

ULTRASONIC STUDIES OF ION-SOLVENT INTERACTIONS OF TETRAALKYLAMMONIUMBROMIDE IN MIXED SOLVENT OF DMF WITH PROPYLENE CARBONATE MIXTURES AT 303.15K

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ABSTRACT

Ultrasonic velocity (U), viscosity (η) and density (ρ) for tetraethylammoniumbromide (Et_4NBr), tetrapropylammoniumbromide (Pr_4NBr) and tetrabutylammoniumbromide (Bu_4NBr) in mixed solvent of N,N-dimethylformamide (DMF) + propylene carbonate (3:1 ratio) at 303.15K. Some acoustical and transport parameters namely adiabatic compressibility (β), apparent molar compressibility (ϕ_K), apparent molar volume (ϕ_V), limiting apparent molar compressibility (ϕ_K^0), limiting apparent molar volume (ϕ_V^0) and their constants (S_K , S_V), viscosity A and B coefficients of Jones-Dole equation have been calculated from the experimental data. The results of the derived parameters have been discussed in terms of ion-solvent interactions between the components of mixture.

Keywords: Ultrasonic velocity, Apparent molar volume, Viscosity coefficient.

1. INTRODUCTION

In recent years, the studies of acoustical properties of aqueous mixed electrolytic solutions have been found to be useful in understanding the specific ion-ion and ion-solvent interaction in solutions. The accurate measurement of density, viscosity, ultrasonic velocity and hence the derived parameters such as adiabatic compressibility, apparent molar compressibility and apparent molar volume will give significant information regarding the state of affairs in a solution. Such studies on binary electrolytes have been made by many researchers (Dowall et al., 1974; Dack et al., 1975; Cassel et al., 1974; Masanobu Janado et al., 1981; Robinson et al., 1962). However, ultrasonic velocity studies on ternary electrolytes have not received as much attention as that of binary electrolytes (Prasad et al., 1977; Prakash, et al., 1977). Since physico-chemical studies of binary electrolytes cannot be so useful to get a definite conclusion regarding the structural properties and the type of interaction involved the study of ternary electrolytes in gaining much importance now-a-days. Ionic association and electrostatic interactions are the prime factors that must be considered in these electrolytes. The study of transport properties of electrolytic solutions gives useful information regarding ion-solvent interactions (Jerzy Matecki et al., 1999;

Elena et al., 1999). Viscosity studies of electrolytic solutions in mixed solvent systems is one of the most fundamental transport properties that play a vital role in understanding the solution behaviour of the electrolytes (David Feakins et al., 1974). Dimethylformamide (DMF) is the organic compound and it is used as a solvent with low evaporation rate and also it can be used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibres, films and surface coatings. Propylene carbonate is a polar and an aprotic solvent. It is frequently used as a high-permittivity component of electrolytes in lithium batteries, usually together with a low-viscosity solvent. Tetraalkylammoniumbromides is useful in many reactions which are “transfer rate limited”. It is also used as a template for zeolites.

It is evident from the prevailing literature that very few attempts have been made to study the molecular interactions among the electrolytes in non-aqueous mixed solvent mixtures. With the view of growing interest an attempt has been made to elucidate the ion-solvent interactions of tetraalkylammoniumbromide in mixed solvent of DMF and propylene carbonate mixtures at 303.15K by measuring viscosity, density and ultrasonic velocity. From the experimental values, the acoustical parameters such as adiabatic compressibility, apparent molar compressibility, apparent molar volume limiting apparent molar compressibility, limiting apparent molar volume and their constants S_K and S_V and viscosity

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A and B coefficients of Jones-Dole equation have been computed to shed more light on such interactions.

2. MATERIALS AND METHODS

Analytical reagent (AR) grade and spectroscopic reagent (SR) grade with minimum assay of 99.9% of tetraethylammoniumbromide, tetrapropylammoniumbromide, tetrabutylammoniumbromide, N,N-dimethylformamide and propylene carbonate were obtained from E-Merck, Germany and SdFine chemicals, India was used as such without further purification. Binary solvent mixture of dimethylformamide with propylene carbonate (3:1) were made by volume and used on the day they were prepared. Solution of tetraalkylammoniumbromides in the concentration range of 0.02-0.1 mol·dm⁻³ were made by mass on the molarity concentration scale with a precision of $\pm 1 \times 10^{-4}$ g on a electronic digital balance (Model: SHIMADZU AX200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kg·m⁻³. An Ostwald's Viscometer (10ml capacity) was used for the viscosity measurement and efflux time was determined using a digital Chronometer to within ± 0.01 s. An ultrasonic interferometer having the frequency 3MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F-81) with an overall accuracy of $\pm 0.1\%$ has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with an accuracy of ± 0.1 K.

