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Short Communication

Studies on Molecular Interactions of Some Electrolytes in Water by Volumetric and Viscometric Measurements at T = (303.15 to 323.15 K)

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Abstract

The viscosities and densities of potassium chloride, potassium nitrate, magnesium chloride, and magnesium nitrate have been measured at 303.15, 308.15, 313.15, 318.15 and 323.15 K in aqueous solution. The viscosity data were analyzed by using Jones–Dole equation. The values of apparent molar volume, limiting apparent molar volume have been evaluated from the density data. The results were interpreted in the light of ion–ion and ion–solvent interactions and of structural effects of the solutes in solution.

Keywords: Density; Apparent molar volume; Viscosity; Jones–Dole equation.

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1. Introduction

The volumetric behavior of solutes has been proven to be very useful in elucidating the various interactions occurring in aqueous solutions [1]. Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes and temperature of solutions have been employed as a function of studying ion-ion and ion-solvent interactions [2]. It has been found by a number of workers [3-5] that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid’s viscosity depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

The main ionic solutes in bio-fluids are the alkali cations viz; Na^+ and K^+ with Mg^{2+} in small amounts and the common anions are the NO_3^- and Cl^-. The high concentration data of the studied electrolytes is available in literature but the low concentration data for the similar type of electrolytes is the least. Our future objective is to investigate the

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interactions between studied electrolytes and protein denaturing agents such as sodium dodecyl sulfate, dodecyl trimethyl ammonium bromide, cetyl trimethyl ammonium bromide, etc. The addition of electrolytes to the surfactant solution could effectively reduce the critical micelle concentration of surfactants and also increase the detergency. Considering this, the present investigation have been undertaken to provide better understanding of the nature of these electrolytes at lower concentration (~0.003 to ~ 0.01 molkg^{-1}) in aqueous medium and to through light on ion-solvent interactions.

2. Experimental

2.1. *Chemicals*

Potassium chloride, KCl (> 99%, Thomas Baker, India), potassium nitrate, KNO_3 (> 99.5 %, E. Merck, Germany), magnesium chloride, $MgCl_2.6H_2O$ (> 98%, E. Merck, Germany) and magnesium nitrate, $Mg(NO_3)_2.7H_2O$ (> 99%, Thomas Baker, India) were used after drying over P_2O_5 in desiccators.

2.2. *Density measurements*

The reagents were always placed in the desiccators over P_2O_5 to keep them in dry atmosphere. Freshly distilled water with specific conductance of ~10^{-6} $\Omega^{-1}.cm^{-1}$ was used for preparing aqueous solution. All the aqueous solutions of electrolytes were made by weight and molalities (*m*) were converted into molarities (*C*) using the standard expression [6]. It is to be mentioned, water of hydration was taken into consideration for calculating the molalities of $MgCl_2$ and $Mg(NO_3)_2$:

$$C=1000\rho\cdot m/\,(1000 + mM_2)$$

where ρ and M_2 are the solution density and molecular weight of an electrolyte. A Mettler PM-200 electronic balance with an accuracy of ±0.0001 g was used for the mass determination. It is apparent that densities changed only in the fourth decimal. This is attributed to the very low concentration of the electrolytes.

The densities (ρ) were measured with an Ostwald-sprengel type pycnometer having bulb volume of 10×10^{-6} m^3 .The pycnometer was calibrated at 303.15 to 323.15 K with doubly distilled water. Averages of triplicate measurements were taken into account.

2.3. *Viscosity measurements*

The viscosities were measured at the stuided temperature using an Ostwald`s suspended level type viscometer which has a flow time of about 214s for water at 303.15 K. The viscometer was calibrated with water. The density and viscosity measurements were carried out in the same water bath (±0.01K).

3. Results and Discussion

3.1. *Apparent molar volume*

The measured densities of electrolytes in water are listed in Table 1 as functions of concentration and temperature. The apparent molal volumes of electrolytes in aqueous systems at 303.15 K to 323.15 K are shown in Table 1. The apparent molar volume of a solute in solution, generally denoted by φ_{v} was calculated by the following equation:

$$\varphi_v = \left[\frac{M_2}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right] \tag{1}$$

