

Viscosity and density of binary electrolytes in aqueous solutions

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Abstract. Viscosities and densities of binary electrolytic solutions at different compositions have been measured at 298.15 K. Values of apparent molal volume, (ϕ_v), relative viscosity, (η_{rel}) and free energy of activation, ($\Delta\mu^{0\ddagger}$) have been deduced from density and viscosity data. Results show that there are short range and weak interactions in these binary systems.

Keywords. Binary electrolytes; apparent molal volume; relative viscosity; free energy of activation.

1. Introduction

Studies of viscosities and densities of aqueous and non-aqueous solutions have been reported (Parmar and Khanna 1986). It has been found by a number of workers that addition of electrolyte either makes or breaks the structure of a liquid. The making or breaking of the structure of fluid has been considered as a measure of solute–solvent and solute–solute interactions.

Recently Manohar and Atkinson (1992) carried out EMF measurements on mixtures of electrolytic systems at various ionic strengths at 25°C. The results were analysed in terms of the Harned equation and Pitzer formalism. Patil *et al* (1994, 1995) have determined the relative viscosity of mixed electrolyte solutions for the systems KBr–NaBr, KBr–Bu₄NBr, NaCl–NaBr and NaCl–Bu₄NBr at different ionic strengths and varying electrolyte mole fractions at 25°C. The data were used to calculate viscosity B-coefficient of the total electrolyte as a function of solute mole fraction. Structural interactions of non-ionic solutes with ionic ones in different solvents are important in many fields of chemistry. Studies on such interactions of electrolytes in aqueous and non-aqueous solvents are very significant and useful in investigating their physico-chemical behaviour. In chemical engineering, concentrated aqueous electrolytic mixtures, whose thermodynamic properties are known, are of considerable importance. In recent years, a number of workers (Parmar and Rao 1990) have utilized density and viscosity data to deduce thermodynamic properties (apparent molal volume, relative viscosity and free energy of activation of viscous flow) for a number of solutions containing mixtures of electrolytes.

An attempt has been made here to determine the densities and viscosities of aqueous binary systems of electrolytes, viz. BaCl₂ + MgCl₂, CH₃COOK + KCl, NaCl + NaNO₃, Na₂SO₄ + NaCl and KCl + KNO₃, in concentrated solutions at 298.15 K. A number of thermodynamic parameters have been deduced from these data,

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which are utilized to study various interactions taking place in solutions of mixed electrolytes.

2. Experimental

The chemicals used for the present investigations KCl, NaCl, MgCl₂ (Analar BDH, 99.9% purity), Na₂SO₄, MgSO₄, CH₃COOK, CH₃COONa, (ACS grade of 99.8% purity) were used as such without further purifications.

2.1 Solution compositions

Densities and viscosities of aqueous solutions of binary systems—BaCl₂ + MgCl₂, CH₃COOK + KCl, NaCl + NaNO₃, Na₂SO₄ + NaCl, and KCl + KNO₃—at different compositions—0.45 + 0.05, 0.40 + 0.10, 0.30 + 0.20, 0.25 + 0.25, 0.20 + 0.30, 0.10 + 0.40 and 0.05 + 0.45 mol—prepared by weight dilution using double distilled water at 298.15 K.

2.2 Method

Densities and viscosities of concentrated binary solutions have been measured with the help of a bicapillary pycnometer and an Ostwald type viscometer at 298.15 K. The values were accurate within $\pm 0.1\%$ kg m⁻³ and $\pm 0.1\%$ kg m⁻¹ s⁻¹ respectively.

