions in the solution (an ionic atmosphere of oppositely charged ions) would stiffen the solution, i.e., increase its viscosity [16].

Since these forces are proportional to the square root of the concentration in very dilute solution, it led to Jones and Dole putting the expression for the relative fluidity $\varphi/\varphi_0 = 1/(\eta/\eta_0)$ in the form:

$$\varphi/\varphi_0 = 1 + A'C^{1/2} + B'C$$

Where C is the molar concentration of the electrolyte in mole dm^{-3} . They expected the coefficient, A' , to be negative and the coefficient, B' , to be either positive or negative. Later authors inverted the original Jones-Dole expression and recast it in terms of the relative viscosity (rather than fluidity)

$$\eta/\eta_0 = 1 + AC^{1/2} + BC$$

As mentioned above, the term A depends on the interionic forces and can be evaluated theoretically. The term B depends on ion-solvent interactions and is related to the volumes of the ions

1.14. The viscosity B coefficient

The B coefficient is an important empirical constant determined by ion-solvent or solute-solvent interaction and solvent-solvent interaction, and which measures the solvation effects, hydrodynamic effects and ionic influence on solvent structure. The values of the B coefficient are obtained from

$$\eta/\eta_0 = 1 + AC^{1/2} + BC$$

hence:

$$B = [(\eta/\eta_0) - 1 - AC^{1/2}] / C$$

A structure making solute is expected to have a positive value of B in the given solvent, whereas a structure breaker may have a less positive or negative B value. Most of the early studies of the B coefficients were done on aqueous solutions and showed that some electrolytes are able to decrease the relative viscosity to that of pure water. Cox and Wolfenden [17] were the first scientists who reported an explanation of the “apparent negative viscosity” or negative B values. According to their statement the negative B values are due to the ions, which break the water (or other solvent) structure and Sutherland [16] suggested that the depolymerization of triple water molecules $(H_2O)_3$, to form single molecules by the dissolved salt caused the diminution in viscosity. On the other hand, an increase in viscosity is attributed to the addition of the smaller ions of the salt.

A more useful analysis of this data can be carried out by splitting the B coefficients into ionic contributions B_+ and B_- . Gill and Sharma [18] have proposed an indirect method to carry out this separation in non-aqueous solvent mixtures using the following equations:

$$B (BU_4N^+) / B (Ph_4B^-) = [5.00/5.35]^3 \text{ -----}2$$

and

$$B (BU_4N^+) + B (Ph_4B^-) = B (BU_4NBPh_4) \text{ -----}3$$

Where BU_4N^+ is tetrabutyl ammonium ion and Ph_4B^- is tetraphenyl borate ion. Thus by using equations 2 and 3, the B coefficients have been divided into ionic B_+ and B_- .

1.15. Activation and Gibbs Free Energy of viscous flow

To gain more insight in to the mechanism of polar solvation, we will also concentrate on the relationship of temperature with viscosity. Viscosity has inverse relation with the temperature while activation energy is independent of temperature. The relationship between temperature and viscosity is given by the Arrhenius equation.

$$\log \eta = \log A + E_{\eta} / (2.303 RT) + C$$

In this equation η is the viscosity of the solution, T is the Kelvin temperature, R is the gas constant and E_{η} is activation energy of diffusion in that solution and A and C are the constants for that solutions. The activation energy can be obtained from the slope of a plot of log of η versus reciprocal temperature.

Similarly the free energy ΔG for viscous flow can be determined by the equation:

$$\Delta G = RT \ln \eta V / hN$$

Where h is the planks constant, N is the Avogadro's number, and V is the volume of 1 mole of the solution [19].

CHAPTER 2

2.1. Literature Survey

Electrostatics forces of both attraction and repulsion are the dominant interaction forces in electrolyte solutions. Ions are charged particles, and charges interact with other charges. So there will be ion-ion, as well as ion-solvent, interactions in the solution. In a dilute solution ion-ion or solute-solute interactions may be neglected and we may then consider a solute to be surrounded only by solvent.

A very crude and approximate model for ion-solvent interactions was suggested by Born in 1920 [20]. In the Born model, an ion is viewed as a rigid sphere bearing a charge and the solvent is taken to be a structure less continuum. The Born model assumes that the charge on the ion is responsible for ion-solvent interactions. So the interactions between the solvent and the ion are considered to be electrostatic in origin. A detailed examination reveals that the Born values for the heats of ion-solvent interactions are numerically too high, in some cases nearly 50% high. The Born model over simplifies the problem, but one must see the model in its historical perspective. It was proposed at a time when the existence of charged particles in the solution was questioned. Indeed, the Born approach to ion-solvent interactions gave answers of the same order of magnitude as did experiments which helped to confirm the hypothesis that ions exist in solution. In historical perspective, the simple Born model may be recognized as an important step towards the understanding of ion-solvent interactions. To go further one has to consider about the nature and the structure of the solvent close

to an ion. Thus a new strategy for understanding ion-solvent interactions must be mapped. For this one must understand the structure of the bulk solvent, far away from the ion as well as the structure of the solvent near the ion.

Bernal and Fowler [21] explained that the structural changes in solvent near the ion and away from the ion were regions of different solvation, which is the basis of ion-solvent interactions. The aim of their work on the “ion- dipole model” was to take a structural microscopic view of the ion inside the solvent. The spherically symmetrical electric field of the ion may take water dipoles out of the water lattice and make them orient around the ion by columbic forces, that arise from the polar nature of the water molecules which form the primary solvated ion. The water structure just outside the primary hydration sheath is broken to some extent, but further away, the normal network structure of water obtains. This picture of the structure of the solvent around the ion was used as the basis of the ion-dipole theory of solvation, which is the principal basis of ion-solvent interactions.

A similar conclusion was put forward independently by Frank and Evans [11] from a re-analysis of the entropy of hydration. Frank and Evans imagined that an ion, which is small or multiply- charged or both (such as Li^+ , F^- , Mg^{+2}) might bring additional structure (entropy loss) to solvent molecules close to these ions. The net structure making influence of these ions was also observed in the region far from the ion. On the other hand they also observed that large and singly - charged ions such as I^- , Cs^+ have a large net structure breaking effect.

Gurney [12] went further and observed that at any rate it is possible to make entropy data, the basis for assigning an orderly gradation of net structure-altering influence to a considerable number of ions. According to Gurneys view

cations smaller or more highly charged than K^+ are net structure formers. K^+ is slightly structure breaking and this tendency increases through Rb^+ and Cs^+ . F^- is a structure former and other halide anions are structure breakers and increase this tendency is due to the increase in their size. NO_3^- and ClO_4^- are strongly structure breaking and OH^- is a structure former ion.

The study of transport properties of electrolytic solutions gives useful information regarding ion-solvent interactions. In most of the cases in the literature, the transport properties of electrolyte solutions are studied using the conductance method. The second method for the study of transport properties of electrolytic solutions is to measure the viscosities of the solutions [18].

The viscosity of an electrolyte solution and in particular the B -coefficients of the Jones-Dole equation indicate the degree of ion-solvent interactions in the solution [13]. The B -coefficients and their ion additive properties are known to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles.

2.2. Viscosity and the B -coefficients of ions in solution.

The change in the viscosity of electrolytic solutions depends on the inter-ionic forces and particularly on ion-solvent interactions. The ion-solvent interaction or B coefficients of the Jones-Dole [13] expression for the relative viscosities of electrolytic solutions provides very useful primary data about the solvation of the ions and their effects on the structure of the solvent in the vicinity of the solute particles.

Despite the above general conclusions about the B -coefficients of the ions in solution, no fundamental theory is available to express B -coefficients in terms of ionic parameters and the solvent properties. Such a theory would presumably need to use something like Debye-Huuckel theory in conjunction with expressions for ion-dipole interactions, ion-ion interactions and dipole-dipole interactions and also suitable mass transport equation.

In the absence of such fundamental theory, the present study confines itself to adding to the experimental data which express B -coefficients as function of viscosity in those solvent mixtures which have not hitherto been investigated and which present particular interest.

A large collection of the data on ionic B -coefficients is available for aqueous and non-aqueous solvents at different temperatures. The B -coefficient has been determined only in polar solvents such as acetonitrile, acetone, pyridine, nitrobenzene and many others [14]. Data on the change of viscosity of water with temperature and pressure is available but inadequate information has been published concerning non-aqueous solvents [22].

The changes in viscosity according to Jones-Dole expression ($\psi/\eta_r = \eta/\eta_o = 1 + AC^{1/2} + BC$) are resulted from the interpretation of data for dilute aqueous solutions of electrolytes. Jones-Dole observed that the electrostatic forces, which tend to maintain a quasilattice of the ions in the solutions would stiffen the solution i.e. an increase its viscosity. Since these forces varies directly to the square root of the concentration in very dilute solutions. This relation was expressed by Jones-Dole as relative fluidity, $\psi/\psi_o = 1/(\eta/\eta_o)$ in the form $\psi/\psi_o = 1 + A'C^{1/2} + B'C$ where C is the molar concentration of the electrolyte in mol dm^{-3} .

Jones-Dole found [13] plots of $(\eta/\eta_o-1)/C^{1/2}$ to be straight line with a negative intercept (A). Afterwards authors inverted the original Jones-Dole expression and recast it in terms of the relative viscosity rather than fluidity.

$$\eta/\eta_o = 1 + AC^{1/2} + BC \text{ ----- } 1$$

This equation is the version in use nowadays.

In equation 1, the term A depends on inter-ionic forces and can be evaluated due to sufficiently low concentration $< 0.5 \text{ mol dm}^{-3}$ from the intercept of the straight-line dependence of the left hand side of the equation below.

$$[(\eta/\eta_o-1)]/C^{1/2} = A + B C^{1/2} \text{ ----- } 2$$

It can also be calculated theoretically, if the equivalent conductivities of the constituent ions are known [23]. The value of the slope plotted between concentration and relative viscosities represents the value of B -coefficient of Jones – Dole expression.

B -coefficient values for a number of salts of low charge type (1:1 and 1:2) aqueous electrolytes consisting of small ions are generally smaller than $0.2 \text{ dm}^3 \text{ mol}^{-1}$ e.g. $B(\text{KCl}, \text{aq}) = 0.014 \text{ dm}^3 \text{ mol}^{-1}$ at $25 \text{ }^\circ\text{C}$. For some aqueous salts such as CsNO_3 they are negative e.g. $B(\text{Cs NO}_3, \text{aq}) = -0.090 \text{ dm}^3 \text{ mol}^{-1}$. B -coefficients are commonly larger and positive for salts containing multivalent ions. For large hydrophobic ions in aqueous solutions and for some salts in non-aqueous solutions B coefficients are larger and almost positive. For example, $B(\text{LuCl}_3, \text{aq})$ and $B[(\text{C}_4\text{H}_9)_4 \text{NaCl}, \text{aq}] = 0.66$ and $1.27 \text{ dm}^3 \text{ mol}^{-1}$ respectively. B -coefficients can be measured by careful maintenance of a constant temperature

with an accuracy of 0.15% for 0.95 mol dm⁻³ aqueous KCl at 65 °C [24] as cited in the exemplary work of Out and Los.

The *B*-coefficient [17] describes exclusively the ion solvent interaction. Its validity for all solvents at all temperatures can not be predicted due to the previously discussed lack of fundamental equations for the *B*-coefficients. In practice viscosities (and hence *B*-coefficients) of electrolytes are often measured at concentrations where ion-ion interactions (*A*-coefficients) are also important and strictly linear extrapolations cannot be made to infinite dilution using Eq. 2 mentioned above.

In non aqueous solvents, even at low concentrations at which *B* value is determined, partial association of the electrolyte takes place in case of sufficiently low relative permittivities [25]. Only the fraction α is then in the form of solvated ions, the rest being 1- α , being ion paired. This must be taken into account, by eq.3

$$[(\eta/\eta_0)-1-A(\alpha C)^{1/2}]/\alpha C = B_i + B_p(1-\alpha)/\alpha \text{-----} 3$$

The splitting of electrolyte *B*-coefficients into their ionic contributions cannot be done by direct measurement. However it is possible to split the measured electrolyte *B*-coefficients into the ionic contributions on the basis of their additivity [26]. Cox and Wolfenden [17] were the first to use such an approach for splitting of electrolyte *B*-coefficients into their ionic contributions in aqueous solutions. Their considerations give the qualitatively around the Einstein's [27] relationship for suspensions of spherical particles.

$$\eta = \eta_0(1 + 2.5v)$$

Here v is the aggregate volume of the particles in a unit volume (1cm^3) of the solution. The coefficient of v in the above equation is 2.5 for spherical particles; it will be larger than 2.5 in cases of particles having other shapes. The magnitude of the ionic B -coefficient is then supposed to be proportional to the molar hydrated volume of the ion. This should hold in particular for an ion for which the temperature coefficient of the mobility u obeys the Stoke's law, which depends on $d\eta_o/dT$ only, with a constant Stokes radius r_s . $u = \lambda^\infty / |z| F = [F/6\pi N_A] / \eta_o r_s$

$$r_s = [(F^2/6\pi N_A)/\eta_o] |z| / \lambda^\infty$$

The B coefficients of such an ion, is proportional to its hydrated ionic volume, would in turn be proportional to the cube of its Stokes radius, r_s , and inversely proportional to the cube of the ion mobility u or cube of the equivalent conductivity λ^∞ . For this study Cox and Wolfenden [17] selected the electrolyte, LiIO_3 , which has a pair of ions, Li^+ and IO_3^- , which obeyed the expectation that the ionic B -coefficients of Li^+ and IO_3^- should vary inversely with the cube of the ionic mobility of the given ions. The B -coefficient value of the LiIO_3 is 0.283 at 18°C and was split into two contributions, viz. 0.147 for Li^+ and 0.136 for IO_3^- .

$$B(\text{Li}^+)/B(\text{IO}_3^-) = u^3(\text{IO}_3^-)/u^3(\text{Li}^+) = \lambda^\infty(\text{IO}_3^-)^3/\lambda^\infty(\text{Li}^+)^3$$

From this relationship they calculated B -coefficients for many ions involved in electrolytes for which accurate data had been available at the time at 18°C and assumed it also to hold at 25°C . Asmus [28] was also agreed with this assumption.

The splitting of electrolyte B -coefficients into the ionic contribution for aqueous solutions at 25°C was demonstrated by Gurney [12] as,

$$B(\text{K}^+) = B(\text{Cl}^-)$$

His method for splitting of electrolyte B -coefficients into the ionic contribution for aqueous solutions was based on the fact that the ratios $(\lambda^\infty \eta_o)_{18^\circ\text{C}} / (\lambda^\infty \eta_o)_{0^\circ\text{C}}$ for the aqueous potassium and the chloride ions are nearly equal. The values of ionic B -coefficients of aqueous potassium and the chloride ions presented by Gurney at 0°C was $-0.050\text{dm}^3\text{mol}^{-1}$ and at 18°C was $-0.014\text{dm}^3\text{mol}^{-1}$. The arguments presented by Gurney [4] in the final estimation discarded the direct relationship to the “hydrated volume” as proposed by Cox and Wolfenden [17] in favour of the equivalence of the mobilities of the selected ions. Gurney [12] followed the assumption of Bingham [29], for the approximate equal fluidity of the potassium and chloride ions as indicated by their conductance (at 25°C).

Kaminsky [26] preferred Gurney’s convention to Cox and Wolfenden’s [17] and observed the mobility data for the ions of LiIO_3 at temperature other than 18°C . The mobilities u of potassium and chloride ions differ by $<3\%$ in the temperature range (15 - 42.5°C) used by Kaminsky [26]. The ionic B -coefficients of K^+ and Cl^- in aqueous solutions are -0.0200 at 15°C , -0.0070 at 25°C , $+0.0049$ at 35°C and $+0.0121$ at 42.5°C . However the Gurney [12], Cox and Wolfenden [17] scale for the ionic B -coefficients are in good agreement. This assumption that $B(\text{K}^+) = B(\text{Cl}^-)$ in aqueous solutions at all temperatures has since been used and employed by a sizeable number of investigators and there have been few challengers to this procedure.

Nightingale [30] proposed aqueous rubidium or Cesium chlorides as having more nearly equal λ^∞ values of the cation and anion than potassium

chloride. Jenkins and Pritchett [31] attempted to approach the problem in a novel way employing Fajans [32] principle. They concluded that cesium iodide can play a better role and give appropriate results of ionic B -coefficients as compare to that of potassiumchloride. The B -coefficients of the following salts have been measured by Krumgalz [33]: (KNO_3 , NH_4NO_3 , RbBr , RbI , CsBr and CsI). For most of the salts, over the temperature range 0-55 °C the percentage deviations of the ratios of $(\lambda_+^\infty)^3 / (\lambda_-^\infty)^3$ from unity and did not exceed 10 %. Overall the least deviations were observed in rubidium bromide, at room temperature and it was not more than 2%. Hence

$$B(\text{Rb}^+) = B(\text{Br}^-)$$

This change from potassium chloride to rubidium bromide represents a very small modification that is only $-0.002\text{dm}^3 \text{mol}^{-1}$ for cations and $+0.002\text{dm}^3 \text{mol}^{-1}$ for anions.

A major problem with these modes of splitting of the electrolyte B -coefficients in to their ionic contributions (whether based on KCl or RbBr) is that, they are applicable to aqueous solutions only. In other solvents the ratios of mobilities of the relatively small ions differ considerably from unity, and further more their B -coefficients are much larger, hence large errors could accrue from this approach to the assignment of ionic values if used for non-aqueous solvents. Only in isolated instances have partitioning assumptions, which have been employed for aqueous media been retained for non-aqueous systems. One example is the adaptation of the Gurney-Kaminsky assumption by Criss and Mastroiana for Methanol [34].

For acetonitrile solutions, Tuan and Fuoss [35] suggested the similar mobilities of the ions of tetrabutylammonium tetraphenylborate as a basis for the splitting of the B -coefficients.

$$B(\text{Bu}_4\text{N}^+) = B(\text{BPh}_4^-) = \frac{1}{2} B(\text{Bu}_4\text{NBPh}_4)$$

They observed that for large ions such as Bu_4N^+ and BPh_4^- the splitting of the B -coefficients are in good agreement and confirm that the model ought to be satisfactory in these cases. But for smaller ions the B values are larger than the computed values.

For other than univalent cations and anions having similar mobilities (λ^∞ values) in given solvents e.g. tetraethylammonium and iodide in *N*-methylpropionamide, the splitting of the B -coefficients has been determined by Tuan and Fuoss, and Gopal and Rastogi respectively [35, 36], with the help of the ratio of the cubes of their limiting equivalent conductivities.

$$B(\text{Et}_4\text{N}^+)/B(\text{I}^-) = \lambda^\infty(\text{Et}_4\text{N}^+)^3 / \lambda^\infty(\text{I}^-)^3$$

Yao and Bennion [37] preferred a different basis for the splitting of the B -coefficients in dimethylsulfoxide using the following expression:

$$B(\text{iPe}_3\text{BuN}^+) = B(\text{BPh}_4^-),$$

because of the equal spherical size and low surface charge density of the ions involved. This reference pair was subsequently employed by several authors for nonaqueous solvents, such as TMS, HMPT and EC [38]. The emphasis thus

shifted from the mobilities to the volumes of the ions affecting the viscosity of the solution.

A popular splitting mode recently adopted by Thompson [39] for non-aqueous solvents at any temperature is

$$\begin{aligned} B(\text{cation})/B(\text{anion}) &= V_{\text{vdW}}(\text{cation}) / V_{\text{vdW}} B(\text{anion}) \\ &= r_{\text{vdW}}(\text{cation})^3 / r_{\text{vdW}} B(\text{anion})^3 \end{aligned}$$

For example;

$$B(\text{Bu}_4\text{N}^+)/B(\text{BPh}_4^-) = r_{\text{vdW}}(\text{Bu}_4\text{N}^+)^3 / r_{\text{vdW}} B(\text{BPh}_4^-)^3$$

The value chosen for the van der Waals radii may differ from worker to worker: Thompson *et al.* used 5.35 and 5.00 Å as the van der Waals radii of the anion and cation, yielding $(5.00/5.35)^3 = 0.816$ for the ratio of their B -coefficients, Lawrence *et al.*, [40] used instead 5.72 and 5.64 Å for the radii of these ions respectively, yielding a ratio of 0.959 for the B -coefficients. Lawrence *et al.*, discussed a variation of this method in his further work [41].

Studies by Gill [42, 43] and by Gill and Sekhri [44] confirm that the ionic radii of Bu_4N^+ and BPh_4^- in a number of non-aqueous and mixed non-aqueous solvents remain constant and equal to 5.00 and 5.35 Å respectively, within an average uncertainty of $\pm 2\%$. In their method, Bu_4NBPh_4 , which is composed of bulky and spherical cation and anion, is used as reference electrolyte. Based on this, Gill [18] proposed the following equations.

$$\begin{aligned} B(\text{Bu}_4\text{NBPh}_4) &= B(\text{Bu}_4\text{N}^+) + B(\text{BPh}_4^-) \\ B(\text{BPh}_4^-) / B(\text{Bu}_4\text{N}^+) &= r_{(\text{BPh}_4^-)}^3 / r_{(\text{Bu}_4\text{N}^+)}^3 \\ B(\text{BPh}_4^-) / B(\text{Bu}_4\text{N}^+) &= (5.35/5.00)^3 \end{aligned}$$

$$B(\text{BPh}_4^-) / B(\text{Bu}_4\text{N}^+) = 1.225$$

This method was tested for the resolution of the viscosity B -coefficients of electrolytes into the contributions of individual ions using some viscosity measurements in non-aqueous solvents. Gill [18] calculated the B_+ values for $\text{Bu}_4\text{N}^+ = 0.78 \text{ dm}^3 \text{ mole}^{-1}$ in TMS, $\text{Bu}_4\text{N}^+ = 0.47 \text{ dm}^3 \text{ mole}^{-1}$ in ethylene carbonate (EC) and $\text{Bu}_4\text{N}^+ = 0.1.12 \text{ dm}^3 \text{ mole}^{-1}$ in HMPT respectively which coincide with the values ascribed by Sacco and coworkers [45] $\text{Bu}_4\text{N}^+ = 0.79 \text{ dm}^3 \text{ mole}^{-1}$ in TMS [32], $\text{Bu}_4\text{N}^+ = 0.46 \text{ dm}^3 \text{ mole}^{-1}$ in EC [46] and $\text{Bu}_4\text{N}^+ = 0.1.12 \text{ dm}^3 \text{ mole}^{-1}$ in HMPT [47].

Many other workers used the similar convention for the splitting the B -coefficients into the ionic components by using the reference electrolyte Bu_4NBPh_4 .

2.3. Viscosity B -coefficients in Aqueous Solutions.

Accurate determination of the viscosities of the dilute aqueous solutions of several electrolytes at 18 °C and 25 °C has been made [12, 27]. Stokes and Mills [48] while summarizing the state of knowledge of the viscosity of aqueous electrolyte solutions also gave numerical data mainly for the monovalent alkali metal, tetraalkylammonium, and halide ions. Divalent alkaline earth and transition metal ions have also been studied [49]. Data on rare earth cations [50] and several new ionic B -coefficients have been reported in recent times [51]. While the effects of ions for the water structure making and breaking have also been studied by many scientists [47, 52, 53].

The values of B -coefficients at 25 °C for inorganic ion and organic ions are listed by Sacco *et al.*, and Desnoyers and Perron [54, 55], ionic B -coefficients values of picrate [34], alkylsulphates [56], alkylsulphonates, alkylammonium ion and longer alkyl chains have been reported [57, 58]. Data at temperatures other than 25 °C for instance 18 °C, [59], 60 °C [60, 61], 65 °C [62], 75 °C 85 °C [60, 63] have been reported. Lack of suitable theory creates problems in the splitting of the electrolyte B -coefficients into the ionic contributions at each temperature. However most of the data have been reported by the original authors according to the widely accepted convention $B(K^+) = B(Cl^-)$ and their values are reported.

The pressure dependence of the B -coefficient of NaCl at 10, 25 and 50 °C was studied [62] and it was found that the values of B -coefficient increases with pressure up to 100 MPa at 10 and 25°C but remains approximately constant at 50°C. At higher pressure at all temperatures B decreases with increasing pressure. This has been attributed due to the decreasing structure of the water (broken by chloride and enhanced by the sodium ions), as either pressure or temperature or both are increased.

Few workers have also paid their attention for the determination of relative viscosities of dilute electrolyte solutions in heavy water, D₂O. The data at 25 °C for tetraalkylammonium bromides and iodides [64, 65] are reported as $B(Et_4N^+) = 0.36 \text{ dm}^3 \text{ mol}^{-1}$, $B(Br^-) = -0.05 \text{ dm}^3 \text{ mol}^{-1}$ and $B(I^-) = -0.07 \text{ dm}^3 \text{ mol}^{-1}$. Similarly at 25 °C and 40 °C for lithium $B(Li^+) = 0.15 \text{ dm}^3 \text{ mol}^{-1}$ and $0.13 \text{ dm}^3 \text{ mol}^{-1}$, sodium $B(Na^+) = 0.08 \text{ dm}^3 \text{ mol}^{-1}$ and $0.08 \text{ dm}^3 \text{ mol}^{-1}$, potassium $B(K^+) = -0.02 \text{ dm}^3 \text{ mol}^{-1}$ and $0.00 \text{ dm}^3 \text{ mol}^{-1}$, cesium $B(Cs^+) = -0.07 \text{ dm}^3 \text{ mol}^{-1}$ and $0.00 \text{ dm}^3 \text{ mol}^{-1}$ chloride $B(Cl^-) = -0.02 \text{ dm}^3 \text{ mol}^{-1}$ and $-0.00 \text{ dm}^3 \text{ mol}^{-1}$ at 25 and 40 °C respectively. Potassium $B(K^+) = -0.02 \text{ dm}^3 \text{ mol}^{-1}$ and iodide $B(I^-) = -0.10 \text{ dm}^3 \text{ mol}^{-1}$ at 25 °C was also determined by Ibuki and Nakahara [66].

Most of the early determinations of the B - coefficients were done in aqueous solutions and it was noted that some electrolytes decrease the viscosity relative to that of pure water. For example cesium nitrate has $B = -0.092 \text{ dm}^3 \text{ mole}^{-1}$ at 25°C [67] and cesium iodide $B = -0.258 \text{ dm}^3 \text{ mole}^{-1}$ at 0°C [68]. Cox and Wolfenden [17] were the first to reach this effect to the water structure. They reported that the negative value of B -coefficient is due to the depolymerization of the solvent water. This effect has been described by Franks Evans [11] as the “structure breaking effect” or the destruction of the structure of water by the ionic field. A similar hypothesis of Bernal and Fowler [21] is that, this behaviour is due to the rise in its structural temperature. As the temperature rises, there is less structure in water [69], and a similar effect is caused by ions having negative values of B -coefficients. Kaminsky [70] in his work showed that there is a relationship between the temperature dependence of the viscosity of aqueous solutions and the ion – solvent interaction. From their experimental results, they showed that $B < 0$ or $B > 0$. $B < 0$ means that the viscosity of the solution becomes less than that of the solvent. Gurney [12] also spoke of a loosening of the water structure for ions with $B < 0$ at room temperature. The effect of temperature on viscosities for aqueous di-isopropanolamine solutions were also studied over the temperature range of 25 to 70°C [71].

Viscosity B -coefficients of aqueous solutions of sodium carboxylates, sodium formate, acetate, propionate, n-butyrate, n- pentanoate, and trichloroacetate have also been determined at 30°C , 35°C and 40°C . The results have been interpreted in terms of the effect of these largely hydrophobic solutes on the structure of water [72].

2.4. Viscosity *B*- coefficients in Non- aqueous Solutions.

The non-aqueous solvents in which viscosity *B*-coefficients have been determined are all polar, but their properties differ considerably. Thus Buckely and Mariott [73] have proposed that the viscosity of the solution depends on the nature of the solvent, its structured ness [74], and its protic or dipolar aprotic nature.

More than twenty non-aqueous solvents, [54, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84] have been used for the determination of *B*-coefficients for different electrolytes at various temperatures and a relationship between the temperature and the ion-solvent interaction has been developed. The *B*- coefficient measurements in methanol at 25 °C indicate that dB/dT is the temperature dependence of the *B* coefficients. The temperature dependence of the *B*-coefficients dB/dT for the chloride salts of Li, Na, Cs are tabulated in Table 2.1. [85].

Table. 2.1. Viscosity *B*-Coefficients of salts in $\text{dm}^3 \text{mol}^{-1}$ in Methanol at various temperatures

Salt	25°C	30°C
LiCl	0.828	0.822
NaCl	0.796	0.794
CsCl	0.563	0.557
Et ₄ NBr	0.56/0.48	
Pr ₄ NBr	0.70/0.66	
Bu ₄ NBr	0.84/0.85	

It is noted that the sign of dB/dT in most cases is negative. The temperature coefficient has assign opposite to that of *B*-coefficients. It is interesting to note that negative *B*-coefficients signifying water structure breaking at ambient temperatures, becomes less negative or even positive as the

temperature is increased. Nightingale [30] placed great weight on the temperature coefficients of solutions and classified ions in four classes.

1. Structure making ions with $B > 0$ and $dB/dT < 0$.
2. Anomalous structure making ions with $B > 0$ but $dB/dT > 0$.
3. Structure breaking ions with $B < 0$ and $dB/dT > 0$.
4. Large structure making ions with “aperipheral hydration” with $B > 0$ and $dB/dT < 0$.

“A peripheral hydration” means that the ion is unhydrated the energy change for the movement of water molecule away from the ion being much less than the energy for its moving away from another water molecule.

Similarly dB/dT for tetraalkylammoniumbromide is almost zero or slightly positive. No viscosity measurements have been found for Rb salts in methanol during this survey. The lack of values for Et_4NaCl and Et_4NaI as well as their bromine counterpart make the further study of Et_4^+ salts important.

B -coefficients of NaI at 25 °C in 1- propanol and 2- propanol have been reported [65] as $B(NaI) = 0.826 \pm 0.010$ and $0.842 \pm 0.009 \text{ dm}^3 \text{ mol}^{-1}$ respectively. The same authors Bare and Skinner [65] have reported that the B -coefficients of Na, K, and ammonium halides in 1-Butanol at 25 °C. They have also produced the viscosity data for tetraalkylammonium ion series i.e. tetra-methyl, tetra-ethyl and tetra-butyl ammonium ions. These values are given in Table. 2.2.

Table. 2.2. Ionic B -Coefficients in $\text{dm}^3 \text{mol}^{-1}$ in Butanol at 25 °C.

Ion	B	Ion	B
Na^+	1.13	Et_4N^+	0.31
K^+	0.96	Bu_4N^+	0.72
NH_4^+	0.92	Cl^-	0.39
Me_4N^+	0.15	Br^-	0.33

The viscosity of the B - coefficient of NaI in Glycerol at 25 °C has been measured by Bare and Skinner [65]. This appeared to have positive B -coefficients values. B (NaI) = $0.357 \pm 0.005 \text{ dm}^3 \text{ mol}^{-1}$ while Crickard and Skinner [76] reported the values B (KI) = -0.185 and B (CsI) = $-0.408 \text{ dm}^3 \text{ mol}^{-1}$. Values for some tetralkylammonium iodides at 25 °C have been published by Gopal *et al.*, [86] and tabulated in Table 2.3.

Table. 2. 3. B -Coefficients of salts in $\text{dm}^3 \text{mol}^{-1}$ in Glycerol at 25 °C.

Ion	B values
Et_4N^+	-0.68
Pr_4NI	-2.90
Bu_4N^+	-1.90

The viscosity B -coefficient of various salts, including bis (2,9-dimethyl-1, 10-phenanthroline) copper (I) perchlorate in acetone at 25 °C have been measured [87]. Comparisons of the viscosity and conductance of several salts in acetone and N, N-dimethylformide regarding viscosity and conductance at 25 °C have been made [87, 88]. However the bromide salts of lithium, rubidium and cesium in acetone have not been investigated adequately.

