Ultrasonic, Volumetric and Viscometric Studies of Monochloroacetic Acid in Water-Isopropanol Solvent Mixtures at 25, 30 and 35°C

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Ultrasonic velocity, density and viscosity of monochloroacetic acid (MCAA) solutions in 10, 30, 50, 70, 90 and 100 wt. % isopropanol-water have been determined at 298.15, 303.15 and 308.15 K. Viscosity and density data of these solutions are analysed with Jones-Dole and Masson equations respectively. The viscosity coefficients A and B, the limiting apparent molar volume (ϕ_v^0) and experimental slope (S_k), ultrasonic velocity (U) and derived parameters, namely adiabatic compressibility (β_{ad}), apparent molar compressibility (ϕ_k), intermolecular free length (L_f), specific acoustic impedance (Z), and solvation number (S_n) throw light on the solute-solvent and solute-solute interactions. Effect of temperature variation on these interactions is discussed.

INTRODUCTION

Accurate thermodynamic (heat capacity, heat of mixing, vapour pressure, solubility, density, surface tension and ultrasonic velocity) and transport (viscosity, conductivity) properties of working fluids are very often required. The density and ultrasonic velocity data are important basic properties to analyse mass transfers and compressibility of industrially potential fluids.

Transport properties of electrolytes in aqueous, nonaqueous and mixed solvents are of interest in various technologies like high energy density batteries, photo-electro-chemical cells, electro-deposition, and wet electrolytic capacitors and in electro-organic synthesis[1]. Viscosity, density and ultrasonic velocity measurements of electrolyte solutions are excellent tools to detect solute-solvent and solute-solute interactions. These interactions in the case of electrolytes in water-*n*-alkanol mixtures have been studied by many workers, but such investigations in water-isoalcohol solvent mixtures are scanty. It has been reported[2] that isopropyl alcohol differs considerably from *n*-propyl alcohol in the manner it undergoes protonation by solvated proton (H_3^+O). Therefore the density, viscosity and ultrasonic behaviours of the electrolytes are expected to show completely different behaviours in water-isopropanol mixtures. Hence, in order to investigate solute-solvent and solute-solute interactions in MCAA solutions in water-isopropanol, the present investigation of density, viscosity and ultrasonic

velocity measurements of MCAA solutions in aqueous isopropanol of different dielectric constants is undertaken. In addition, an attempt has been made to study the effect of the addition of MCAA on intermolecular interactions leading to hydrogen bond formation between water and isopropanol molecules[3].

EXPERIMENTAL

Monochloracetic acid (MCAA) was purified as reported earlier[4]. Isopropanol was dried by refluxing with fused calcium oxide for 8–10 h and finally distilled using a fractionating column. Triple-distilled water was used to mix (by weight) with purified isopropanol to give mixtures of different dielectric constants[5]. Solutions of different molarities of MCAA were prepared afresh by dissolving the acid in the solvent mixture. Ultrasonic velocity, viscosity and density of these solutions were measured in a thermostated water bath having thermal stability of ± 0.01°C, using M-82 interferometer having frequency of 1.5 MHz, suspended level Ubbelohde viscometer and bicapillary pycnometer with an accuracy of 0.03%, ± 0.0003 Cp and ± 0.0001 gm/ml respectively. The efflux times were measured with a stop watch correct to 0.01 second.

RESULTS AND DISCUSSION

The apparent molar volumes (ϕ_v) of MCAA in water-isopropanol solvent mixtures at all temperatures, calculated from their density data, obeyed Masson equation

$$\phi_v = \phi_v^0 + S_v \sqrt{C} \tag{1}$$

The intercepts (ϕ_v^0) and slopes (S_v) of linear plots of ϕ_v versus $\sqrt{C}$ for all temperatures, are recorded in Table-1.

