Review of Solute-Solute and Solute-Solvent Interactions in Solutions of Different Solutes in Mixed Solvents at Different Temperatures and Different Concentrations and Determined the Physicochemical Quantities

P. C. Verma and Hana Mengistu
The College of Natural and Computational Science
Department of Chemistry, Wollega University Nekemte
Ethiopia

ABSTRACT
The present review is carried out in connection with the work on physicochemical studies of systems involving mixed solvents and the main object of the review has been to arrive at the nature of solute-solvent interactions from these studies. The solute-solvent interaction in solutions of different electrolytes in water and aqueous solvents has been deduced from the values of limiting apparent molar volume (density measurement), the B-coefficient of the Jones – Dole equation (viscosity measurement) and from conductance review at different concentrations and at different temperatures. Furthermore, the Gibbs free energies of activation of viscous flow per mole of solvent, \( \Delta \mu_1^# \) and per mole of solute, \( \Delta \mu_2^# \), entropies, \( \Delta S^0 \) and enthalpies, \( \Delta H^0 \) of activation of viscous flow were also calculated and discussed in terms of transition state theory. The solubility of solutes in mixed solvents depends primarily on the solvation of the solutes or their constituent ions by the components of the solvent mixtures. Complications may arise if different crystal solvates are formed or if solute-solute interactions are appreciable.

Key words: Mixed solvents, concentrations, thermodynamic properties, viscosity, conductance, density.

INTRODUCTION
Solute-solvent interactions are of current interest in all branches of chemistry. The Solute-solvent interactions provide a better understanding of the nature of the solute and solvent therefore, whether the solute modifies or distorts the structure of the solvent [1-6]. Investigation on solute-solvent interaction studies have been a subject of active interest among physical chemists and mostly the inferences regarding these interactions are drawn from conductance, molar volume data and viscosity data together [7]. Literature is full of such studies in pure solvents. Studies in mixed solvents are of considerable interest because peculiar results are obtained in most of the solvent systems. The solute-solvent interactions provide a better understanding of the nature of the solute and solvent therefore, whether the solute modifies or distorts the structure of the solvent [8].

The present review is carried out with a view to investigate solute-solvent interactions are drawn from conductance, molar volume data and viscosity measurement. The study of apparent molar volumes of electrolytes at infinite dilution, parameter of Jones-Dole equation and their dependence on temperature, molar conductance at infinite dilution and Walden product (viscosity and conductance) studies can furnish useful information on the nature of solute-solvent interaction [9]. The aims of such attempts have been to obtain better parameters of solvent polarity by choosing solvent-dependent standard systems and examining the changes in parameters of that system when the solvent is changed. Solvents can be classified in many ways including their polarity, acidity, electron pair or proton-donating properties, etc. Some solvent scales are defined to describe individual intermolecular interactions in liquid media; others do not separate specific properties and are referred to as general polarity scales [10]. These interactions can play a large role in determining ground-state and excited-state structure, dynamics, kinetics, and branching ratios. A key problem has been to monitor and separate the different types of interactions (hydrogen bonding, \( \pi - \pi \)
stacking, electrostatic interactions, etc.) occurring between solute and solvent. The incomplete understanding of solute-solvent interactions has been exacerbated by the lack of structurally-specific probes; typically, the effect of solvent on excited-state relaxation processes is followed by fluorescence lifetime measurements, elucidated the role of the solvents on the kinetics of excited-state relaxation processes, little direct information is provided on the specific solute-solvent interactions responsible for those kinetics [11]. The solubility of solutes in mixed solvents depends primarily on the solvation of the solutes or their constituents ions by the components of the solvents mixtures. Complications may arise if different crystal solvents formed. Solvent mixtures (mixed solvents) play important roles in chemical industries and in research laboratories. The value of mixed solvents comes about, for example, through the enhancement of chemical reactivity by increasing reactant solubility or product separation [12].

The present investigation was done to study thermodynamic properties in solutions involving mixed solvent and to reach a particular system to be selected for the various investigations, a review of the literature of the mass and transport properties in混合 solvent was done. For the sake of convenience, these thermodynamic properties are reviewed in the three sections such as density, conductance and viscosity measurement [13-17].

OBJECTIVES OF THE REVIEW

The specific objective of this review to:

➢ To review solute-solvent interaction of different solutes in mixed solvents solutions by using thermodynamic property of measurement of such as; viscosity measurement, density measurement and conductance measurement at different, temperatures and concentrations.

