Mutual Comparison Studies of Mono and Di Cations in Binary and Ternary Aqueous Electrolytes Solution at 298.15 K

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Abstract

Densities and viscosities of binary and ternary electrolytes solution have been determined experimentally at 298.15 K. The results obtained from density and viscosity measurement have been used to calculate apparent molar volume \( \phi \), partial molar volume \( \phi^\circ \) at infinite dilution, relative viscosities \( \eta_{rel} \), A and B coefficients, and free energies of activation of viscous flow of solvent \( \Delta \mu^0 \) and solute \( \Delta \mu^2 \). The results are discussed in terms of the dehydration effect of the weak ion-ion and strong ion-solvent interactions. The properties of these systems are discussed in terms of the charge, size, and hydrogen bonding effect.

Keywords: Potassium chloride, barium chloride, magnesium chloride, magnesium sulphate, apparent molar volume, Jones-Dole coefficients, and free energies of activation

1. Introduction

We present in this paper, the study of interaction electrolytes in the aqueous medium, there has been an increased interest in the physicochemical properties of aqueous electrolyte media to understand the role played by the biological molecules in the living organism [1-6]. Disarrangement of water and electrolyte balance in living systems causes a wide variety of health problems. In physiological media such as blood, membranes, cellulose fluids, etc., the dipolar character of ions such as \( \text{Na}^+, \text{K}^+, \text{Mg}^{2+} \), and \( \text{Cl}^- \) etc., dissolved in body water has an important bearing on their biological functions. In recent years, a number of workers have utilized density and viscosity data to deduce the thermodynamic properties (relative viscosity, Jones-Dole coefficient, and free energy of activation of viscous flow) for a number of mixtures solutions [7-10]. Structural interactions of non-ionic solutes with ionic ones in different solvents are important in many fields of chemistry and biochemistry. Very recently, we have made a systematic effort to investigate the ultrasonic and volumetric properties of amino acids in concentrated glucose and mannose solution [11-13]. It was found that NaCl CaCl\(_2\) and MgCl\(_2\) increase the apparent molar volume and decrease the adiabatic compressibility of electrolytes solution. This increase could be attributed to the interactions of the ions of the NaCl, KCl, CaCl\(_2\), and MgCl\(_2\) electrolytes.
and aqueous glucose and mannose, causing the transfer of hydrated water molecules to the bulk state. In the present paper, we report densities, \( \rho \), and viscosities \( \eta \) of binary and ternary aqueous electrolytes solution have been determined experimentally at 298.15 K. From these experimental data a number of thermodynamic parameters namely, apparent molal volume; partial molar volume at infinite dilution; Jones- Dole equation calculate A and B coefficients and free energies of activation of viscous flow of solute and solvent respectively have been calculated. These parameters were utilized a mutual comparison interaction study of mono and di cations in binary and ternary electrolytes solution at 298.15 K.

2. Experiments
2.1 Chemical and Preparation
Potassium Chloride, barium chloride, magnesium chloride, and magnesium sulphate (99.9% purity) were procured from Merck and S d Fine Ltd. The viscosities and densities of the aqueous electrolytes solution at various concentrations as well as in double-distilled de-ionized water were measured experimentally. All the solutions were prepared by mass in a dry box and were stored in special air-tight bottles and kept in dark to avoid photochemical degradation. The weighing was done on an Afcozet ER-120A electronic balance with an accuracy \( \pm 0.1 \) mg.

2.2 Measurement of density and viscosity
The densities were measured with a single capillary pycnometer (made of Borosil glass) of bulb capacity of \( 8 \times 10^{-6} \) m\(^3\). The marks of the stems were calibrated using double distilled water at 298.15 K. The pycnometer was kept for about 30 minutes in a thermostatic water bath so that the thermal fluctuation in density was minimized. The viscosity measurements were carried out by Ubbelohde type suspended level viscometer which was first calibrated with doubled distilled water. The viscometer was allowed to stand in an electronically controlled thermostatic water bath for 30 minutes to minimize the thermal fluctuation. The time of fall was recorded with a stop-watch of least count 0.1 s. At least three-time records were obtained, and the average value was used as the experimental flow time. Poiseuille’s equation was employed to calculate the viscosity of the water + electrolyte solutions.

\[
\eta = \frac{\pi \rho h g r^4 t}{8 l V} = \rho \beta t
\]

Here \( \rho \) is the density of the electrolytes solutions, \( h \) is the height of the column in the viscometer, \( g \) is the acceleration due to gravity, \( r \) is the radius of the capillary, \( l \) is the length of capillary and \( t \) is the time of fall of the solution of volume \( V \). The term \( h, g, r, l \), and \( V \) are constant for a given viscometer, therefore, these have been replaced by single term \( \beta \). The temperature of the water bath was maintained at 30\({}^\circ\)C. The viscosity and density data were found to be accurate within \( \pm 0.1 \) % and \( \pm 0.01\)% respectively.