The apparent molar volume at infinite dilution, (φ_v^0) was calculated using least square fit to the linear plots of experimental values of φ_{v} versus square root of molal concentration ($\sqrt{m}$) using the following Masson equation [7]:

$$\varphi_{\mathrm{v}} = \varphi_v^0 + S_{\mathrm{v}}\sqrt{m} \tag{2}$$

where S_{v} is the experimental slope, which is sometimes considered to be the volumetric pairwise interaction coefficient [8-9]. The limiting apparent molal volume (φ_v^0) and S_{v} values along with standard error are given in Table 3. It is evident from the table that the values of S_{v} are positive for electrolytes in water at different temperatures. Since S_{v} is a measure of ion-ion interactions, the result indicates the presence of very strong ion-ion interactions. The limiting apparent molal volume (φ_v^0) which is taken to be the partial molal volume at infinite dilution of electrolytes in aqueous solutions reflects the true volume of the solute and the volume change arising from solute-solvent interactions. Among the electrolytes studied (KCl, KNO_3, $MgCl_2$ and $Mg(NO_3)_2$), the φ_v^0 value obtained for $Mg^{2+}Cl^-/NO_3^-$ is observed to be abnormally higher than those of the other electrolytes (shown in Table 3). This abnormality may be accounted for by the fact that Mg^{2+} can form an octahedral complex with water. The variation of φ_v^0 with the molality of electrolytes can be rationalized in terms of cosphere overlap model [10]. According to the model, the overlap of the cospheres of two ions or polar groups or an ion with that of hydrophilic groups always produces a positive volume change. On the other hand, the overlap of the cospheres of an ion with that of hydrophobic groups results in a negative volume change. The temperature dependence of limiting apparent molal volume, φ_v^0 for electrolyte plus water solutions can be expressed by the following expression:

$$\varphi_v^0 = a_0 + a_1T + a_2T^2 \tag{3}$$

where, T is temperature in Kelvin. The limiting apparent molar expansibilities (φ_E^0) can be obtained by differentiating Eq. (3) with respect to temperature.

$$\varphi_E^0 = (\partial\varphi_v^0/\partial T)_\mathrm{p} = a_1 + 2a_2T \tag{4}$$

The limiting apparent molar expansibilities (φ_E^0) for electrolytes plus water obtained using Eq. (4) at different temperatures are given in Table 4. It is found that φ_E^0 values decrease with rising temperature for KCl and KNO_3. This may be considered as an indication of the fact that the structure of the solvent is weakened by the elevation of temperature, that is, some solvent molecules may be released from the loose solvation layers of the solute. The effect is that the removal of solvent molecules favors solute–solute interactions causing less electrostriction around electrolytes. On the other hand, opposite behavior has been observed for $MgCl_2$ and $Mg(NO_3)_2$.

Table 1. Densities and apparent molar volume of studied electrolytes in water at different temperatures.