TABLE-1

ϕ_v^0 AND S_v AT ALL COMPOSITIONS AND AT ALL TEMPERATURES

Temp. °C	ϕ_v^0 cm³ mol⁻¹	S_v cm³ lit¹ᐟ² mol⁻³ᐟ²	ϕ_v^0 cm³ mol⁻¹	S_v cm³ lit¹ᐟ² mol⁻³ᐟ²	ϕ_v^0 cm³ mol⁻¹	S_v cm³ lit¹ᐟ² mol⁻³ᐟ²
	0 wt % i-PrOH		10 wt % i-PrOH		30 wt % i-PrOH	
25	60.50	1.88	55.00	38.15	33.00	52.63
30	60.66	1.92	56.25	38.46	36.00	48.00
35	62.68	1.98	59.00	29.41	46.50	32.70
	50 wt % i-PrOH		70 wt % i-PrOH		90 wt % i-PrOH	
25	50.00	12.22	6.50	12.50	59.00	46.43
30	60.00	10.60	44.75	25.00	60.75	11.54
35	66.00	5.00	54.00	15.00	63.50	5.67

Recently it has been shown that ϕ_v^0 results from four contributions[6, 7]

$$\phi_v^0 = V_{vw} + V_f + V_s + V_h \qquad (2)$$

where V_{vw} is the intrinsic or the Van der Waal's volume, V_f, the void volume, V_s, the contribution from solute-solute-solvent interactions and V_h, that from hydrophobic hydration. Taking $(V_{vw} + V_f)$ to be same in aqueous isopropanol as in water, the expected changes in $(V_s + V_h)$ should explain the observed trends in ϕ_v^0. The $(V_s + V_h)$ for MCAA in water-isopropanol can be given as

$$(V_s + V_h) \text{ in water-isopropanol} = V_{ss} - V_{sw} + V_{i\,PrOH\,i\,PrOH}$$
$$- V_{s\,i\,PrOH} + V_{ww} \qquad (3)$$

where s stands for solute MCAA, w for water and i-PrOH for isopropanol. The increasse in ϕ_v^0 with increase of temperature can be attributed to decrease in $-V_{sw}$ and $-V_{s\,i\,PrOH}$ due to favoured salt-salt (V_{ss}) interactions. Contributions from changes in V_{ww} and $V_{i\,PrOH\,i\,PrOH}$ can be taken as relatively small[8].

The possibility of positive S_v values is accounted for strong electrostatic ion-ion interactions due to large size of acetate ion which results in interionic penetration[9] leading to ion-ion interactions.

The applicability of Jones-Dole equation is shown by linear plot $\eta_r - 1/\sqrt{C}$ *vs* $\sqrt{C}$ at all temperatures. The values of constants A and B given by the intercept and slope of the plots respectively are given in Table 2. 'A' values are small but positive in solutions in 10, 70 and 90 wt % isopropanol indicating negligible solute-solute interactions. However, unexpected negative values of 'A' in MCAA solutions in 30, 50 and 100 wt % isopropanol cannot be explained on Falkenhagen theory. This anomalous behaviour of MCAA in these solutions as regards the sign of 'A' is similar to that obtained for MCAA in other mixed solvents[10,11].

TABLE-2

'A' AND 'B' PARAMETERS OF JONES-DOLE EQUATION AT DIFFERENT
COMPOSITIONS AND DIFFERENT TEMPERATURES

Wt % i-PrOH	A	B	A	B	A	B
	25°C		30°C		35°C	
10	0.026	−0.031	0.040	−0.050	0.056	−0.760
30	−0.142	0.136	−0.112	0.100	−0.130	0.025
50	−0.044	0.038	−0.047	0.037	−0.048	0.035
70	0.057	−0.061	0.065	−0.064	0.059	−0.052
90	0.014	−0.013	0.013	−0.009	0.015	−0.003
100	−0.014	−0.030	−0.030	−0.038	−0.017	−0.020

The positive 'B' and negative $\dfrac{dB}{dT}$ values for MCAA in solutions in 30 and 50 wt % isopropanol indicate strong solute-solvent interactions making MCAA as structure promoter[12] in these solvent mixtures. However, negative 'B' and positive

$\frac{dB}{dT}$ values for MCAA in solutions in 10, 70 and 100 wt % isopropanol suggest that MCAA behaves as structure breaker in these solvent mixtures[12].