Few measurements of the viscosity of electrolytes dissolved in acetic acid have been carried out at 25°C and 35°C [78, 89]. No values have been assigned to rubidium and chloride ions due to lack of data for their respective salts.

Several authors [54, 81] have studied the B -coefficients of many salts in acetonitrile at 25°C but only the data of Ibuki and Nakahara [53] deals with the temperatures at 15 °C and 35 °C. In 1989 Lawrence *et al.*, [41] also used acetonitrile as a solvent with different salts (Bu₄NBu₄B, Bu₄NBr, Bu₄NI, Ph₄PBr, Ph₄PI, NaI, NaPh₄B and for the homologous series from Et₄NBr to Hept₄NBr) at 25°C and 35 °C. Ionic B values for the bromide and iodide ions have been calculated from the B -coefficients for the tetra-alkylammonium solutions and are compared with those obtained from the tetraphenylphosphonium solutions [41]. Similarly Nirmal and Bijan [90] have also been used acetonitrile as solvent for measurements of viscosity of few symmetrical tetra alkyl ammonium salts at 15, 25, 35 and 45 °C. In another study for B -coefficients at 25 °C and 35 °C by few researchers for the same electrolytes as mentioned above have used N,N – dimethyl formamide as solvent [52]. A number of studies of the viscosity B -coefficients of salts in dimethyl sulfoxide at various temperatures have been carried out [82, 91, 92, 93]. The data have been split in to ionic B -coefficients using the alternative approaches such as [B (BuN⁺) = B (BBu₄⁻) and B (Ph₄P⁺) = B (BPh₄⁻)].

Viscosity B -coefficients in nitrobenzene and nitromethane have been measured at 25°C [35, 94] B (Bu₄NBr) = 0.75 dm³ mol⁻¹. They also obtained B (Bu₄N⁺) = 0.58 and B (BPh₄⁻) = 0.71; B (Br⁻) = 0.17 dm³ mol⁻¹, B (Et₄NCl) = 0.54, B (Et₄NBr) = 0.046 and B (Et₄NI) = 0.005 dm³ mol⁻¹ at 30 °C. Tominage [87] measured the viscosity B -coefficients of some perchlorates at 25 °C in nitrobenzene.

B -coefficients of several salts in the tetramethylene sulfone at different temperatures have been determined and it was found that dB/dT is less than zero for cations [93, 95]. The negative temperature coefficients for all cations

examined have been ascribed [95] to their structure making behaviour increasing for the tetralkylammonium ions from MeN^+ to Hx_4N^+ , but decreasing with increasing size of alkali metal cation except Li^+ .

Sacco *et al.*, [45] calculated the viscosity B -coefficients for many salts mentioned in Table 2.4 in sulfolane at 30 °C, 40 °C, and 50 °C. The data have been split in to ionic B -coefficient assuming that $B_{\text{Li Am}_3\text{BuN}^+} = B_{\text{BPh}_4^-} = B_{\text{Li Am}_3\text{BuNBPh}_4/2}$ and concluded that cations are solvated to a greater extent than anions because sulfolane is a dipolar aprotic solvent.

Table. 2.4. The B Coefficients of the salts in Sulfolane at 30, 40 and 50 °C.

Salt	B 30 °C	B 40 °C	B 50 °C
TABBPh ₄	1.90 ± 0.01	1.68 ± 0.01	1.50 ± 0.01
NaBPh ₄	2.25 ± 0.03	2.01 ± 0.03	1.84 ± 0.03
NaClO ₄	1.13 ± 0.01	1.12 ± 0.01	1.05 ± 0.01
Bu ₄ NClO ₄	0.72 ± 0.01	0.64 ± 0.01	0.57 ± 0.01
Bu ₄ NI	0.83 ± 0.01	0.74 ± 0.01	0.65 ± 0.01
Bu ₄ NBr	0.85 ± 0.01	0.75 ± 0.02	0.69 ± 0.01
Bu ₄ NCl	0.78 ± 0.02	0.69 ± 0.02	0.63 ± 0.02
TABI	0.99 ± 0.02	0.89 ± 0.02	0.80 ± 0.02
LiClO ₄	1.00 ± 0.02	0.95 ± 0.02	0.93 ± 0.01
RbClO ₄	0.97 ± 0.001	0.90 ± 0.01	0.86 ± 0.01
CaClO ₄	0.84 ± 0.01	0.80 ± 0.01	0.75 ± 0.01

Viscosities of several univalent electrolytes in hexamethylphosphotriamide (HMPT) at 25 °C have been measured [47]. Data was analysed by the Jones – Dole equation $B(\text{Li}^+) = 1.134 \text{ dm}^3 \text{ mol}^{-1}$, $B(\text{Na}^+) = 1.171 \text{ dm}^3 \text{ mol}^{-1}$, potassium $B(\text{K}^+) = 0.888 \text{ dm}^3 \text{ mol}^{-1}$, $B(\text{Rb}^+) = 0.883 \text{ dm}^3 \text{ mol}^{-1}$, $B(\text{Cs}^+) = 0.870 \text{ dm}^3 \text{ mol}^{-1}$ and $0.00 \text{ dm}^3 \text{ mol}^{-1}$ chloride $B(\text{Cl}^-) = 0.738 \text{ dm}^3 \text{ mol}^{-1}$ and it is found that the alkali metal cations are solvated by HMPT due to the fact that HMPT is a dipolar aprotic solvent. Viscosities of cinnamic acid solutions in pure methanol, ethanol and 1- butanol for various concentrations and at different temperatures

from 30 to 50 °C were measured and ion-solvent interactions were determined in terms of Jones – Dole B -coefficients and found that the cinnamic acid behaves as a structure breaker in absolute methanol and ethanol but as a structure maker in 1-butanol [96]. Viscosities of alkali metal chlorides and bromides in methoxyethanol at 25°C and 35°C have been determined. They found that the viscosity B -coefficient was positive and decreases as the size of the alkali metal ion increased except sodium halides [25, 97].

The behaviour of the electrolytes tetraethylphosphoniumiodide and tetraethylammoniumiodide in the nonaqueous solvents methanol, ethanol, 1-propanol, 1-butanol, acetonitrile and 2-propanone was determined at 25°C. The B -coefficient for each salt was shown to be solvent dependent [98].

The same type of behaviour was observed in the studies of the viscosity B -coefficient of salts in dimethylsulfoxide [99, 100]. The B values for the cations generally decrease as the ionic radius increases except that the value for sodium is less than that of potassium. $B(\text{Li}^+) = 0.608$, $B(\text{Na}^+) = 0.53$, $B(\text{K}^+) = 0.544$, $B(\text{Rb}^+) = 0.523$, $B(\text{Cs}^+) = 0.492 \text{ dm}^3 \text{ mol}^{-1}$. This order is explained by considering the fact that the ions with high charge density interact more strongly with the solvent molecules and generate larger hydrodynamic entities which cause greater obstruction to the viscous flow of the solvent [101].

2.5. Viscosity B -coefficients in Binary solvent mixtures.

To analyze ion-solvent interactions, great interest has been paid on the behavior of the solution of electrolytes in pure solvents and in binary solvent mixtures. Solvent parameters such as dielectric constant and viscosity in mixed

solvents can be varied to a desired value therefore ion solvation can be better understood in mixed solvents than in pure solvents. The pure solvents as mentioned earlier can be classified as protic and aprotic solvents and the binary system may comprise one of the following.

1. A protic solvent mixed with a protic solvent e.g. water with methanol, or
2. a protic solvent mixed with an aprotic solvent e.g. water with acetonitrile, or
3. an aprotic solvent mixed with an aprotic solvent e.g. dimethylacetamide with acetonitrile.

2.6. Protic solvent mixed with a Protic solvent.

The measurements of the viscosity B coefficient for alkali metal chlorides in propan-1-ol-water mixtures at 25 and 35 °C have been reported by Joseph Crudden *et al.*, [102]. The high precision density measurements were used to determine the relative viscosities of the solutions.

The viscosity B coefficients of sodium tartarate solutions in aqueous acidic methanol using 10-50% mixtures of various concentrations at 25 °C, 30 °C, 40 °C and 45 °C have been measured by Fahim *et al.*, [103]. The viscosity data was analyzed in term of ion solvent interactions. All the B coefficient values of sodium tartarate solutions were found positive.

Another study has been reported by Fahim *et al.*, [104] for the electrolytes, succinates of Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and the tetramethylammonium ion in acidic aqueous methanol mixtures at various temperatures. It was observed that the viscosity B coefficient increased with the temperature, which shows that succinate solutions behave as a structure breaker in acidic aqueous methanol. Pandharinath *et al.*, [105] have been measured the coefficients B -coefficients and

ionic B -coefficients of reference salts tetra alkyl, ammonium chlorides in (0-100) mass water and methanol at 25 °C.

Piekarski and Tkaczyk [106] have reported some thermo chemical properties of electrolyte solutions in 2- alkoxyethanol-water mixtures for NaI at 25 °C. Quintana *et al.*, [107] have been reported the data for ethanol-water mixtures at various temperatures. The viscosities of the associated electrolytes Na₂SO₄ and Mg SO₄ were measured in water rich mixtures of ethanol and water. The B coefficient values for these mixtures using (0- 30%) of ethanol varies in the range of B (Na⁺) = (0.086-0.082) dm³ mol⁻¹ and B (Mg²⁺) = (0.408-0.395) dm³ mol⁻¹. The ion solvent interaction increases in the Mg SO₄ and decreases in Na₂SO₄ as the dielectric constant of the medium decreases.

Viscosity, density and conductivity measurements on KI and KCl solutions in the water-t-butyl alcohol system at 26°C were performed by A. Kacperska and S. Taniewska-Osińska [108] up to 70 and 50 mol % of alcohol. The values of the A and B coefficients in the Jones-Dole equation were calculated. All the values for these B coefficients were found positive. The experimental criterion B (K⁺) = B (Cl⁻) was applied to obtain the ionic B coefficients. In the water- rich region the values of ionic B coefficients were decreased with the size of ions as they do in water.

The viscosity of KCl in a mixture of polyvinyl alcohol and water (1.0g.L⁻¹ to 5. 0g.L⁻¹) was measured at different concentration of salts at various temperatures ranging from 303 K to 320 K at intervals of 5 K. Ionic interactions in terms of Jones-Dole coefficients A and B were interpreted as function of salt concentration and temperature. The positive and large values of B -coefficients led to the conclusion that the strong association exists between water and polyvinyl

alcohol [109]. The apparent molar volumes and viscosities of NaCl, NH₄Cl, CuCl₂, CuSO₄ and MgSO₄ in pure water and water + Urea mixtures were studied and their dependence on temperature and concentration were also observed by Motin [110].

2.7. Protic solvent mixed with an Aprotic solvent.

Viscosity measurements of solutions of NaI in water-tetrahydrofuran mixtures were performed at 20, 25 and 30 °C [111]. Viscosities of a number of electrolytes were measured in acetonitrile and methanol mixtures at 25 °C by Gill and Chauhan [112]. The viscosity data was analyzed by the Jones-Dole equation to evaluate the *A* and *B* coefficients of the electrolytes. The *B* coefficients for electrolytes were positive and were split up into the individual ionic contributions *B*₊ and *B*₋, using a model proposed by Gill and co-workers [18].

Haase and Tillmann in 1995 [113] investigated the mixing properties of the liquid system 2-propanol + cyclohexane at 25 °C over the entire range of compositions. They concluded that the relative viscosity of the liquid system 2-propanol + cyclohexane increases with the increase in the mole fraction of 2-propanol. Measurements of the density and viscosity of hexamethylphosphoramide (HMPA)-water mixtures and the solutions of NaI in these mixtures were performed at numerous temperatures and it was found that the viscosity increases with the increased in the concentration of HMPA by S. Taniewska-Osińska and M. Józwiak [114]. When searching for information on the solvation behavior of ions in mixed solvents the viscosity data played an important role. The viscosities of tetrabutylammonium, tetraphenyl-borate (Bu₄NBPh₄), tetrabutylammoniumiodide (Bu₄NI), sodium tetraphenyl-borate

(NaBPh₄), tetrabutylammonium perchlorate (Bu₄NClO₄), copper perchlorate (CuClO₄) and silver nitrate (AgNO₃) in pyridine – methanol mixtures were measured at 25 °C. The viscosity *B* coefficient data was again splitted into ionic *B* coefficients. Ionic *B*₊ and *B*₋ coefficients of Bu₄N⁺ and Ph₄B⁻ in pyridine – methanol mixtures were found to decrease with an increase in the concentration of methanol. Similar behavior of these two ions was also observed in pyridine – acetonitrile mixtures at different temperatures [115]. The *B*₋ coefficients for I⁻, ClO₄⁻ and NO₃⁻ in pyridine – methanol mixtures were relatively small and showed a slight increase with the increase in the concentration of methanol. The results showed a weak solvation of these anions in pyridine – methanol mixtures which were enhanced in the methanol- rich region of the mixtures. The *B*₊ coefficients for Cu⁺ and Ag⁺ remained constant in the pyridine rich regions and decreased in methanol. It was concluded by Gill and Bakshi [116] that there is preferential solvation of Ag⁺ and Cu⁺ in pyridine.

2.8. Aprotic solvent mixed with an Aprotic solvent

The viscosities of tetrabutylammoniumtetrphenylborate (Bu₄NBPh₄), tetrabutylammoniumiodide (Bu₄NI), tetrabutylammoniumnitrate (Bu₄N NO₃), sodium tetrphenylborate (NaBPh₄), sodium perchlorate (NaClO₄), potassium perchlorate (KClO₄), potassium iodide (KI) and silver nitrate (AgNO₃) were measured in acetone and N, N-dimethylformamide mixtures at 25 °C. Viscosity *B* coefficients for all the electrolytes in acetone + N, N-dimethylformamide mixtures are large and positive which is a common feature in most non- aqueous solvents. In dipolar aprotic solvents, the structure- breaking contribution is negligible with the result that the *B*₋ coefficients are positive and large [18].

The solvation behavior of copper (1) perchlorate (CuClO_4) was investigated in binary mixtures of 3-hydroxypropionitrile- acetonitrile and propionitrile - acetonitrile mixtures at 25 °C. For these measurements the viscosities of tetrabutylammoniumtetraphenylborate (Bu_4NBPh_4), tetrabutylammonium perchlorate (Bu_4NClO_4) and copper perchlorate (CuClO_4) were observed. The viscosity results showed that Cu^+ is better solvated by acetonitrile and ClO_4^- by propionitrile and 3-hydroxypropionitrile in propionitrile – acetonitrile and 3-hydroxypropionitrile- acetonitrile mixtures respectively. This behavior was investigated by Gill *et al.* [117].

Viscosities of tetrabutylammoniumtetraphenylborate (Bu_4NBPh_4), tetraethylammoniumbromide (Et_4NBr), tetrabutylammoniumiodide (Bu_4NI), tetraethylammoniumiodide (Et_4NI), tetrapropylammoniumiodide (Pr_4NI) and tetrapropylammoniumbromide (Pr_4NBr) in acetonitrile and acetonitrile– dioxane, solvent mixtures have been reported by Syal *et al.* [118]. It has been found that B_{\pm} values for these ions increase with the increase of dioxane content in acetonitrile – dioxane mixtures, which indicates that there is no preferential solvation in acetonitrile – dioxane, solvent mixtures.

Viscosity B -coefficients of the alkali-metal bromides LiBr , NaBr , KBr , RbBr , CsBr , tetrabutylammoniumbromide (Bu_4NBr), and tetrabutylammoniumtetraphenylborate (Bu_4NBPh_4), in 3-hydroxypropionitrile (3HPN)- acetonitrile (AN) mixtures over the entire composition range at 25 °C were measured and it was found that the B -coefficients of all electrolytes reported by Zamir and. Quickenden [119] were positive. The values of B -coefficients of alkali metal bromides in 3-hydroxypropionitrile (3HPN)- acetonitrile (AN) mixtures show a small decrease as the crystal radii increase, except for NaBr . NaBr has a somewhat higher B -coefficient value $B(\text{Na}^+) = 0.27 \text{ dm}^3 \text{ mol}^{-1}$ than

that of LiBr $B(\text{Li}^+) = (0.23) \text{ dm}^3 \text{ mol}^{-1}$. This has been attributed to the fact that the ions with high charge density interact more strongly with the solvent molecule, which decreases the viscous flow of the solvent. Similar results have been observed in some other non-aqueous solvents [120].

2.9. Activation Energy of viscous flow

The temperature dependence of the solution viscosity enables the activation energy of the diffusion of ions through the solution to be determined. The Arrhenius equation gives:

$$\log \eta = \log A + E_{\eta}/2.303 RT + C$$

Where η = viscosity of coefficients, E_{η} is the activation energy, R is universal gas constant, T is the temperature while A and C are constants for the given binary solvent mixtures.

The energies of activation were determined [96] in methanol, ethanol, 1-butanol and cinnamic acid solutions at various concentrations and the results showed that the nature of the solvent affects the energy of activation. So that the activation energy of methanol < ethanol < 1-butanol. This is due to the difference in the size of the molecules and the strength of the interaction existing between the components of the mixtures. The increase in the values of activation energy indicates that dipole interaction and the association of the molecules increases with an increase in the aliphatic chain length of alcohols [121]. Ramadan *et al.*, [122] determined the energy of activation of viscous flow at different mole fractions of ethanol- dioxane mixtures. It was observed that as the viscosity of the mixtures increases the energy of activation decreases. The behaviour of polybutadiene rubber used in local tyre industry was studied by Khan [123] in toluene in temperature range of 15-75 oC with the increment of 10 oC by

viscosity techniques. The viscosity data was used to calculate the energy of activation of viscous flow of polybutadiene and it was noted that the activation of viscous flow of polybutadiene was increased with increase in concentration and also the temperature of the solution. Hafez and co-workers [124] used the dielectric measurements for ethanol- dioxane mixtures at different temperature to calculate the dielectric constant, the dipole moment, the dielectric relaxation and the free energy ΔG of activation. On calculations the authors found that it has constant values with temperature variation. On the other hand it decreases by increasing the non-polar solvent mole fraction, but in all cases it exhibits a negative deviation from unity indicating anti-parallel orientation of the dipoles of the neighbouring molecules, which means that structural variation occurs.

2.10. Gibb's Free Energy of viscous flow

The Gibb's free energy is also an important quantity for analysis of ion-solvent interactions structural properties. The Gibb's free energy ΔG for viscous flow can be determined by the equation proposed by Eyring,

$$\Delta G = RT \ln \eta V / hN$$

Where h is the plank constant, N is the Avogadro number, R is the universal gas constant, and V is the volume of 1 mole of the solution particles. Eyring proposed that the above equation is also applicable to a mixture of two components with the assumption that V is the average molar volume of the mixture and that ΔG is the average free energy of activation, which can be defined by the expression,

$$\Delta G = x_1 \Delta U_1 + x_2 \Delta U_2$$

The viscosity data has also been examined by a few workers in the light of transition state theory of the relative viscosity for dilute electrolyte solutions

purposed by Feakin *et al.*, [125]. According to the theory, the B -coefficients is given as

$$B = (\bar{V}_1^0 - \bar{V}_2^0) / 1000 + \bar{V}_1^0 (\Delta U_2^0 - \Delta U_1^0) / RT / 1000$$

Where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute respectively, as $c \Rightarrow 0$ then $V_1 = V_2$ and $\Delta U_1 = \Delta G$. ΔU_2^0 is the contribution per mole of solute to the free energy of activation of viscous flow of the solution and ΔU_1^0 is the free energy of the activation per mole of the pure solvent. ΔU_2^0 is calculated using the following equation.

$$\Delta G_1 = \Delta U_1^0 = RT \ln(\eta_0 \bar{V}_1^0 / hN) \text{-----} 1$$

$$\Delta G_2 = \Delta U_2^0 = \Delta U_1^0 + RT / \bar{V}_1^0 [1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \text{---} 2$$

Ali *et al.*, [126] observed for MgSO_4 that ΔU_2 have large values as compare to ΔU_1 in formamide-ethyleneglycol mixtures at 25 °C. The free energy of activation of viscous flow ΔU_1 for 20% volume of formamide in formamide-ethyleneglycol mixtures is 17.95 KJ mole^{-1} , while the observed value for ΔU_2 is 118.98 KJ mole^{-1} . Therefore they suggested that there is a strong ion-solvent interaction in the solution and MgSO_4 in formamide + ethyleneglycol mix solvent behaves as structure maker. They also proposed that electrolytes with grater values of ΔU_2 than the values of ΔU_1 are structure maker and vice versa will behave as structure breaker. A similar conclusion regarding MgSO_4 in dioxane + water mixed solvent was observed by Kammappan and Rajendran [127].

Nandi and Hazra [97] have been reported that the values of ΔU_2 for alkali metal cations in 2-methoxyethanol at 25 and 35 °C were decreased in the order: $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ and for anions in the order: $\text{Br}^- > \text{Cl}^-$. ΔU_2 values for the anions are slightly greater than those for the cations except for the Na^+ ion. This suggests that the Na^+ ion interacts with Me more strongly than do the other ions. It was also found that ΔU_2 values for all the ions were positive and greater than the values of ΔU_1 .

Viscosities of several uni-univalent electrolytes in HMPT at 25 °C have been measured by Sacco *et al.* [47]. Data were analyzed by Jones-Dole equation, and the *B*-coefficients and the free energies of activation were discussed in terms of transition state theory. Thus ΔU_2 values for the salts have been calculated and found that these values were positive for all the salts. On the basis of the assumption that $\Delta U_2(\text{TAB}^+) = \Delta U_2(\text{BPh}_4) = \Delta U_2(\text{TABBPh}_4) / 2$ as reported also by other authors [76], ionic free energies of activation of the viscous have been calculated. It may be noted that ΔU_2 was positive for all ions, thus the formation of a transition state was made less favourable by the presence of these ions. ΔU_2 values for alkali cations decreased in the order: $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, and for anions in the order: $\text{Cl}^- = \text{ClO}_4^- > \text{Br}^- > \text{I}^-$. ΔU_2 values for alkali cations were found greater than those for the anions, which showed the fact, that cations were interacted with HMPT more strongly than the anions.

2.11. Objectives.

The knowledge of ion-solvent interactions in aqueous and non-aqueous media is of considerable fundamental and technological importance. The potentialities of non-aqueous solvents in thermodynamic, kinetic and analytical

techniques in organic and inorganic synthesis as well as in industrial applications have been well recognised [70, 97].

In non- aqueous batteries, the choice of electrolyte solution and the optimisation of its salt concentration are two important factors. An electrolyte solution having high specific conductivity and with negligible ion –ion solvent interactions is required to maintain low internal resistance in the cell. Knowledge of the state of association of the electrolytes and the interactions between the solvent molecules is essential for the optimal choice of the solvent and electrolyte. To this end, various classical techniques such as electrical conductivity, viscosity and ultrasonic velocity measurements have been employed to study the status of association of the electrolytes [128, 129].

Dimethylsulfoxide (DMSO) is an aprotic solvent and has useful properties in organic synthesis [130, 131] and important applications in electrochemistry [132]. The physical and the dipolar properties of DMSO make the solvent promising for high-energy-density battery application. The transport behaviour of ions in DMSO, and the role of solvent DMSO solvent molecules in organic reactions both require the understanding of the nature of ion-solvent interactions. Transport parameters of electrolyte solutions such as ionic conductance and viscosity can provide information concerning the nature of the kinetic entities from which the ion-solvent interaction can be inferred [19, 133].

The main theme of this study is to investigate the behavior of the kinetic entities called mobile ions in the proposed solvents water and DMSO. In this study, the reason for the selection of water and DMSO is to observe the physical changes in the behaviour of a protic to aprotic binary solvent system

Considering the structure and dielectric constant of dimethylsulfoxide, studies of salt in mixtures of dimethylsulfoxide with water, acetonitrile and

nitrobenzene could be an ideal approach towards the ion solvent interaction in mixed solvents. These considerations led us to study the solvation properties of 1:1 electrolytes in H₂O, DMSO and H₂O-DMSO mixtures. Water is characterised by protic structure whereas DMSO is aprotic in character [134]. The results from the present study together with solvation values in water and DMSO may reveal characteristic changes (i.e. differences of interaction of electrolytes with solvent molecules) associated with the transfer of electrolytes from the protic (water) to an aprotic solvents (DMSO). After complete search of literature, the main objective of this study is as under.

1. Determination of the density and viscosity data for entire concentration range of alkali metal bromides in water, Dimethylsulfoxide and water – Dimethylsulfoxide mixtures.
2. Effect of temperature on the densities and viscosities of the solvents.
3. Determination of relative viscosities of alkali metal bromides in water, Dimethylsulfoxide and water – Dimethylsulfoxide mixtures.
4. Evaluation of coefficients *A* and *B* of the Jones-Dole equation
5. Determination of ionic *B*₊ and *B*₋ values for cations and anions of alkali metal bromides.
6. Determination of activation energy for cations and anions of alkali metal bromides by viscosity data.
7. Determination of Free energy of viscous flow for of alkali metal bromides.

CHAPTER 3

3.1. Material and Methods

3.1.1. Solvents

For a careful electrochemical work with aqueous solutions highly purified water is needed. Water is commonly contaminated with metals in both dissolved cationic form and in the form of colloidal or particulate matter [135]. It is also contaminated with bacteria [136]. The purification of water has been treated exhaustively in the literature, and reviews have summarized general conclusions and recommended techniques for the ultra-purification and analysis of water [135]. There is a general consensus among investigators that water purified in quartz or in plastic apparatus contains a lower level of cationic impurities than water purified in borosilicate or metal apparatus; secondly storage of purified water for periods exceeding 30 days, even in plastic or Teflon containers, will result in an increase in cationic impurities. So all the precautionary steps for a careful analysis were taken by passing doubly distilled water through a monobed deionizer [133,137,138]. The purified water was stored in plastic containers for periods not exceeding 15 days.

Dimethylsulfoxide (DMSO) has proved to be a particularly versatile and useful solvent since it became commercially available. The purification of DMSO for electrochemical studies has been surveyed by Reddy [139] on the behalf of the IUPAC Commission. Water is the principal impurity in DMSO and the recommended procedure is to remove water with molecular sieve type 5A, followed by distillation.

Dimethylsulfoxide 99% (Fluka) was stored over well-dried 5 Å molecular sieves for several days and then filtered. The solvent was distilled in the presence

of P_2O_5 , and was used for various measurements. Dimethylsulfoxide + water mixtures of compositions 0, 10, 30, 50, 70, 90 and 100 mass % DMSO (corresponding to mole fractions of 0, 0.466, 0.1586, 0.3054, 0.5064, 0.7983, and 1 of DMSO) were prepared by mixing a known mass of water and dimethylsulfoxide in a glass-stoppered flasks

3.1.2. Salts

The MX salts (where M= alkali metals, X = Bromide) were purified by re-crystallization. Then these re-crystallized electrolytes were dried at 130-150 °C for several hours prior to use. Owing to the hygroscopic nature of the bromides, these salts were stored in vacuum desiccators over P_2O_5 [140] for viscometer and conductometric measurements. Bu_4NBPh_4 (Aldrich) was precipitated with water from acetone solution and dried at 70 °C. This salt was also recovered after a set of measurements by precipitation from the DMSO solution using water. Bu_4NBr was purified by conventional methods [139]. Tetrabutylammoniumbromide (Aldrich) m.p: 103 °C was re-crystallized from benzene and n-hexane. The re-crystallized salt was dried at 117 to 120 °C for several hours prior to use.

3.1.3. Density ρ .

Densities of the pure solvents (DMSO and H_2O) and of solvent mixtures (DMSO- H_2O mixture) and of salt solutions were determined by using a specific density bottle of volume 15 cm^3 . The specific density bottle was calibrated using double distilled water and benzene at 25, 30, 35, 40 and 45 °C. The volume of the specific density bottle was corrected for the temperature change over the range studied (25, 30, 35, 40 and 45 °C). The specific density bottle filled with air or

bubble free experimental liquid was kept in a transparent- walled water bath for 10 to 15 min minimum to attain thermal equilibrium. When the level of the meniscus remained unchanged for 15 min the system was considered to be at equilibrium. The specific density bottle was removed from thermostatic water bath, dried and weighed. The density of the solution was calculated by dividing the weight in grams of the liquid by the volume in milliliters of the density bottle. The estimated accuracy of density measurements of solutions was $\pm 0.00001 \text{ gm cm}^{-3}$.

3.1.4. Viscosity, η :

For viscosity measurements, an ubbelholde type glass capillary tube suspended level viscometer was used for all viscosity measurements. A flow time of 450 seconds was detained for distilled water at 25, 30, 35, 40 and 45 °C. Capillary flow measurement involves the liquid or solution draining through a fine bore tube. The viscosity is determined from measured flow rate. The viscometer had a capillary length of 12.2 cm and a capillary diameter of 0.45 mm and was calibrated by using distilled water, n-hexane, methanol and acetone. Cleaning of the viscometer with clean mixture (sulfuric-chromic acid) was done at frequent intervals to ensure proper drainage of the solution.

The viscometer was suspended in a water thermostat maintained at 25, 30, 35, 40 or 45 °C with an uncertainty of ± 0.01 °C. At first 20 cm^3 of the reference liquid of accurately known viscosity η_1 was added from a pipette to the viscometer and its flow time t_1 was obtained. Same procedure was repeated for the liquid of interest to obtain the viscosity η_2 by its rate of flow t_2 . At least tree replicate of each data set reproducible to 0.05 Sec was obtained, results were

averaged and standard deviation and errors were determined. The overall accuracy of viscosity measurements was estimated to be ± 0.01 .

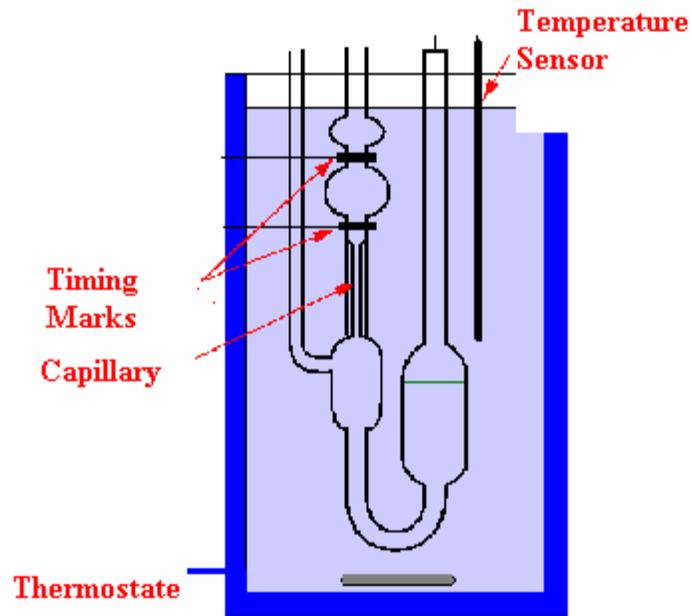


Fig 3.1: Ubbelohde dilution viscometer.

Viscosity values η_2 were determined from measurements of flow times t_1 and t_2 of liquids of the respective densities ρ_1 and ρ_2 using the following relation

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}$$

The absolute viscosities of DMSO, H₂O, DMSO-H₂O mixtures and their solutions with alkali metal bromides were determined at 25, 30, 35, 40 and 45 °C. Viscosities were measured at series of concentration for each alkali metal bromide; the lowest concentration being 0.01mole per liter and the highest concentration was about 0.4 moles per liter, which was found empirically to be the practical limit of the linear relationship that is the Jones Dole Equation. Experimental values of viscosities of the solution $\eta_1 = \eta$ and of solvents (H₂O, DMSO, H₂O-DMSO mixtures) as η_0 are used to determine the relative viscosities η_r or ψ of the solution which was used in Jones Dole equation.

$$(\psi/\eta_r = \eta/\eta_0 = 1 + AC^{1/2} + BC)$$

Experimental values of densities and viscosities were used to calculate the A and B coefficients in the Jones Dole equation and free energies of viscous flow ($\Delta \mu_1$) per mole of solvent and energy of activation in pure solvent and all the solvent mixtures at temperatures 25, 30, 35, 40 and 45 °C. The free energy ΔG for viscous flow was determined by using the equation

$$\Delta G = RT \ln \eta V / hN$$

Where the values of R the universal gas constant 8.315 J mol⁻¹, h the Planks constant 6.63 x 10⁻³⁴ and N the Avogadro's number 6.023 x 10²³ were used to determine the free energy f viscous flow of water, DMSO and DMSO-water mixtures at 25, 30, 35, 40 and 45 °C. V is the partial volume of the solvents

(DMSO and H₂O) were determined at all the five temperatures by using the expression

$$V = M/d$$

M is the molecular weight of the solvent. Molecular weight of DMSO is 78.13 and of H₂O is 18.015 and d is the density of the solvent at given temperature. The calculated partial molar volumes for DMSO and H₂O) at 25 °C were 71.67 cm³ and 18.066 cm³ mole⁻¹ respectively.