3. Results and discussion
The densities and viscosities of binary and ternary electrolytes solution have been determined experimentally at 298.15 K and are presented in Table 1. It is observed from Table 1 that densities \( \rho \) and viscosities \( \eta \) for all the binary systems increase with the increase in molalities of KCl, BaCl\(_2\), and MgCl\(_2\). The values of \( \rho \) and \( \eta \) of these systems aqueous NaCl + KCl, BaCl\(_2\) + MgCl\(_2\), and MgCl\(_2\) + MgSO\(_4\) are recorded in Table 2. The values of \( \rho \) and \( h \) are varied with the concentration of electrolytes in all the systems under investigation, which appear to be due to hydrophobic properties of solutes i.e. H-bond forming. The changes in the structure of solvent or solution as a result of H-bond formation lead to a decrease in intermolecular free length [13]. The solute may occupy the interstitial spaces insolvent or get solvated forming new weaker bonds. It was suggested [14-16] that what is experimentally observed for any system, reflects the compromise
between the tendency for the ion and the water to interact with each other and the inclination of the solutes to associate with the solvent.

### Table 1: Densities (ρ) and viscosities (η), relative viscosities (η_{rel}) and apparent molal volume (ø_v) of concentrated aqueous KCl, BaCl_2 and MgCl_2 at 298.15K

| C (mol·L⁻¹) | ρ (×10⁻³ kg m⁻³) | η (×10⁻¹ Nm⁻²s) | η_{rel} (×10²) | ø_v (×10⁶ m³mol⁻¹) |
|------------|-----------------|-----------------|----------------|------------------|
|            |                 |                 |                |                  |
| Aqueous KCl|                 |                 |                |                  |
| 0.10       | 1.001           | 0.6531          | 0.7673         | 35.66            |
| 0.20       | 1.004           | 0.6740          | 0.7918         | 40.17            |
| 0.30       | 1.009           | 0.6896          | 0.8102         | 34.99            |
| 0.40       | 1.014           | 0.7353          | 0.8639         | 32.40            |
| 0.50       | 1.020           | 0.7934          | 0.9321         | 28.84            |
| Aqueous BaCl_2|             |                 |                |                  |
| 0.10       | 1.012           | 0.6188          | 0.7270         | 85.52            |
| 0.20       | 1.027           | 0.5954          | 0.6995         | 90.04            |
| 0.30       | 1.049           | 0.5677          | 0.6670         | 71.48            |
| 0.40       | 1.062           | 0.5417          | 0.6364         | 87.28            |
| 0.50       | 1.086           | 0.5102          | 0.5994         | 66.71            |
| Aqueous MgCl_2|             |                 |                |                  |
| 0.10       | 1.007           | 0.4617          | 0.5424         | 104.81           |
| 0.20       | 1.009           | 0.4115          | 0.4835         | 144.32           |
| 0.30       | 1.018           | 0.3945          | 0.4635         | 134.09           |
| 0.40       | 1.025           | 0.2975          | 0.3495         | 133.99           |
| 0.50       | 1.030           | 0.2095          | 0.3046         | 137.94           |

The viscosity data were used to calculate the relative viscosity using Jones-Dole equation [17]

\[
\eta_{rel} = \frac{\eta}{\eta_0} = \left[ 1 + Am^{1/2} + Bm \right] \quad (2)
\]

Where \( \eta \) and \( \eta_0 \) are the viscosities of the solutions and solvent respectively. \( B \) is the Jones-Dole coefficient [17], an empirical constant, and is the measure of ion-solvent interaction. Its values depend on the size and shape of the solute particles.