3. Results and discussion

Densities, viscosities, relative viscosities and other parameters of aqueous solutions of binary systems (BaCl₂ + MgCl₂; CH₃COOK + KCl; NaCl + NaNO₃; Na₂SO₄ + NaCl; KCl + KNO₃) at different compositions (0.45 + 0.05; 0.40 + 0.10; 0.30 + 0.20; 0.25 + 0.25; 0.20 + 0.30; 0.10 + 0.40; 0.05 + 0.45 mol) are presented in table 1. The values of density of these systems increase and decrease with different compositions. The change in structure of solvent or solutions as a result of H-bond formation or disruption leads to decrease or increase in intermolecular free length. Hydrophobic (structure making) or hydrophilic (structure breaking) character of the solute i.e. H-bond forming or disrupting properties are thus correlated to changes in density or viscosity. Solutes can occupy the interstitial spaces (cavities) of solvents. Solutes which increase the density of water therefore appear to be hydrophobic, and those that decrease the density are hydrophilic. Study of ion hydration is most significant for understanding the structural properties of solutions. Hydration of ion occurs as a result of ion-solvent interaction. Water molecules form a symmetrical tetrahedron or octahedron around the ion with the appropriate end of the dipole pointing to the centre of the ion.

Apparent molal volumes, ϕ_v , were calculated using the equation,

$$\phi_v = [1000/m\rho^0(\rho^0 - \rho)] + [M_r/\rho^0], \quad (1)$$

where ρ and ρ^0 are the densities of the solutions and solvent and M_r is given by

$$M_r = n_1 M_1 + n_2 M_2 / (n_1 + n_2). \quad (2)$$

n_1, n_2 are the number of moles of components and M_1, M_2 are the molecular weights of the solutes. The positive values of the apparent molal volume at different molalities are given in table 1. The limiting apparent molal volume shows almost a linear relationship with $m^{1/2}$ with the concentration range studied in each case. It has been represented by

$$\phi_v = \phi_v^0 + S_r m^{1/2}. \quad (3)$$

Table 1. Variation of ρ , η , η rel, and ϕ_v with different compositions in water solvent at 298.15 K.

Molality (<i>m</i>) (mol.kg ⁻¹)	Density (ρ) $\times 10^{-3}$ (kg m ⁻³) $\rho^0 = 0.9971$	Viscosity (η) $\times 10^{-3}$ (kg m ⁻¹ s ⁻¹) $\eta^0 = 0.8512$	Relative viscosity (η rel) $\times 10^{-3}$	Apparent molal volume (m ³ mol ⁻¹) (ϕ_v) $\times 10^{-6}$
BaCl₂ + MgCl₂				
0.45 + 0.05	1.052	0.1047	0.1231	110.56
0.40 + 0.10	1.053	0.0526	0.0617	110.42
0.30 + 0.20	1.054	0.0203	0.0239	110.34
0.25 + 0.25	1.055	0.1733	0.2076	108.34
0.20 + 0.30	1.056	0.1644	0.1932	108.57
0.10 + 0.40	1.07	0.1532	0.1799	78.25
0.05 + 0.45	1.075	0.3008	0.3534	68.23
CH₃COOK + KCl				
0.45 + 0.05	1.017	0.5668	0.6659	46.72
0.40 + 0.10	1.017	0.6761	0.7942	46.32
0.30 + 0.20	1.018	0.7844	0.9215	43.31
0.25 + 0.25	1.018	0.8384	0.9849	44.32
0.20 + 0.30	1.015	0.8506	0.9992	50.33
0.10 + 0.40	1.015	0.8673	1.018	49.73
0.05 + 0.45	1.016	0.8488	0.9972	49.53
NaCl + NaNO₃				
0.45 + 0.05	1.018	0.4238	0.4979	29.47
0.40 + 0.10	1.019	0.5332	0.6264	29.07
0.30 + 0.20	1.021	0.5599	0.6578	24.06
0.25 + 0.25	1.016	0.5635	0.6621	34.08
0.20 + 0.30	1.018	0.571	0.6708	30.07
0.10 + 0.40	1.017	0.5135	0.6033	32.08
0.05 + 0.45	1.016	0.3651	0.4289	32.88
Na₂SO₄ + NaCl				
0.45 + 0.05	1.043	0.0867	0.1019	8.5
0.40 + 0.10	1.04	0.0479	0.0563	14.52
0.30 + 0.20	1.036	0.0422	0.0495	24.04
0.25 + 0.25	1.035	-0.1778	-0.2088	24.55
0.20 + 0.30	1.034	0.0112	0.0132	25.52
0.10 + 0.40	1.032	-0.1716	-0.2005	26.42
0.05 + 0.45	1.031	-0.3087	-0.3627	27.42
KCl + KNO₃				
0.45 + 0.050	1.025	0.5621	0.6604	32.21
0.40 + 0.10	1.024	0.7619	0.8952	34.21
0.30 + 0.20	1.023	0.7721	0.9071	36.22
0.25 + 0.25	1.022	0.7782	0.9142	38.23
0.20 + 0.30	1.021	0.6062	0.7121	40.23
0.10 + 0.40	1.018	0.8107	0.9524	46.25
0.05 + 0.45	1.019	0.6952	0.8168	44.25