The variation of sound velocity with concentration, C, of a solute is given by

$$\frac{dU}{dC} = -\frac{U}{2}\left[\frac{1}{\beta_{ad}} \cdot \frac{d\beta_{ad}}{dC} + \frac{1}{\rho} \cdot \frac{d\rho}{dC}\right] \tag{4}$$

Magnitudes of positive values of $\frac{1}{\rho} \cdot \frac{d\rho}{dC}$ are smaller than negative magnitudes of $\frac{1}{\beta_{ad}} \cdot \frac{d\beta_{ad}}{dC}$, making $\frac{dU}{dC}$ positive in solutions in 10, 30 and 100 wt % isopropanol. However, in solutions in 50, 70 and 90 wt % isopropanol, $\frac{1}{\rho} \cdot \frac{d\rho}{dC}$ as well as $\frac{1}{\beta_{ad}} \cdot \frac{d\beta_{ad}}{dC}$ are positive making $\frac{dU}{dC}$ negative. Thus the fact that increase of velocity (U), decrease of adiabatic compressibility (β_{ad}), decrease of intermolecular free length (L_f), increase of specific acoustic impedance (Z), and decrease of solvation number (S_n) with increase of molar concentration of MCAA in 10, 30 and 100 wt % isopropanol at all temperatures is indicative of the increase of intermolecular forces with the addition of MCAA forming aggregates of solvent molecules around solute ions[13] supports the strong solute-solvent interactions due to which structural arrangement is affected[14]. Decrease of velocity (U), increase of adiabatic compressibility, increase of intermolecular free length (L_f), decrease of specific acoustic impedance (Z), and increase of solvation number (S_n) with increase of MCAA concentration in 50, 70 and 90 wt % isopropanol at all temperatures supports the existence of solute-solute interactions in these solutions. Similar behaviour is observed at other temperatures.

Apparent molar compressibility values (ϕ_k) vary linearly with $\sqrt{C}$ at all temperatures obeying Gucker's limiting law

$$\phi_k = \phi_k^0 + S_k \sqrt{C} \tag{5}$$

The intercepts (ϕ_k^0) and slpes (S_k) of linear plots of ϕ_k versus $\sqrt{C}$ are listed in Table-3. The negative ϕ_k^0 and positive S_k values in solutions in 10, 30 and 100 wt % isopropanol indicate strong electrostrictive solute-solvent interactions, while positive ϕ_k^0 and negative S_k values in 50, 70 and 90 wt % isopropanol suggest that solvent molecules are loosely attached to solute. Near constancy of ϕ_k^0 with temperature, irrespective of its sign is explained on Frank and Wen model as explained previously[15].

The adiabatic compressibilities of MCAA solutions are found to obey Bachem's relation

$$\beta_{ad} = \beta_{ad}^0 + AC + BC^{3/2} \tag{6}$$

β_{ad}, β_{ad}^0 and C have their usual meanings[15]. Constants 'A' and 'B' are intercepts and slopes of linear plots of $(\beta_{ad} - \beta_{ad}^0)/C$ versus $\sqrt{C}$ are included in Table 3.

TABLE-3

ϕ_k^0, S_k, A AND B PARAMETERS FOR MCAA IN DIFFERENT COMPOSITIONS AND DIFFERENT TEMPERATURES

Wt% i-PrOH	$A \times 10^{12}$	$B \times 10^{12}$	$\phi_k^0 \times 10^9$	$S_k \times 10^9$
		25°C		
10	−17.4	0.33	−13.0	0.04
30	−5.5	0.16	−3.7	0.12
50	4.5	−0.20	6.6	−0.40
70	11.8	−0.10	15.7	−0.08
90	12.5	−0.06	16.4	−0.10
100	−15.1	0.01	−8.9	8.80
		30°C		
10	−16.1	0.12	−11.5	0.05
30	−6.3	0.11	−5.1	0.11
50	11.7	−0.07	15.7	−0.68
70	9.8	−0.09	11.5	−0.11
90	5.9	−0.06	11.1	−0.14
100	−20.1	−0.03	−12.7	17.86
		35°C		
10	−15.3	0.50	−8.5	0.04
30	−7.7	0.10	−3.2	0.15
50	14.0	−0.06	16.8	−0.07
70	17.3	−0.04	19.1	−0.52
90	7.5	−0.05	13.1	−0.09
100	−6.5	0.20	−10.2	18.00

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