$m\times10^{-2}$ ($\mathrm{molkg^{-1}}$)	T/K=303.15		T/K=308.15		T/K=313.15		T/K=318.15		T/K=323.15	
	$\rho\times10^{-3}$ ($\mathrm{kgm^{-3}}$)	$\varphi_\mathrm{V}\times10^{6}$ ($\mathrm{m^3mol^{-1}}$)	$\rho\times10^{-3}$ ($\mathrm{kgm^{-3}}$)	$\varphi_\mathrm{V}\times10^{6}$ ($\mathrm{m^3mol^{-1}}$)	$\rho\times10^{-3}$ ($\mathrm{kgm^{-3}}$)	$\varphi_\mathrm{V}\times10^{6}$ ($\mathrm{m^3mol^{-1}}$)	$\rho\times10^{-3}$ ($\mathrm{kgm^{-3}}$)	$\varphi_\mathrm{V}\times10^{6}$ ($\mathrm{m^3mol^{-1}}$)	$\rho\times10^{-3}$ ($\mathrm{kgm^{-3}}$)	$\varphi_\mathrm{V}\times10^{6}$ ($\mathrm{m^3mol^{-1}}$)
KCl										
0.3209	0.995815	29.09	0.994201	31.37	0.992376	31.89	0.990385	33.83	0.988202	35.10
0.3885	0.995845	29.23	0.994230	31.54	0.992404	32.06	0.990413	33.94	0.988229	35.30
0.4985	0.995893	29.54	0.994277	31.74	0.992448	32.56	0.990458	34.16	0.988273	35.49
0.6959	0.995979	29.87	0.994360	32.16	0.992528	32.89	0.990539	34.34	0.988352	35.67
0.8075	0.996027	30.06	0.994406	32.42	0.992572	33.17	0.990584	34.50	0.988396	35.82
0.9511	0.996089	30.22	0.994466	32.57	0.992645	31.67	0.990642	34.63	0.988452	36.01
KNO_3										
0.3067	0.995859	39.10	0.994247	41.16	0.99242	42.01	0.990427	45.23	0.988244	46.66
0.3997	0.995916	39.18	0.994303	41.33	0.992474	42.16	0.99048	45.39	0.988296	46.84
0.5019	0.995979	39.15	0.994365	41.34	0.992533	42.32	0.990538	45.53	0.988353	46.98
0.6997	0.996099	39.40	0.994483	41.63	0.992648	42.38	0.990648	46.01	0.988462	47.32
0.8615	0.996197	39.53	0.994579	41.82	0.992739	42.77	0.990738	46.22	0.988551	47.49
1.0325	0.996300	39.68	0.994679	42.09	0.992847	41.88	0.990832	46.47	0.988643	47.80
1.2658	0.996440	39.86	0.994818	42.13	0.992978	42.36	0.990961	46.65	0.988767	48.20
1.5135	0.996588	40.02	0.994962	42.38	0.993112	43.05	0.991096	46.89	0.988899	48.46
$MgCl_2$										
0.3022	0.995964	105.56	0.994349	109.49	0.992527	107.95	0.990536	111.98	0.988353	113.82
0.4000	0.996057	106.08	0.994442	109.58	0.992620	107.90	0.990628	112.08	0.988445	113.68
0.5000	0.996152	106.42	0.994536	109.85	0.992714	108.09	0.990718	112.93	0.988538	113.79
0.7000	0.996342	106.77	0.994723	110.24	0.992901	108.41	0.990903	113.16	0.988724	113.87
0.7995	0.996436	106.96	0.994822	109.62	0.992994	108.52	0.990988	114.10	0.988816	113.97
0.8994	0.996530	107.12	0.994908	110.59	0.993086	108.74	0.991094	112.53	0.988909	113.94
$Mg(NO_3)_2$										
0.3029	0.995962	159.67	0.994351	162.35	0.992521	163.59	0.990531	167.33	0.988348	169.28
0.4005	0.996055	159.93	0.994438	164.00	0.992615	162.69	0.990621	167.43	0.988437	169.38
0.5059	0.996155	160.16	0.994536	164.24	0.992713	162.80	0.990718	167.51	0.988533	169.45
0.7003	0.996337	160.74	0.994716	164.56	0.992892	163.15	0.990856	173.33	0.988708	169.77
0.8141	0.996443	161.00	0.994821	164.70	0.992997	163.23	0.991000	167.74	0.988811	169.80
0.9263	0.996547	161.24	0.994924	164.85	0.993101	163.23	0.991102	167.83	0.988912	169.86

Hepler [11] developed a technique of examining the sign of $[\partial\varphi_E^0/\partial T]_\mathrm{P}$ for various solutes in terms of the long range structure making or breaking ability of solutes in aqueous solution using the general thermodynamic expression:

$$[\partial\varphi_E^0/\partial T]_\mathrm{P} = \left[\frac{\partial^2\varphi_v^0}{\partial T^2}\right]_p \tag{5}$$

The sign of $\left[\dfrac{\partial^2 \varphi_v^0}{\partial T^2}\right]_p$ i.e. second derivative of limiting apparent molal volume of solution with respect to temperature at constant pressure which corresponds to structure making or breaking properties of solution was determined. The value of $\left[\dfrac{\partial^2 \varphi_v^0}{\partial T^2}\right]_p$ has been found to be negative for KNO_3 and KCl suggesting structure breaking property and the positive value for $MgCl_2$ and $Mg(NO_3)_2$ suggesting structure making property. Roy *et al.* [12] reported negative value of $\left[\dfrac{\partial^2 \varphi_v^0}{\partial T^2}\right]_p$ for KNO_3 in water which agrees with our estimated value.

Table 2. Viscosity of studied electrolytes in aqueous solutions as a function of concentration at various temperatures.