S_v is the experimental slope. Values of partial molal volume at infinite dilution, ϕ_v^0 or \bar{V}_2^0 , and slopes, S_v , for such systems in concentrated aqueous solutions are given in table 2. The positive values of ϕ_v^0 or \bar{V}_1^0 indicate greater solute-solvent interactions. The slopes S_v are found to be positive in case of the systems $\text{NaNO}_3 + \text{NaCl} + \text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{H}_2\text{O}$, thereby indicating strong ion-ion interactions and they have greater complex ion-forming ability. The negative values of S_v obtained in the case of systems $\text{BaCl}_2 + \text{MgCl}_2 + \text{H}_2\text{O}$, $\text{CH}_3\text{COOK} + \text{KCl} + \text{H}_2\text{O}$ and $\text{KCl} + \text{KNO}_3 + \text{H}_2\text{O}$ indicate that ion-ion interactions are very weak and that the systems have less complex ion-forming ability.

The ionic strength (μ) of a solution is a measure of the electrical intensity due to the presence of ions in solution. It is given by half the sum of all the terms obtained by multiplying the molality of each ion by the square of its valency,

$$\mu = 1/2(m_1 z_1^2 + m_2 z_2^2), \quad (4)$$

where m_1 and m_2 are molalities and z_1, z_2 are the valencies of the various ions present in solutions. Ionic strengths of binary systems depend on the molalities and valencies of the ions in solution. They increase and decrease with varying composition and nature of the ion in solution. For any electrolyte, lowering of compressibility depends upon the ionic strength of the solution.

Viscosity data are analysed with Jones-Dole equation

$$\eta_{\text{rel}} = \eta/\eta^0 = 1 + Am^{1/2} + Bm, \quad (5)$$

where, η_{rel} is the relative viscosity of the binary systems, A and B are the Falkenhagen and the Jones-Dole coefficients. The viscosities and relative viscosities of various binary systems in aqueous solutions of $\text{BaCl}_2 + \text{MgCl}_2 + \text{H}_2\text{O}$, $\text{CH}_3\text{COOK} + \text{KCl} + \text{H}_2\text{O}$, $\text{NaNO}_3 + \text{NaCl} + \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{H}_2\text{O}$ and $\text{KCl} + \text{KNO}_3 + \text{H}_2\text{O}$ at different molalities are given in table 1. These values of viscosity depend on the compositions of the electrolytic mixtures. The values of coefficient A are positive in the case of binary systems $\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{H}_2\text{O}$ and $\text{KCl} + \text{KNO}_3 + \text{H}_2\text{O}$, which indicate that ion-ion interactions are greater, and are negative in the case of binary systems $\text{BaCl}_2 + \text{MgCl}_2 + \text{H}_2\text{O}$, $\text{CH}_3\text{COOK} + \text{KCl} + \text{H}_2\text{O}$ and $\text{NaNO}_3 + \text{NaCl} + \text{H}_2\text{O}$, indicating that ion-ion interactions here are weaker and that these are less efficient at complex ion formation. B coefficients for the respective systems are positive which indicate greater ion-solvent interactions and show that they behave as "structure makers". The negative value for the system $\text{NaNO}_3 + \text{NaCl} + \text{H}_2\text{O}$ indicates that ion-solvent interactions are weaker and that the system behaves as a "structure breaker".