### Table 2: Densities (ρ) and viscosities (η), relative viscosities (η_{rel}) and apparent molal volume (ø_v) of concentrated aqueous NaCl + KCl, BaCl_2 + MgCl_2 and MgCl_2 + MgSO_4 at 298.15K

| m (mol·L⁻¹) | ρ (×10⁻³ kg m⁻³) | η (×10⁻¹ Nm⁻²s) | η_{rel} (×10²) | ø_v (×10⁶ m³mol⁻¹) |
|------------|-----------------|-----------------|----------------|------------------|
|            |                 |                 |                |                  |
| Aqueous NaCl + KCl|             |                 |                |                  |
| 0.40 + 0.10 | 1.016           | 0.5445          | 0.6397         | 28.82            |
| 0.30 + 0.20 | 1.015           | 0.5503          | 0.6465         | 30.83            |
| 0.20 + 0.30 | 1.015           | 0.5885          | 0.6913         | 30.83            |
| 0.10 + 0.40 | 1.018           | 0.6879          | 0.8083         | 24.81            |
| Aqueous BaCl_2 + MgCl_2|             |                 |                |                  |
| 0.40 + 0.10 | 1.053           | 0.1526          | 0.1617         | 110.42           |
| 0.30 + 0.20 | 1.054           | 0.1203          | 0.1239         | 110.34           |
| 0.20 + 0.30 | 1.056           | 0.1644          | 0.1932         | 108.57           |
| 0.10 + 0.40 | 1.071           | 0.1532          | 0.1799         | 78.25            |
| Aqueous MgCl_2 + MgSO_4|             |                 |                |                  |
| 0.40 + 0.10 | 1.031           | 0.1253          | 0.1298         | 157.18           |
| 0.30 + 0.20 | 1.036           | 0.2225          | 0.2614         | 147.55           |
| 0.20 + 0.30 | 1.042           | 0.5033          | 0.5931         | 135.52           |
| 0.10 + 0.40 | 1.034           | 0.3477          | 0.4085         | 151.56           |
The A is the Falkenhagen coefficient [18] which indicates ion-pair electrostatic interactions. They were obtained by a least-square treatment as the intercepts and slopes of the linear plots of \( \eta /\eta_0 - 1/m_{1/2} \) versus \( m_{1/2} \) and their values are given in Table 2.

The viscosity, \( \eta \), of dilute solution of non-electrolytes is represented by

\[ \eta = \eta_0 (1+Bm) \]  \hspace{1cm} (3)

For a dilute solution of unsolvated spherical colloidal suspension, has derived by Einstein relation

\[ \eta_{rel} = 1+2.5\phi \]  \hspace{1cm} (4)

Where \( \phi \) is the volume fraction of the solute[19] . If this equation is valid or amino acids, Eq. (3) becomes

\[ \eta_{rel} = 1+0.0025V_hm \]  \hspace{1cm} (5)

Where \( V_h \) is the hydrodynamic volume. Since the \( Am_{1/2} \) term in Eq. 2 can be assumed to be negligible in a dilute solution, the following relation holds

\[ B= 0.0025V_h \]  \hspace{1cm} (6)

Hakin et. al[20] may be assumed that the partial molar volume at infinite dilution of the unsolved solute particle in a continuum solvent. The more B values in the mixed solvent might mean a more hydrodynamic volume in the mixed solvent.

A perusal of Table 3 shows that all the values of A coefficients are negative except MgCl2+ MgSO4+ H2O system and those of B coefficients are positive for all the binary and ternary systems under investigation, thereby suggesting the ion-ion interactions are weak and ion-solvent interactions are strong. The positive value of B indicates increased interaction between these polar ends and ions of the electrolytes. Iqbal et al [21 & 22] have estimated that the contraction of water around the appositively charged group is caused by electrostatic ion- solvent interaction and is called electrostriction.

**Table 3: Falkenhagen coefficient, (A), Jones Dole coefficient, (B), experimental slope (S_v), partial molar volume at infinite dilution (\( \varphi_0^\phi \)) Free energy of activation per mole of solvent, (\( \Delta \mu_1^{0#} \)) and solute (\( \Delta \mu_2^{0#} \)) of binary and ternary systems at 298.15 K.**