Thermodynamic properties and solute-solvent interaction in aqueous mixed solvents

Thermodynamic Properties can be measured by using different property at different temperatures such as:

- Viscosity measurements
- Conductance measurements
- Density measurements

1. Viscosity measurements

Viscosity is a composite of a solution's mass transport properties. Viscosity of often referred to as a thickness of fluid. You can think of water (low viscosity) and honey (high viscosity). In this study we measured the absolute viscosity for each of the materials [18]. The viscosity of solution is resistant to flow which is due to internal friction of layers which retards the velocity of other layers. In general, the frictional forces are more at the wall of tube as compare to central part of tube. That’s why the central layer flows faster than peripheral layers [19]. Viscosity greatly influences diffusion of species which are dissolved or dispersed in a media such as an ionic liquid. Viscosity is very temperature dependent. Viscosity of a liquid decreases with increasing temperature. It is closely linked to the internal structure of liquids. The course of viscosity varies considerably with temperature. The temperature dependence has always decreasing character which is in most cases possible to express by the empirical Arrhenius mathematical function in the form [20].

\[
\eta = A e^{\frac{E_a}{RT}}
\]  

Where \(\eta\) is dynamic viscosity (Pa.s); \(A\) is the pre-exponential factor (Pa.s); \(E_a\) is the exponential constant that is known as activation energy (J/mol); \(R\) is the gas constant (J/mol K) and \(T\) is the absolute temperature (K) [21]. The value of \(A\) can be approximated as the infinite temperature viscosity (\(\eta_0\)), which is exact in the limit of infinite temperature. Hence, equation (1) can be rewritten in the following form

\[
\eta = \eta_0 e^{\frac{E_a}{RT}}
\]  

Equations (1) and (2) are basically equivalent. Although equation (1) gives a more accurate representation of the fluid since the pre-exponential value is better defined there. However, equation (2) is not yet in its simplest form. In addition to this, which is used to represent the stability of the liquid system, is reported as unreliable in discriminating oil viscosity – temperature stability [22]. The relative viscosities of the mixed solutions were analyzed with the help of the Jones-Dole [23].
\[ \eta_r = \eta / \eta_0 + 1 + A \sqrt{C} + BC \] 

(4)

Where \( \eta_r \) is the relative viscosity, \( \eta \) is the viscosity of the solution, \( \eta_0 \) is the viscosity of the solvent, \( C \) is the molar concentration and \( A \) and \( B \) are constants characteristic of the solute electrolyte. A coefficient represents the contribution from inter-ionic electrolytic force. The \( B \) coefficient is said to be a measure of the effective hydrodynamic volume of the solvated ions and to donate the order structure the values of \( A \) and \( B \) of equation (4) are determined from the intercept and slope of \( (\eta / \eta_0 - 1) / \sqrt{C} \) versus \( C^{1/2} \) [24].

2. Conductance Measurements

Measurement of solution conductance is a classical electro analytical technique that finds application in a variety of chemical and biochemical studies, we can measured by modern conductometer [25]. For example, conductance can be used to assess solvent purity, determine relative ionic strengths of solutions (including functioning as a detector for ion chromatography), monitor dissolution kinetics and the approach to equilibrium for partially soluble salts, determine critical micelle concentrations, follow the course of some enzymatic reactions, as well as to provide basic thermodynamic data for electrolyte solutions. Conductivity measurement of the ionic liquid and mixtures of the ionic liquid with water in solvent at different temperatures showed increase in conductivity due to the presence of the ionic liquid in water and mixed solvent volume decrease in other co solvents [26]. Conductivity is a measure of the concentration of ions in solution. By completing the circuit shown in Figure 1, we can measure the conductivity of the solution in the beaker. The conductivity is proportional to the current that flows between the electrodes. For current to flow, ions must be present in solution to carry the charge from one electrode to another. Increasing the number of ions in solution will increase the amount of charge that can be carried between electrodes and will increase the conductivity. The units’ micro Siemens/cm (\( \mu \)S/cm) and milli Siemens/cm (mS/cm) are most commonly used to describe the conductivity of aqueous solutions [27].