For DMSO-H₂O mixtures the partial molar volumes were determined at different temperatures by using the following expression.

$$V = M_{av}/d$$

Where M_{av} is the average molecular weight of the solvent H₂O and DMSO. Average molecular weight of the mixtures were determined by using the expression

$$M_{av} = M_1 \times M_2 / (W_1M_1 + W_2M_2)$$

M_1 = Molecular wt. of DMSO

M_2 = Molecular wt. of H₂O

W_1 = Mol fraction of DMSO

W_2 = Mol fraction of H₂O

The energy of activation and the effect of temperature on viscosity were determined by the following relation.

$$\eta = A e^{E_\eta/RT}$$

Where the E_η is the energy of activation of viscous flow, which is required to transfer one gm mole of the solute from one position of the equilibrium to another.

CHAPTER 4

4.1. Results & Discussion

The measured physical parameters like densities (ρ_o) and viscosities (η_o) for Dimethyl sulfoxide (DMSO), water (H₂O) and DMSO –H₂O mixtures containing 100, 60, 40, 20 and 0 % mole DMSO are reported in Table 1 for temperatures of 25 °C with the increment of 5 °C up to 45 °C. The data obtained in this study for densities (ρ_o) and viscosities (η_o) of the pure solvents H₂O and DMSO at 25 °C and at the other mentioned temperatures coincided with the values obtained by other authors [5]. However, the densities (ρ_o) in different composition of mixtures at other temperatures were measured for the first time in this study and literature data are not available for comparison.

The plots of densities (ρ_o) and viscosities (η_o) versus weight percentage of DMSO are presented in Fig 4.1-4.5. The plots of densities (ρ_o) show small deviations from linearity in mixture 1 (60 % DMSO). The trend in the physical properties of these binary solvent mixtures can be explained by starting from the lowest concentration of DMSO (i.e. 0, 20, 40, 60), where the addition of DMSO causes a slight increase in densities of the solvent mixtures, which indicates small structural effects in DMSO –H₂O mixtures. The above structural effects of aq. solvent mixtures may be due to high dielectric constant of water, which alters the densities of the solvent mixtures.

In this study, the same trend is observed in the plots of viscosities. Similar changes in viscosity were also found by other researchers. The viscosity of water- dioxane [141], water- dialkylated amide [142, 143], and water- alcohol [144], should a sharp maximum or minimum in the plots of viscosity versus solvent compositions. It is observed that at 60% composition of DMSO, the viscosity of the DMSO –H₂O mixture is at its maximum for all the five temperatures indicating the highest molecule packing in this region. This causes the hindrance in the flow of solvent mixture which results in the increase in viscosities binary solvent mixture.

A preliminary literature survey has shown us clearly the different conclusions, some authors have affirmed that DMSO has a capacity to enhance the water structure, while others argue that DMSO has structure-breaking ability due to its viscosity, density and refractive index [9], infra red spectroscopy and heat of mixing measurements [145]. However, in the present study it is observed that the addition of small quantities of DMSO to water, affects the structure of water, which influences the viscosities and densities of the mixed binary solvents.

4.2. Viscosity Measurements of electrolytic solutions

Relative viscosities, viscosities and the densities of LiBr, NaBr, KBr, RbBr and CsBr have been measured in the concentration range $(15-1000) \times 10^{-4}$ mol dm⁻³ in DMSO, H₂O and DMSO-H₂O mixtures over the entire composition range and reported in Tables 2- 26 at 25, 30, 35, 40 and 45 °C.

The results of the measurements of the relative viscosities η_r , of aqueous and non-aqueous electrolyte solutions are found to fit the Jones Dole equation [13].

$$\eta_r = \eta/\eta_0 = 1 + AC^{1/2} + BC$$

In this equation, η and η_0 are the viscosities of the solution and the pure solvent or solvent mixtures respectively, C is the molar concentration and A and B are the constants and are characteristic of the solvent and the salt.

Table 1. Densities (ρ_o) and viscosities (η_o) for DMSO, H₂O and DMSO–H₂O mixtures at 25, 30,35, 40 and 45 °C.

Wt % DMSO	Mol fraction	Density g/cm ³	Viscosity CP
25 °C			
100 % pure DMSO	1.00	1.09541	1.966
60 % DMSO + 40 % water	0.2570	1.08231	3.421
40 % DMSO + 60 % water	0.1333	1.05347	2.221
20 % DMSO + 80 % water	0.0545	1.02420	1.340
100 % Pure H ₂ O	0.0000	0.99715	0.890
30 °C			
100 % pure DMSO	1.00	1.09013	1.809
60 % DMSO + 40 % water	0.2570	1.08111	3.421
40 % DMSO + 60 % water	0.1333	1.05247	2.221
20 % DMSO + 80 % water	0.0545	1.01970	1.3117
100 % Pure H ₂ O	0.0000	0.99710	0.8003
35 °C			
100 % pure DMSO	1.00	1.08538	1.6523
60 % DMSO + 40 % water	0.2570	1.0728	3.10500
40 % DMSO + 60 % water	0.1333	1.0453	1.92100
20 % DMSO + 80 % water	0.0545	1.0152	1.05372
100 % Pure H ₂ O	0.0000	0.99366	0.75910
40 °C			
100 % pure DMSO	1.00	1.08538	1.55884
60 % DMSO + 40 % water	0.2570	1.06521	2.84611
40 % DMSO + 60 % water	0.1333	1.04012	1.6182
20 % DMSO + 80 % water	0.0545	0.9984	0.9572
100 % Pure H ₂ O	0.0000	0.9684	0.6214
45 °C			
100 % pure DMSO	1.00	1.0745	1.4875
60 % DMSO + 40 % water	0.2570	1.06001	2.77532
40 % DMSO + 60 % water	0.1333	1.03801	1.49756
20 % DMSO + 80 % water	0.0545	0.9792	0.8482
100 % Pure H ₂ O	0.0000	0.95321	0.53467

Table 2. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of LiBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 25 °C.

C Mol dm ⁻³	Density (ρ) g cm ⁻³	Viscosity (η) cP	Relative Viscosity (η_r)	C Mol dm ⁻³	Density (ρ) g cm ⁻³	Viscosity (η) cP	Relative viscosity (η_r)
LiBr in 100.00 %DMSO				LiBr in 20 % DMSO + 80 % Water			
0.019	1.0969	2.0086	0.1573	0.13	1.02633	1.35223	0.0766
0.025	1.0973	2.0182	0.1664	0.19	1.02698	1.35508	0.0799
0.033	1.0978	2.0385	0.2047	0.26	1.02756	1.35776	0.0814
0.040	1.0985	2.0536	0.2228	0.36	1.02866	1.36225	0.0865
0.049	1.0990	2.0655	0.2277	0.44	1.02959	1.36499	0.0882
LiBr in 60 % DMSO + 40 %Water				LiBr in 100.00 %Water			
0.016	1.09230	3.54164	0.2765	0.014	0.99823	0.90605	0.1518
0.021	1.09482	3.55945	0.2822	0.019	0.99940	0.90899	0.1539
0.026	1.09689	3.57962	0.2887	0.025	0.99960	0.91309	0.1547
0.032	1.09999	3.59789	0.2911	0.035	0.99980	0.91712	0.1599
0.046	1.10992	3.64706	0.2972	0.045	1.00067	0.92118	0.1627
LiBr in 40 % DMSO + 60% Water							
0.016	1.07230	2.29664	0.2670				
0.021	1.07482	2.30723	0.2709				
0.026	1.07689	2.31910	0.2733				
0.032	1.08000	2.33058	0.2774				
0.046	1.08007	2.35451	0.2814				

Table 3. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of LiBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 30 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm ⁻³	g cm ⁻³	cP	(η_r)	Mol dm ⁻³	g cm ⁻³	cP	(η_r)
LiBr in 100.00 %DMSO				LiBr in 20 % DMSO + 80 % Water			
0.016	1.09263	1.85830	0.2150	0.013	1.02183	1.34312	0.0778
0.022	1.09612	1.87123	0.2317	0.018	1.02548	1.34560	0.0809
0.029	1.09792	1.88938	0.2621	0.024	1.02646	1.34819	0.0834
0.045	1.09992	1.92044	0.2889	0.034	1.02756	1.35256	0.0875
0.049	1.10083	1.92830	0.2993	0.042	1.35558	1.35558	0.0900
LiBr in 60 % DMSO + 40 %Water				LiBr in 100.00 %Water			
0.016	1.09230	3.54074	0.2789	0.013	0.99857	0.81402	0.1528
0.021	1.09482	3.56092	0.2832	0.016	0.99940	0.81583	0.1553
0.027	1.09689	3.58289	0.2875	0.021	0.99960	0.81832	0.1570
0.031	1.09999	3.59571	0.2898	0.030	0.99980	0.82264	0.1599
0.049	1.10992	3.64904	0.2998	0.035	1.00067	0.82466	0.1617
LiBr in 40 % DMSO + 60% Water							
0.016	1.07224	2.29558	0.2676				
0.020	1.07452	2.30511	0.2699				
0.026	1.07686	2.31848	0.2733				
0.031	1.07966	2.32880	0.2766				
0.046	1.08003	2.35547	0.2834				

Table 4. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of LiBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 35°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
LiBr in 100.00 %DMSO				LiBr in 20 % DMSO + 80 % Water			
0.019	1.08686	1.70100	0.2154	0.013	1.01732	1.06305	0.0764
0.025	1.08725	1.71570	0.2416	0.019	1.01799	1.06544	0.0808
0.032	1.08772	1.73302	0.2721	0.026	1.01806	1.06788	0.0841
0.041	1.08847	1.74581	0.2785	0.036	1.01816	1.07103	0.0869
0.049	1.08897	1.75886	0.2900	0.044	1.01827	1.07361	0.0905
LiBr in 60 % DMSO + 40 %Water				LiBr in 100.00 %Water			
0.016	1.07385	3.16587	0.1550	0.014	0.99137	0.77115	0.1366
0.021	1.07482	3.17523	0.1580	0.019	0.99172	0.77334	0.1379
0.023	1.07652	3.17980	0.1599	0.020	0.99227	0.77441	0.1412
0.032	1.07679	3.19630	0.1656	0.030	0.99237	0.77807	0.1433
0.049	1.07779	3.22648	0.1760	0.036	0.99259	0.78287	0.1470
LiBr in 40 % DMSO + 60% Water							
0.016	1.06232	1.98251	0.2511				
0.021	1.06430	1.99096	0.2541				
0.026	1.06630	2.00074	0.2568				
0.032	1.06730	2.00074	0.2607				
0.046	1.06930	2.03089	0.2678				

Table 5. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of LiBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 40 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
LiBr in 100.00 %DMSO				LiBr in 20 % DMSO + 80 % Water			
0.019	1.08686	1.60522	0.2176	0.013	1.00135	0.96567	0.0764
0.025	1.08725	1.61858	0.2414	0.019	1.00439	0.96784	0.0807
0.032	1.08772	1.62936	0.2521	0.026	1.00806	0.97007	0.0841
0.041	1.08847	1.64670	0.2775	0.036	1.01116	0.97325	0.0887
0.049	1.08897	1.65895	0.2889	0.044	1.01130	0.97569	0.0926
LiBr in 60 % DMSO + 40 %Water				LiBr in 100.00 %Water			
0.016	1.06538	2.90182	0.1547	0.014	0.96867	0.63127	0.1366
0.021	1.06558	2.91041	0.1578	0.019	0.96897	0.63311	0.1385
0.023	1.06588	2.91466	0.1599	0.020	0.96927	0.63393	0.1412
0.032	1.06618	2.93012	0.1662	0.030	0.96967	0.63693	0.133
0.049	1.06679	2.95780	0.1765	0.036	0.96990	0.64092	0.1475
LiBr in 40 % DMSO + 60% Water							
0.016	1.04230	1.67003	0.2511				
0.021	1.04430	1.67734	0.2550				
0.026	1.04631	1.68561	0.2577				
0.032	1.04730	1.69343	0.2614				
0.046	1.04930	1.71104	0.2686				

Table 6. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of LiBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 45 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm ⁻³	g cm ⁻³	cP	(η_r)	Mol dm ⁻³	g cm ⁻³	cP	(η_r)
LiBr in 100.00 %DMSO				LiBr in 20 % DMSO + 80 % Water			
0.019	0.9544	1.5277	0.1974	0.013	0.97960	0.85549	0.0741
0.026	0.9546	1.5411	0.2267	0.019	0.98010	0.85765	0.0808
0.032	0.9548	1.5522	0.2421	0.026	0.98110	0.85961	0.0841
0.041	0.9550	1.5638	0.2525	0.036	0.98220	0.86240	0.0885
0.049	0.9551	1.5775	0.2720	0.044	0.98380	0.86443	0.0917
LiBr in 60 % DMSO + 40 %Water				LiBr in 100.00 %Water			
0.016	1.06261	2.83938	0.1540	0.014	0.95662	0.54319	0.1372
0.021	1.06351	2.83770	0.1570	0.019	0.95754	0.54485	0.1400
0.023	1.06421	2.84244	0.1606	0.020	0.95782	0.54537	0.1402
0.032	1.06651	2.85698	0.1657	0.030	0.96032	0.54818	0.1441
0.049	1.07131	2.88452	0.1770	0.045	0.96234	0.55158	0.1485
LiBr in 40 % DMSO + 60% Water							
0.016	1.03848	1.53526	0.2514				
0.021	1.03855	1.54195	0.2551				
0.026	1.03866	1.54957	0.2579				
0.032	1.03873	1.55682	0.2618				
0.046	1.03891	1.57326	0.2697				

Table 7. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of NaBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 25°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
NaBr in 100.00 %DMSO				NaBr in 20 % DMSO + 80 % Water			
0.009	1.09621	1.99975	0.1699	0.0159	1.02756	1.35392	0.0850
0.013	1.09758	2.01232	0.2079	0.0189	1.02798	1.35611	0.0855
0.033	1.09991	2.05174	0.2406	0.0235	1.02866	1.35800	0.0859
0.049	1.10080	2.08337	0.2689	0.0323	1.02958	1.36122	0.0867
0.056	1.10211	2.11210	0.3136	0.0419	1.03154	1.36433	0.0875
NaBr in 60 % DMSO + 40 % Water				NaBr in 100.00 % Water			
0.0162	1.09437	3.55328	0.3031	0.0106	0.99940	0.89559	0.0576
0.0205	1.09497	3.57045	0.3046	0.0136	0.99961	0.89638	0.0599
0.0258	1.09688	3.59032	0.3081	0.0245	0.99982	0.89883	0.0612
0.0315	1.10003	3.60983	0.3108	0.0354	1.00067	0.90084	0.0628
0.0456	1.10992	3.65504	0.3203	0.0484	1.00363	0.90290	0.0643
NaBr in 40 % DMSO + 60% Water							
0.0167	1.08231	3.36175	0.3383				
0.0206	1.08482	3.38020	0.3439				
0.0257	1.08688	3.39954	0.3456				
0.0315	1.09000	3.41926	0.3468				
0.0428	1.09006	3.45411	0.3499				

Table 8. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of NaBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 30 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm ⁻³	g cm ⁻³	cP	(η_r)	Mol dm ⁻³	g cm ⁻³	cP	(η_r)
NaBr in 100.00 %DMSO				NaBr in 20 % DMSO + 80 % Water			
0.011	0.96860	0.62398	0.0404	0.014	1.02756	1.34456	0.0853
0.013	0.96873	0.62424	0.0408	0.017	1.02798	1.34624	0.0869
0.020	0.96891	0.62526	0.0435	0.026	1.02866	1.34882	0.0883
0.034	0.96939	0.62670	0.0459	0.032	1.02959	1.35283	0.0915
0.048	0.96998	0.62792	0.0478	0.041	1.03150	1.35648	0.0940
NaBr in 60 % DMSO + 40 %Water				NaBr in 100.00 %Water			
0.0153	1.09530	3.54872	0.3021	0.011	0.99940	0.80510	0.0582
0.0196	1.09631	3.56677	0.3046	0.014	0.99960	0.80582	0.0589
0.0228	1.09789	3.58017	0.3081	0.024	0.99980	0.80797	0.0612
0.0305	1.10383	3.60681	0.3108	0.035	0.1.0006	0.80978	0.0628
0.0356	1.11359	3.62550	0.3167	0.048	1.00363	0.81162	0.0643
NaBr in 40 % DMSO + 60% Water							
0.016	1.08430	2.31094	0.3413				
0.019	1.08682	2.32503	0.3429				
0.022	1.08889	2.33377	0.3445				
0.031	1.09200	2.35630	0.3488				
0.041	1.09407	2.37943	0.3532				

Table 9. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of NaBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 35°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
NaBr in 100.00 %DMSO				NaBr in 20 % DMSO + 80 % Water			
0.009	1.08862	1.70149	0.3118	0.014	1.01755	1.06220	0.0676
0.013	1.08877	1.71340	0.3306	0.019	1.01798	1.06381	0.0696
0.023	1.08921	1.74324	0.3635	0.024	1.01886	1.06526	0.0715
0.029	1.09028	1.75741	0.3715	0.032	1.01928	1.06784	0.0746
0.036	1.09526	1.77452	0.3890	0.042	1.02150	1.07038	0.0773
NaBr in 60 % DMSO + 40 %Water				NaBr in 100.00 %Water			
0.016	1.07386	3.17398	0.1736	0.011	0.98989	0.76213	0.0384
0.021	1.07388	3.18336	0.1763	0.013	0.99012	0.76269	0.0418
0.025	1.07679	3.19271	0.1794	0.020	0.99076	0.76385	0.0435
0.029	1.07905	3.20188	0.1815	0.034	0.99213	0.76548	0.0451
0.041	1.07992	3.22382	0.1899	0.048	0.99291	0.76677	0.0458
NaBr in 40 % DMSO + 60% Water							
0.016	1.05532	1.94390	0.0952				
0.020	1.05682	1.94785	0.0975				
0.026	1.05683	1.95165	0.0995				
0.031	1.05808	1.95538	0.1025				
0.042	1.05988	1.96277	0.1070				

Table 10. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of NaBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 40°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
NaBr in 100.00 %DMSO				NaBr in 20 % DMSO + 80 % Water			
0.009	1.08862	1.60592	0.3166	0.014	1.00176	0.96480	0.0666
0.013	1.08878	1.61646	0.3306	0.019	1.00459	0.96624	0.0686
0.023	1.08921	1.64441	0.3627	0.024	1.00886	0.96769	0.0715
0.029	1.09029	1.65860	0.3739	0.032	1.01183	0.97029	0.0762
0.036	1.09526	1.67380	0.3880	0.042	1.01435	0.97263	0.0788
NaBr in 60 % DMSO + 40 %Water				NaBr in 100.00 %Water			
0.016	1.06539	2.90934	0.1736	0.011	0.96860	0.62398	0.0404
0.021	1.06554	2.91843	0.1775	0.013	0.96873	0.62424	0.0408
0.025	1.06577	2.92651	0.1794	0.020	0.96891	0.62526	0.0435
0.030	1.06591	2.93607	0.1839	0.034	0.93939	0.62670	0.0459
0.041	1.06620	2.95509	0.1900	0.048	0.96998	0.62792	0.0478
NaBr in 40 % DMSO + 60% Water							
0.016	1.04430	1.63735	0.0945				
0.021	1.04606	1.64062	0.0966				
0.026	1.04768	1.64428	0.1005				
0.031	1.04881	1.64782	0.1048				
0.042	1.05191	1.65377	0.1071				

Table 11. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of NaBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 45°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
NaBr in 100.00 %DMSO				NaBr in 20 % DMSO + 80 % Water			
0.009	1.07560	1.53267	0.3181	0.014	0.97960	0.85505	0.0676
0.013	1.07590	1.54251	0.3306	0.019	0.97990	0.85634	0.0696
0.023	1.07600	1.56937	0.3635	0.023	0.98020	0.85764	0.0725
0.029	1.07640	1.58217	0.3715	0.032	0.98050	0.85988	0.0766
0.036	1.07680	1.59755	0.3890	0.042	0.98090	0.86210	0.0800
NaBr in 60 % DMSO + 40 %Water				NaBr in 100.00 %Water			
0.016	1.06005	2.83686	0.1733	0.009	1.07560	1.53267	0.3181
0.021	1.06008	2.84537	0.1763	0.013	1.07590	1.54252	0.3306
0.025	1.06012	2.85372	0.1794	0.023	1.07600	1.56937	0.3635
0.029	1.06015	2.86193	0.1815	0.029	1.07640	1.58214	0.3715
0.040	1.06019	2.88154	0.1899	0.036	1.07680	1.59755	0.3890
NaBr in 40 % DMSO + 60 %Water							
0.016	1.03806	1.50511	0.0942				
0.020	1.03809	1.50814	0.0965				
0.026	1.03813	1.51153	0.1005				
0.031	1.03816	1.51418	0.1025				
0.042	1.03819	1.52039	0.1076				

Table 12. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of KBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 25 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
KBr in 100.00 %DMSO				KBr in 20 % DMSO + 80 % Water			
0.009	1.09644	1.99592	0.1601	0.016	1.02426	1.34131	0.0059
0.015	1.09761	2.01785	0.2179	0.020	1.02427	1.34172	0.0073
0.039	1.10068	2.05317	0.2247	0.025	1.02428	1.34196	0.0076
0.050	1.10189	2.08545	0.2722	0.031	1.02429	1.34248	0.0090
0.057	1.10255	2.11294	0.3121	0.036	1.02430	1.34267	0.0091
KBr in 60 % DMSO + 40 %Water				KBr in 100.00 %Water			
0.012	1.08266	3.42658	0.0152	0.010	0.99672	0.89386	0.0389
0.020	1.08297	3.43157	0.0217	0.013	0.99685	0.89427	0.0382
0.025	1.08301	3.43460	0.0250	0.024	0.99718	0.89550	0.0372
0.031	1.08305	3.43833	0.0286	0.035	0.99755	0.89623	0.0353
0.036	1.08325	3.44182	0.0320	0.048	0.99788	0.89680	0.0331
KBr in 40 % DMSO + 60 %Water							
0.014	1.05454	2.22405	0.0116				
0.021	1.05465	2.26625	0.0162				
0.024	1.05473	2.22740	0.0184				
0.031	1.05486	2.22945	0.0215				
0.043	1.05501	2.23310	0.0266				

Table 13. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of KBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 30°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
KBr in 100.00 %DMSO				KBr in 20 % DMSO + 80 % Water			
0.009	1.09644	1.83701	0.1624	0.016	1.02920	1.33244	0.0077
0.015	1.09761	1.85588	0.2139	0.020	1.02998	1.33263	0.0077
0.039	1.10698	1.89748	0.2477	0.025	1.03100	1.33284	0.0079
0.050	1.11269	1.91935	0.2732	0.031	1.03159	1.33306	0.0080
0.057	1.11493	1.93862	0.2991	0.036	1.03263	1.33323	0.0081
KBr in 60 % DMSO + 40 %Water				KBr in 100.00 %Water			
0.012	1.08530	1.08530	0.0152	0.010	0.99672	0.80350	0.0389
0.020	1.08731	1.08731	0.0227	0.013	0.99687	0.80387	0.0382
0.025	1.08889	1.08889	0.0255	0.024	0.99718	0.80497	0.0372
0.031	1.09004	1.09004	0.0295	0.035	0.99765	0.80570	0.0358
0.036	1.09159	1.09159	0.0322	0.048	0.99788	0.80632	0.0341
KBr in 40 % DMSO + 60 %Water							
0.014	1.08430	2.22402	0.1115				
0.021	1.08730	2.22625	0.0142				
0.024	1.08889	2.22740	0.0164				
0.031	1.09200	2.22859	0.0187				
0.043	1.09807	2.23038	0.0245				

Table 14. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of KBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 35°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
KBr in 100.00 %DMSO				KBr in 20 % DMSO + 80 % Water			
0.010	1.08875	1.69410	0.2598	0.015	1.05514	1.05526	0.0120
0.015	1.08891	1.71137	0.2903	0.012	1.05548	1.05584	0.0142
0.024	1.08961	1.73150	0.3099	0.020	1.05566	1.05622	0.0156
0.040	1.09062	1.76773	0.3500	0.025	1.05602	1.05691	0.0175
0.056	1.09146	1.79904	0.3741	0.040	1.05626	1.05743	0.0190
KBr in 60 % DMSO + 40 %Water				KBr in 100.00 %Water			
0.011	1.07324	3.11051	0.0166	0.010	0.98989	0.76215	0.0390
0.020	1.07397	3.11647	0.0260	0.012	0.98990	0.76240	0.0385
0.024	1.07458	3.11850	0.0279	0.020	0.98993	0.76318	0.0373
0.030	1.07505	3.12130	0.0301	0.025	0.98996	0.76362	0.0371
0.034	1.07525	3.12556	0.0348	0.040	0.99006	0.76459	0.0357
KBr in 40 % DMSO + 60 %Water							
0.014	1.04613	1.92446	0.0152				
0.020	1.04633	1.92642	0.0199				
0.024	1.04653	1.92753	0.0219				
0.030	1.04669	1.92928	0.0247				
0.041	1.04701	1.93213	0.0286				

Table 15. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of KBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 40 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm ⁻³	g cm ⁻³	cP	(η_r)	Mol dm ⁻³	g cm ⁻³	cP	(η_r)
KBr in 100.00 %DMSO				KBr in 20 % DMSO + 80 % Water			
0.010	1.08675	1.59889	0.2641	0.015	0.99987	0.95861	0.0012
0.015	1.08781	1.61438	0.2892	0.020	0.99994	0.95914	0.0014
0.024	1.08891	1.63352	0.3100	0.023	1.00020	0.95962	0.0016
0.040	1.09062	1.66548	0.3428	0.030	1.00053	0.96039	0.0192
0.056	1.09246	1.69690	0.3731	0.034	1.00065	0.96084	0.0205
KBr in 60 % DMSO + 40 %Water				KBr in 100.00 %Water			
0.011	1.06757	2.85119	0.0167	0.010	0.96989	0.62387	0.0390
0.020	1.06997	2.85666	0.0261	0.012	0.96990	0.62407	0.0385
0.024	1.07158	2.85848	0.0279	0.020	0.96993	0.62471	0.0372
0.030	1.07305	2.86149	0.0310	0.025	0.96996	0.62507	0.0371
0.034	1.07525	2.86495	0.0348	0.040	0.97006	0.62590	0.0360
KBr in 40 % DMSO + 60 %Water							
0.014	1.04020	1.62113	0.0153				
0.020	1.04031	1.62300	0.0209				
0.024	1.04040	1.62390	0.0227				
0.030	1.04053	1.62512	0.0245				
0.041	1.04077	1.62790	0.0296				

Table 16. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of KBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 45 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm ⁻³	g cm ⁻³	cP	(η_r)	Mol dm ⁻³	g cm ⁻³	cP	(η_r)
KBr in 100.00 %DMSO				KBr in 20 % DMSO + 80 % Water			
0.009	1.09632	1.52542	0.2618	0.015	0.97967	0.84932	0.0106
0.015	1.09641	1.54071	0.2903	0.020	0.97983	0.84980	0.0131
0.024	1.09648	1.55880	0.3099	0.023	0.97999	0.85009	0.0145
0.040	1.09672	1.58918	0.3424	0.030	0.98016	0.85085	0.0179
0.056	1.09689	1.61882	0.3719	0.034	0.98027	0.85135	0.0200
KBr in 60 % DMSO + 40 %Water				KBr in 100.00 %Water			
0.011	1.06006	2.78008	0.0160	0.010	0.95682	0.53722	0.0469
0.020	1.06014	2.78558	0.0260	0.012	0.95694	0.53746	0.0467
0.024	1.06018	2.78739	0.0279	0.020	0.95762	0.53817	0.0458
0.030	1.06024	2.78990	0.0301	0.025	0.95813	0.53855	0.0455
0.036	1.06028	2.79370	0.0348	0.040	0.95935	0.53942	0.0442
KBr in 40 % DMSO + 60 %Water							
0.014	1.03842	1.50025	0.0152				
0.020	1.03846	1.50178	0.0198				
0.024	1.03848	1.50265	0.0219				
0.030	1.03851	1.50401	0.0247				
0.041	1.03857	1.50647	0.0293				

Table 17. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of RbBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 25°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
RbBr in 100.00 %DMSO				RbBr in 20 % DMSO + 80 % Water			
0.011	1.09692	1.99692	0.1507	0.015	1.02422	1.34131	0.0059
0.020	1.09830	2.01924	0.1911	0.020	1.02426	1.34172	0.0073
0.027	1.10008	2.03943	0.2284	0.024	1.02428	1.34196	0.0078
0.030	1.10037	2.04721	0.2384	0.026	1.02429	1.34204	0.0078
0.046	1.10251	2.08514	0.2566	0.033	1.02433	1.34232	0.0081
RbBr in 60 % DMSO + 40 %Water				RbBr in 100.00 %Water			
0.011	1.08255	3.42548	0.0179	0.010	0.99669	0.89301	0.0341
0.015	1.08278	3.42954	0.0212	0.013	0.99684	0.89349	0.0331
0.021	1.08301	3.43282	0.0251	0.020	0.99703	0.89526	0.0310
0.023	1.08320	3.43559	0.0271	0.025	0.99728	0.89616	0.0300
0.028	1.08345	3.43708	0.0304	0.038	0.99779	0.89657	0.0270
RbBr in 40 % DMSO + 60 %Water							
0.013	1.05441	2.22435	0.0132				
0.014	1.05453	2.22462	0.0137				
0.019	1.05478	2.22610	0.0165				
0.021	1.05492	2.22681	0.0179				
0.025	1.05508	2.22784	0.0194				

Table 18. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of RbBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 30°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
RbBr in 100.00 %DMSO				RbBr in 20 % DMSO + 80 % Water			
0.011	1.09254	1.83920	0.1597	0.015	1.01994	1.33214	0.059
0.020	1.09771	1.86052	0.2012	0.020	1.02007	1.33255	0.0073
0.026	1.10691	1.87657	0.2284	0.024	1.02018	1.33278	0.0078
0.030	1.11093	1.88439	0.2404	0.026	1.02028	1.33286	0.0079
0.056	1.13493	1.92274	0.2663	0.033	1.02036	1.33315	0.0081
RbBr in 60 % DMSO + 40 %Water				RbBr in 100.00 %Water			
0.011	1.08259	3.42753	0.0179	0.010	0.99608	0.89341	0.0320
0.015	1.08273	3.42989	0.0212	0.013	0.99608	0.89373	0.0314
0.021	1.08300	3.43381	0.0261	0.020	0.99614	0.89427	0.0301
0.023	1.08305	3.43527	0.0273	0.025	0.99617	0.89457	0.0294
0.028	1.08333	3.43849	0.0304	0.038	0.99624	0.89503	0.0272
RbBr in 40 % DMSO + 60 %Water							
0.013	1.05449	2.22430	0.0130				
0.014	1.05453	2.22462	0.0137				
0.019	1.05478	2.22622	0.0169				
0.021	1.05482	2.22681	0.0179				
0.025	1.05502	2.22784	0.0194				

Table 19. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of RbBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 35°C .