| Electrolytes | A \( (m^3/mol^{1/2}) \) | B \( S_v \) \( (m^3/mol^1) \) | \( \varphi_0^\phi \times 10^{-6} \) \( (m^3/mol^1) \) | \( \Delta \mu_2^{0#} \times 10^{-4} \) (KJ mol\(^{-1}\)) | \( \Delta \mu_1^{0#} = 9.05 \times 10^{-4} \) (KJ mol\(^{-1}\)) |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Binary system** | | | | | |
| Aqueous KCl | -6.127 | 5.171 | -20.07 | 20.80 | 20.70 |
| Aqueous BaCl2 | -10.460 | 15.98 | -38.90 | 39.45 | 1.09 |
| Aqueous MgCl2 | -5.927 | 5.928 | -78.0 | 46.10 | 74.52 |
| **Ternary system** | | | | | |
| NaCl + KCl + H2O | -2.80 | 0.094 | +48.07 | 57.80 | 1.95 |
| BaCl2+ MgCl2 + H2O | -1.96 | 0.080 | -33.32 | 24.7 | 20.72 |
| MgCl2+ MgSO4+ H2O | +4.96 | 1.528 | 99.10 | 94.32 | 21.33 |
A mutual comparison of the KCl, BaCl$_2$, and MgCl$_2$ shows that values of B are larger in the case of BaCl$_2$ and MgCl$_2$ than KCl. The Ba$^{+2}$ and Mg$^{+2}$ ion being smaller in size has an intense force field and hence a strong hydration co sphere around it. Therefore hydration of BaCl$_2$ and MgCl$_2$ (ion-solvent) will be much more than that of KCl. Further to this effect is superimposed the effect of the interaction of cations (K$^+$, Ba$^{+2}$ and Mg$^{+2}$) and anion (Cl$^-$) with negative and positive charge centers of water respectively (ion-ion interaction). The double charge on Ba$^{+2}$ and Mg$^{+2}$ results in an intense electric field and thus, the possibility of interactions with water are larger in the case of an aqueous BaCl$_2$ + MgCl$_2$ ternary system. The hydration behavior of aqueous electrolytes considered the following interactions (a) Akhtar [4] as the opposite ions of water nature which may be hydrophilic, the cations (K$^+$, Ba$^{+2}$ and Mg$^{+2}$) and anion (Cl$^-$) are hydrated in an electrostatic manner (b) the overlap of hydration groups co spheres of the terminal (K$^+$, Ba$^{+2}$, Mg$^{+2}$ and Cl$^-$) and the adjacent groups result in volume change. Table 3 shows that the values of B are positive and greater in binary systems than the ternary systems which indicate strong solute-solvent interactions.

The apparent molal volume, $\phi_v$, were calculated from measured density data of binary and ternary electrolytes solutions have been determined experimentally at 298 K and are presented in Table 1 using the following equation:

$$\phi_v = \frac{1000 (\rho^0 - \rho)}{m \rho \rho^0} + \frac{M}{\rho} \quad (7)$$

Where $M$ is the molecular mass of the solutes, $\rho^0$ and $\rho$ are densities of solvent and solution. The calculated values of $\phi_v$ of these binary and ternary systems are given in Table 1. In these cases where molality dependence of $\phi_v$, having definite trend points, The $\phi_v$ values increase due to reduction in the electrostriction effect at terminals, whereas it decreases due to disruption of side group hydration by that of the charged end. The linear variation was obtained by least-square fitting to the following Masson equation (17).

$$\Phi_v = \phi_0^v + S_v \sqrt{m} \quad (8)$$

The quantity $S_v$ is the experimental slope and the Masson type equation gives us an important quantity called partial apparent molal volume $\phi_0^v$ at infinite dilution. The quantity provides the solute-solvent interactions, and each solute molecule can only interact with solvent molecules that are surrounded. The derived values $\phi_0^v$ of along with $S_v$ are summarized in Table 3. Table 3 shows that the values of $\phi_0^v$ are positive of these binary and ternary systems which indicate ion-solvent interactions are strong. The variation of $\phi_0^v$ with the concentration of electrolytes can be explained in terms of the cosphere overlap model. According to this model, the overlap of the cospheres of two ions or polar groups or an ion with hydrophilic groups always produces a positive volume change. The values of $\phi_0^v$ are less in presence of mono metal ion (K$^+$) than those of divalent ions (Ba$^{+2}$ and Mg$^{+2}$). Mutual comparison of these electrolytes shows the values of $\phi_0^v$ are larger in the case of Ba$^{+2}$ and Mg$^{+2}$ than in K$^+$. The Ba$^{+2}$ and Mg$^{+2}$ ions are being smaller in size, has an intense force field and hence strong hydration co sphere around them therefore, hydration of MgCl$_2$ and BaCl$_2$ (Solute - solvent interaction) will be much more than that of KCl which is in good agreement with the results reported in glucose – alcohol-water mixture (Landge et al 2013)[23].