Theory and Calculations

Using the measured data, the following volumetric, compressibility and transport parameters have been calculated using the standard relations.

$$\text{Adiabatic Compressibility } \beta = \frac{1}{U^2 \rho} \quad \dots(1)$$

The apparent molal compressibility has been calculated from relation,

$$\varphi_K = \frac{1000}{m\rho_0} (\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0} \right) \quad \dots(2)$$

where β , ρ and β_0 , ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molal concentration of the solute, and M the molecular mass of the solute. φ_K is the function of m as obtained

by Gucker (1933) from Debye Huckel theory (Debye et al., 1923) and is given by

$$\varphi_K = \varphi_K^0 + S_K m^{1/2} \quad \dots(3)$$

where φ_K^0 is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. φ_K^0 and S_K of equation (3) have been evaluated by the least square method.

The apparent molal volume φ_V has been calculated using the relation

$$\varphi_V = \left(\frac{M}{\rho} \right) - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \quad \dots(4)$$

The apparent molal volume φ_V has been found to differ with concentration according to Masson (1929) empirical relation as

$$\varphi_V = \varphi_V^0 + S_V m^{1/2} \quad \dots(5)$$

where φ_V^0 is the limiting apparent molal volume at infinite dilution and S_V is a constant and these values were determined by least square method.

The viscosity A and B coefficients for the amino acids in aqueous 1,4-dioxane solutions were calculated from the Jones-Dole equation (Jones et al., 1929).

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad \dots(6)$$

where, η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute. A is determined by the ionic attraction theory of Falkenhagen-Vernon and therefore also called Falkenhagen coefficient (1932), B or Jones-Dole coefficient is an empirical constant determined by ion-solvent interactions.

3. RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) for different molar concentration of tetraethylammoniumbromide (Et₄NBr), tetrapropylammonium-bromide (Pr₄NBr) and tetrabutylammoniumbromide (Bu₄NBr) in binary solvent mixtures of N,N-dimethylformamide (DMF) with propylene carbonate (PC) at 303.15K are shown in Table 1. The values of adiabatic compressibility (β), apparent molar compressibility (φ_K), apparent molar

volume (φ_v), limiting apparent molar compressibility (φ_K^0), limiting apparent molar volume (φ_v^0), and their constants (S_K , S_v), and viscosity of A and B coefficients of Jones-Dole equation are presented in Tables 2 and 3.

In all the three system (Table 1) the values of density and ultrasonic velocity are increases with increase in molar concentration of tetraalkylammoniumbromides. The density increases with increasing the concentration of solute (salts) suggest, a moderate strong electrolytic nature in which the solute tends to attract the solvent (DMF + PC) molecules. Molecular interactions are thus responsible for the observed increase in density and ultrasonic velocity in these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration. Table 2 shows the variation of adiabatic compressibility with molar concentration of tetraalkylammoniumbromides at 303.15K. The values of adiabatic compressibility are decreases with increase in molar concentration of solute in all systems studied. The decrease in adiabatic compressibility is attributed to the influence of the electrostatic field of the ions (N^+ , Br^-) on the surrounding solvent molecules so called electrostriction. The increasing electrostrictive compression of water around the molecules results in a large decrease in the compressibility of solutions. The decrease in compressibility implies that there is enhanced molecular association in these systems on increase in solute content, as the new entities (formed due to molecular association) become compact and less compressible (Fort et al., 1965). The increase in velocity and decrease in compressibility were attributed to the formation of hydrogen bonds between solute and solvent molecules.

The following observations have been made on φ_K and φ_v (Table 2) of the tetra alkylammoniumbromides in mixed solvent mixtures of DMF with propylene carbonate at 303.15K.