C Mol dm^{-3}	Density (ρ) g cm^{-3}	Viscosity (η) cP	Relative Viscosity (η_r)	C Mol dm^{-3}	Density (ρ) g cm^{-3}	Viscosity (η) cP	Relative Viscosity (η_r)
RbBr in 100.00 %DMSO				RbBr in 20 % DMSO + 80 % Water			
0.011	1.08775	1.68165	0.1699	0.014	1.01546	1.05511	0.0101
0.027	1.08877	1.70051	0.2061	0.020	1.01558	1.05539	0.0112
0.027	1.08897	1.71230	0.2221	0.024	1.01566	1.05558	0.0114
0.030	1.08997	1.72189	0.2430	0.026	1.01574	1.05568	0.0115
0.056	1.09197	1.75852	0.2723	0.033	1.01578	1.05596	0.0127
RbBr in 60 % DMSO + 40 %Water				RbBr in 100.00 %Water			
0.011	1.07485	3.11561	0.0322	0.010	0.98987	0.76213	0.0390
0.014	1.07495	3.11866	0.0367	0.013	0.98989	0.76245	0.0380
0.020	1.07505	3.12250	0.0398	0.020	0.98999	0.76315	0.0372
0.023	1.07514	3.12469	0.0418	0.024	0.99003	0.76352	0.0370
0.028	1.07514	3.12880	0.0458	0.035	0.99013	0.76428	0.0360
RbBr in 40 % DMSO + 60 %Water							
0.013	1.04610	1.92616	0.0235				
0.014	1.04613	1.92654	0.0244				
0.015	1.04620	1.92695	0.0249				
0.020	1.04634	1.92855	0.0275				
0.025	1.04652	1.93027	0.0305				

Table 20. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of RbBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 40°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
RbBr in 100.00 %DMSO				RbBr in 20 % DMSO + 80 % Water			
0.011	1.08775	1.58693	0.1726	0.014	0.99904	0.95836	0.0101
0.020	1.08877	1.60428	0.2061	0.020	1.00558	0.95873	0.0112
0.028	1.08977	1.61541	0.2221	0.024	1.00966	0.95891	0.0115
0.030	1.08997	1.61986	0.2259	0.026	1.10118	0.95909	0.0122
0.046	1.09197	1.65900	0.2722	0.033	1.01707	0.95942	0.0127
RbBr in 60 % DMSO + 40 %Water				RbBr in 100.00 %Water			
0.011	1.06885	2.85583	0.0322	0.010	0.96949	0.76213	0.0389
0.014	1.06895	2.85863	0.0367	0.013	0.96956	0.76245	0.0379
0.020	1.06905	2.86214	0.0397	0.020	0.96968	0.76315	0.0372
0.023	1.06914	2.86421	0.0419	0.024	0.96974	0.76352	0.0369
0.028	1.06924	2.86792	0.0457	0.035	0.96997	0.76428	0.0352
RbBr in 40 % DMSO + 60 %Water							
0.013	1.04016	1.61824	0.0233				
0.014	1.04023	1.61824	0.0244				
0.015	1.04031	1.61825	0.0252				
0.020	1.04053	1.61826	0.0281				
0.025	1.04072	1.61829	0.0305				

Table 21. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of RbBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 45°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
RbBr in 100.00 %DMSO				RbBr in 20 % DMSO + 80 % Water			
0.011	1.09642	1.51502	0.1770	0.014	0.97970	0.84924	0.0101
0.020	1.09652	1.53091	0.2061	0.020	0.97987	0.84956	0.0112
0.027	1.09658	1.54152	0.2221	0.024	0.98002	0.84972	0.0115
0.030	1.09660	1.54934	0.2384	0.026	0.98014	0.84989	0.0122
0.056	1.09690	1.58094	0.2725	0.033	0.98028	0.85026	0.0133
RbBr in 60 % DMSO + 40 % Water				RbBr in 100.00 %Water			
0.011	1.06011	2.78480	0.0322	0.010	0.95683	0.53673	0.0382
0.014	1.06031	2.78754	0.0367	0.013	0.95695	0.53700	0.0378
0.020	1.06051	2.79096	0.0398	0.020	0.95764	0.53751	0.0374
0.023	1.06071	2.79292	0.0418	0.024	0.95831	0.53777	0.0372
0.028	1.06091	2.79686	0.0463	0.035	0.95944	0.53832	0.0363
RbBr in 40 % DMSO + 60 % Water							
0.013	1.03854	1.50158	0.0235				
0.014	1.03855	1.50188	0.0244				
0.015	1.03856	1.50219	0.0249				
0.020	1.03861	1.50345	0.0275				
0.025	1.03865	1.50495	0.0312				

Table 22. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of CsBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 25°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
CsBr in 100.00 %DMSO				CsBr in 20 % DMSO + 80 % Water			
0.021	2.01450	2.01450	0.1691	0.010	1.02426	1.34142	0.0076
0.031	2.03074	2.03074	0.1875	0.015	1.02427	1.34171	0.0083
0.037	2.04559	2.04559	0.2095	0.020	1.02427	1.34203	0.0089
0.054	2.07381	2.07381	0.2369	0.026	1.02428	1.34235	0.0093
0.076	2.10960	2.10960	0.2657	0.031	1.02429	1.34268	0.0099
CsBr in 60 % DMSO + 40 %Water				CsBr in 100.00 %Water			
0.012	1.08283	3.41998	0.0101	0.009	0.99674	0.89360	0.0381
0.020	1.08295	3.42843	0.0165	0.010	0.99685	0.89373	0.0377
0.025	1.08301	3.43032	0.0199	0.013	0.99703	0.89408	0.0364
0.031	1.08311	3.43153	0.0231	0.020	0.99736	0.89469	0.0343
0.036	1.08319	3.43526	0.0257	0.026	0.99759	0.89502	0.0330
CsBr in 40 % DMSO + 60 %Water							
0.010	1.05438	3.22458	0.0111				
0.014	1.05453	3.22636	0.0140				
0.019	1.05478	3.22839	0.0165				
0.021	1.05482	3.22922	0.0174				
0.025	1.05492	3.23076	0.0191				

Table 23. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of CsBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 30°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
CsBr in 100.00 %DMSO				CsBr in 20 % DMSO + 80 % Water			
0.021	1.09024	1.84913	0.1519	0.010	1.02024	1.33226	0.0081
0.031	1.09046	1.86860	0.1875	0.015	1.02027	1.33258	0.0086
0.037	1.09076	1.88129	0.2067	0.020	1.02029	1.33285	0.0089
0.054	1.09114	1.90263	0.2235	0.026	1.02032	1.33320	0.0094
0.076	1.09171	1.93546	0.2542	0.031	1.02035	1.33341	0.0095
CsBr in 60 % DMSO + 40 %Water				CsBr in 100.00 %Water			
0.012	1.08187	3.41998	0.0101	0.009	0.99711	0.80322	0.0374
0.020	1.08195	3.42843	0.0166	0.010	0.99711	0.80333	0.0370
0.025	1.08201	3.43032	0.0205	0.013	0.99713	0.80367	0.0361
0.031	1.08205	3.43153	0.0235	0.020	0.99716	0.80430	0.0347
0.036	1.08212	3.43526	0.0257	0.026	0.99718	0.804648	0.0338
CsBr in 40 % DMSO + 60 %Water							
0.010	1.05249	2.22347	0.0111				
0.014	1.05255	2.22469	0.0140				
0.019	1.05267	2.22610	0.0165				
0.021	1.05272	2.22680	0.0178				
0.025	1.05278	2.22775	0.0192				

Table 24. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of CsBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 35 °C.

C Mol dm ⁻³	Density (ρ) g cm ⁻³	Viscosity (η) cP	Relative Viscosity (η_r)	C Mol dm ⁻³	Density (ρ) g cm ⁻³	Viscosity (η) cP	Relative Viscosity (η_r)
CsBr in 100.00 %DMSO				CsBr in 20 % DMSO + 80 % Water			
0.020	1.08725	1.69490	0.1810	0.010	1.01547	1.05447	0.0070
0.026	1.08775	1.70277	0.1898	0.014	1.01548	1.05486	0.0090
0.030	1.08845	1.71018	0.2010	0.020	1.01549	1.05542	0.0114
0.044	1.08945	1.72824	0.2201	0.026	1.01551	1.05607	0.0137
0.056	1.09095	1.75068	0.2525	0.031	1.01552	1.05654	0.0151
CsBr in 60 % DMSO + 40 %Water				CsBr in 100.00 %Water			
0.011	1.07287	3.10658	0.0050	0.009	0.98985	0.69422	0.0415
0.020	1.07295	3.11087	0.0133	0.010	0.98987	0.69732	0.0412
0.024	1.07299	3.11155	0.0135	0.013	0.98991	0.70592	0.0409
0.030	1.07305	3.11481	0.0181	0.020	0.98996	0.71608	0.0400
0.034	1.07310	3.11724	0.0213	0.026	0.99001	0.72418	0.0395
CsBr in 40 % DMSO + 60 %Water							
0.010	1.04633	1.93148	0.0546				
0.014	1.04653	1.93410	0.0572				
0.019	1.04678	1.93705	0.0599				
0.021	1.04690	1.93803	0.0605				
0.025	1.04710	1.84016	0.0630				

Table 25. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of CsBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 40 °C.

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm ⁻³	g cm ⁻³	cP	(η_r)	Mol dm ⁻³	g cm ⁻³	cP	(η_r)
CsBr in 100.00 % DMSO				CsBr in 20 % DMSO + 80 % Water			
0.020	1.08735	1.59899	0.1810	0.010	1.00546	0.95788	0.0070
0.026	1.08775	1.60642	0.1898	0.014	1.00768	0.95823	0.0090
0.030	1.08845	1.61341	0.2010	0.020	1.01260	0.95875	0.0114
0.044	1.08945	1.63044	0.2201	0.026	1.01751	0.95933	0.0137
0.056	1.09095	1.65067	0.2499	0.031	1.01952	0.95980	0.0153
CsBr in 60 % DMSO + 40 % Water				CsBr in 100.00 % Water			
0.011	1.06777	2.84756	0.0050	0.009	0.96882	0.62389	0.0417
0.020	1.06795	2.85149	0.0133	0.010	0.96885	0.62402	0.0416
0.024	1.06805	2.85211	0.0135	0.013	0.96890	0.62435	0.0409
0.030	1.06818	2.85536	0.0187	0.020	0.96897	0.62487	0.0390
0.034	1.06825	2.85734	0.0210	0.026	0.96904	0.62518	0.0380
CsBr in 40 % DMSO + 60 % Water							
0.010	1.04613	1.62703	0.0546				
0.014	1.04643	1.62923	0.0572				
0.019	1.04673	1.63172	0.0599				
0.021	1.04682	1.63255	0.0605				
0.025	1.04701	1.63437	0.0631				

Table 26. The density (g cm^{-3}), viscosity (cP) and relative viscosity (η_r) of CsBr in dimethyl sulphoxide (DMSO), water (H_2O) and different mixtures of DMSO and water at 45°C .

C	Density (ρ)	Viscosity (η)	Relative Viscosity	C	Density (ρ)	Viscosity (η)	Relative Viscosity
Mol dm^{-3}	g cm^{-3}	cP	(η_r)	Mol dm^{-3}	g cm^{-3}	cP	(η_r)
CsBr in 100.00 %DMSO				CsBr in 20 % DMSO + 80 % Water			
0.020	1.09576	1.52585	0.1810	0.010	0.98029	0.84893	0.0083
0.026	1.09594	1.53294	0.1898	0.014	0.98038	0.84915	0.0092
0.030	1.09611	1.53961	0.2010	0.020	0.98046	0.84946	0.0104
0.044	1.09644	1.55589	0.2201	0.026	0.98053	0.84983	0.0117
0.056	1.09697	1.57488	0.2491	0.031	0.98046	0.85015	0.0129
CsBr in 60 % DMSO + 40 %Water				CsBr in 100.00 %Water			
0.011	1.06019	2.77674	0.0050	0.009	0.96204	0.53680	0.0414
0.020	1.06221	2.78049	0.0131	0.010	0.96257	0.53690	0.0412
0.024	1.06342	2.78130	0.0138	0.013	0.96424	0.53720	0.0409
0.030	1.06462	2.78458	0.0191	0.020	0.96676	0.53773	0.0400
0.034	1.06582	2.78627	0.0213	0.026	0.96884	0.53803	0.0393
CsBr in 40 % DMSO + 60 %Water							
0.010	1.03832	1.50573	0.0546				
0.014	1.03844	1.50777	0.0572				
0.019	1.03856	1.51007	0.0599				
0.021	1.03865	1.51102	0.0614				
0.025	1.03876	1.51249	0.0630				

The A - coefficient accounts for ion-ion interactions and the B parameter is a measure of the ion solvent interactions. In all the cases, the plots of $\Psi = (\eta - \eta_0) / \eta_0 C^{1/2}$ versus $C^{1/2}$ (Figs 4.6-4.30) are found to be linear over the whole concentration range studied. The A and B coefficients in each case were obtained from intercepts and slopes of these plots by the method of least squares.

The values of the A - coefficients obtained at 25, 30, 35, 40 and 45 °C are listed in Table 27. An irregular variation is observed in A - coefficient values for all electrolytes in various compositions of solvent mixtures. A - coefficient values vary with composition of solvent and with the temperature of solution respectively. The negative as well as positive values of “ A ” shows incomplete dissociation and ion-association. Smaller values of A –coefficient at higher composition of water in binary solvent mixtures imply that ion hydration is greater than ion-ion interaction.

The B coefficient values obtained at 25, 30, 35, 40 and 45 °C for various salts in the different solvent mixtures are listed in Table 28. It is found that the viscosity B - coefficients for all the electrolytes in pure DMSO are large and positive. It is also noted that the viscosities of the solutions are increased with an increase in the concentration of electrolytes, which is a common feature in most non-aqueous solvents like sulpholane (TMS) [45]; hexamethylphosphotriamide (HMPT) [47]; acetonitrile (AN) [146]; propylene carbonate (PC) [147, 148]; tetramethylurea (TMU) [146, 149]; Methanol [64]; N-methylformamide [155]; and ethylenecarbonate (EC) [46]. The large and positive values of viscosity B - coefficients indicate the structure making effect of ions on the DMSO solvent.

Table 27. Viscosity $A \times 10^2$ ($\text{dm}^{3/2} \text{mol}^{-1/2}$) coefficients of the Jones-Dole equation for some electrolytes in DMSO mixtures at 25, 30, 35, 40 and 45 °C.

mol% DMSO	LiBr	NaBr	Kbr	Rbr	CsBr
25 °C					
100 % pure DMSO	2.8661	9.8062	9.2664	6.7103	5.7656
60 % Mix 1	25.1940	27.1670	-0.6577	-0.3397	-1.0086
40 % Mix 2	24.6540	32.3120	-0.8768	-0.3218	-0.2357
20 % Mix 3	6.1982	8.7822	-0.0234	-0.1705	0.4539
0 % Pure H ₂ O	13.7910	5.2054	4.3917	4.0855	4.5900
30 °C					
100 % pure DMSO	10.495	10.8680	9.7182	80.011	5.1552
60 % Mix 1	25.194	27.5610	-0.6655	20.306	-1.025
40 % Mix 2	24.446	32.1680	-0.6889	14.71	-0.265
20 % Mix 3	6.2351	8.3825	0.0669	3.752	0.6003
0 % Pure H ₂ O	14.111	5.0302	4.2926	-5.0063	4.2738
35 °C					
100 % pure DMSO	10.414	24.024	17.742	77.957	7.1603
60 % Mix 1	12.664	14.506	-0.4928	20.683	-1.4653
40 % Mix 2	22.614	7.6161	-0.2794	15.142	4.0501
20 % Mix 3	6.0458	5.3827	-0.1673	3.8031	-0.4093
0 % Pure H ₂ O	12.436	3.4786	4.2137	-3.1916	4.4441
40 °C					
100 % pure DMSO	10.586	24.636	19.3614	74.503	7.5413
60 % Mix 1	12.526	14.523	-0.5158	20.743	-1.5004
40 % Mix 2	22.581	7.3198	-0.289	0.1578	4.034
20 % Mix 3	5.6927	4.8472	-0.5351	4.2114	-0.4352
0 % Pure H ₂ O	12.419	3.3949	4.1804	-4.0002	4.7717
45 °C					
100 % pure DMSO	9.2297	24.845	19.303	73.208	7.6562
60 % Mix 1	12.338	14.441	-0.5997	21.403	-1.5349
40 % Mix 2	22.458	7.2625	-0.3952	16.5	3.9948
20 % Mix 3	84.443	4.9405	-0.8029	0.1501	0.1947
0 % Pure H ₂ O	12.398	3.3515	4.9878	-2.105	4.6603

Table 28. Viscosity B ($\text{dm}^3 \text{mol}^{-1}$) coefficients of the Jones-Dole equation for some electrolytes in DMSO mixtures at 25, 30, 35, 40 and 45 °C.

mol% DMSO	LiBr	NaBr	KBr	RbBr	CsBr
25 °C					
100 % pure DMSO	0.92944	0.83699	0.83800	0.82867	0.76429
60 % Mix 1	0.21167	0.20173	0.20013	0.19992	0.18800
40 % Mix 2	0.16664	0.13318	0.17194	0.14284	0.13545
20 % Mix 3	0.12651	0.08782	0.05053	0.03696	0.29902
0 % Pure H ₂ O	0.11482	0.05205	-0.04727	-0.06815	-0.08101
30 °C					
100 % pure DMSO	0.87964	0.80682	0.81084	0.80011	0.75020
60 % Mix 1	0.21560	0.21100	0.20406	0.20306	0.19050
40 % Mix 2	0.18203	0.15567	0.14906	0.14710	0.13834
20 % Mix 3	0.13643	0.10225	0.00751	0.03752	0.20411
0 % Pure H ₂ O	0.10913	0.05304	-0.03903	-0.05006	-0.05620
35 °C					
100 % pure DMSO	0.86298	0.78512	0.79489	0.77957	0.74459
60 % Mix 1	0.22087	0.21857	0.20799	0.20683	0.19200
40 % Mix 2	0.19405	0.14944	0.15674	0.15142	0.13961
20 % Mix 3	0.14354	0.11508	0.11157	0.03803	0.10903
0 % Pure H ₂ O	0.10752	0.05340	-0.03217	-0.03192	-0.03104
40 °C					
100 % pure DMSO	0.83111	0.75006	0.75080	0.74503	0.72111
60 % Mix 1	0.23022	0.22210	0.21087	0.20743	0.19502
40 % Mix 2	0.20003	0.17009	0.16071	0.15779	0.14100
20 % Mix 3	0.17006	0.15003	0.14081	0.04211	0.11118
0 % Pure H ₂ O	0.11009	0.06400	-0.02943	-0.04000	-0.06065
45 °C					
100 % pure DMSO	0.81008	0.73681	0.75078	0.73208	0.71410
60 % Mix 1	0.24040	0.22222	0.21423	0.21403	0.19806
40 % Mix 2	0.21010	0.17080	0.15502	0.16500	0.14506
20 % Mix 3	0.18000	0.15008	0.15009	0.15010	0.06084
0 % Pure H ₂ O	0.11500	0.06401	-0.02800	-0.02105	-0.048203

It is clear from the literature that in dipolar aprotic solvents [118], the structure breaking contribution is negligible due to the positive and large values of the B –coefficients that come from the tendency of the ions to attract the solvent molecules around themselves centrosymmetrically. When an ion is introduced in to a liquid, it interacts with the solvent dipole to form the solvent sheath, and cause the alteration in the liquid structure and the orientation of the molecules surrounding the ion. The degree to which the ion alters the neighboring solvent structure depends on the ionic charge, size, and shape.

According to literature [151] the interaction energy between a small alkali metal ion and the solvent dipole in DMSO is at least six times greater than the solvent- solvent (DMSO-DMSO) interaction. The same effect is observed in the present study which shows that the interaction of small alkali metal ions especially Li^+ and Na^+ with DMSO is much stronger than the DMSO-DMSO interaction. These strong interactions immobilize neighboring DMSO molecules and produce large obstructions to their flow, which results in an increase in solution viscosity and causes large B -coefficients values which measure the structure making contribution. It is clear from Table 28 that the B -coefficient values of LiBr in DMSO are larger than the B -coefficient values of CsBr. The experimentally observed values of the viscosity B - coefficients for the salts LiBr, NaBr, KBr, RbBr and CsBr in pure DMSO are in good agreement with the available literature values at 25, 35 and 45 °C and the direct comparison of the present B -coefficient values with the literature values are shown in Table 29. The values of the B - coefficients of alkali metal bromides in pure DMSO at all observed temperatures show a small decrease from LiBr to CsBr. With the rise of temperature the B values decreases, indicating that they behave as a structure maker in DMSO. The decrease in B - coefficient values

is due to the increase in crystal radii of alkali metals. Similar behavior has been observed in some other non-aqueous solvents [38, 141, 146, 153, 154].

Table 29. Comparison of. Viscosity B -coefficients ($\text{dm}^3 \text{mol}^{-1}$) of electrolytes in DMSO with literature values at 25, 35 and 45 °C.

Ions	25 °C		35 °C		45 °C	
	Lit	Our	Lit	Our	Lit	Our
LiBr	0.907	0.929 ±0.004	0.860	0.863 ±0.002	0.820	0.810 ±0.003
NaBr	0.833	0.837 ±0.004	0.783	0.785 ±0.001	0.739	0.737 ±0.002
KBr	0.843	0.838 ±0.002	0.796	0.795 ±0.001	0.757	0.751 ±0.004
RbBr	0.822	0.828 ±0.004	0.779	0.780 ±0.002	0.744	0.732 ±0.002
CsBr	0.791	0.764 ±0.003	0.748	0.745 ±0.001	0.714	0.714 ±0.001

We will now examine the studies of B - coefficients in binary solvent (DMSO- H_2O) mixtures tabulated in Table 28. For all the alkali metal bromides, a gradual and regular decrease in the values of the B - coefficients is observed as the DMSO content is decreased. Decrease in B - coefficient values show, that the ions cause weaker orientation effects in the solvation layer. In the water rich region the values of B - coefficients are changed gradually with the solvent composition and smaller B - values are then found in DMSO- H_2O system at all the five temperatures. The same trend is observed in the study of KCl and KBr dissolved in H_2O -HMPT (hexamethyl phosphoric triamide) binary mixtures [152] and in another study of the salts NaCl, NaBr, NaI and KCl in H_2O -DMSO mixtures [154].

It is observed in Table 28 that in water the B -coefficients for LiBr and NaBr have small and positive values, which increase with the increase in the concentration of the electrolyte while the B -coefficients values for KBr, RbBr and CsBr are observed to be negative in water.

It is well known that in highly structured solvents, salts like CsBr, CsI, KBr and KI cause B to be negative [70]. The solvents in which negative B values are found [38,70,155], all have molecules capable of forming hydrogen bonding in three dimensions and water is the prime example. The situation is different in the case of LiBr and NaBr. In these salts the B values are positive and due to cations Li^+ and Na^+ which are small and therefore have high surface charge densities. Consequently, such ions will strongly orient adjacent water molecules. The degree of the orientation around the ion in the successive shells and the dielectric saturation will fall off with distance from the ion as shown in Fig; 2 .1, the bulk structure of the solvent being re-established at large distances. So the B -coefficients values of these salts are found to be positive and this trend was also observed during the literature survey [63].

The present measurements of B for alkali metal bromides in pure water at the given temperatures are in good agreement with those by [24, 38]. Direct comparison of B - values from our studies in pure water with those available in the literature is presented in Table 30.

The values of the B -coefficients of the reference salts are presented in Table 3. These values are large and positive in pure DMSO. Relative viscosity data has shown an increase which follows the increase in the concentration of the reference salts in DMSO. The B -coefficients values decrease slightly with the increase in the temperature.

Table 30. Comparison of Viscosity B -coefficients ($\text{dm}^3 \text{mol}^{-1}$) of electrolytes in H_2O with literature values at 25, 35 and 45 °C.

Temp °C	LiBr		NaBr		KBr	
	our	Lit	our	Lit	our	Lit
25	0.1448 ± 0.001	0.113 ¹	0.0521 ± 0.004	0.05	-0.0473 ² ± 0.003	-0.047
30	0.109 ± 0.003	0.109 ¹	0.053 ± 0.002	0.05	-0.039 ± 0.004	-0.034
35	0.1075 ± 0.002	0.109	0.0534 ± 0.004	0.06	-0.032 ± 0.002	-0.030
40	0.1101 ± 0.001	0.112	0.064 ± 0.003	0.07	-0.029 ± 0.002	-0.011
45	0.115 ± 0.003	0.115	0.064 ± 0.004	0.07		

Table 31. B coefficients of reference salts $\text{BU}_4 \text{NBPh}_4$ and in $\text{BU}_4 \text{NBr}$ in DMSO at 25,30,35, 40 and 45 °C.

Temperature	$B/\text{dm}^3 \text{mol}^{-1}$	
	$\text{BU}_4 \text{NBPh}_4$	$\text{BU}_4 \text{NBr}$
25 °C	1.270 ± 0.001	0.901 ± 0.003
30 °C	1.265 ± 0.003	0.882 ± 0.002
35 °C	1.259 ± 0.002	0.876 ± 0.002
40 °C	1.254 ± 0.003	0.853 ± 0.002
45 °C	1.213 ± 0.002	0.835 ± 0.003

It is clear from Table 31 that in general, the values of the B -coefficients found in the present study are consistent with the literature values for similar substances. B -coefficients values are comparable with the literature values [40].

The B -coefficients of alkali metal bromide in different compositions of DMSO in the present work are positive and much higher than water. DMSO is generally considered bulkier and less structured than water. A solute with positive B -coefficients in a given solvent is considered to have a structure making effect. On the other hand in the case of B -coefficients of alkali metal bromides in different compositions of binary solvent mixtures (DMSO) and in pure water, less positive and negative values were observed respectively. A solute with less positive and negative B -coefficient in a given solvent is considered to be a structure breaking solute. The present results indicate that all salts in an aqueous medium having negative B -coefficients behave as structure breakers, while in DMSO all salts having positive B -coefficient values behave as structure makers. In DMSO-H₂O mixtures the B -coefficient values are less positive showing the weak structure making effect.

4.3. Ionic B -coefficients

To achieve a better understanding of ion-solvent interactions, it is necessary to split the B -coefficients into the individual ionic B -coefficients, B_+ and B_- . However, there is no experimental method related to viscosity which separately determines the ionic B -coefficients. A number of methods have been suggested by various workers [38] to split B -coefficients of electrolytes into the contributions of the individual ions.

Most of these methods depend upon the choice of the reference salt for which cation-solvent and anion-solvent interactions may be considered equal. This criterion is realized for large polyatomic ions that are minimally solvated, so we chose the tetra butyl ammonium tetra phenyl borate and tetrabutylammoniumbromide. In the present work we have used the Gill and Sharma approach [18] to resolve viscosity B -coefficients into the contributions of individual ions. This method like the method of Krumgalz [38] is based on the assumption that BU_4N^+ and Ph_4B^- ions with large alkyl groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constants. Studies by Gill *et al.*, [43, 44] confirm that the ionic radii of BU_4N^+ and Ph_4B^- in non-aqueous solvents and in non-aqueous mixed solvents remain constant and equal to 5.00 and 5.35Å respectively, with an average uncertainty of $\pm 2\%$.

The splitting of B into ionic B_{\pm} have been resolved by the equation

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{BU}_4\text{N}^+}} = \frac{r^3_{\text{Ph}_4\text{B}^-}}{r^3_{\text{BU}_4\text{N}^+}} = \frac{(5.35)^3}{(5.00)^3} \quad 3$$

$$B_{\text{(exp) Bu}_4\text{NBPh}_4} = B_{\text{Ph}_4\text{B}^-} + B_{\text{BU}_4\text{N}^+} \quad 4$$

Using the equation 3 and 4, the B -coefficients have been divided in to ionic B_+ and B_- . The values are shown in Table 32. This Table shows that the ionic B_+ and B_- values for BU_4N^+ , Ph_4B^- and Br^- ions decrease with increasing temperature from 25 to 45 °C. The B_+ values for cations from Li^+ to Cs^+ are decreasing as the ionic radius increases, except for K^+ . The ionic B -coefficient B_+ value for Na^+ is 0.5070 and for K^+ is 0.508 dm^3/mol at 25 °C respectively. So K^+ has slightly higher B_+ values than Na^+ and these values are in good agreement with the literature values [152]. The same pattern of B_+ values of

Na⁺ and K⁺ is observed in other non-aqueous solvents [150,152] and the similar inversion, in which K⁺ has slightly higher B_+ values than Na⁺ is observed at four other temperatures, viz 30, 35, 40 and 45 °C during this study.

Table 32. Ionic B_{\pm} coefficients of ions in DMSO at 25, 30, 35, 40 and 45 °C.

	$B_{\pm}/\text{dm}^3\text{mol}^{-1}$							
	BU ₄ N ⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	BPh ₄ ⁺	Br ⁻
25 °C	0.5708 ± 0.002	0.5994 ± 0.001	0.5070 ± 0.002	0.5080 ± 0.001	0.4987 ± 0.003	0.4343 ± 0.002	0.6992 ± 0.002	0.3300 ± 0.002
30 °C	0.5685 ± 0.003	0.5662 ± 0.003	0.4934 ± 0.002	0.4974 ± 0.001	0.4876 ± 0.001	0.4368 ± 0.002	0.6965 ± 0.003	0.3135 ± 0.001
35 °C	0.5660 ± 0.001	0.5530 ± 0.003	0.4751 ± 0.004	0.4849 ± 0.001	0.4695 ± 0.003	0.4346 ± 0.002	0.6933 ± 0.002	0.3100 ± 0.002
40 °C	0.5636 ± 0.001	0.54171 ± 0.003	0.4607 ± 0.002	0.4614 ± 0.002	0.4556 ± 0.003	0.4317 ± 0.001	0.6964 ± 0.001	0.2894 ± 0.003
45 °C	0.5452 ± 0.002	0.5202 ± 0.002	0.4470 ± 0.002	0.4609 ± 0.001	0.4422 ± 0.001	0.4243 ± 0.003	0.6678 ± 0.001	0.2898 ± 0.002

The reason for this inversion can be explained by the suggestion of Bicknel [156] that both of these ions have high charge densities and therefore strongly oriented solvent molecules creating a sheath of firmly attached solvent. This leads to larger values for the ionic B_{\pm} -coefficients for Na⁺ and K⁺, but the K⁺ ion complex would be slightly larger than the Na⁺ complex, which results in larger B_{\pm} coefficients for K⁺ than Na⁺.

The B_{\pm} -coefficients in Table 32 for other ions are less than those of Na⁺ and K⁺ and decreases with an increase in ionic size since the small charge density of the larger ions cause's only weak orientation effects in the primary solvation sheath. Therefore small distortion of the solvent structure in the vicinity of such larger ions leads to small B_{\pm} -coefficient values.

This above method of splitting of electrolyte B -coefficients in to ionic contributions is not applicable in aqueous solutions. Gurney's method [12] for aqueous solution was thus used. This method simply assumes that the positive and negative ion contributions are simply equal and thus:

$$B(\text{K}^+) = B(\text{Cl}^-) = \frac{1}{2} B(\text{KCl})$$

This sub division cannot be applied in the case of organic solvents because the behavior of the ions in the non-aqueous solvents is entirely different [40, 52]. The Gurney approach is used in the present study whenever water-rich solutions are involved. Many other researchers have adopted the same practice in their studies for water rich solvent mixtures [154]. Using the Gurney approach, the values of the ionic B -coefficients for the ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and Br^-) in pure water and in DMSO- H_2O mixtures at 25, 30, 35, 40 and 45 °C were obtained and are reported in Table 33.

In DMSO- H_2O mixtures where the mole percentage of DMSO is 60%, 40% and 20%, all electrolytes have small positive ionic B -coefficient values which increase with the increase of temperature indicating that all these electrolytes have a structure breaking component. This character is due to the Br^- ion because it has a smaller ionic B -coefficient value and also has negative values in 40% and 20%, DMSO- H_2O mixtures.