When two electrodes are immersed in a solution and a potential is applied across them, a current will be produced in the external circuit that connects the two electrodes. The mechanism of electrical communication between the two electrodes in solution is the movement of ions in the solution. The magnitude of the current observed generally obeys Ohm’s Law [28].

\[ E = I R \]  

(5)

\[ 1/R = K A / L \]  

(6)

Where \( E \) is the applied potential, \( I \) is the current measured, and \( R \) is the resistance of the solution between the two electrodes.
conductivity, $\Lambda_0$ [29]. This parameter represents the molar conductivity for a compound that would hypothetically be measured in the limit of infinite dilution. In practice, such values are obtained by fitting experimental data of an equation known as Kohlrausch’s Law:

$$\Lambda_m = \Lambda_0 - k\sqrt{c}$$

(7)

The limiting equivalent conductance, $\Lambda_0$ at different temperature is evaluated from Onsager’s plots [29], and with the help of Owens’s method [30]. This is based on the conductance equation,

$$\Lambda_m = \Lambda_0 \cdot SC^{1/2} + AC \log C + BC$$

(8)

Where $S$ is the limiting Onsager slope, $C$ is the concentration, $A$ and $B$ are constants. In any event, experimental values of $A$ have been carefully determined for many salts as a function of concentration in very dilute solutions, and the intercept values of the resulting plots obtained. Conductivity is concentration dependent, measured values for different solutions are not easy to compare directly. For this reason, a quantity called the molar conductivity (or sometimes equivalent conductivity). The molar conductivity is symbolized by $\Lambda_m$ and it is defined as the solution conductivity ($\kappa$) normalized by the total ionic concentration ($C$).

$$\Lambda_m = \kappa /C$$

(9)

3. Density Measurements

Density is a measure of the “compactness” of matter within a substance and is defined by the equation:

$$\text{Density} = \text{mass}/\text{volume}$$

(10)

The density of a solution is a relative measurement of the mass of an object compared against the space that it occupies. Finding a solution’s density is a simple task. Once measurements have been taken to determine the volume and mass of the solution, it is easy to calculate the density of the solution. The densities of solutions of solute and aqueous mixed solvent at the corresponding solubilising in different temperatures were determined by using a specific gravity bottle (25 mL capacity) as described elsewhere [31]. The extrapolation of the apparent molar volume of electrolytes to infinite dilution and the expression for the concentration dependence of the apparent molar volume is given by equation [32]. The apparent molar volume, $\Phi_v$, is calculated from the density

$$\Phi_v = \frac{1000(d_0 - d)}{m \cdot d_0} + \frac{M^2}{d}$$

(11)

Where $\Phi_v$ represents the molar volume of electrolyte, $d$ the density of the solution, $d_0$ is density of the solvent, $m$ the molality of the solution, $M_2$ the molecular weight of the electrolyte. The density of the solutions can be represented by Roots equation:

$$\frac{d - d_0}{c} = A - B\sqrt{C}$$

(12)

Where $A$ and $B$ are the constants of the Roots equation [33]. On plotting d-d$_0$/c versus$v$\sqrt{C}. A straight line should be obtained and we get straight line in each case. Values of $A$ and $B$ evaluated from the intercept and slope.

The apparent molar volume has been found to vary linearly with the square root of the concentration.

$$\Phi_v = \Phi^0_v + S\sqrt{C}$$

(13)

Where $\Phi^0_v$ is the limiting apparent molar volume and $S$ is the experimental slope. Here $\Phi^0_v$ is the measure of solute-solvent interactions. The $\Phi_v$ of electrolytes using Masson’s equation and found that it adequately represents the concentration dependence of the $\Phi_v$ of electrolytes over a wide temperatures and concentrations ranges.
RESULTS AND DISCUSSION

Viscosity Measurements

1. Viscosity – Temperature Relationship

The viscosity of all of solutions decreased as the temperature increased. This could be due to the energy obtained to overcome the resistance to flow, which may be due to the attractive forces among the solution of molecules. The relative viscosities of the mixed solutions were analyzed by using extended Jones-dole [20] equation of the form. From above equation (4) where η is the relative viscosity of the solution, η and η₀ are the viscosities of ternary solutions and the mixed solvent, respectively, A and B are the Jones-Dole coefficients, respectively [34-36]. Coefficient A results from the electrostatic interactions between the ions and accounts for the solute-solute interactions and B is attributed to the influence on the hydrogen bond structure by the ion and provides information about the solvation of solutes, which reflects the (solute-solvent) interactions [37-39]. The ionic B-coefficient is proportional to the partial molar entropy of the hydration and a positive B-coefficient is a measure of the effective hydrodynamic volume or co-sphere of the hydrated ion [40-41]. The values of A and B have been obtained as the intercept and slope from linear regression of [(η/η₀-1)/V] versus C¹/², which were found almost linear in these systems. A-coefficients are much smaller in magnitude as compared to B-coefficients, suggesting weak solute-solute and strong solute-solvent interactions in these solutions. Values of B-coefficients are larger in % aqueous solvent than those in % aqueous solutions due to greater hydrophilic-ionic group interactions. B-coefficients increase when the water is replaced by another mixed solvent, i.e. solute act as water structure-maker by H-bonding. B-coefficients increases with increasing concentration of solvent, the reason may be that the friction increases to prevent water flow at increased solute concentration. Thus, trends observed in the values of coefficients A and B support the behaviors of Φv, Φo, S, which suggest stronger solute-solvent interactions as compared to solute-solute interactions in these solutions.