According to the transition state theory of the relative viscosities of electrolytic solutions proposed by Feakins et al [24], the B- coefficient given as

$$B = \frac{\langle V_1^0, V_2^0 \rangle}{1000 + \langle V_1^0 \rangle} + \langle \Delta \mu_2^{0#} - \Delta \mu_1^{0#} \rangle / RT \quad (9)$$
Where $\bar{V}_1^0$ and $\bar{V}_2^0$ is the partial molar volumes of the solvent and solute at infinite dilution, respectively, $\Delta \mu_1^{0\#}$ is the free energy of activation per mole of the solvent and $\Delta \mu_2^{0\#}$ is the free energy of activation per mole of the solute. The $\Delta \mu_1^{0\#}$ and $\Delta \mu_2^{0\#}$ were calculated from the equation

$$\Delta \mu_1^{0\#} = RT \ln \left( \frac{n_1^{0\#} \bar{V}_1^0}{hN_A} \right)$$

$$\Delta \mu_2^{0\#} = \Delta \mu_1^{0\#} + RT/\bar{V}_1^0 \left[ 1000 \text{B} - (\bar{V}_1^0 - \bar{V}_2^0) \right]$$

Where R, h, and N are the gas constant, Planck's constant and constant respectively and T is the absolute temperature. The values of $\Delta \mu_1^{0\#}$ and $\Delta \mu_2^{0\#}$ for different compositions of aqueous electrolytes are given in Table 3. Table 3 shows that $\Delta \mu_2^{0\#}$ is larger than $\Delta \mu_1^{0\#}$ suggesting that the formation of the transition state is accompanied by the breaking and distortion of the intermolecular bonds. Moreover, the greater values of $\Delta \mu_2^{0\#}$ than $\Delta \mu_1^{0\#}$ suggest that the metal chlorides understudy, behave as structure makers/promoters in different concentration ranges of electrolytes. Greater values of $\Delta \mu_2^{0\#}$ have also been reported in mixtures of Ni, Cu, Co, and Zn chlorides in aqueous glycine [23].

A comparison of $\Delta \mu_1^{0\#}$ and $\Delta \mu_2^{0\#}$ values of the two solutes result in the structure making ability of Ba$^{2+}$ and Mg$^{2+}$ is greater than K$^+$ which may be due to stronger solute-solvents interaction in BaCl$_2$ and MgCl$_2$ solutions. Therefore the hydration of BaCl$_2$ and MgCl$_2$ will is much greater than that of KCl. The dication charge on Ba$^{2+}$ and Mg$^{2+}$ results in intense electric field and the radius of Bar$^{2+}$ and Mg$^{2+}$ ions is smaller than that of K$^+$ thus the possibility of interactions with Aqueous MgCl$_2$ and MgSO$_4$ is larger in this ternary systems than NaCl + KCl + H$_2$O and BaCl$_2$+ MgCl$_2$+ H$_2$O which causes disruption of the intermolecular bonds of the solvent, thereby decreasing the values of $\Delta \mu_2^{0\#}$.

Thus the trends and magnitude of the various parameters obtained from viscosity measurement are reported in this paper. The studies suggest that ion- solvent interactions are stronger and ion-ion interactions are weak. The extent of interactions and structure-making ability is greater in the case of BaCl$_2$ and MgCl$_2$. The dB/dT is a better criterion for determining the structure-making/breaking nature of any electrolyte rather than simply the B- coefficient.

4. Conclusion

The volumetric and viscometric studies have been used to the solute –solute and solute-solvent interaction in these binary and ternary systems. It can be concluded that the existence of ionic interaction in aqueous electrolytes solution is a strong structure maker. Mutual comparison of these electrolytes shows the values of B and $\phi$ are larger in the case of Ba$^{2+}$ and Mg$^{2+}$ than in K$^+$. The Ba$^{2+}$ and Mg$^{2+}$ ions are being smaller in size, have an intense force field, and hence strong hydration co sphere around them therefore, hydration of MgCl$_2$ and BaCl$_2$ (solute-solvent interaction) will be much more than that of KCl.

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