In DMSO- H_2O mixtures, the B -coefficient increases with an increase in DMSO content. The addition of dimethylsulphoxide to water causes the breaking of water structure by formation of DMSO- H_2O bonds which leads to a less structured solvent. There is thus a decrease in the structure breaking ability of the ions compared with that of pure water.

Table 33. Ionic B_{\pm} coefficients of ions in Mix 1, Mix 2, Mix 3 and water at 25, 30, 35, 40 and 45 °C.

	Li ⁺	Na ⁺	B _± /dm ³ mol ⁻¹				
			K ⁺	Rb ⁺	Cs ⁺	Br ⁻	Cl ⁻
60 % Mix 1							
25 °C	0.1745	0.1646	0.163	0.16279	0.15087	0.03713	0.163
30 °C	0.177	0.1724	0.155	0.1645	0.1519	0.0386	0.1655
35 °C	0.1809	0.1786	0.168	0.1668	0.1520	0.0400	0.168
40 °C	0.1894	0.1812	0.170	0.1666	0.1542	0.0409	0.170
45 °C	0.1982	0.1800	0.172	0.1718	0.1558	0.0422	0.172
40 % Mix 2							
25 °C	0.1557	0.12224	0.161	0.1319	0.12451	0.01094	0.1610
30 °C	0.1956	0.1691	0.1625	0.1605	0.1518	-0.01300	0.1625
35 °C	0.2023	0.1577	0.165	0.1597	0.1479	-0.08000	0.1650
40 °C	0.2000	0.1764	0.167	0.0079	0.1473	-0.00629	0.1670
45 °C	0.2156	0.1763	0.1705	0.1705	0.1505	-0.00500	0.1705
20 % Mix 3							
25 °C	0.1490	0.11029	0.0730	0.05942	0.05237	-0.0225	0.6992
30 °C	0.2294	2.343	0.1005	0.1305	0.1134	-0.0930	0.6965
35 °C	0.1570	0.1285	0.1250	0.0515	0.1225	-0.0130	0.6933
40 °C	0.2143	0.1942	0.1850	0.0863	0.1554	-0.0440	0.6964
45 °C	0.2454	0.2155	0.2155	0.0669	0.1263	-0.0650	0.6678
Water							
25 °C	0.1491	0.08632	0.009	-0.0362	-0.0474	-0.0343	-0.009
30 °C	0.1492	0.09307	-0.001	-0.0901	-0.0962	-0.0400	-0.001
35 °C	0.1357	0.08160	0.004	-0.0610	-0.0592	0.0282	-0.040
40 °C	0.1305	0.08443	0.009	-0.0604	0.0461	-0.0204	-0.009
45 °C	0.1290	0.07801	0.014	-0.03505	-0.03421	-0.0140	-0.014

A complete comparison of the present study with the literature is not possible because of meager published ionic B -coefficient values for alkali bromides in DMSO-H₂O mixtures at the given temperatures. The measured ionic B -coefficient values of the ions in water are in good agreement with the values already reported in the literature and the latter are reported in Table 34. In this study it is observed that all the values of ionic B -coefficients of (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) are positive and small showing the weak structure making effects associated with the increase in ionic radius in DMSO-H₂O mixtures [17]. It is also observed that Br⁻ ions maintain negative B -coefficient values in all DMSO-H₂O mixtures, except in 60% DMSO mole fraction. From this it can be concluded that Br⁻ ion behaves as a structure breaker in water and in all DMSO-H₂O mixtures except in 60% DMSO mole fraction mixtures.

The low B_{\pm} values of alkali metal ions and Br⁻ ions in water (Table 33) are due to the breakdown of the tetrahedral structural of water and the formation of strongly structured solvated ion. It is observed that this behavior is more dominant in ions with larger ionic radius [157]. The sequence for the alkali metals for structure breaking effects is in the order of Cs⁺ > Rb⁺ > K⁺, . Li⁺ and Na⁺ ions with particularly large field intensities and with positive B -coefficient values indicate not only an attachment of water molecules to the ions but exert an ordering influence on more remote water molecules [70]. Li⁺ has higher B -coefficient values than Na⁺ showing more structure making capacity. While Cs⁺, Rb⁺, K⁺ and Br⁻ ions have a structure- disrupting influence, so that the viscosity of the solution is reduced and negative ionic B values appear. Cs⁺ and Rb⁺ with larger negative B -coefficient values are stronger structure breakers than K⁺.

Table 34. Comparison of ionic B coefficients of ions in water at 25, 30, 35, 40, 45 °C.

		25	30	35	40	45
Li ⁺	Our	0.1491	0.1492	0.1357	0.1305	0.1290
	Lit	0.147 ¹	0.138 ²	0.135 ²	0.132 ²	0.129 ²
Na ⁺	Our	0.08632	0.09307	0.0816	0.08443	0.07801
	Lit	0.086 ¹	0.084 ¹	0.084 ¹	0.084 ¹	0.084 ¹
K ⁺	Our	0.009	0.001	0.004	0.009	0.014
	Lit	0.009	-0.001 ²	-0.004	0.009 ²	0.014 ²
Rb ⁺	Our	-0.0362	-0.0901	-0.061	-0.0604	-0.03505
	Lit	-0.033	–	–	–	–
Cs ⁺	Our	-0.0474	-0.0962	-0.0592	0.0461	-0.03421
	Lit	-0.046 ²	–	–	–	–
Br ⁻	Our	-0.0343	-0.04	-0.0282	-0.0204	-0.014
	Lit	-0.632 ²	-0.033 ¹	-0.026 ¹	-0.026 ¹	-0.014 ¹

1. Kaminsky, M. *Z. Phys. Chem. (Frankfurt)* 12, 206 (1957).

2. Sacco, A., D. Giglio, A. D. Atti, A, Pettrella. *J. Chem. Soc., Faraday Trans. 1* 77, 2693 (1981).

4.4. Viscosity and the Activation Energy for viscous flow

The activation energy for the viscous flow is the energy required to transfer one mole of solute from one position of equilibrium to another. Activation energy can be explained that each molecule in a liquid may be regarded as occupying roughly an equilibrium position, and before it can pass

through another such position in the direction of flow, it must acquire a definite energy of activation. This energy is also associated with the inter-atomic and inter molecular forces. In general, the higher this energy, the greater is the viscosity of the liquid although other factors also play important role. The relationship between viscosity and energy of activation is given by the following expression [15].

$$\eta = A e^{E_{\eta}/RT}$$

or

$$\log \eta = \log A + E_{\eta}/2.303 RT$$

Where E_{η} is the activation energy for viscous flow and A is constant pre-exponential factor. R is gas constant and T is the absolute temperature.

In the present work, the activation energy for viscous flow of LiBr, NaBr, KBr, RbBr and CsBr at various concentrations in pure DMSO, pure water and DMSO-water mixtures were determined by Arrhenius plots of $\log \eta$ against the reciprocal of absolute temperature. The results are tabulated in Tables 35-39 respectively. The representative plots of apparent energy of activation (E_{η}), $\log \eta$ versus $1/T$ are linear for all alkali metal bromides in DMSO, water and DMSO-water mixture.

Results indicate that the energy of activation is influenced by the concentration of the salts and the composition of the solvent mixtures. It is noted that the energy of activation for the salts (LiBr, NaBr, KBr, RbBr and CsBr) is increased by an increase in their concentration, which coincides with the trends observed by Fahimuddin *et al.* [103].

An increase in activation energy with an increase in concentration is due to the fact that at higher concentrations the ions will cause obstruction to the flow of ions, which will make it difficult to produce vacant sites in the solvent matrix resulting in high values of activation energy. So it is observed that the energy of activation for CsBr is greater than for RbBr, KBr, NaBr and LiBr in DMSO and DMSO-water mixture with some variation in mixture No 2 (40% DMSO-water) for NaBr and RbBr.

Table 35. Activation energy E_{η} (KJ/mol) for viscous flow of LiBr in dimethyl sulphoxide (DMSO), water (H₂O) and different mixtures of DMSO and water.

Conc	E_{η}	Conc	E_{η}	Conc	E_{η}
DMSO		Mix 1		Mix 2	
0.018	10.965	0.016	10.215	0.016	17.673
0.025	10.966	0.021	10.324	0.020	17.678
0.032	10.968	0.024	10.524	0.026	17.698
0.042	11.004	0.031	10.497	0.031	17.703
0.049	11.005	0.049	10.707	0.045	17.710
Mix 3			Water		
0.013	19.623	0.013	20.090		
0.019	19.604	0.018	20.087		
0.027	19.535	0.021	20.226		
0.035	19.589	0.031	20.217		
0.043	19.573	0.043	20.096		

Table 36. Activation energy $E\eta$ (KJ/mol) for viscous flow of NaBr in dimethyl sulphoxide (DMSO), water (H₂O) and different mixtures of DMSO and water.

Conc	$E\eta$	Conc	$E\eta$	Conc	$E\eta$
DMSO		Mix 1		Mix 2	
0.009	10.555	0.018	10.230	0.016	30.969
0.012	10.515	0.020	10.319	0.020	31.110
0.027	10.674	0.025	10.416	0.025	31.244
0.037	11.046	0.030	10.564	0.031	31.489
0.044	11.127	0.041	10.724	0.042	31.779
Mix 3			Water		
0.014	19.709	0.011	20.110		
0.019	19.709	0.013	20.127		
0.023	19.713	0.022	20.175		
0.032	19.709	0.035	20.178		
0.042	19.704	0.047	20.190		

Table 37. Activation energy $E\eta$ (KJ/mol) for viscous flow of KBr in dimethyl sulphoxide (DMSO), water (H₂O) and different mixtures of DMSO and water.

Conc	$E\eta$	Conc	$E\eta$	Conc	$E\eta$
DMSO		Mix 1		Mix 2	
0.009	10.695	0.011	9.491	0.014	17.359
0.015	10.735	0.020	9.463	0.021	17.356
0.030	11.077	0.025	9.461	0.024	17.354
0.044	10.835	0.031	9.456	0.031	17.351
0.057	10.529	0.036	9.420	0.041	17.337
Mix 3			Water		
0.015	19.585	0.010	19.993		
0.020	19.570	0.013	19.997		
0.024	19.560	0.022	20.002		
0.031	19.533	0.029	20.012		
0.035	19.514	0.044	19.972		

Table 38. Activation energy E_{η} (KJ/mol) for viscous flow of RbBr in dimethyl sulphoxide (DMSO), water (H₂O) and different mixtures of DMSO and water.

Conc	E_{η}	Conc	E_{η}	Conc	E_{η}
DMSO		Mix 1		Mix 2	
0.011	11.066	0.011	9.399	0.013	17.366
0.020	11.096	0.015	9.400	0.014	17.366
0.027	11.220	0.020	9.391	0.017	17.392
0.030	11.203	0.023	9.389	0.021	17.380
0.054	11.063	0.028	9.352	0.028	17.370
Mix 3			Water		
0.015	19.589	0.010	18.429		
0.020	19.585	0.013	18.429		
0.024	19.585	0.020	18.457		
0.026	19.577	0.025	18.472		
0.033	19.570	0.037	18.447		

Table 39. Activation energy E_{η} (KJ/mol) for viscous flow of CsBr in dimethyl sulphoxide (DMSO), water (H₂O) and different mixtures of DMSO and water.

Conc	E_{η}	Conc	E_{η}	Conc	E_{η}
DMSO		Mix 1		Mix 2	
0.021	11.084	0.011	9.451	0.010	29.094
0.028	11.283	0.020	9.504	0.014	29.056
0.033	11.415	0.025	9.517	0.019	29.012
0.048	11.529	0.035	9.500	0.021	28.998
0.064	11.763	0.035	9.500	0.025	28.971
Mix 3			Water		
0.010	19.612	0.009	20.002		
0.015	19.610	0.010	20.000		
0.020	19.600	0.013	19.993		
0.026	19.587	0.020	19.983		
0.031	19.577	0.026	19.976		

Another researcher [158] has observed the same type of variation in 7% aqueous butanol mixture of NaCl.

It is also concluded that with the increase in the size of solute particles, the energy of activation increases. This is again based on the; hole theory, that holes are necessary for solvents [159,160] to flow, and greater size of solute particles produce less vacant sites and give increase in viscosity and high values of energy of activation.

It can also be seen from Table that the values of the energy of activation of the flow are greater for all alkali metal bromides in water than DMSO. This can be explained by the presence of a network of hydrogen bonds which accounts for very high viscosities because the energy required to produce a hole will be large.

4.5. Free Energy of Activation for Viscous Flow

Free energy is the energy available to do work. The free energy of activation for viscous flow ΔG can be determined by the equation

$$\Delta G = \Delta U_l = RT \ln \eta V / hN$$

Where h is the Planks constant, N is the Avogadro's number, R is the universal gas constant, and V is volume occupied by 1 mole of pure solvent particles [19]. ΔU_l is the free energy of activation per mole of the pure solvent. For pure solvents DMSO and H₂O, the molar volumes are determined by.

$$V = M/d$$

Where “ M ” is the molecular weight of DMSO or H₂O and “ d ” is the density of the DMSO or H₂O.

For solvent mixtures DMSO - H₂O, the average molecular weight (M_{av}) is used to calculate the molar volume of DMSO - H₂O mixtures.

$$V = M_{av} / d$$

$$M_{av} = M_1 M_2 / (w_1 M_1 + w_2 M_2)$$

M_1 and M_2 are the molecular weights of DMSO and H₂O respectively w_1 and w_2 are the mole fractions of DMSO and H₂O. The calculated average “molecular weights” of 60, 40, and 20% DMSO - H₂O mixtures are 42.0598, 54.0761 and 66.1075 respectively.

The results obtained for the free energy of activation for viscous flow are listed in Table 40 for DMSO - H₂O mixtures, 60, 40, and 20% DMSO - H₂O mixtures at 25, 30, 35, 40 and 45 °C. The values of free energy for DMSO and H₂O at 25 and 35°C can be found in literature [40, 161] and are in good agreement with those measured in the present work. It is also seen in Table 40 that in DMSO and in DMSO rich mixtures (60%) the free energy of activation for viscous flow increases with temperature. A decrease in free energy of activation for viscous flow is also observed in water and water rich mixtures. The same trend is also observed in the literature [162] during the study of the free energy of activation of acid solutions in pure and mixed solvents at 25, 30 and 35°C.

Table 40. Gibbs free energy of activation $\Delta\mu^1$ (KJ/mol) for viscous flow of dimethyl sulphoxide (DMSO), water (H₂O) and different mixtures of DMSO and water at different temperatures.

Temp	DMSO	Water	Mix 1	Mix 2	Mix3
25	14.51	9.158	14.39	14.012	13.387
30	14.57	9.059	14.64	14.249	13.508
35	14.59	9.06708	14.65	14.130	13.19
40	14.68	8.7603	14.68	13.926	13.44
45	14.813	8.54462	14.86	13.949	13.15

4.6. Conclusion

The salvation (ion- solvent interactions) of various salts (LiBr, NaBr, KBr, RbBr and CsBr) in pure solvents (DMSO and Water) and in solvent mixtures (DMSO + Water) is determined at different concentrations by the help viscosity data. The influence of temperature on this study is also observed. The data is analyzed with the help of Jones- Dole Equation.

In the present study, the large and positive values of viscosity *B*-coefficients (ion- solvent interactions) indicate the structure making effect of electrolytes on the DMSO solvent and it is also clear that in DMSO (dipolar aprotic) solvent, the structure breaking contribution is negligible. With the rise of temperature the *B* values decreases, indicating that they behave as a structure maker in DMSO.

The values of *B*- coefficients are changed gradually with the solvent composition and smaller *B*- values are then found in DMSO- H₂O system at all the five temperatures. Decrease in *B*- coefficient values show, that the ions cause weaker orientation effects in the solvation layer.

On splitting the B - coefficients into ionic B - coefficients it is concluded that Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ behave as structure makers in DMSO and in DMSO- H_2O system and this character is more strong in Li^+ , Na^+ than the other alkali metal ions. K^+ , Rb^+ , Cs^+ behave as structure breakers while Li^+ and Na^+ as structure former in H_2O .

It is also observed that Br^- ions maintain negative B -coefficient values in all DMSO- H_2O mixtures except in 60% DMSO mole fraction. From this it can be concluded that Br^- ion behaves as a structure breaker in water and in all DMSO- H_2O mixtures except in 60% DMSO mole fraction mixtures.

It is observed that the values of the energy of activation of the flow are greater for all alkali metal bromides in water than DMSO. It is also noted that the energy of activation for the salts (LiBr , NaBr , KBr , RbBr and CsBr) is increased along with the increase in their concentration.

It is also concluded that the free energy of activation for viscous flow decreases in water and water rich mixtures. An increase in the free energy of activation for viscous flow is also observed with the increase in temperature.

4.7. Future Plan

In future the present work can be extended to alkali metal iodides and alkaline earth metal bromides to analyze the effect of ion size on viscosity *B*- coefficients and on transition state parameters.

This work can also be extended for the study of salvation process in biologically important macro-molecules. Many of these macro-molecules are charged at various positions along the structures and small counter ions will be present to balance the charge on the biological molecule. Carboxylate groups can be present, for instance as the Ca^{+2} , Mg^{+2} or Na^{+} salts and protonated amino groups will be balanced by ions such as Cl^{-} or OH^{-} . Through this study fast transportation of essential electrolytes by the choice of suitable solvents will be helpful to improve biological functions when it is needed.

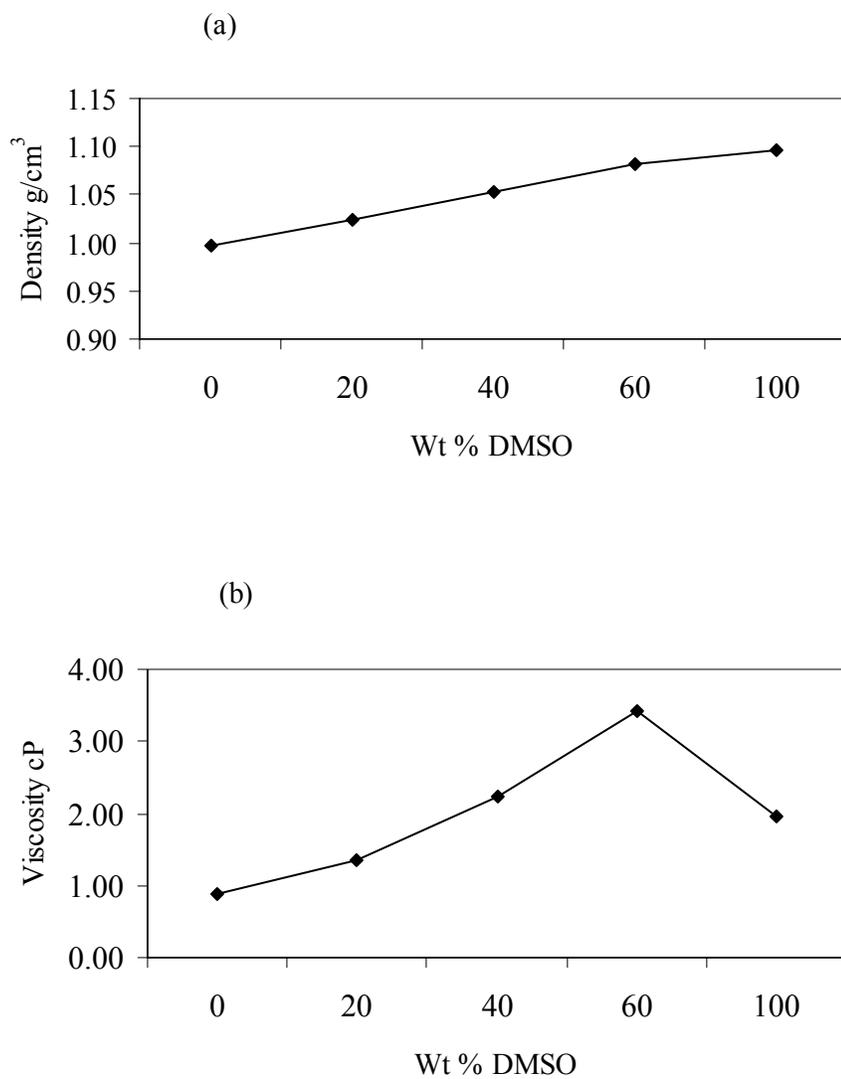


Fig 4.1. Density (a) and viscosity (b) verses wt % DMSO in DMSO-H₂O mixture at 25 °C.

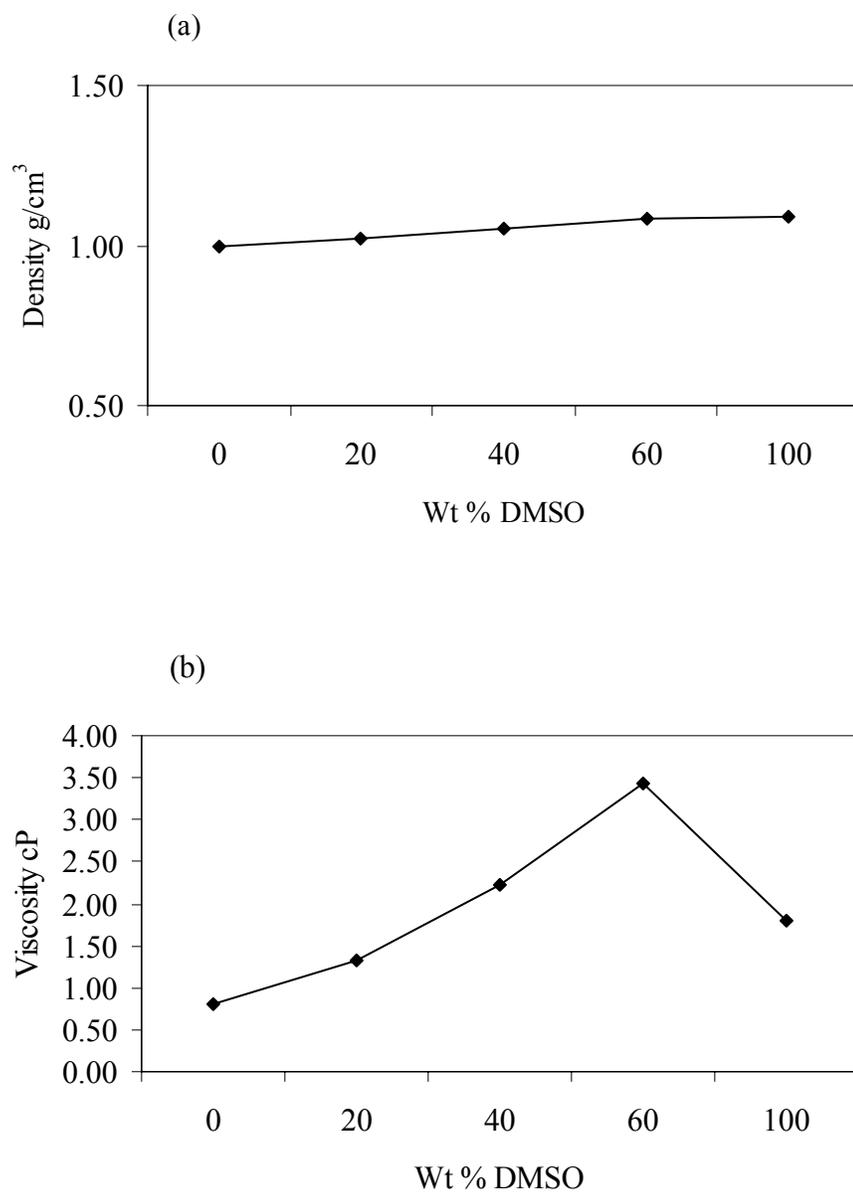


Fig 4.2. Density (a) and viscosity (b) verses wt % DMSO in DMSO-H₂O mixture at 30 °C.

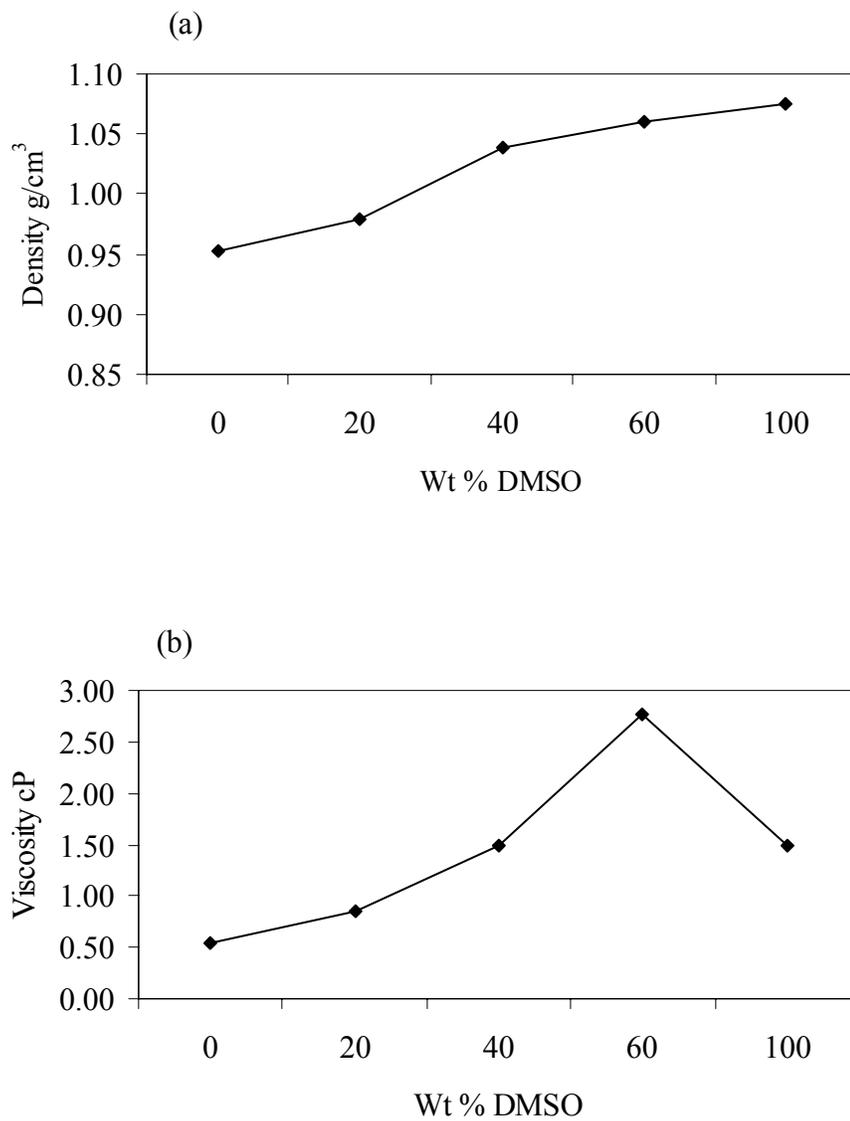


Fig. 4.3. Density (a) and viscosity (b) versus wt % DMSO in DMSO-H₂O mixture at 35 °C.

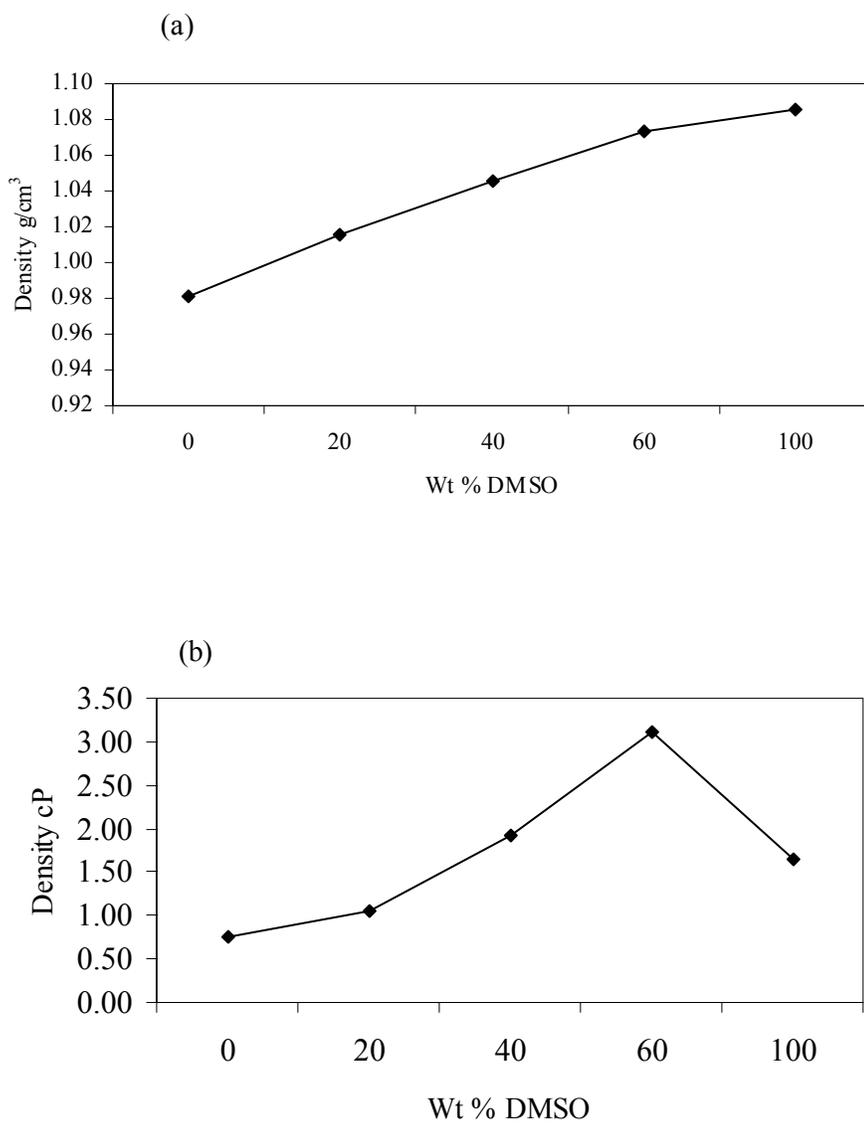


Fig 4.4. Density (a) and viscosity (b) verses wt % DMSO in DMSO-H₂O mixture at 40 °C.

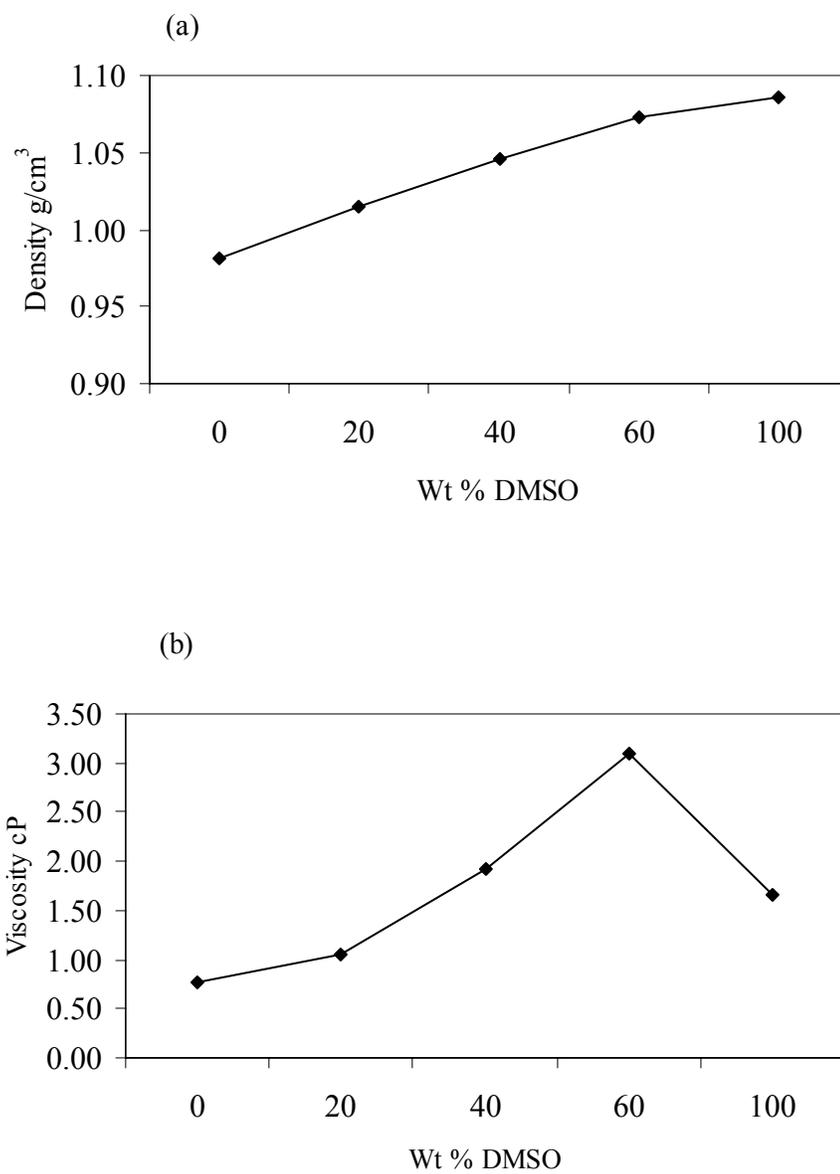


Fig. 4.5. Density (a) and viscosity (b) verses wt % DMSO in DMSO-H₂O mixture at 45 °C.