2. Using different-temperature Viscosity

The viscosity – temperature stability was investigated by comparing it’s the original in different temperatures. When temperature increase in solution, the viscosity decrease that means the solute-solvent interaction was decrease. So the solution move free then the viscosity of solution decreases. The viscosity data (Table 1) has been analyzed on the basis of Jones- Dole relation:

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Temperature(°C)</th>
<th>A (mol⁻¹·cm³⁻¹)</th>
<th>B (mol⁻¹·cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte in water</td>
<td>35</td>
<td>0.007</td>
<td>0.166</td>
</tr>
<tr>
<td>Electrolyte in %</td>
<td>40</td>
<td>0.01</td>
<td>0.181</td>
</tr>
<tr>
<td>Aqueous solvent</td>
<td>45</td>
<td>0.144</td>
<td>0.183</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.035</td>
<td>0.258</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>-0.2</td>
<td>0.243</td>
</tr>
</tbody>
</table>

Parameter A of Jones-Dole equation represents the contribution from solute-solute interactions. The values of A, shows that solute-solvent interactions for an electrolyte in some wt. % of aqueous solutions decreases with increase in temperature, which may be due to more salvation of solute ions. The B parameter which measures the structure making/breaking capacity of an electrolyte in a solution also contain a contribution from structural effects and is responsible for solute-solvent interactions in a solvent. It has been emphasized by a number of workers that dB/dT is more important criteria for determining solute-solvent interactions. Viscosity study of a number of electrolytes has shown that structure-maker will have negative dB/dT and structure-breaker will have positive dB/dT. The temperature effect on B coefficient for an electrolyte in some wt. % of aqueous solutions shows a positive sign of dB/dT. Thus behaves as structure-breaker in some wt. % of aqueous solutions [42-43].
2. Conductance Measurements

2.1. Conductance –Temperature relationships

When a temperature increase the conductance of solutions also increase. That means solute solvent interaction of intermolecular force decrease or the ions of the solutions free move at that condition conductivity increase. For different mixed solvent has different conductivity measurement due to co-solvent effect. For example, in pure ethanol conductance increased slightly with increase in temperature and the conductivity of the solution increased with increase in temperature. The addition of the ionic liquid enhanced the ionic interactions in the solution. But conductivity decreases with increase in temperature and the decrease is non-linear. The addition of the ionic liquid as co solvent also resulted in a decrease in conductivity with increase in temperature which also non-linear. These results show that the addition of a co solvent to an ionic liquid has influenced the ionic association equilibrium of the ionic liquid. The thermodynamics properties of such solutions could be described as solute-solvent interactions.

The conductance data we have taken and analyzed on the basis of Walden product from equation (7). The Walden product data ($\Lambda_{m\varphi}$) have been recorded. The structure making/breaking nature of solute has been determined from temperature coefficient of Walden product. i.e. [$\Lambda_{m\varphi} (\eta_0) / dT$]. The negative temperature coefficient of Walden product for electrolyte in some wt. % of aqueous solutions indicates that electrolyte solution behaves as structure-breaker in some wt. % of aqueous solutions.

3. Density measurement

3.1. Density –Temperature relationships

When the temperature increase the density of solution was decrease as see the equation relationships of density. Partial molar volume is one such property and these volumes of electrolytes in mixed solvents are proved useful in ascertaining the solute-solvent interaction. Since $\Phi v^o$ has been regarded as a measure of solute-solvent interactions by many workers, greater magnitude of $\Phi v^o$ in a solution may be considered quantitatively as a measure of greater solute-solvent interactions [44].