- (i) The values of φ_K and φ_v are all negative over the entire range of molarity.
- (ii) A non-linear variation of φ_K and have been observed throughout the solutes concentration range.
- (iii) The magnitude of in the order: $Et_4NBr > Pr_4NBr > Bu_4NBr$

All the above observations clearly suggest that the negative and values indicate the existence of specific interaction occurring in these systems. A non-linear behaviour of and in all the three system reveals that strengthening of ion-solvent interaction exist in these mixtures. Further, the negative values of indicate electrostrictive solvation of ions (Dhanalakshmi, et al., 1999). From the magnitude of , it can be concluded that, strong molecular interaction is found in Bu_4NBr than the other two salts and hence Bu_4NBr is a more effective structure maker than others.

The limiting apparent molar compressibility due to Masson (1929) and the related constant for all the three systems have been computed using least square method. provides information regarding ion-solvent interaction and , that of ion-ion interaction in the mixtures. From the Table 3, it is observed that values are negative in all the three systems studied. Negative value of for all the systems reinforce our earlier view that the existence of ion-solvent interaction. Values of S_K exhibits positive in all the three systems, suggesting the presence of strong ion-ion interaction in the mixtures. The volume behaviour of a solute at infinite dilution is satisfactorily represented by which is independent of the ion-ion interactions and provides information concerning ion-solvent interactions. It is observed from the Table 3, that the values of in all the three systems are found to be negative. Negative value of indicates smaller ion-solvent interactions present in these systems. It is also observed from the table that the value of for the solution with Et_4NBr is higher than that for the solutions with Pr_4NBr and Bu_4NBr . This indicates the more structure intensifying aspect of the Bu_4NBr than others. The magnitude of is in order: $Et_4NBr > Pr_4NBr > Bu_4NBr$. The values (Table 3) exhibit positive in Bu_4NBr and it found to be negative in Et_4NBr and Pr_4NBr systems. Positive values suggesting the presence of strong ion-ion / solute-solute interaction in the mixtures.

Viscosity is an another important parameter in understanding the structure as well as molecular interactions occurring in the mixtures. From the Table 1, it is observed that the values of viscosity increases with

increase in concentration solutes in all systems studied. This increasing trend indicates the existence of ion-solvent interaction between the components in the mixtures. In order to shed more light on this, the role of viscosity coefficients have been obtained. From the Table 3, it is observed that the values of A and B are positive in all systems studied. Since A is a measure of ionic interaction (Jahagiridhar, et al., 2000) and it is evident that there is a strong ion-ion interaction in the mixtures studied, which is indicated by the positive magnitude. B-coefficient is also known as measure of order and disorder introduced by the solute into the solvent. It is also a measure of ion-solvent interaction and the relative size of the solute and solvent molecules. The behaviour of B coefficient in all the three systems suggests the existence of strong ion-solvent interaction. The magnitude of B values is in the order: $\text{Bu}_4\text{NBr} > \text{Pr}_4\text{NBr} > \text{Et}_4\text{NBr}$. The order of B-coefficients shows that the obstruction of the solvent viscous flow increases with decreased ion charge density and with increased size of the hydrodynamic entity by solvation. This conclusion is an excellent agreement with that drawn from S_v and data and the larger values of B-coefficient indicate structure intensifying property of the solute.

4. CONCLUSION

The present study reports experimental data of density, viscosity and ultrasonic velocity for Et_4NBr , Pr_4NBr and Bu_4NBr in mixed solvent of DMF with propylene carbonate at 303.15K. From these data, some thermodynamical and transport parameters have been calculated and the results have been used to explain the ion-solvent interactions between the mixing components. The existence of ion-solvent and ion-ion interactions resulting in attractive forces promote the structure intensifying tendency of the solute and solvent molecules. From the magnitude of A and B-coefficient, it can be concluded that the existence of ion-solvent interaction is in the order of $\text{Bu}_4\text{NBr} > \text{Pr}_4\text{NBr} > \text{Et}_4\text{NBr}$. This suggests Bu_4NBr mixtures possess strong structure maker than other two salts.