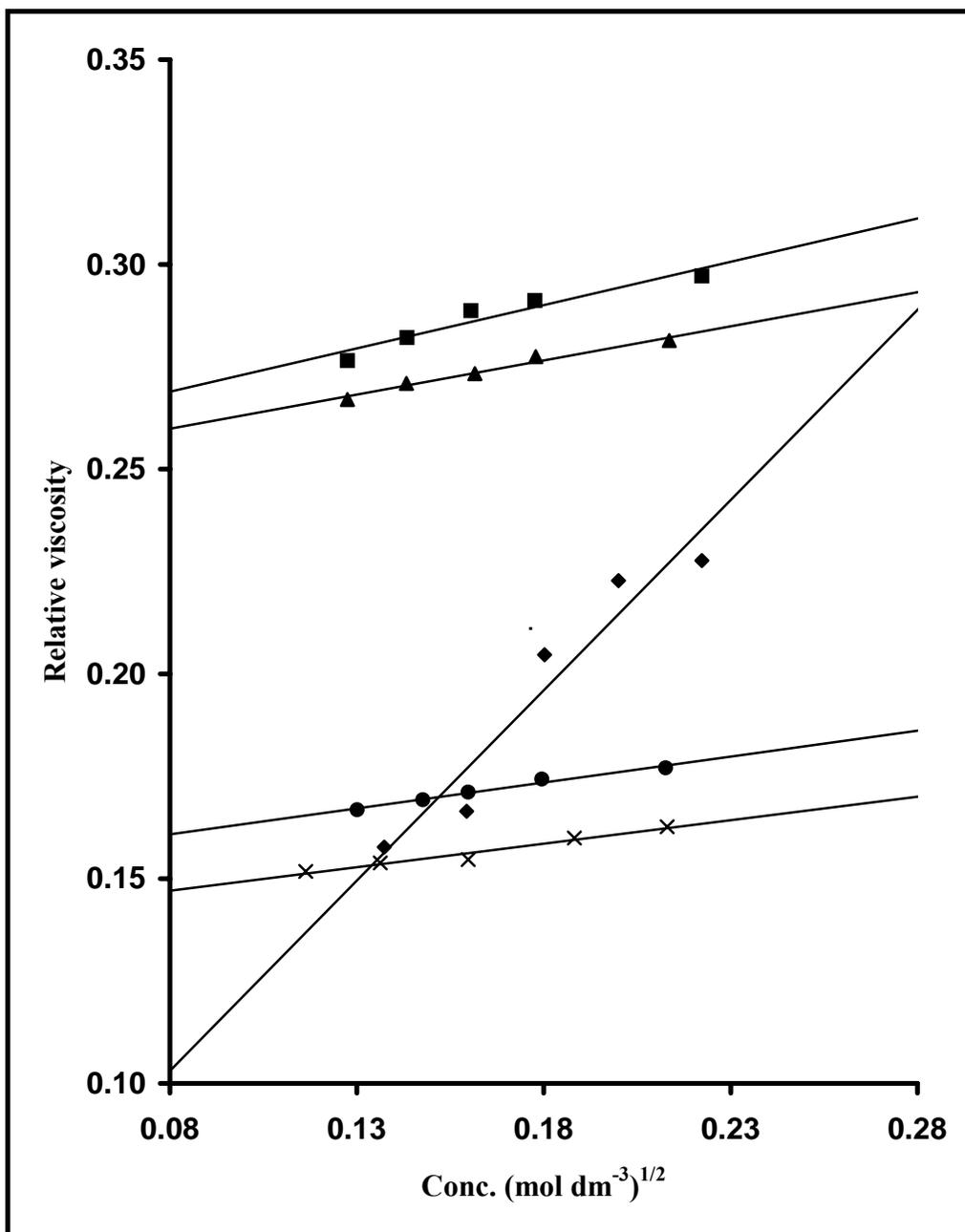


Fig.4.6. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of LiBr at 25 °C. ◆ 100% DMSO, ●, 60 % DMSO, ▲, 40 % DMSO, ●, 20 % DMSO, x 100 % water.

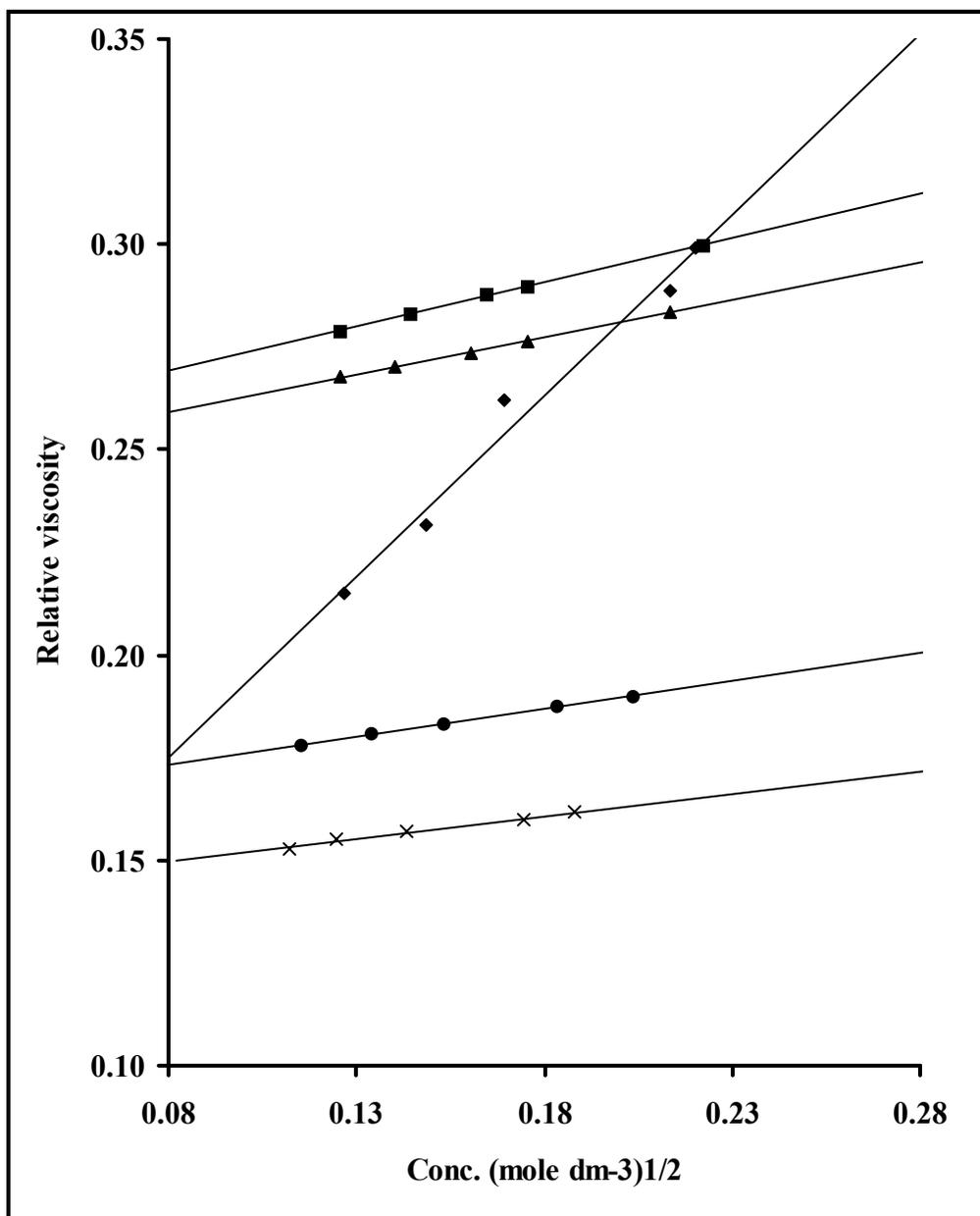


Fig.4.7. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of LiBr at 30 °C. ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

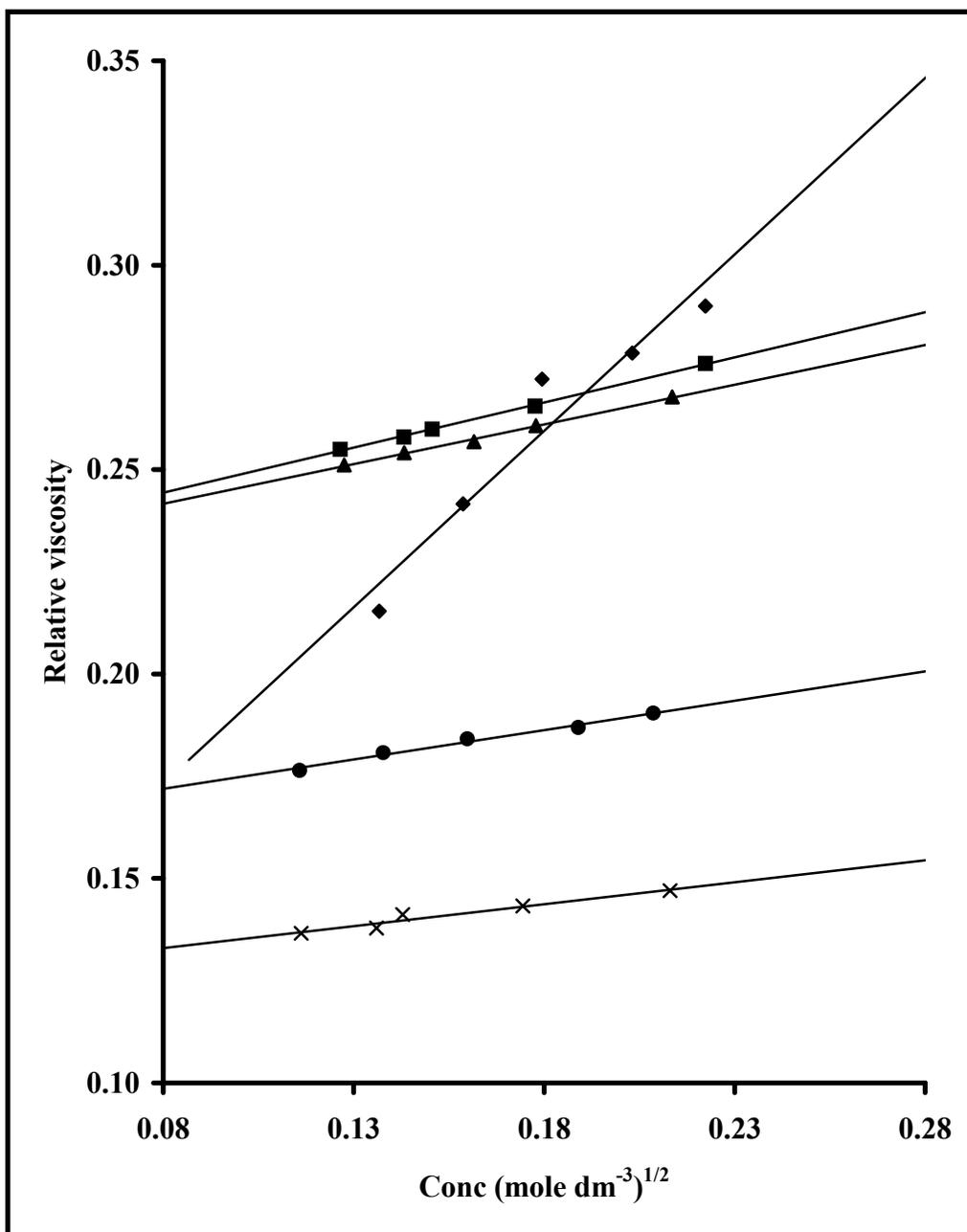


Fig.4.8. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of LiBr at 35°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

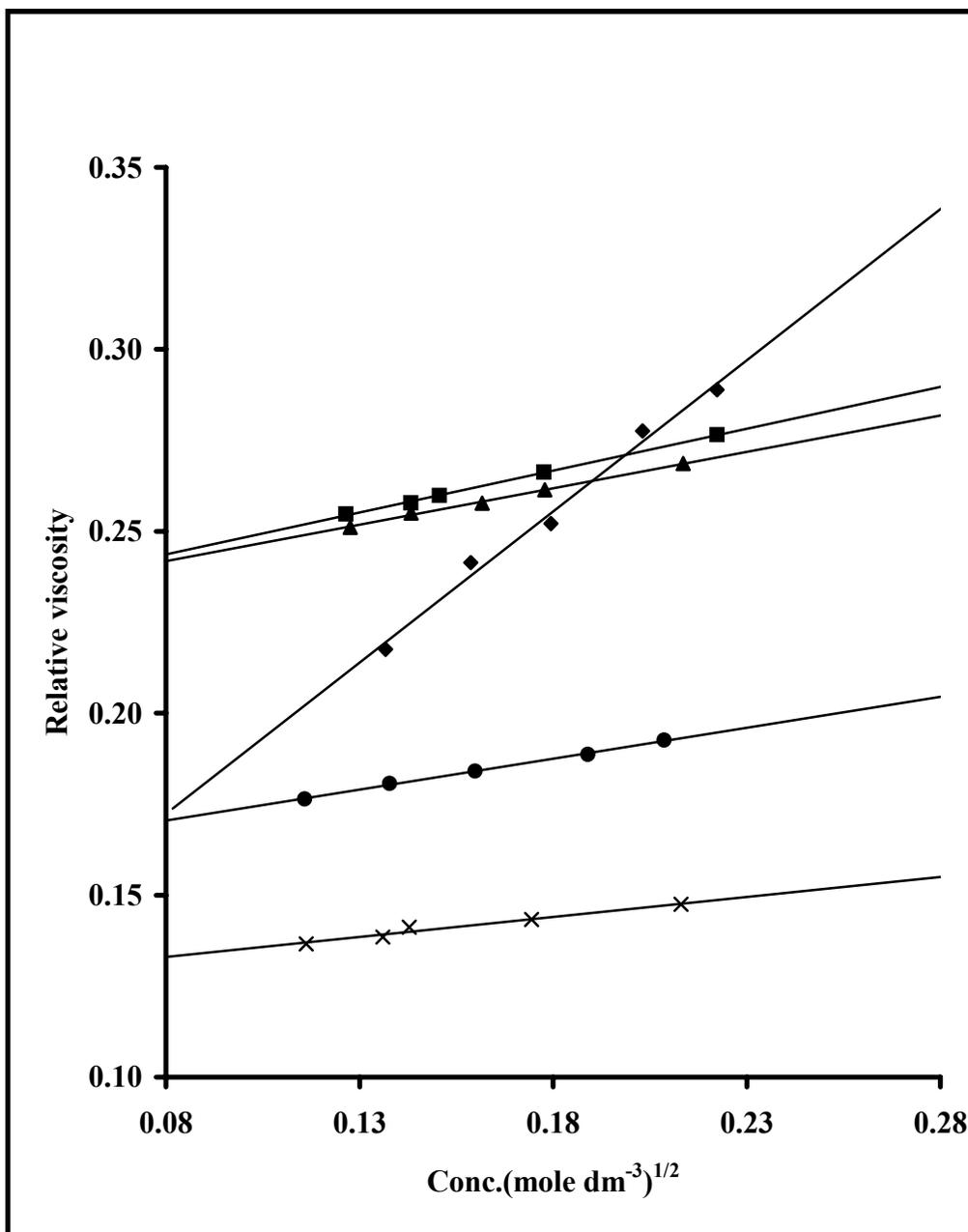


Fig.4.9. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of LiBr at 40°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

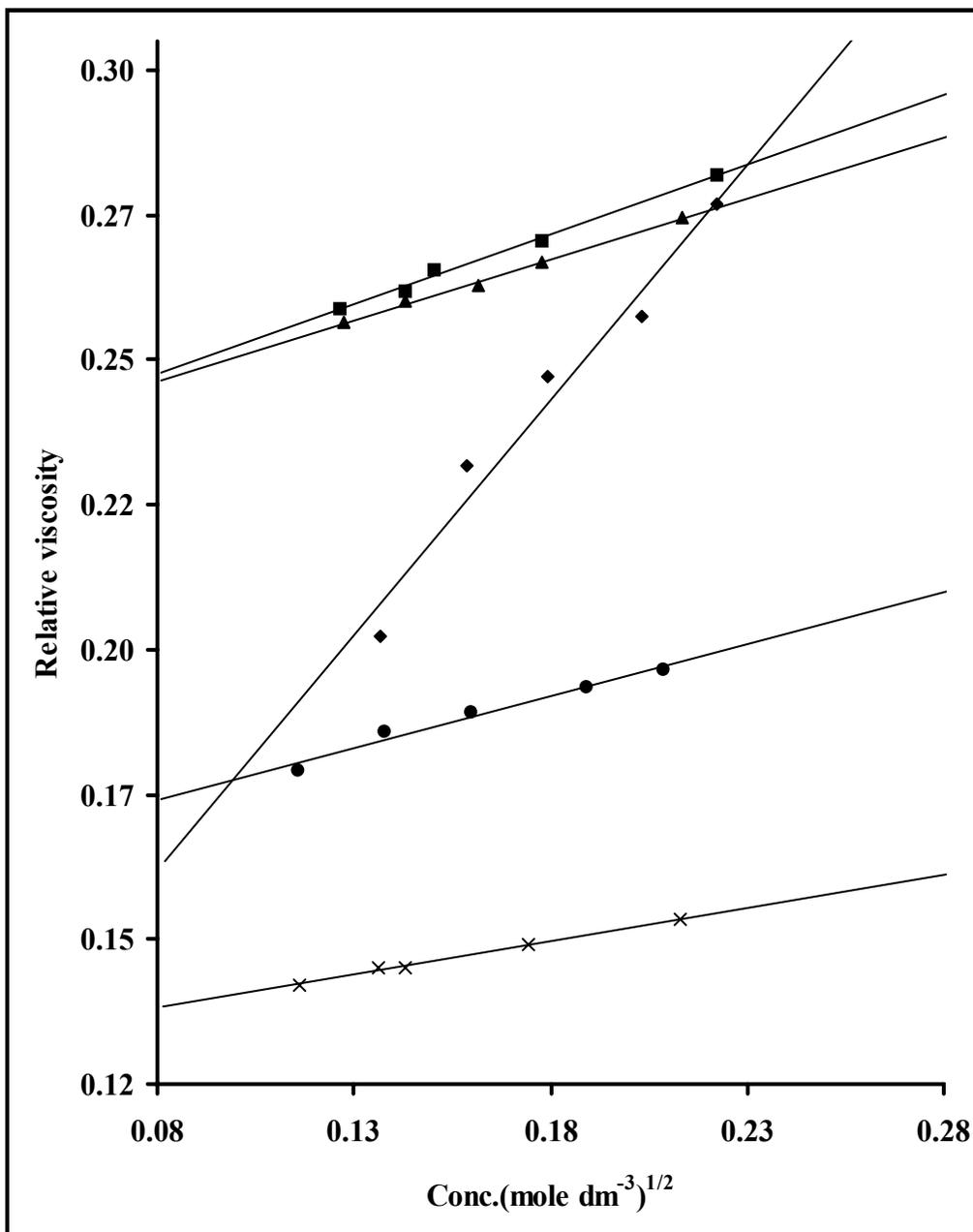


Fig. 4.10. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of LiBr at 45°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

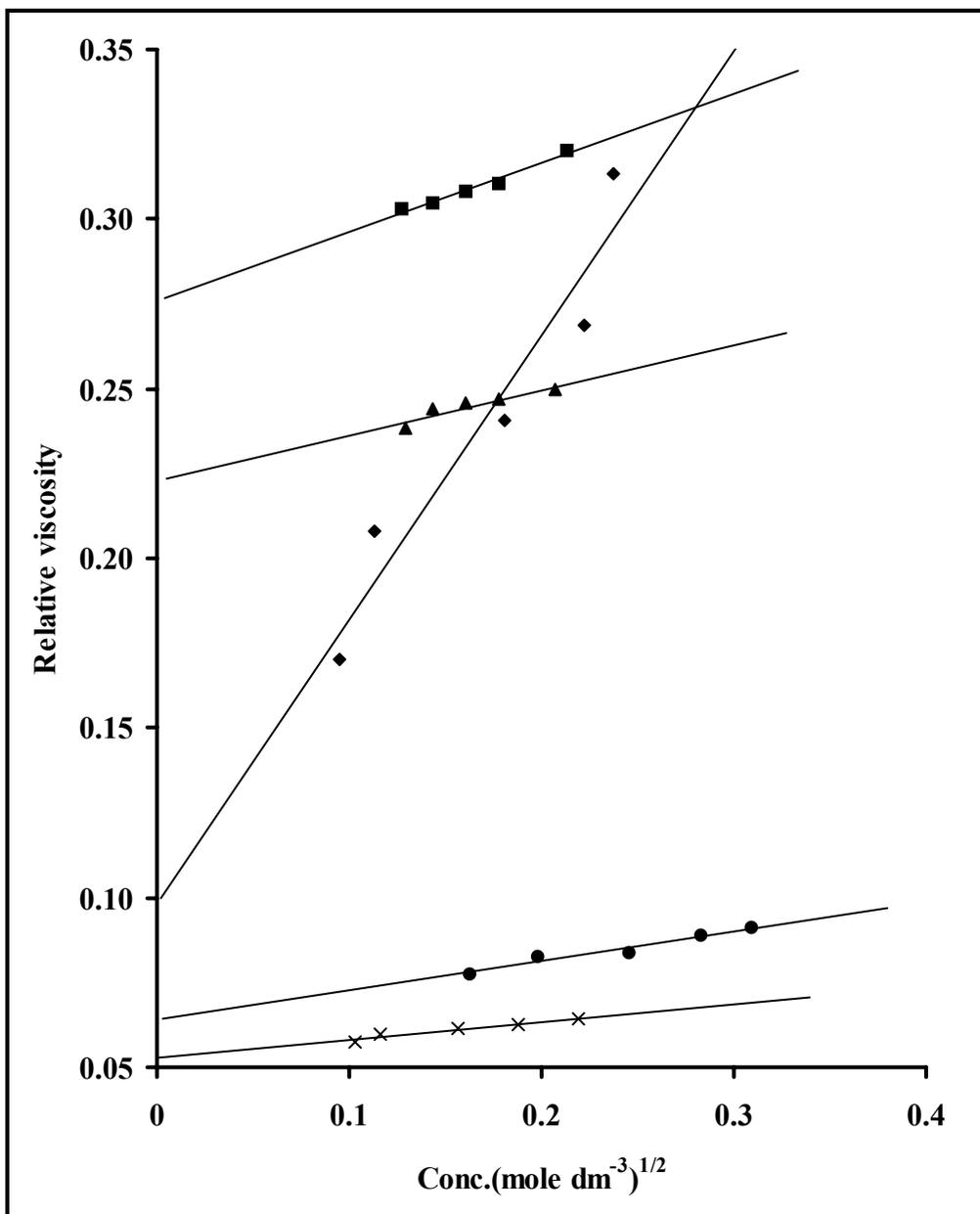


Fig. 4.11. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of NaBr at 25°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

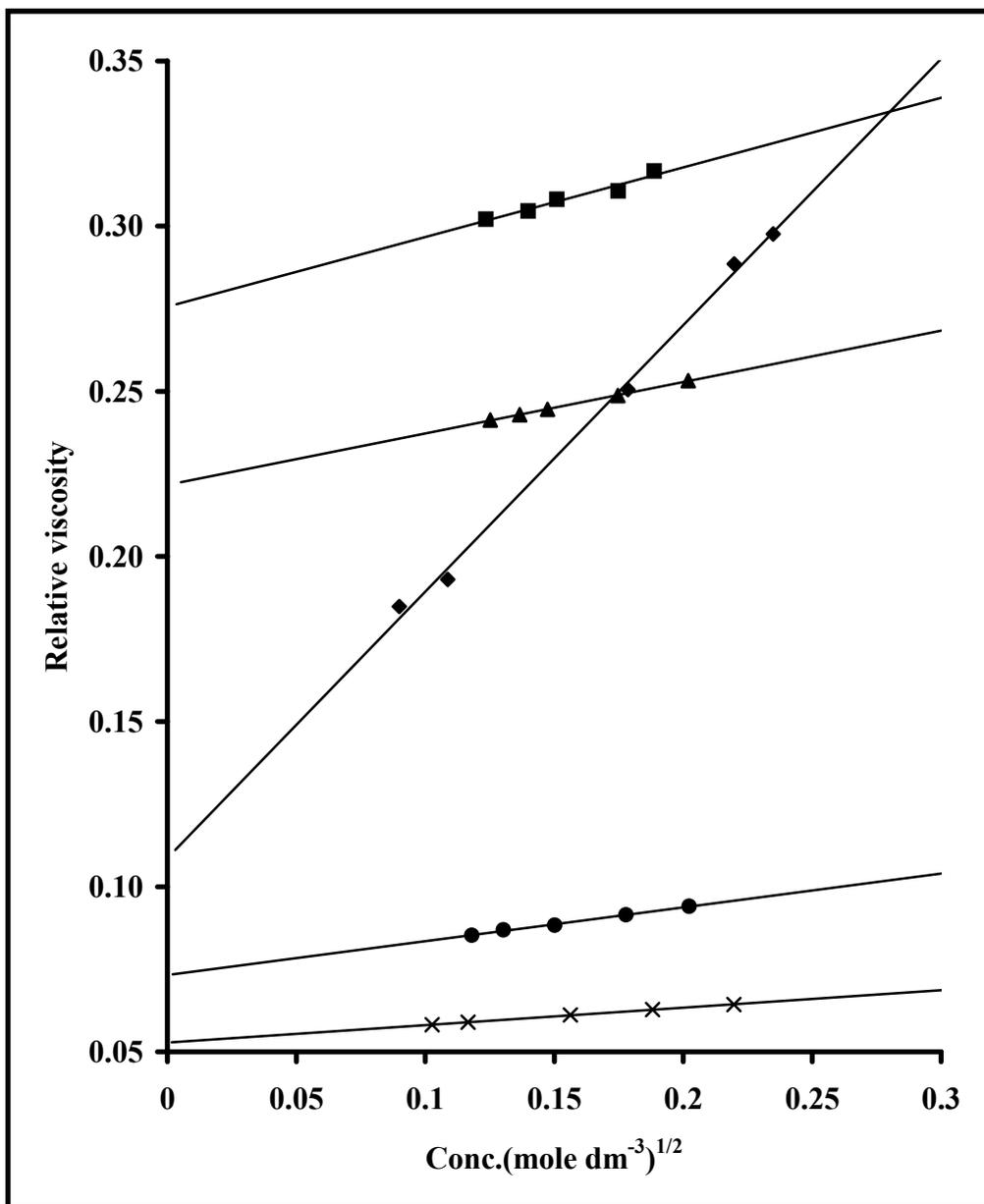


Fig.4.12. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of NaBr at 30°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

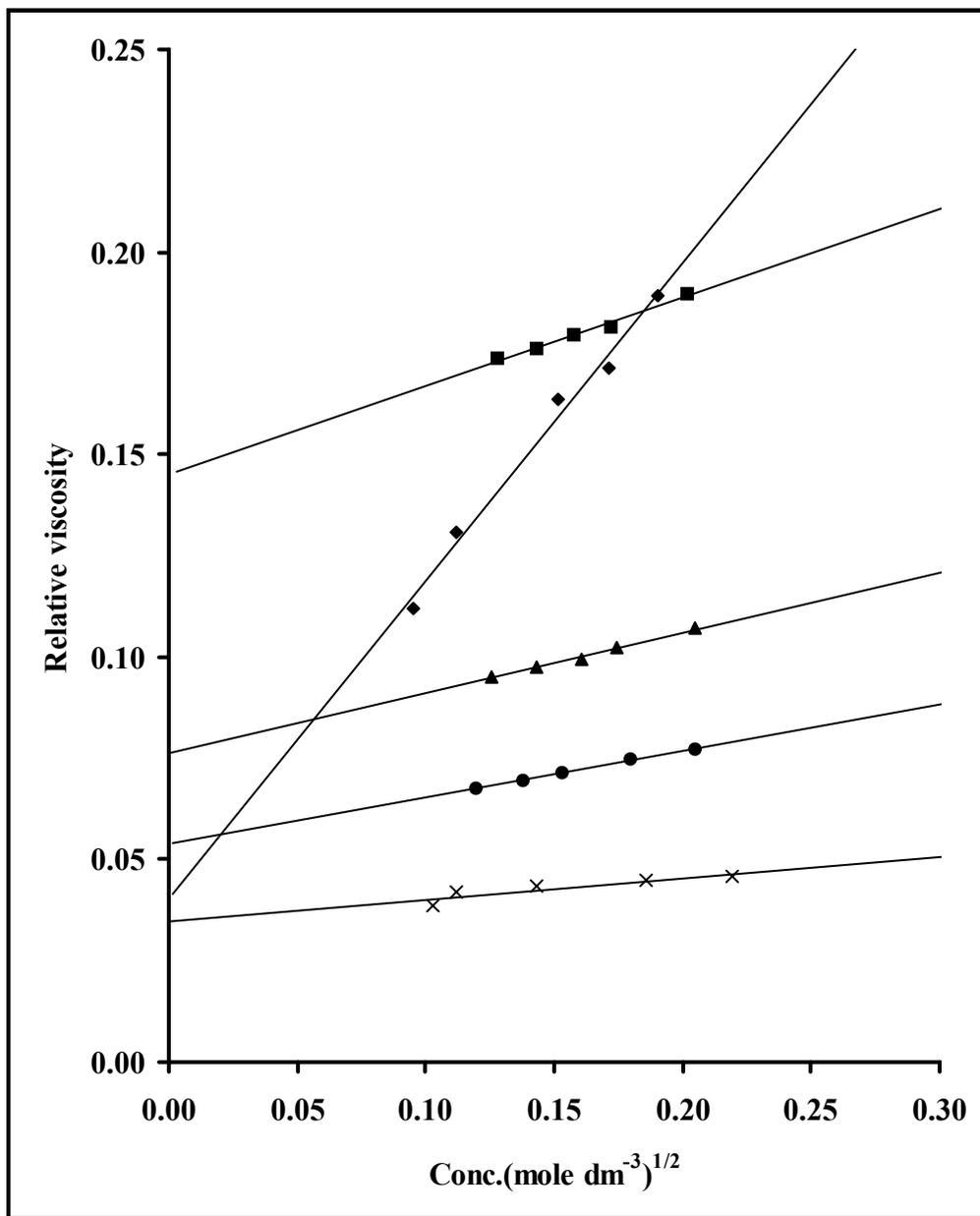


Fig.4.13. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of NaBr at 35°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