In general, negative slope is favored. If the dielectric constant of the medium is high, whether the solvent is polar or non-polar and if the electrostatic solute solvent interaction is weak due to the large ionic size. On the other hand, a positive slope is observed if solute solvent interactions are strong due to low dielectric constant of the medium. Hence, the dielectric constant of the medium plays an important role for observing the sign of the slope. The $\Phi v^o$ is a measure of solute-solvent interactions. The $\Phi v^o$ values for an electrolyte are low and negative and increase with a rise in both the temperature and concentration in wt. % of aqueous solvent. This indicates the presence of solute-solvent interactions and these interactions are further strengthened at higher temperatures and higher concentrations suggesting larger electrostriction at higher temperatures. A quantitative comparison of the magnitude of values shows $\Phi v^o$ values are much greater in magnitude than $S v$ values, for all the solutions. This suggests that solute-solvent interactions dominate over ion–ion interactions in all the solutions and at all experimental temperatures. The values of $\Phi v^o$ decreases with increase in temperature for electrolyte solution wt. % of aqueous solutions indicates the absence of “caging effect and its behavior is just like common electrolyte.

4. Thermodynamics of Viscous Flow

The viscosity data have also been analyzed on the basis of Eyeing transition state theory. Activation parameters, Gibbs free energies of activation per mole of solute and free energies of activation per mole of solvent were calculated according to transition state theory of the relative viscosity proposed by [45- 49]. According to this theory, the B-Coefficient could be expressed by the following equation:

$$B = [(v_1^o - v_2^o) + v_1^o (\Delta \mu_2 - \Delta \mu_1)/RT]/1000$$

Where, $v_1^o$ is the apparent (partial) molar volume of the mixed solvents (aqueous amino acids) and $v_2^o$ is the limiting apparent (partial) molar volume of the solute at infinite dilution, respectively. The free
energy of activation per mole of solvent (\( \Delta \mu^0_1 \)) has been calculated by using the Eyring viscosity relation [50].

Viscosity data has also been analyzed on the basis of transition state theory of relative viscosity of electrolytic solutions as suggested by Eyring. The values of \( \Delta \mu^0_1 \) (Free energy of activation per mole of solvent) and \( \Delta \mu^0_2 \) (Free energy of activation per mole of solute) is calculated by using the following relations:

\[
\Delta \mu^0_1 = RT \ln \left( \frac{\eta_1 v_{10}}{hN} \right) \tag{16}
\]

\[
\Delta \mu^0_2 = -\Delta H^0 + RT/v_{10} [1000B - (v_{10} - \Phi_{s0})] \tag{17}
\]

Where \( R, h \) and \( N \) are gas constant, Planck constant and Avogadro’s number respectively; \( T \) is absolute temperature and \( v_{10} \) is partial molar volume of solvent. The values of \( v_{10}, \Delta \mu^0_1 \) and \( \Delta \mu^0_2 \) are recorded. In the earlier prediction it suggested that for structure maker normally \( \Delta \mu^0_1 < \Delta \mu^0_2 \) and for breaker \( \Delta \mu^0_1 > \Delta \mu^0_2 \). It suggests that solutes behave as structure-breaker in wt. % of solute solutions. This may be due to increase in interactions of solute ions by the solvent molecules as a result of weakening of forces among solvent molecules at transition state. The entropy, \( \Delta S^0 \) and enthalpy, \( \Delta H^0 \) of activation of viscous flow has been calculated using the following relation.

\[
\Delta \mu^0_2 \# = \Delta H^0 - T \Delta S^0 \tag{18}
\]

It was found that the \( \Delta \mu^0_2 \# \) values for Solute in water and aqueous mixed solvent are positive and much larger than those of \( \Delta \mu^0_1 \# \) It has been reported that the larger the value of \( \Delta \mu^0_2 \# \), the greater is the structure making ability of the solute.

**CONCLUSION**

The solute-solvent interactions can be better understood if the bulk properties of the solutes and solvents in their pure state and in the mixed state over wide range of temperature are studied. Solute-solvent interactions can be solved by transport property such as viscosity, conductance, and density. Viscosity calculated by Jones-dole equations. The limiting equivalent conductance evaluating by using different temperatures from Onsager’s with the help of Owens method based on conductance equation. And density (apparent volume) can be calculated from density data by using the equation. A comprehensive model has been developed for calculating the viscosity of concentrated aqueous and mixed-solvent electrolyte solutions.

**ACKNOWLEDGMENT**

We are thankful to Dr Dunkana Negussa, AVP, Wollega university for guidance and encouragement.

**REFERENCES**