m×10^{-2} (molkg^{-1})	*T*/K=303.15	*T*/K=308.15	*T*/K=313.15	*T*/K=318.15	*T*/K=323.15
	η (mPa S)	η (mPa S)	η (mPa S)	η (mPa S)	η (mPa S)
KCl					
0.3209	0.8063	0.7279	0.6616	0.6045	0.5552
0.3885	0.8068	0.7284	0.6621	0.6051	0.5557
0.4985	0.8076	0.7292	0.6629	0.6059	0.5566
0.6959	0.8088	0.7304	0.6641	0.6071	0.5578
0.8075	0.8094	0.7286	0.6647	0.6077	0.5584
0.9511	0.8102	0.7316	0.6655	0.6086	0.5592
KNO_3					
0.3067	0.8152	0.7365	0.6691	0.6139	0.5658
0.3997	0.8175	0.7382	0.6705	0.6157	0.568
0.5019	0.8190	0.7310	0.6722	0.6178	0.5701
0.6997	0.8217	0.7433	0.6752	0.621	0.5737
0.8615	0.8244	0.7449	0.6775	0.6231	0.5761
1.0325	0.8263	0.7472	0.6782	0.6253	0.5785
1.2658	0.8285	0.7492	0.6805	0.628	0.5813
1.5135	0.8305	0.7514	0.6833	0.6304	0.5845
$MgCl_2$					
0.3022	0.8039	0.7343	0.6675	0.6213	0.5775
0.4000	0.8323	0.7545	0.6865	0.6301	0.5975
0.5000	0.8483	0.7723	0.7031	0.6466	0.6196
0.7000	0.8693	0.7896	0.7195	0.6648	0.6244
0.7995	0.8885	0.8071	0.7366	0.6804	0.6481
0.8994	0.9112	0.8198	0.7601	0.6989	0.6697
$Mg(NO_3)_2$					
0.3029	0.8036	0.7327	0.6665	0.6195	0.5575
0.4005	0.8293	0.751	0.6847	0.6272	0.5773
0.5059	0.8454	0.7688	0.7021	0.6449	0.5927
0.7003	0.8685	0.7895	0.721	0.6635	0.6106
0.8141	0.8903	0.8097	0.7356	0.6813	0.6176
0.9263	0.9014	0.8156	0.7458	0.6958	0.6305

Table 3. Standard partial molar volume, experimental slope, values of the parameter *A* and *B* of the Jones-Dole equation for studied mineral electrolytes in water at various temperatures.

T(K)	$S_v \times 10^6$ ($m^3 l^{1/2} mol^{3/2}$)	$\varphi^o_v \times 10^6$ ($m^3 mol^{-1}$)	$\varphi_E \times 10^6$ ($m^3 mol^{-1} K^{-1}$)	$B \times 10^3$ ($m^3 mol^{-1}$)	$A \times 10^{3/2}$ ($m^{3/2} mol^{-1/2}$)
KCl					
303.15	28.17 (±1.03)	27.51 (±0.08)	2.859	-0.0454 (±0.016)	0.1257 (±0.001)
308.15	30.20 (±0.90)	29.66 (±0.07)	2.820	-0.4225 (±0.422)	0.1574 (±0.033)
313.15	9.46 (±17.90)	31.65 (±1.39)	2.781	-0.0554 (±0.019)	0.1535 (±0.002)
318.15	19.45 (±0.79)	32.75 (±0.06)	2.741	-0.0476 (±0.032)	0.1718 (±0.003)
323.15	20.79 (±1.26)	33.97 (±0.10)	2.702	-0.0826 (±0.028)	0.1915 (±0.002)
KNO_3					
303.15	14.28 (±0.88)	38.24 (±0.08)	0.662	-0.3762 (±0.060)	0.3512 (±0.005)
308.15	18.39 (±0.99)	40.12 (±0.09)	0.657	-0.4131 (±1.034)	0.2808 (±0.093)
313.15	9.16 (±5.44)	41.56 (±0.49)	0.653	-0.3453 (±0.102)	0.3773 (±0.009)
318.15	25.61 (±1.02)	43.8 (±0.09)	0.648	-0.3576 (±0.033)	0.4745 (±0.003)
323.15	26.91 (±1.08)	45.11 (±0.10)	0.643	-0.3308 (±0.036)	0.5591 (±0.003)
$MgCl_2$					
303.15	37.04 (±3.14)	103.7 (±0.24)	-1.724	30.383 (±3.834)	-1.4316(±0.296)
308.15	20.37 (±9.52)	108.35 (±0.74)	-1.691	25.860 (±3.041)	-0.9931(±0.235)
313.15	21.22 (±2.80)	106.66 (±0.22)	-1.657	30.026 (±3.350)	-1.2265(±0.258)
318.15	33.44 (±18.83)	110.26 (±1.46)	-1.624	26.256 (±2.025)	-0.7752(±0.156)
323.15	5.414 (±2.03)	113.43 (±0.16)	-1.591	28.738 (±6.249)	-0.4851(±0.481)
$Mg(NO_3)_2$					
303.15	38.86 (±1.40)	157.5 (±0.11)	0.351	28.396 (±3.284)	-1.3380(±0.255)
308.15	49.96 (±13.98)	160.3 (±1.09)	0.354	26.196 (±2.809)	-1.0687(±0.218)
313.15	30.80 (±10.16)	163.05 (±0.79)	0.357	26.362 (±3.044)	-1.0191(±0.236)
318.15	43.06 (±70.33)	165.24 (±5.47)	0.360	26.257 (±1.564)	-0.8338(±0.121)
323.15	15.29 (±1.36)	168.42 (±0.11)	0.362	28.045 (±4.537)	-1.0573(±0.352)