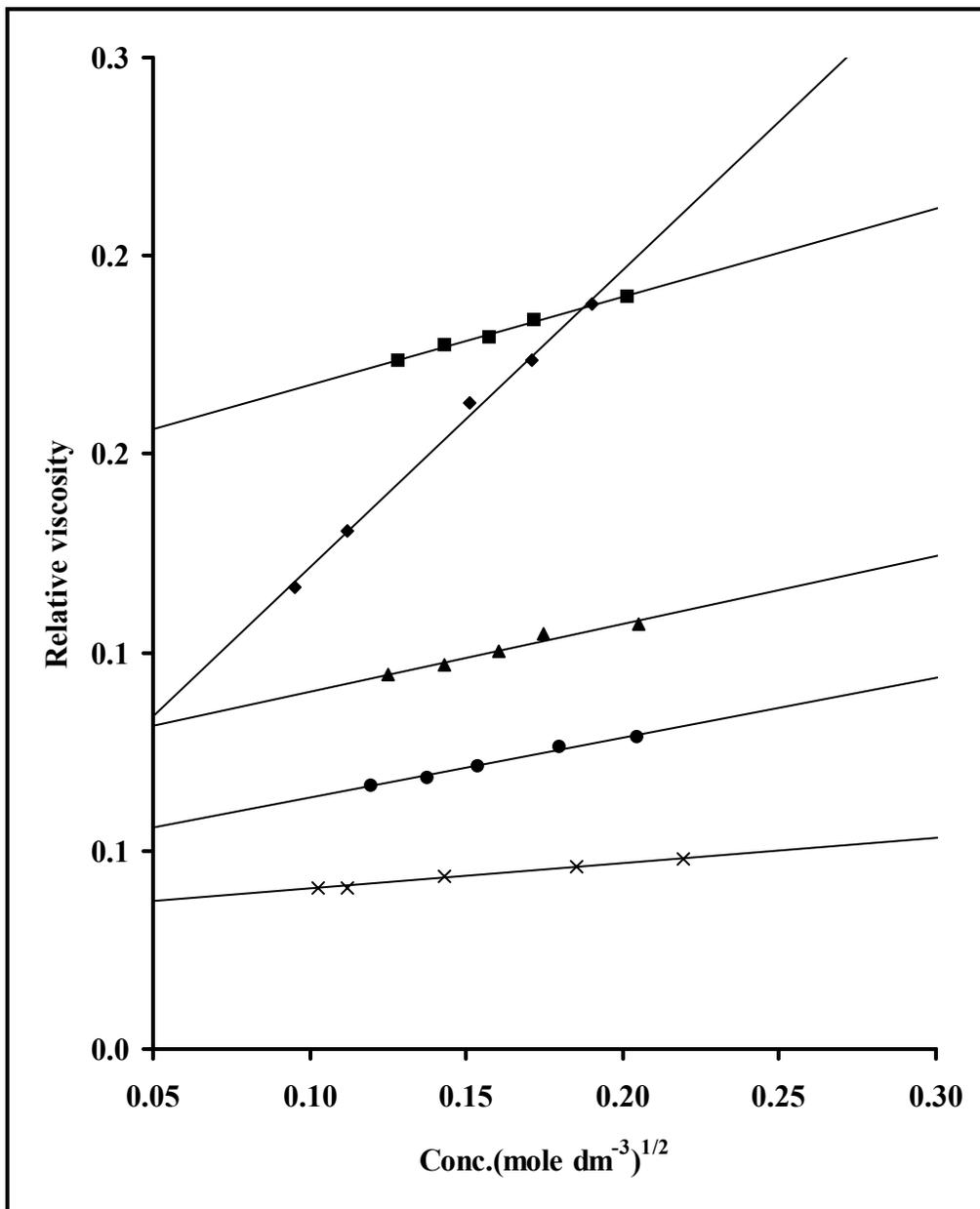


Fig. 4.14. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of NaBr at 40°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

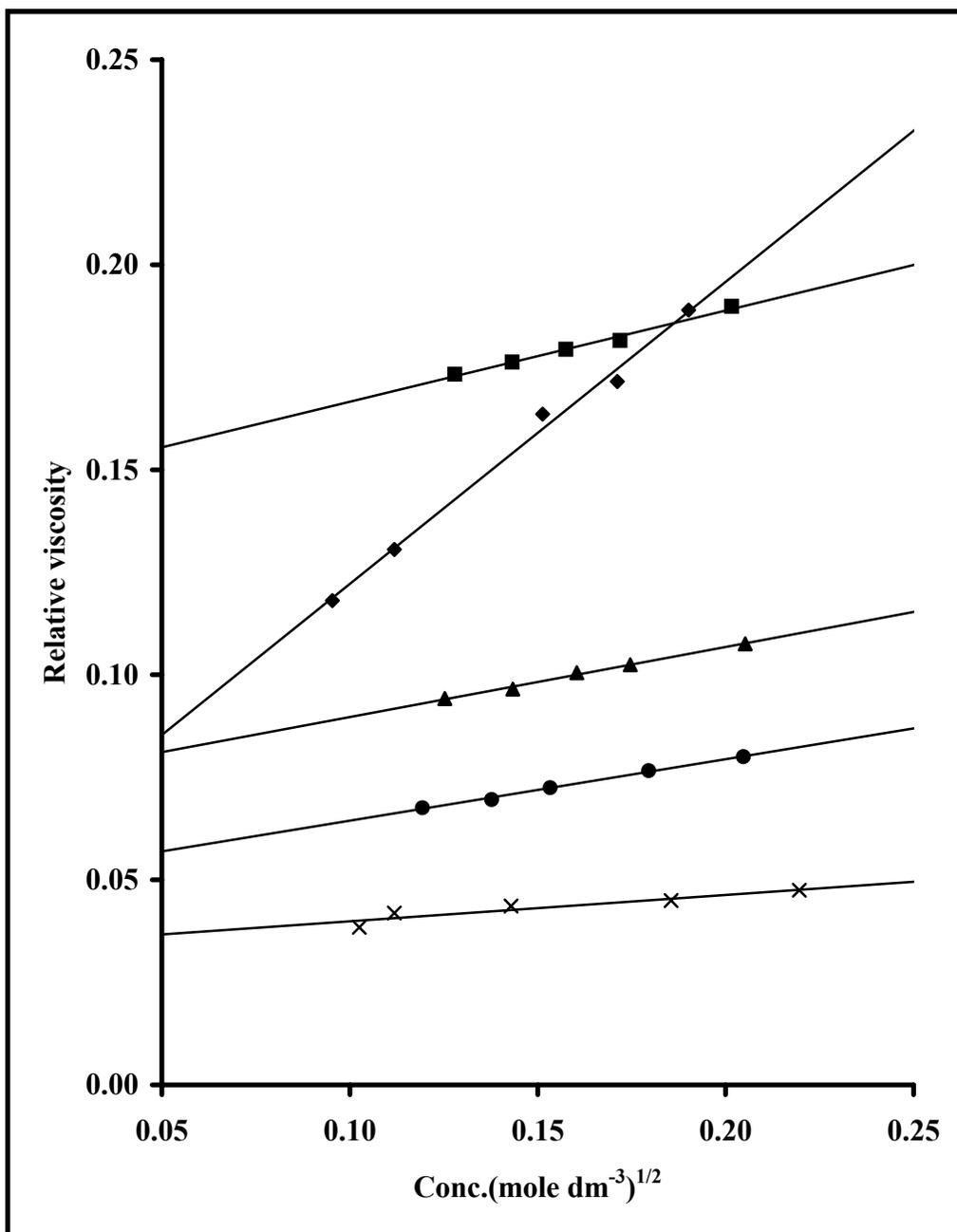


Fig. 4.15. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of NaBr at 45°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

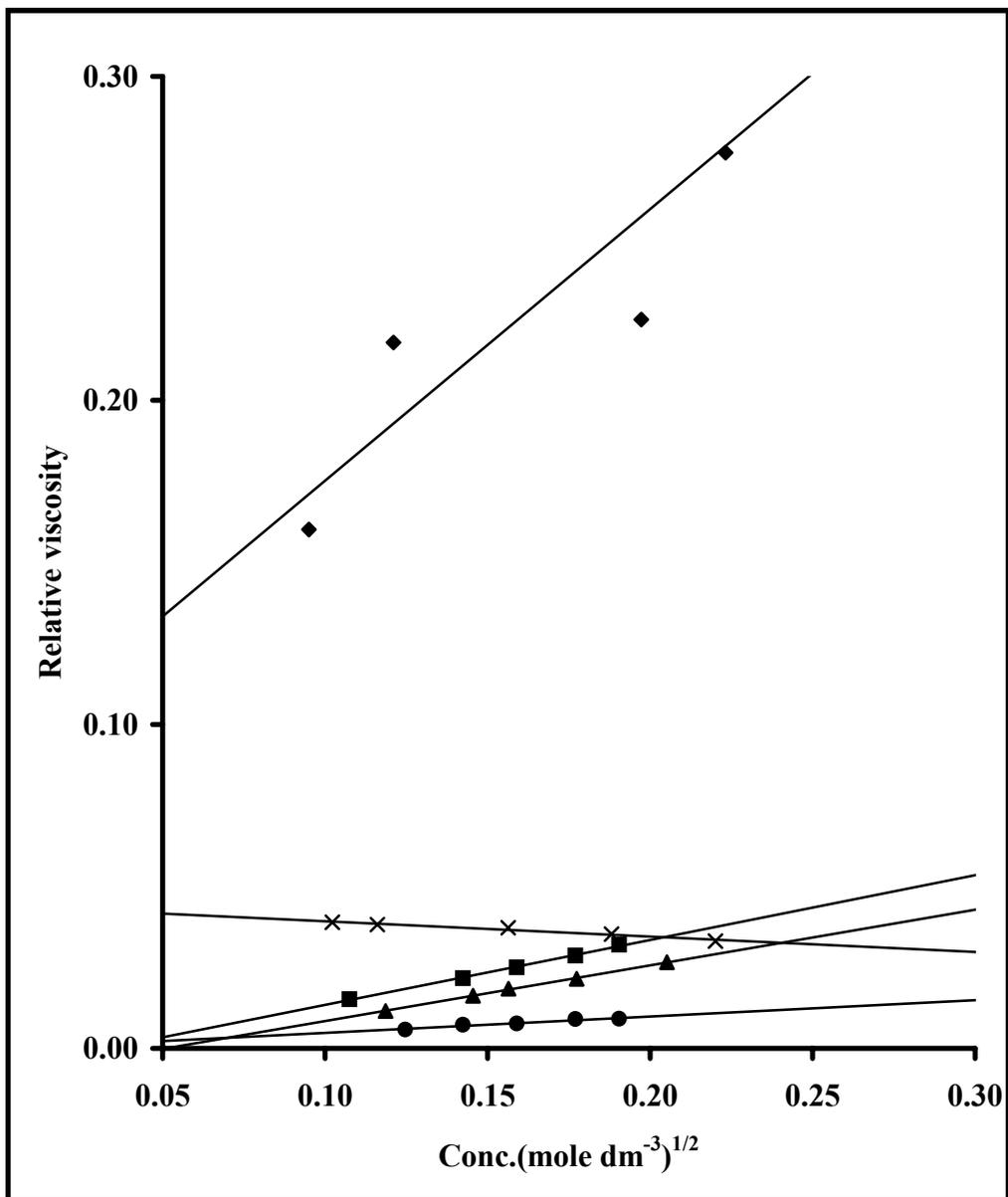


Fig. 4.16. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of KBr at 25°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

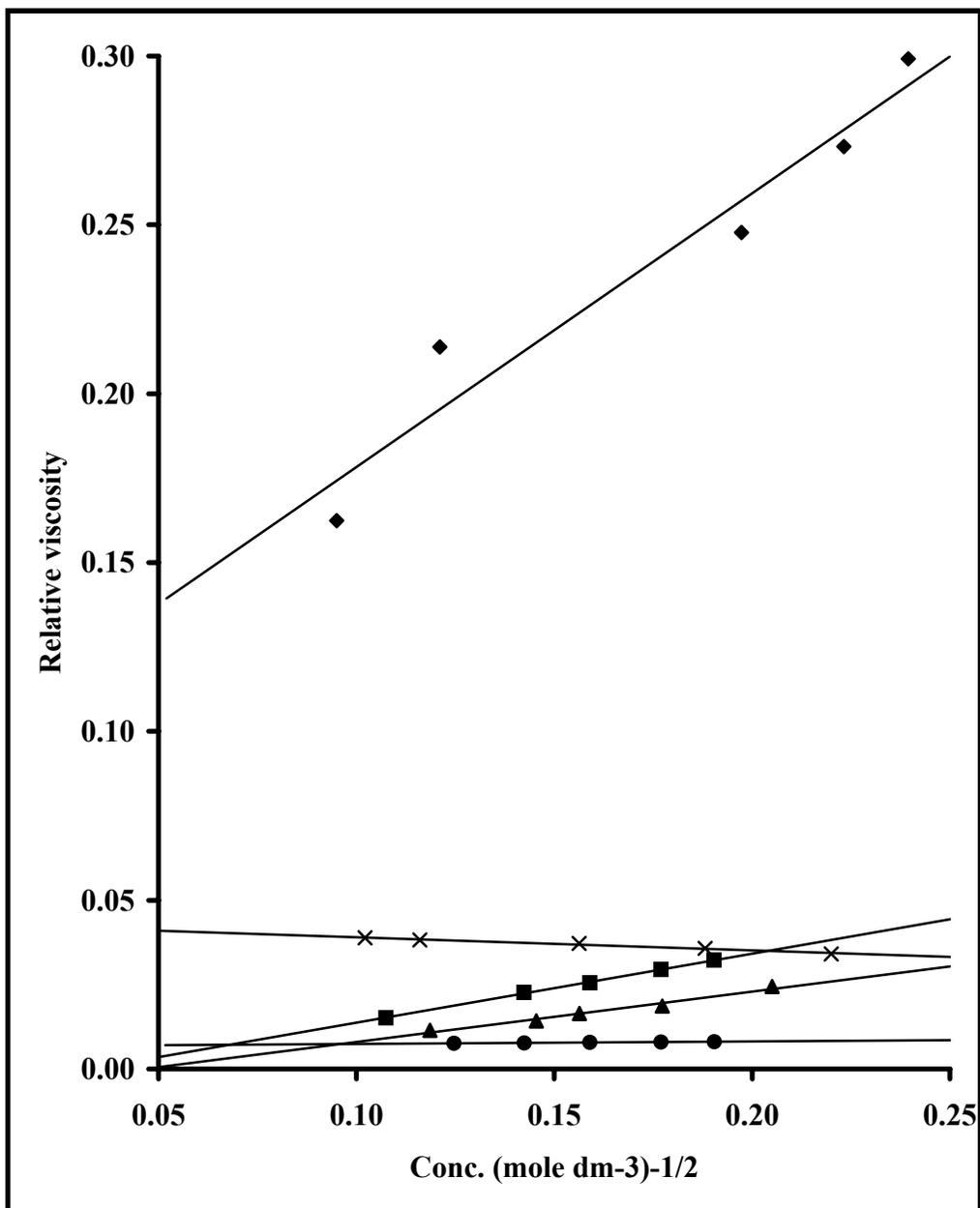


Fig. 4.17. Plot of relative viscosity versus the square root of the concentration in moldm^{-3} of KBr at 30°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

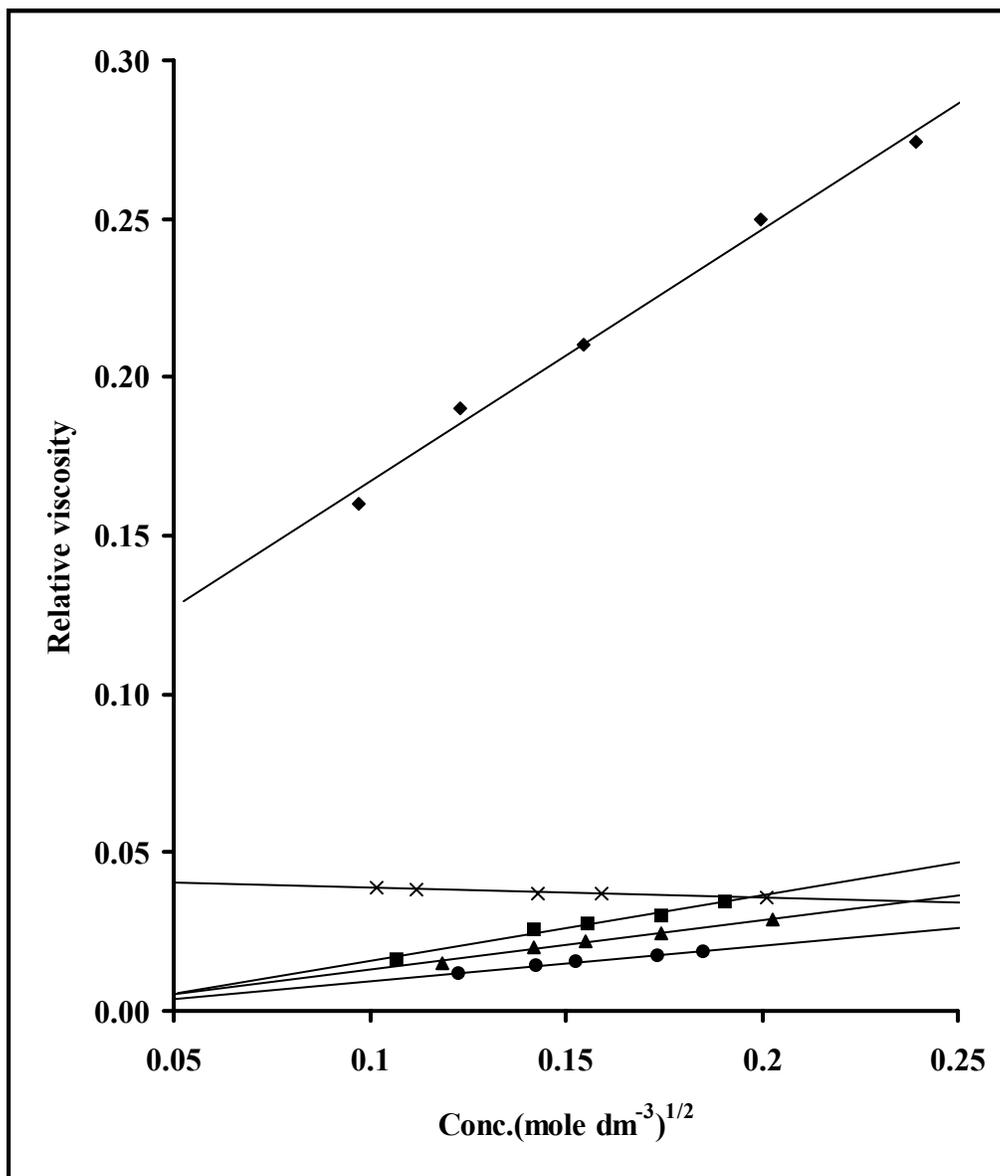


Fig.4.18. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of KBr at 35°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

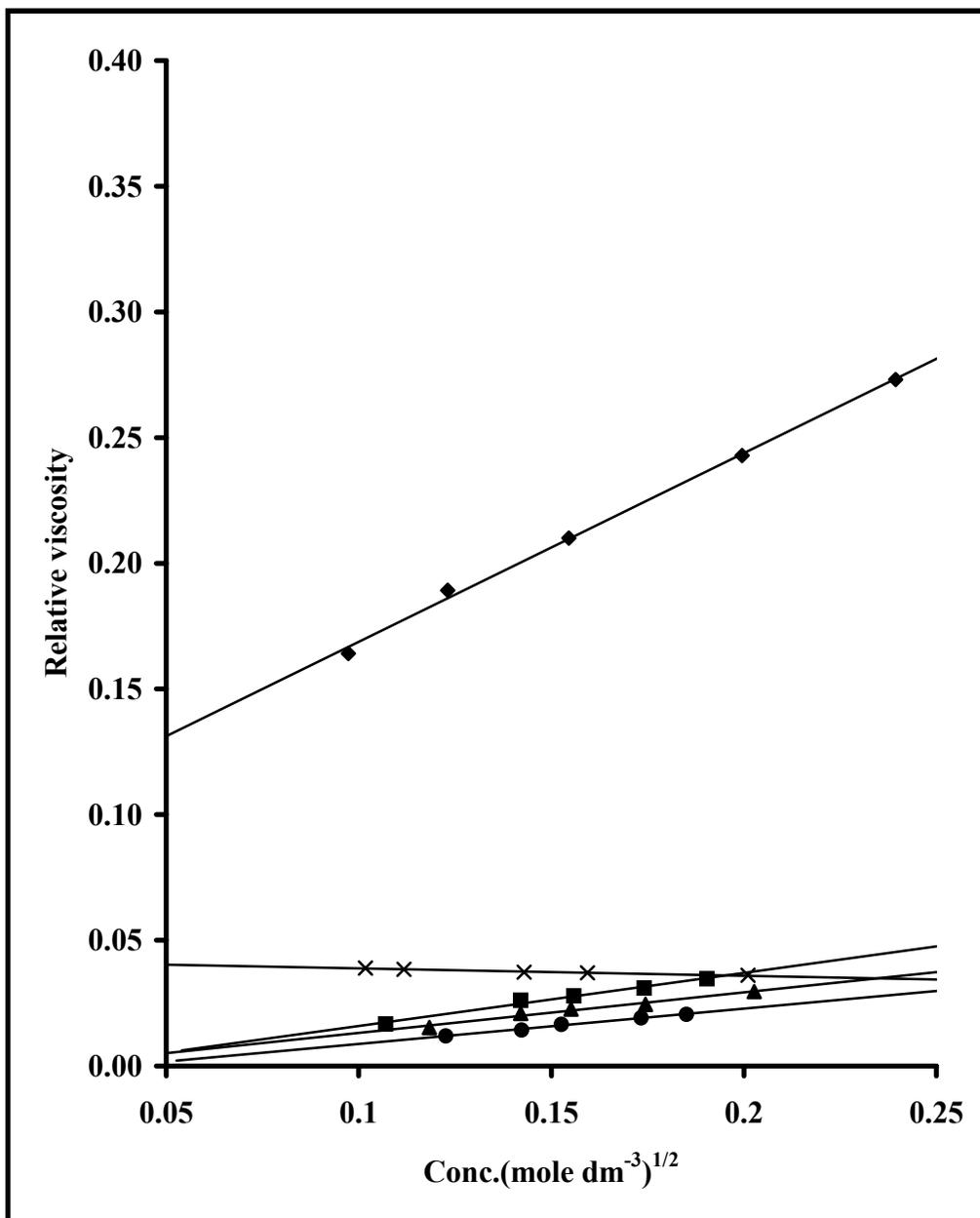


Fig. 4.19. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of KBr at 40°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

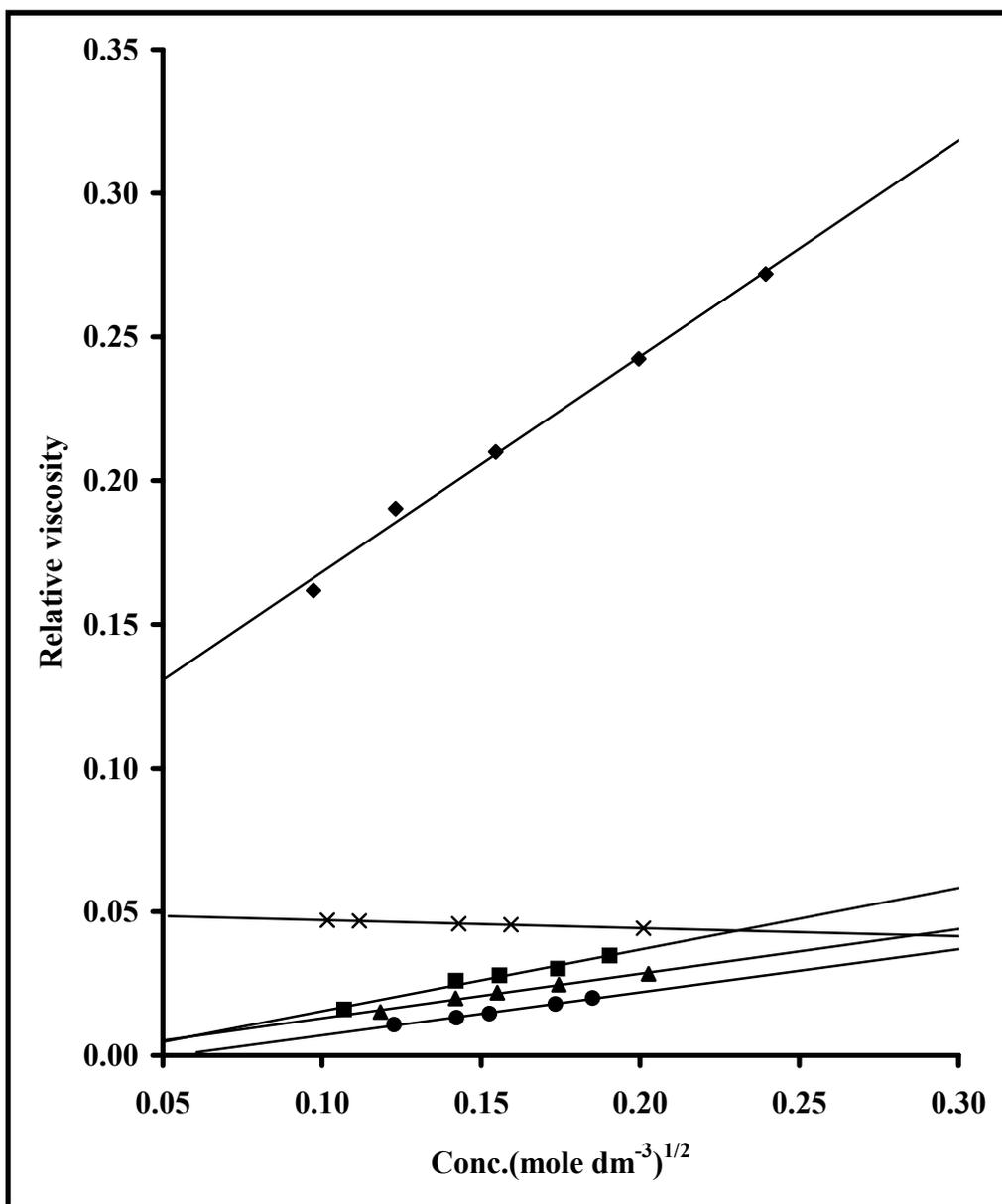


Fig. 4.20. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of KBr at 45°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

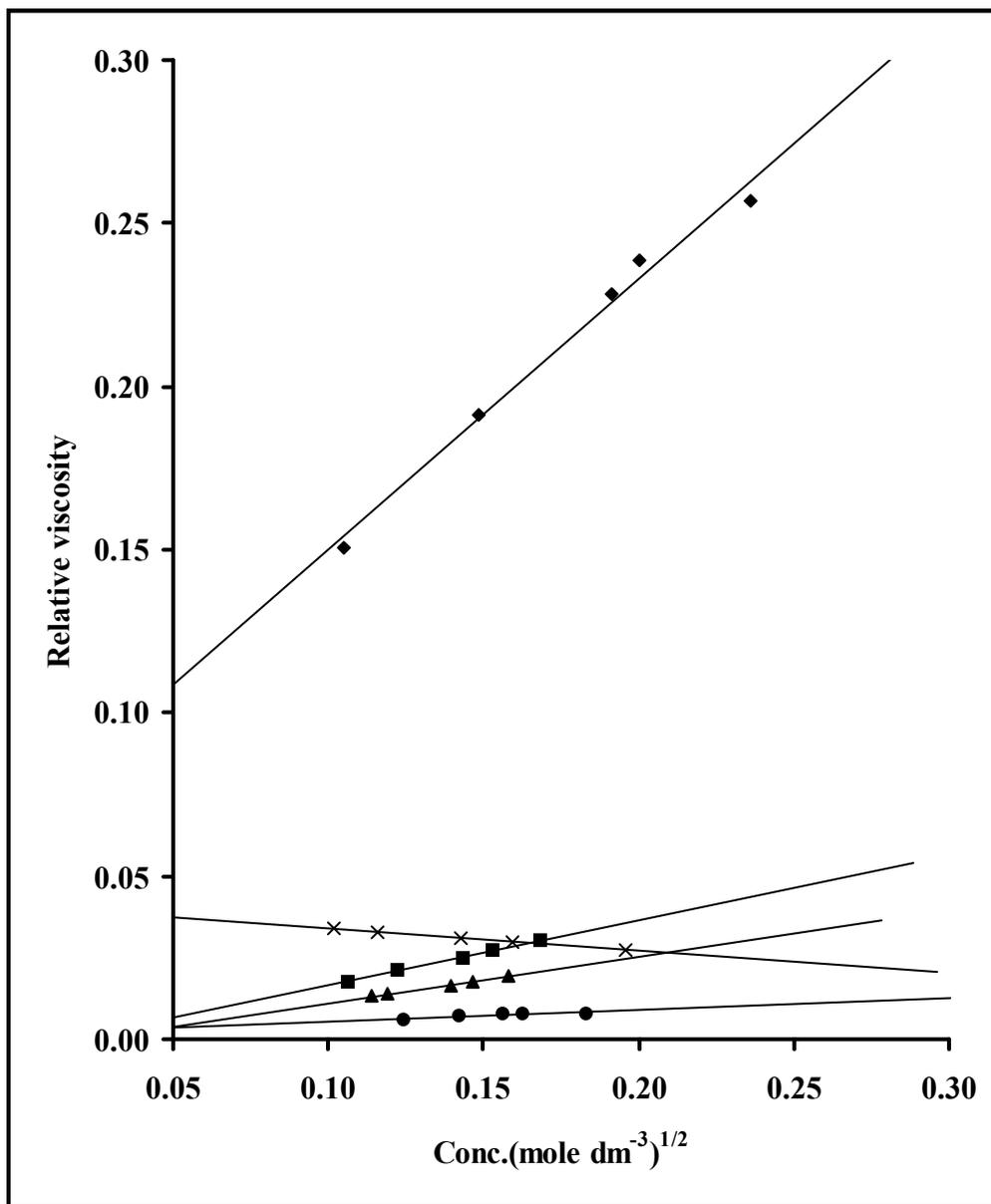


Fig. 4.21. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of RbBr at 25°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

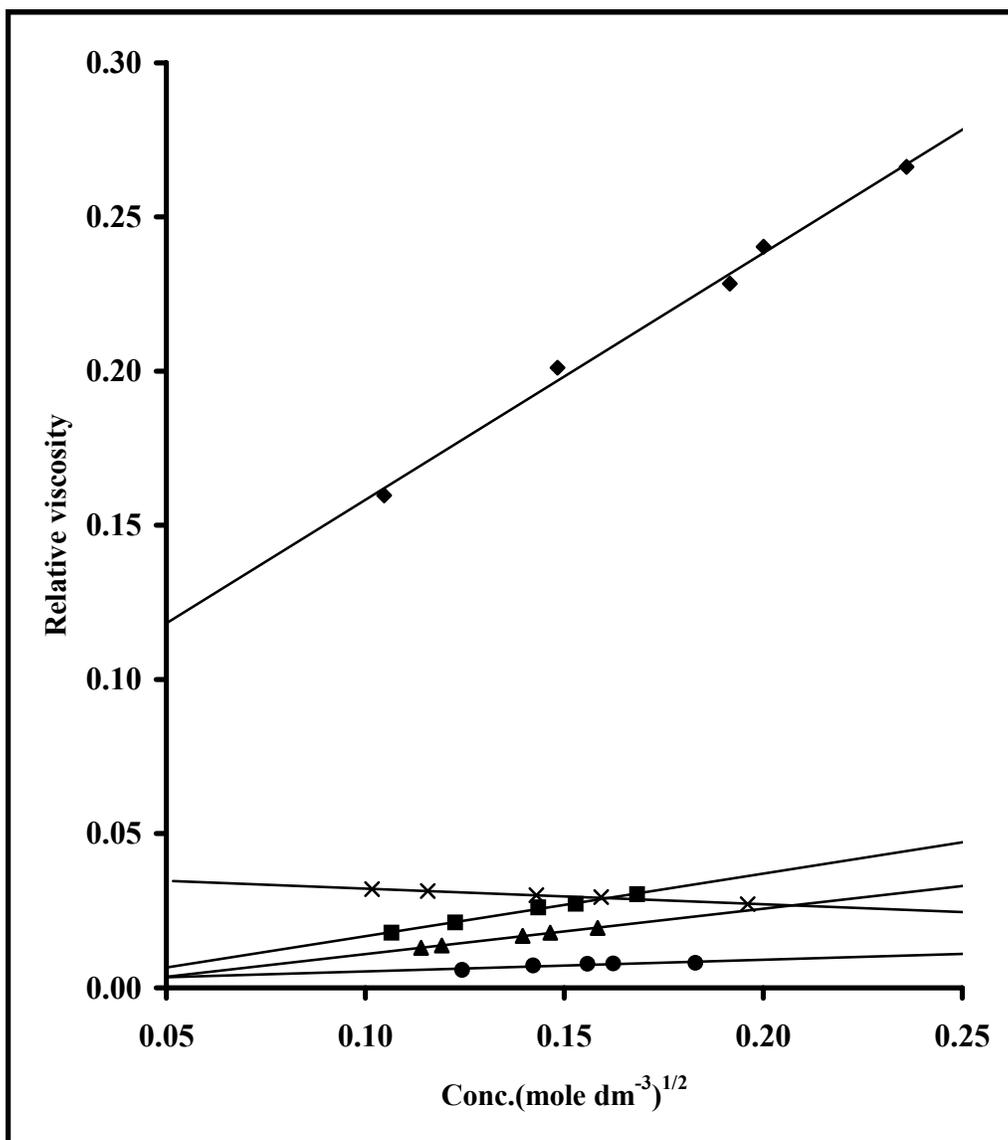


Fig. 4.22. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of RbBr at 30°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