The free energy of activation per mole of solvent, $(\Delta\mu_1^{0\neq})$, and solute, $(\Delta\mu_2^{0\neq})$, are calculated with the help of (6) and (7) respectively,

$$\Delta\mu_1^{0\neq} = RT \ln(\eta_0 \bar{V}_1^0)/hN \quad (6)$$

and

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + (RT/\bar{V}_1^0) * 1000B(\bar{V}_1^0 - \bar{V}_2^0), \quad (7)$$

where h is Planck's constant and N is Avogadro's number.

The activation energy of a reaction is defined as the additional energy which reactant molecules must acquire in order to form the intermediate activated complex for the reaction. The reacting molecules possessing sufficient energy approach each other and there is redistribution of energy and bonds so that the activated complex acquires

Table 2. Values of the parameters *A* and *B* of the Jones-Dole equation, \bar{V}_1^0 , \bar{V}_2^0 , S_v , $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ of $\text{BaCl}_2 + \text{MgCl}_2$, $\text{CH}_3\text{COOK} + \text{KCl}$, $\text{NaNO}_3 + \text{NaCl}$, $\text{Na}_2\text{SO}_4 + \text{NaCl}$ and $\text{KCl} + \text{KNO}_3$ in concentration aqueous solutions at 298.15 K.

Binary systems	<i>A</i> ($m^{3/2} \text{ mol}^{-1/2}$)	<i>B</i> ($m^3 \text{ mol}^{-1}$)	S_v $(m^3 \text{ mol}^{-3/2} \text{ l}^{1/2})$	$\bar{V}_1^0 = 18.05 \times 10^{-6}$ ($m^3 \text{ mol}^{-1}$)	$\bar{V}_2^0 \times 10^{-6}$ ($m^3 \text{ mol}^{-1}$)	$\Delta\mu_1^{0\#} = 9.050 \times 10^{-4}$ (kJ mol^{-1})	$\Delta\mu_2^{0\#} \times 10^{-4}$ (kJ mol^{-1})
$\text{BaCl}_2 + \text{MgCl}_2$	-1.97	0.081	-33.33	125.01		2.75	
$\text{CH}_3\text{COOK} + \text{KCl}$	-3.89	0.409	-100.30	6.19		5.82	
$\text{NaCl} + \text{NaNO}_3$	-3.58	-0.420	08.89	29.32		-6.31	
$\text{Na}_2\text{SO}_4 + \text{NaCl}$	1.57	0.971	16.17	17.43		14.2	
$\text{KCl} + \text{KNO}_3$	0.801	0.506	-33.33	21.56		7.36	

energy to form the intermolecular bond. The values of $\Delta\mu_1^{0\ddagger}$ and $\Delta\mu_2^{0\ddagger}$ are recorded in table 2 for all the binary systems. The values of $\Delta\mu_1^{0\ddagger}$ do not change in the present case. The values of $\Delta\mu_2^{0\ddagger}$ for these systems $\text{BaCl}_2 + \text{MgCl}_2$, $\text{CH}_3\text{COOK} + \text{KCl}$, $\text{KCl} + \text{KNO}_3$ and $\text{MgSO}_4 + \text{Na}_2\text{SO}_4$ in aqueous solutions are greater than $\Delta\mu_1^{0\ddagger}$ and behave as structure makers. The value of $\Delta\mu_2^{0\ddagger}$ for the system $\text{NaNO}_3 + \text{NaCl}$ in aqueous solution is less than $\Delta\mu_1^{0\ddagger}$ which indicates that it is a structure breaker. The positive values show that the formation of the transition state is less favoured in the presence of these systems, meaning thereby that the formation of the transition state is accompanied by the breaking and distortion of intermolecular bonds.

References

- Manohar S, Ananthaswamy J and Atkinson G 1992 *J. Chem. Eng. Data* **37** 459
Parmar M L and Khanna A 1986 *Indian J. Chem.* **A25** 1044, 4122
Parmar M L and Rao C V N 1990 *Indian J. Chem.* **A29** 958
Patil K J, Manwalkar S M and Dhonge S S 1994 *Indian J. Chem.* **A33** 4
Patil K J, Dhonge S S and Manwalkar S M 1995 *Indian J. Chem.* **A34** 950