Table 1. Values of density (ρ) viscosity (η) and ultrasonic velocity (U) of tetraalkylammonium bromides in mixed solvent mixtures at 303.15K

M/ (mol. dm ⁻³)	ρ / (kg m ⁻³)	η / ($\times 10^{-3}$ Nsm ⁻²)	U/(m.s ⁻¹)
System I: Tetraethyl ammonium bromide (Et_4NBr) + [N,N-dimethylformamide + propylene carbonate (3:1)]			
0.00	1002.3	1.113	1418.5
0.02	1003.7	1.125	1423.3
0.04	1005.2	1.129	1429.2
0.06	1006.6	1.135	1433.4
0.08	1007.9	1.137	1437.5
0.10	1009.1	1.144	1444.7
System II: Tetrabutyl Tetrapropyl ammonium bromide (Pr_4NBr) + [N,N-dimethylformamide + propylene carbonate (3:1)]			
0.00	1002.3	1.113	1418.5
0.02	1005.3	1.144	1425.3
0.04	1008.0	1.154	1430.2
0.06	1011.1	1.170	1437.3
0.08	1014.2	1.176	1442.6
0.10	1017.6	1.187	1452.4
System III: Tetrabutyl ammonium bromide (Bu_4NBr) + [N,N-dimethylformamide + propylene carbonate (3:1)]			
0.00	1002.3	1.113	1418.5
0.02	1008.7	1.159	1427.2
0.04	1015.0	1.167	1432.9
0.06	1021.1	1.183	1447.2
0.08	1027.2	1.209	1454.1
0.10	1033.3	1.227	1460.5

Table 2. Values of adiabatic compressibility (β), apparent molal compressibility (ϕ_K) and apparent molal volume (ϕ_V) of tetraalkylammonium bromides in mixed solvent mixtures at 303.15K

M/ (mol. dm ⁻³)	β / ($\times 10^{-10}$ m ³ N ⁻¹)	ϕ_K / ($\times 10^{-7}$ m ³ N ⁻¹)	ϕ_V / ($\times 10^{-3}$ m ³ mol ⁻¹)
System I: Tetraethyl ammonium bromide (Et_4NBr) + [N,N-dimethylformamide + propylene carbonate (3:1)]			
0.00	4.958	234.65	69.37
0.02	4.918	253.34	71.75
0.04	4.871	240.47	70.82
0.06	4.835	230.86	69.08
0.08	4.801	239.45	72.91
0.10	4.752	234.65	69.37
System II: Tetrabutyl Tetrapropyl ammonium bromide (Pr_4NBr) + [N,N-dimethylformamide + propylene carbonate (3:1)]			
0.00	4.958	379.16	148.61
0.02	4.897	340.43	140.78
0.04	4.850	355.88	144.46
0.06	4.788	348.54	146.07
0.08	4.738	374.85	149.75
0.10	4.650	379.16	148.61
System III: Tetrabutyl ammonium bromide (Bu_4NBr) + [N,N-dimethylformamide + propylene carbonate (3:1)]			
0.00	4.958	613.15	316.19
0.02	4.867	579.61	311.77
0.04	4.798	624.96	305.83
0.06	4.676	596.44	301.99
0.08	4.604	574.55	299.01
0.10	4.537	613.15	316.19

Table 3. Values of limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0), constants S_K , S_V and viscosity A and B coefficients of Jones-Dole equation of tetraalkylammoniumbromides in mixed solvent mixtures at 303.15K

Amino acids	$\phi_k^0 / (\times 10^{-4} \text{ m}^3 \text{ mol}^{-1})$	$S_K / (\times 10^{-4} \text{ N}^{-1} \text{ m}^2 \text{ mol}^{-1})$	$\phi_v^0 / (\text{m}^3 \text{ mol}^{-1})$	$S_V / (\text{m}^3 \text{ mol}^{-1})$	A Coefficient $A / (\text{dm}^3 \text{ mol}^{-1/2})$	B Coefficient $B / (\text{dm}^3 \text{ mol}^{-1})$
Tetraethyl ammonium bromide + DMF – propylene carbonate	-2.46	0.24	-68.50	-9.64	0.0645	0.0597
Tetrapropyl ammonium bromide + DMF – propylene carbonate	-3.66	0.27	-143.21	-11.48	0.1874	0.0657
Tetrabutyl ammonium bromide + DMF – propylene carbonate	-6.29	1.33	-331.44	103.25	0.2269	0.2416

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