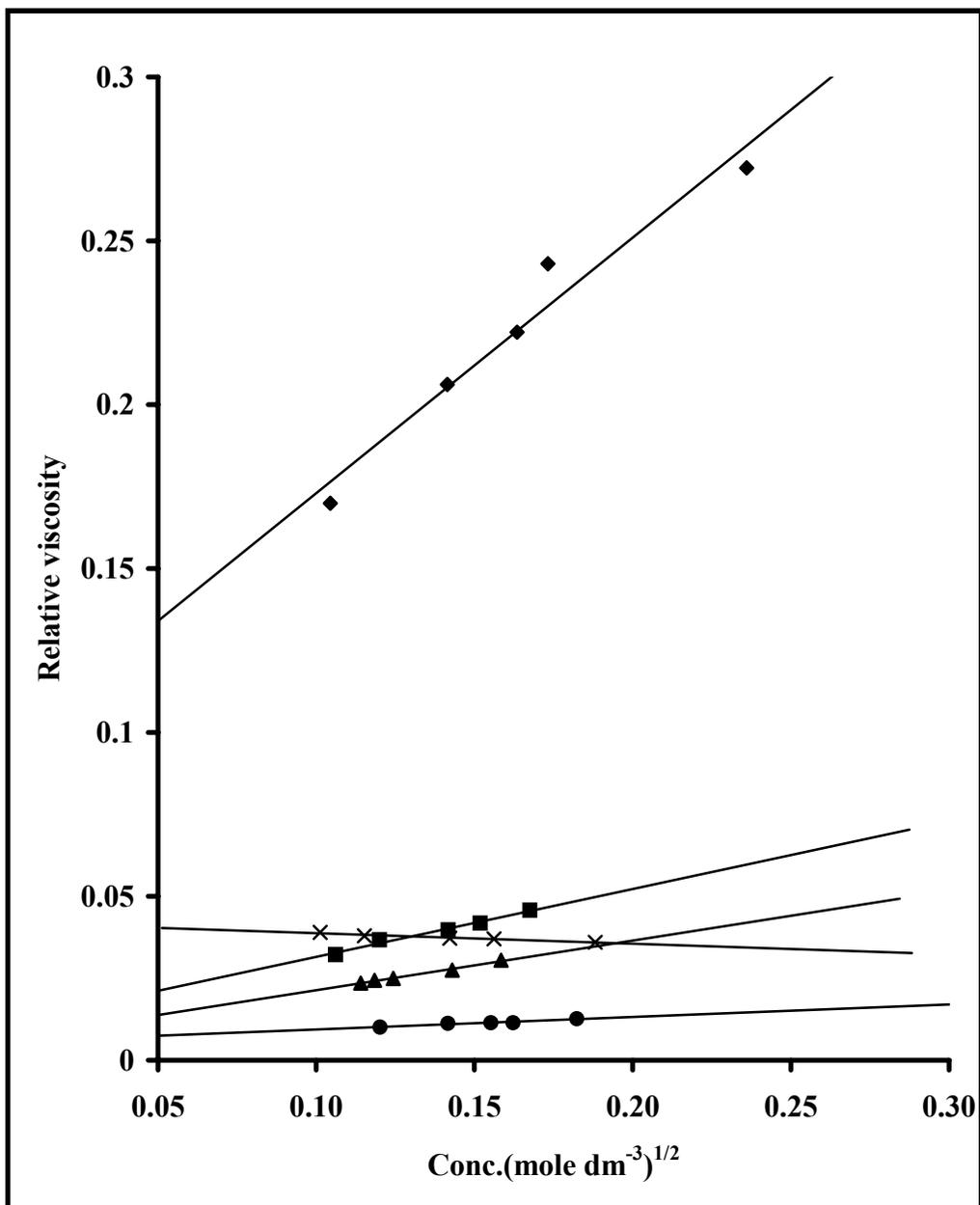


Fig 4.23. Plot of relative viscosity versus the square root of the concentration in moldm^{-3} of RbBr at 35°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

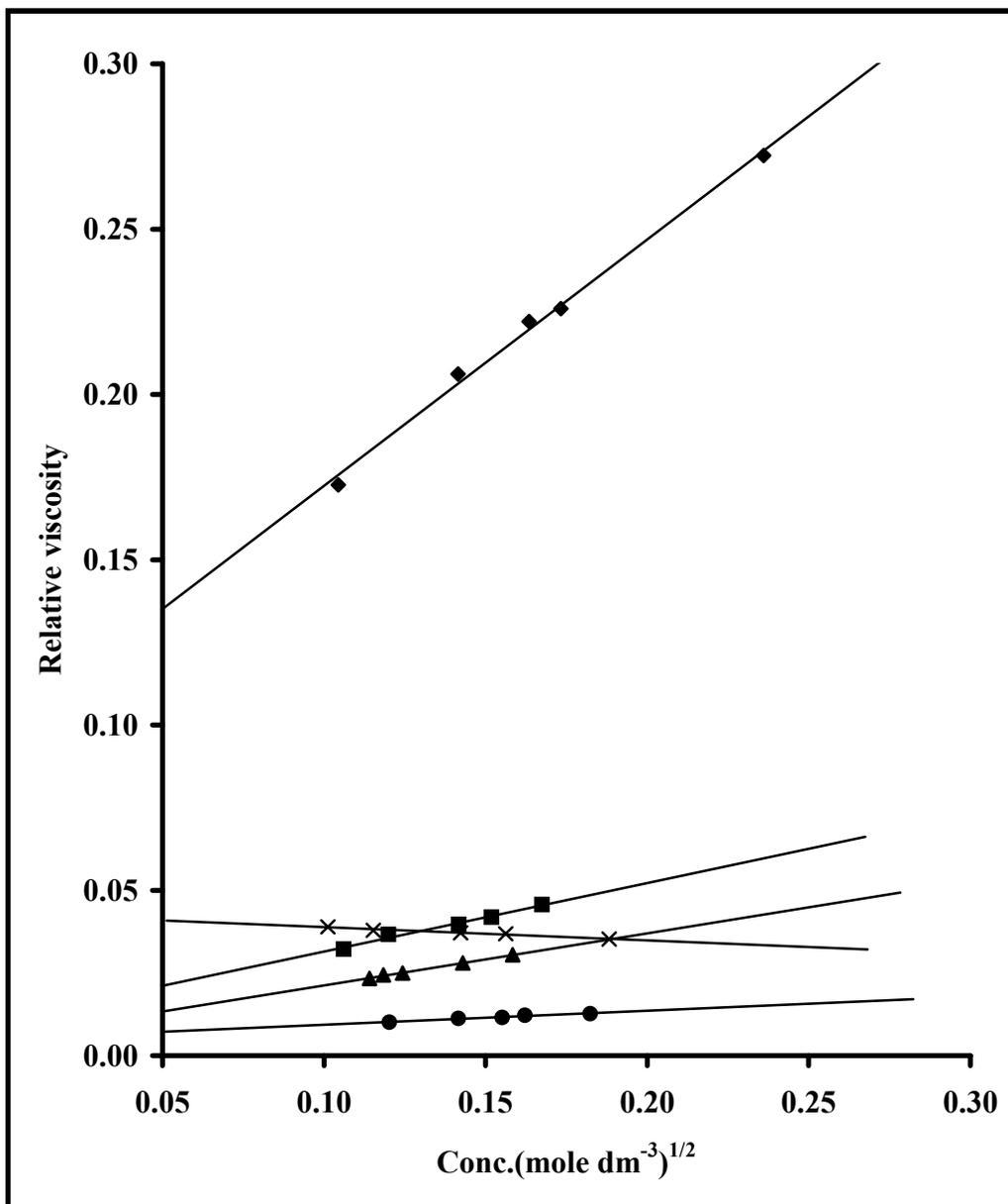


Fig. 4.24. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of RbBr at 40°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

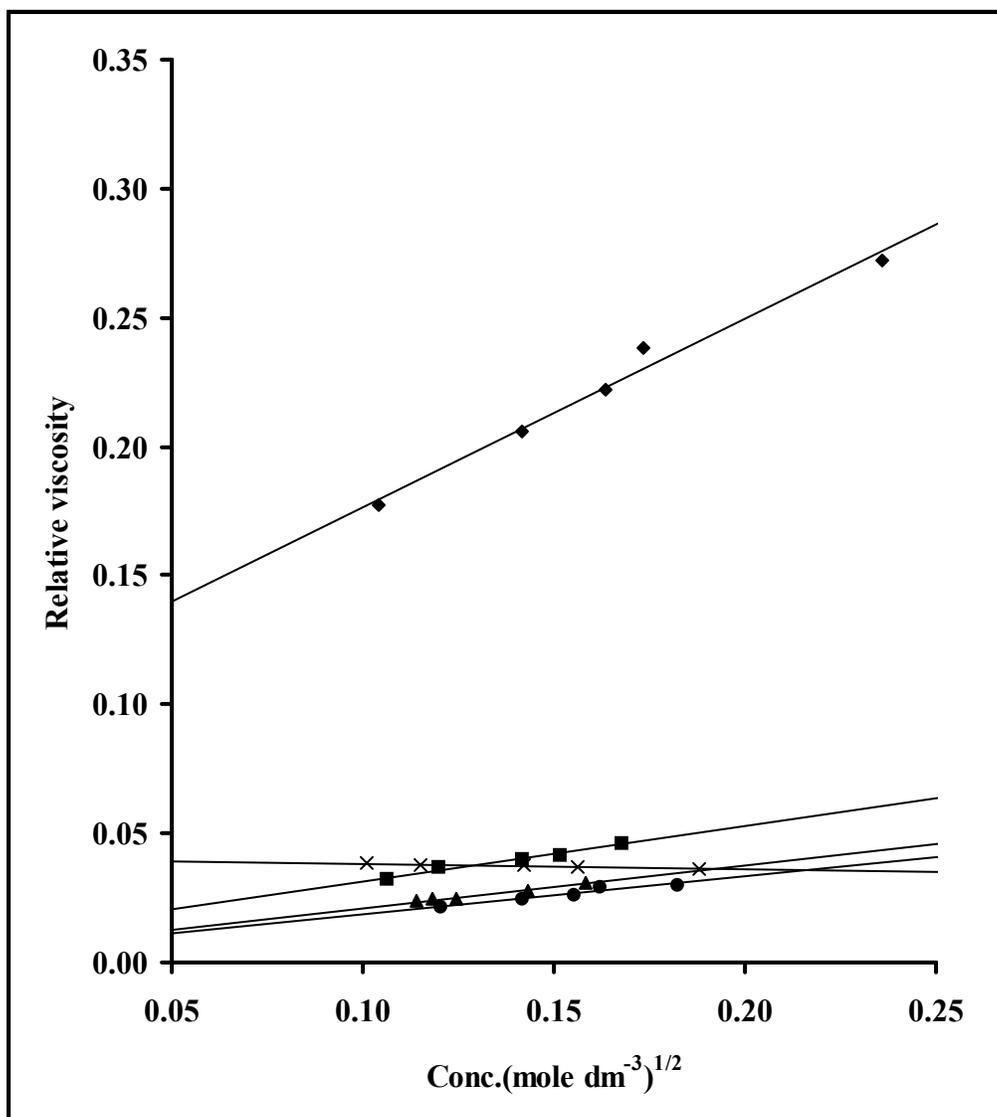


Fig. 4.25. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of RbBr at 45°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

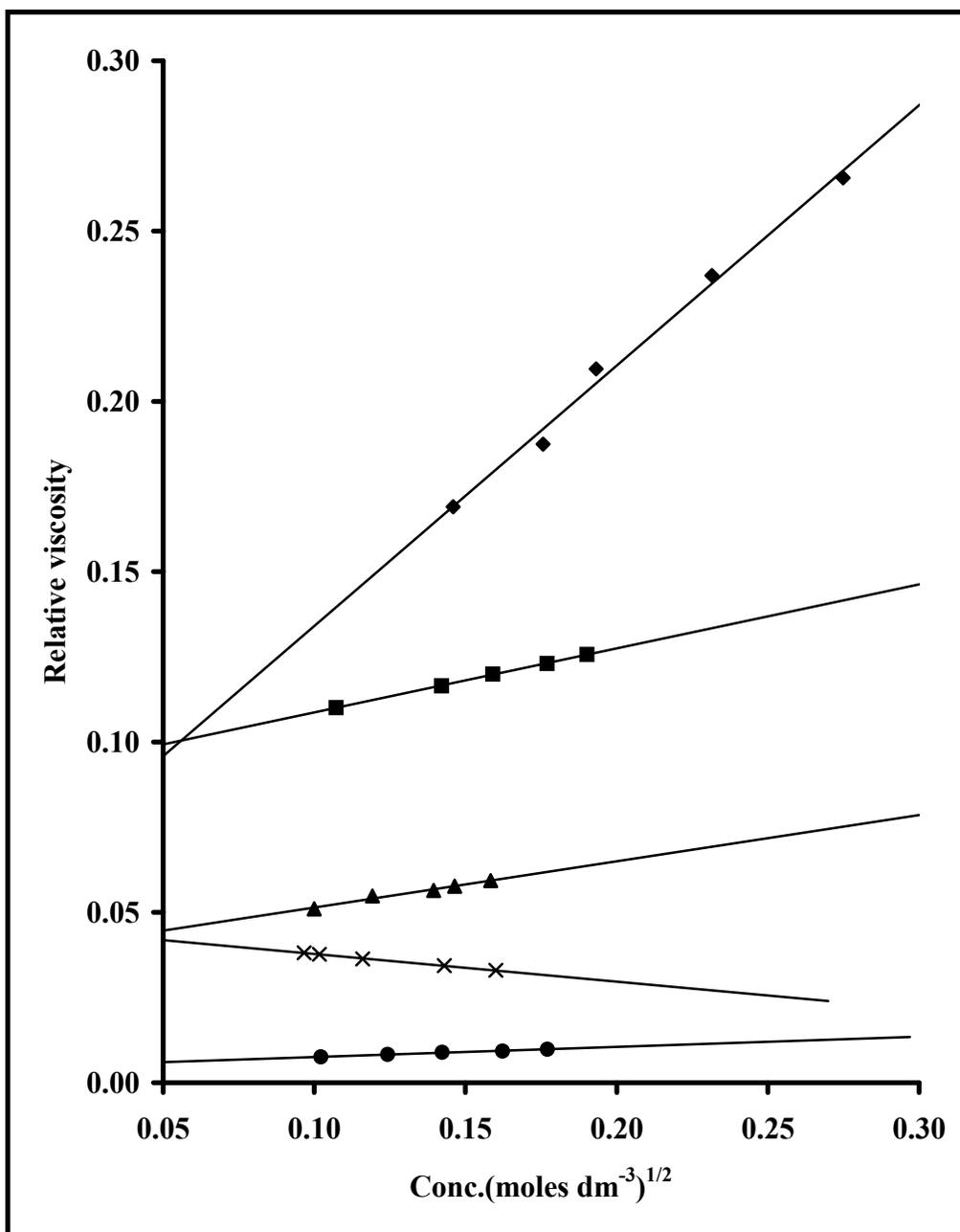


Fig. 4.26. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of CsBr at 25°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

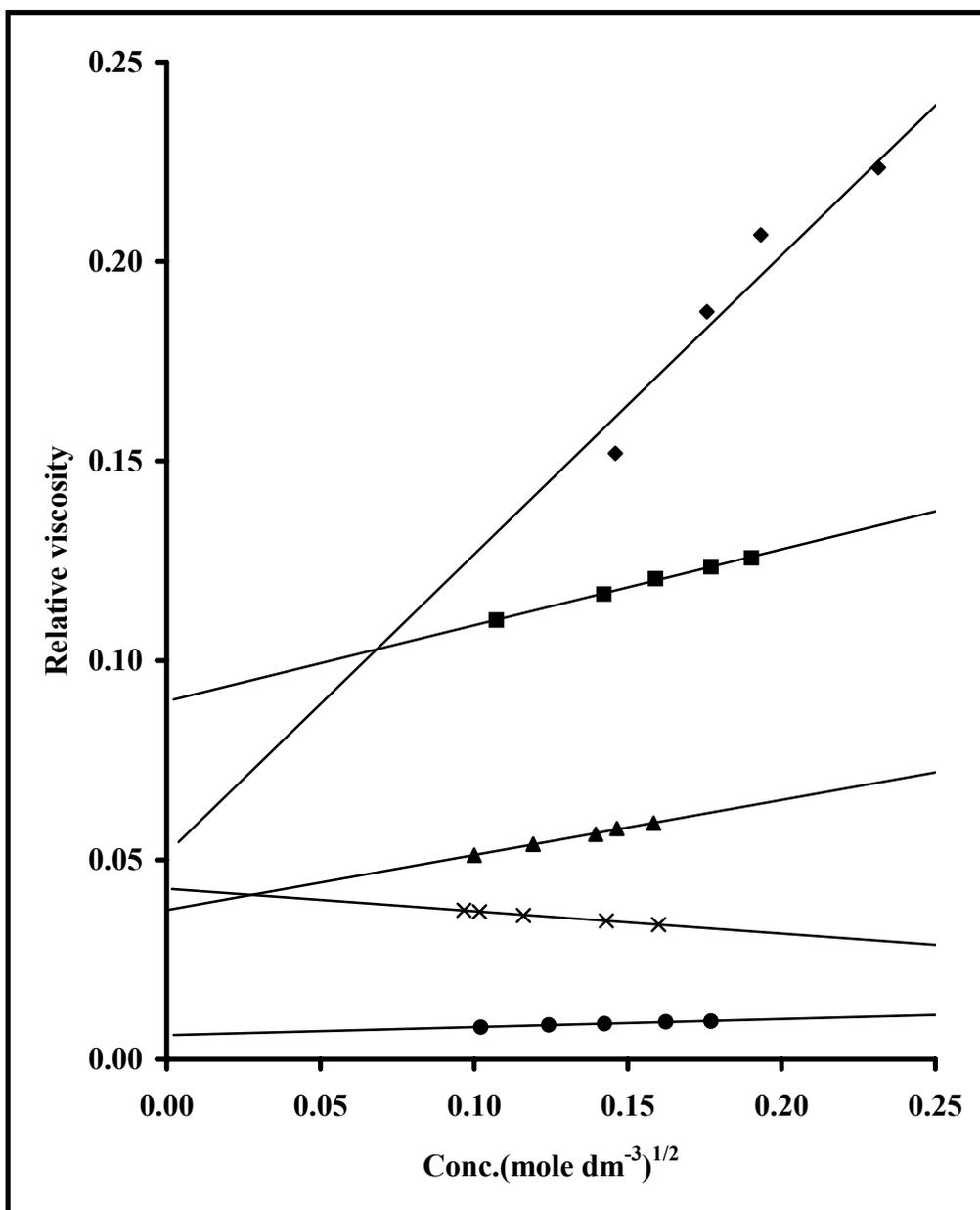


Fig. 4.27. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of CsBr at 30°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

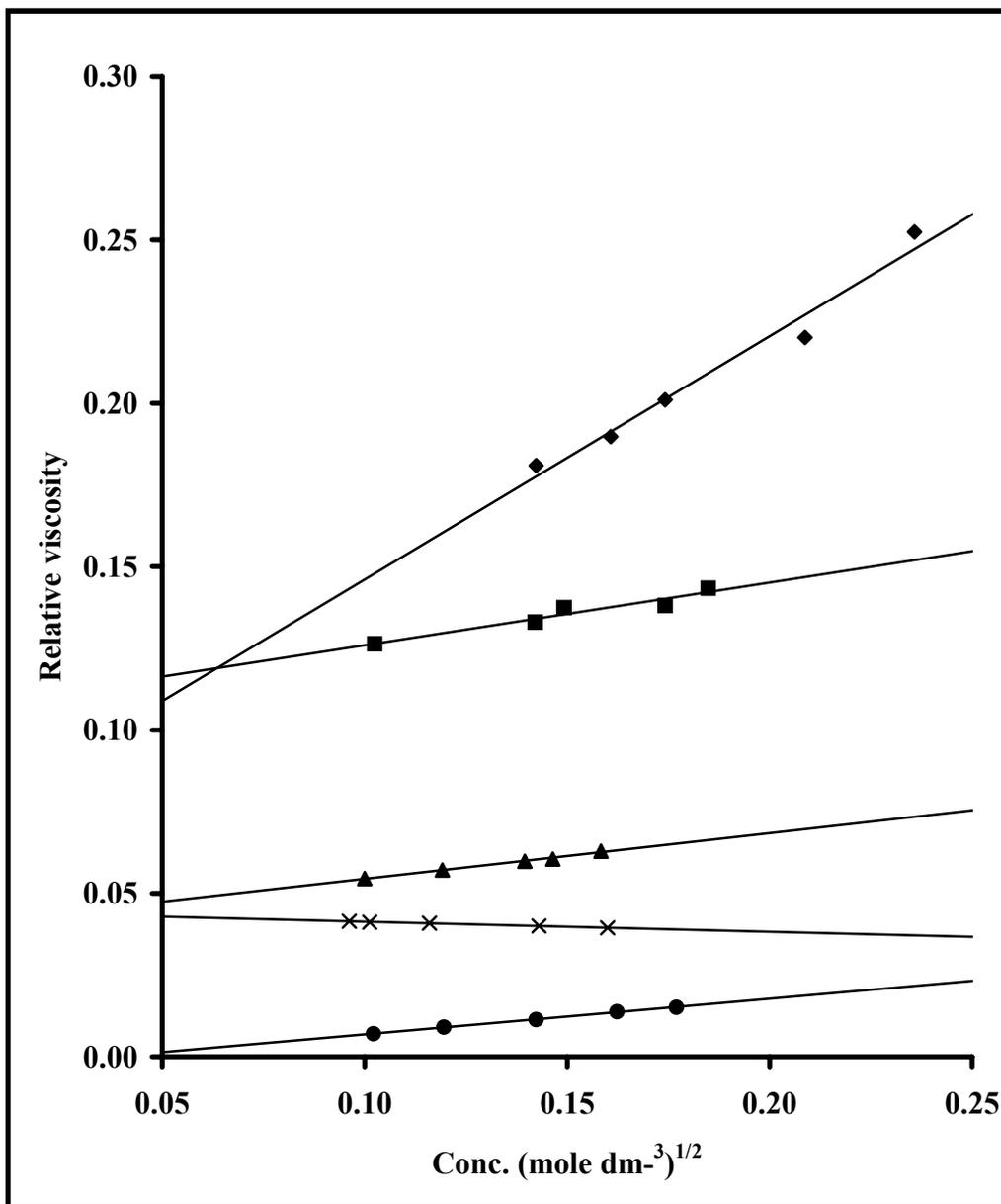


Fig. 4.28. Plot of relative viscosity versus the square root of the concentration in moldm^{-3} of CsBr at 35°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

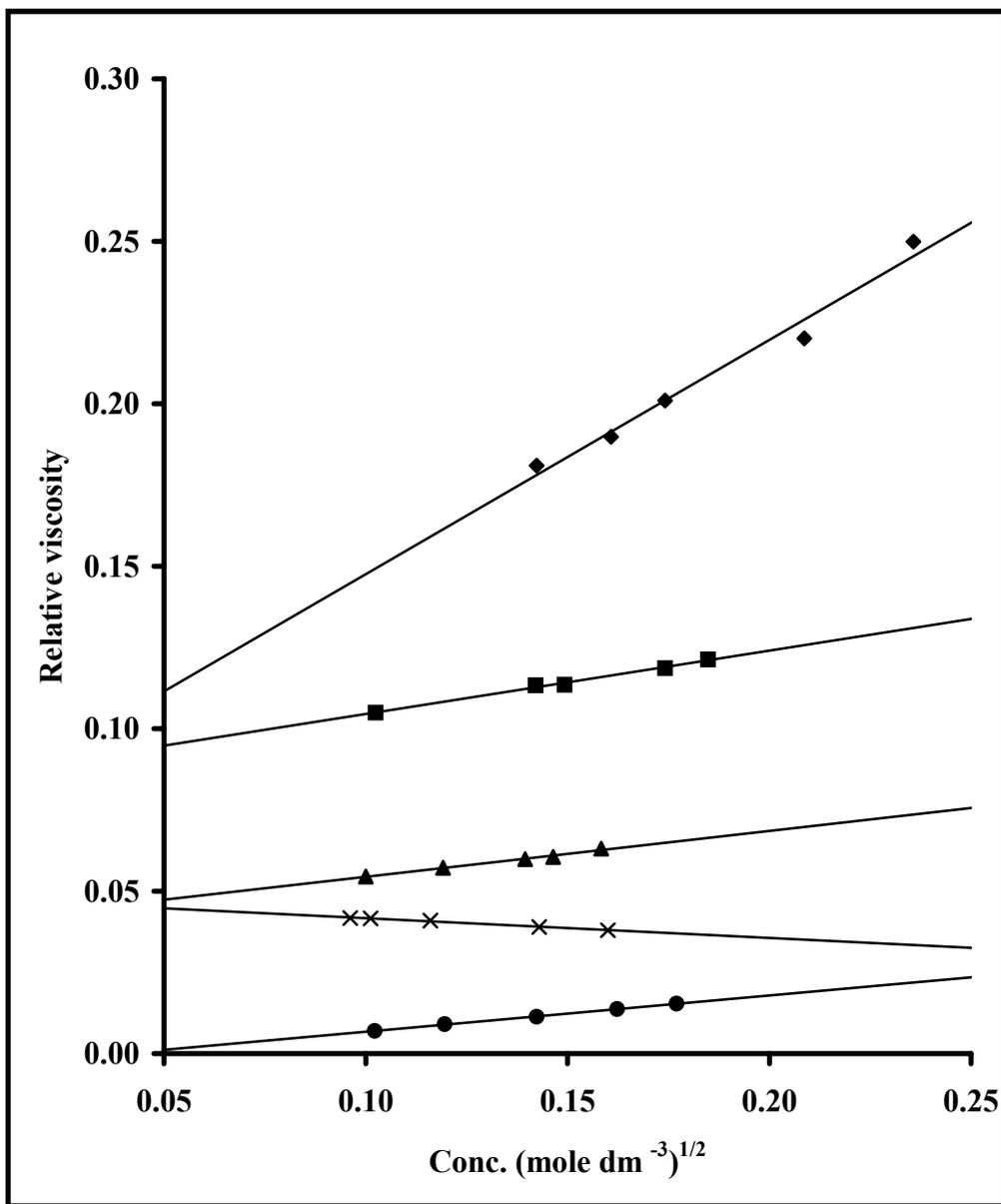


Fig. 4.29. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of CsBr at 40°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

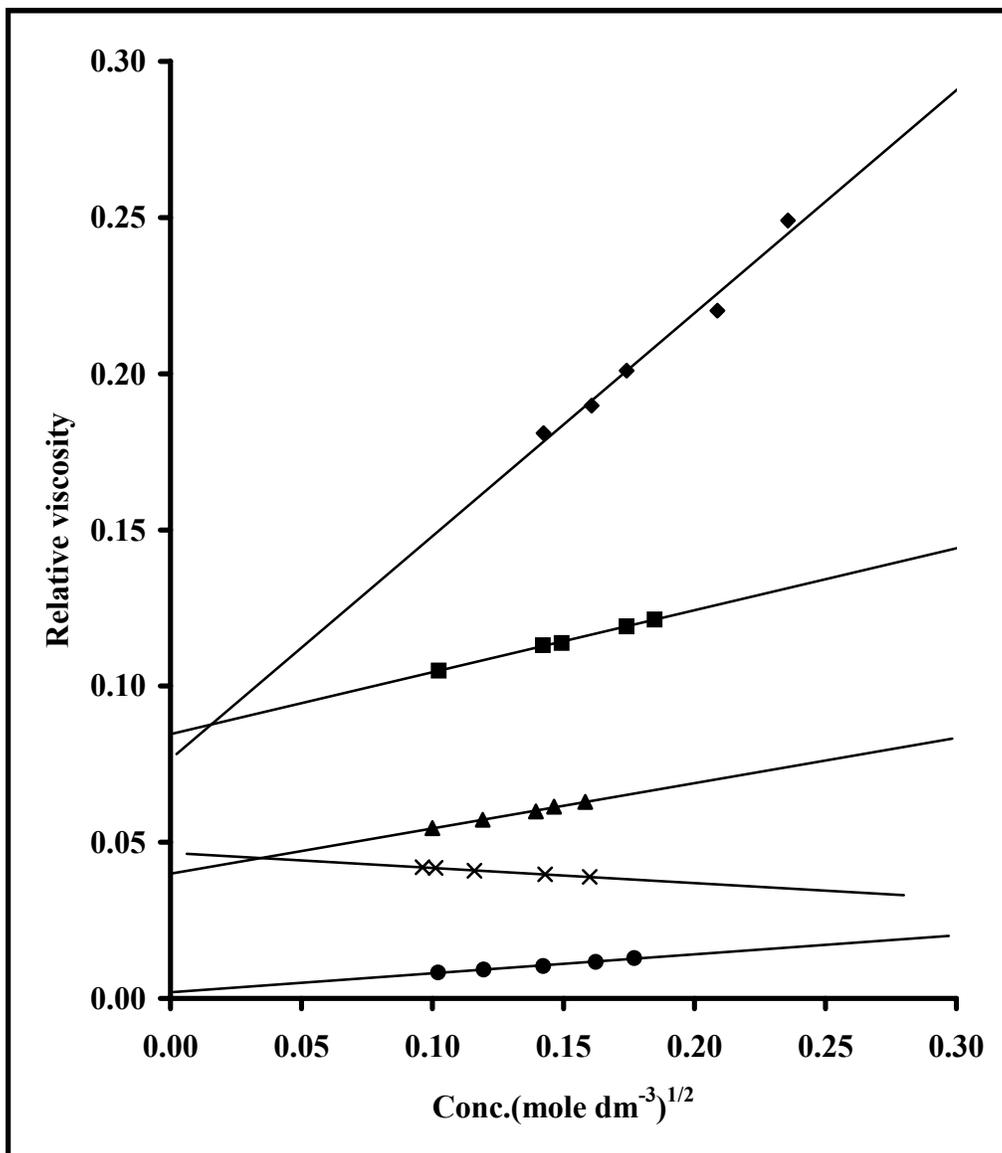


Fig. 4.30. Plot of relative viscosity versus the square root of the concentration in mol dm^{-3} of CsBr at 45°C . ◆ 100% DMSO, ● 60 % DMSO, ▲, 40 % DMSO, ■ 20 % DMSO, X 100 % water.

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