3.2. *Viscosity B-coefficient*

The viscosities of KCl, KNO_3, $MgCl_2{\cdot}6H_2O$ and $Mg(NO_3)_2{\cdot}7H_2O$ in aqueous solutions have been determined at 303.15 to 323.15 K with 5K intervals respectively. The relevant data are shown in Table 2. The viscosity data were analyzed in terms of the semi-empirical Jones-Dole equation [13], after arranging it into a straight line form given below;

$$\frac{\eta}{\eta_o} = 1 + AC^{1/2} + BC \tag{6}$$

where η_r is the relative viscosity and C is the molar concentration, *A* and *B* are the constants characteristic of ion-ion and ion-solvent interactions respectively. The value of η increases with the increase in molarity. As a result, the dynamic equilibrium between monomer water molecule and aggregated water molecule [$nH_2O = (H_2O)_n$] shifts towards right. For The evaluation of the coefficients *A* and *B* from the Jones-Dole Eq. (6), plots of

$(\eta_r\text{-}1)$ versus $\sqrt{C}$ were constructed and were found to be linear within experimental uncertainty over the whole concentration range of electrolyte studied. The values of *A* and *B*-coefficients for the electrolytes are estimated by computerized least-square method and presented in the Table 3, along with uncertainty. Table 3 shows that the values of *A* coefficients are either positive or negative and very small for all the four electrolytes indicating the presence of weak ion-ion interactions, which of course further improve with the rise in temperatures.

Table 4. Values of various co-efficient of Eq. 3, Hepler constant and d*B*/dT for studied electrolytes.

Electrolytes	a_0	a_1	a_2	Hepler constant	d*B*/d*T*
KCl	-839.264	5.2411	-0.0079	-0.00786	0.0060
KNO_3	-162.548	0.9568	-0.0010	-0.00097	0.0029
$MgCl_2$	627.126	-3.7420	0.0067	0.00666	-0.0580
$Mg(NO_3)_2$	51.186	0.1777	0.0006	0.00057	-0.0130

It is also evident from Table 3 that the values of *B*-coefficient, for $MgCl_2$ and $Mg(NO_3)_2$ aqueous solutions are positive and fairly large thereby suggesting the strong ion-solvent interactions. On the other hand, negative values of *B*-coefficient have been found for KCl and KNO_3 which reflects the structure rupturing property. The negative *B*-coefficient value was reported by A. Hammadi *et al*. [14] in aqueous system for KCl. Further the values of *B*-coefficient in aqueous KCl and KNO_3 solutions decrease with the increase in temperature, thereby suggesting that the ion-solvent interactions are weakened with the increase of studied temperatures. On the other hand, the values of the *B*-coefficient for $MgCl_2$ and $Mg(NO_3)_2$ in aqueous solution increase with the rise in temperature, thereby showing the ion-solvent interactions further improve with the increase in temperature. Recently it has been emphasized by many workers that d*B*/d*T* is a better criterion [15] for determining the structure making/breaking nature of any electrolyte rather than simply the *B*-coefficient. The values of d*B*/d*T* were calculated from the slope of the curve obtained by plotting the *B*-coefficient value against temperatures and these values are given in Table 4. It is evident from Table 4 that the positive values of d*B*/d*T* for KCl and KNO_3 showing their structure breaking nature. A perusal Table 3 shows that the *B*-coefficient values of $MgCl_2$ and $Mg(NO_3)_2$ decreases with rising temperature. So derivative of temperature (d*B*/d*T*) is negative. We can classify $MgCl_2$ and $Mg(NO_3)_2$ acts as structure maker in aqueous solution. Haque *et al.* [15] noticed that d*B*/dT value is negative for $MgCl_2$ in methanol. These are in excellent agreement with the conclusions drawn from $[\partial\varphi_v^{0\,2}/\partial T^2]_p$ as discussed earlier.

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