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RESEARCH ARTICLE

Thermodynamics and Viscometric Studies of Monochloroacetic Acid in Water-Isopropanol Solvent Mixtures at 298, 303 and 308 K

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Abstract: Ultrasonic velocity, density and viscosity of monochloroacetic acid (MCAA) solutions in 10, 20, 30, 40, 50, 60, 70, 80, 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 were analysed with John-doles and Masson's equation. The viscosity coefficient A and B, the limiting apparent molar Volume (Φ^0_v) and experimental slop (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 salvation number (S_n) throw light on solute-solvent and solute-solute interactions. Consequence of temperature disparity on these interactions is discussed.

Keywords: Density, Viscosity, Ultrasonic Velocity, Adiabatic compressibility, Apparent molar compressibility, Specific acoustic impedance, Salvation number

Introduction

Precise thermodynamics and transport properties on working fluid are very often obligatory. The density and ultrasonic velocity data are significant basic properties to investigation mass transfers and compressibility of scientifically prospective fluids. Transport properties of electrolytes in aqueous, non-aqueous and mixed solvents are of concern in assorted technologies like high energy density batteries, electro deposition and in electr-oganic synthesis[1]. Viscosity, density and ultrasonic velocity measurements of electrolyte solutions are admirable apparatus to perceive solute-solvent and solute-solute interaction. These interactions in the case of electrolyte in water– *n*-alkanols mixtures have been deliberate by many workers, but such study in water–isoalcohol solvent mixtures are inadequate. It has been reported[2] that isopropyl alcohol differs significantly from *n*-propyl alcohol, the way it undergoes protonation by solvated proton. Therefore viscosity, density and ultrasonic behaviours of the electrolyte are expected to demonstrate entirely different performance in water – isopropanol mixtures. Hence in order to inspect solute- solvent and solute- solute interaction in MCAA solutions in water – isopropanol, the present investigation of viscosity, density and ultrasonic velocity measurements of MCAA solutions in aqueous isopropanol of different dielectric constants is undertaken. In accumulation, an effort has been made to study the consequence of adding of MCAA on intermolecular interactions leading to hydrogen bond formation amid of water and isopropanol molecules[3].

Experimental

MCAA was purified as reported previously[4]. Isopropanol was dried by refluxing with merged calcium oxide for 8-10 hours and ultimately distilled by means of a fractionating column. Triple distilled water was used to merge (by weight) with purified isopropanal to give mixtures of different dielectric constant[5]. Solutions of different molarities of MCAA were arranged again by dissolving acid in the solvent mixtures. Viscosity, density and ultrasonic velocity of the solution were calculated in thermostated water bath having thermal stability of ±0.01 °C, with M-82 interferometer having frequency of 1.5 MH_z, suspended level Ubbelohde viscometer and bicapillary pycnometer with an accuracy of 0.03 %, ±0.03 C_p ±0.001 gm/mL respectively. The efflux times were calculated with stopwatch correct to 0.01 second.

Results and Discussion

The apparent molar volumes (Φv) of MCAA in water – isopropanol solvent mixtures at all temperatures were calculated from there density data, obeyed Masson equation.

$$\Phi v = \Phi_v^{\ 0} + Sv\sqrt{C} \qquad (1)$$

The intercepts (Φ_v) and slopes (S_v) of linear plots of Φv *versus* $\sqrt{C}$ for all temperature 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 cm^3mol^{-1}	Sv cm^3 $L^{1/2}mol^{-3/2}$	Φ_v^0 cm^3mol^{-1}	Sv cm^3 $L^{1/2}mol^{-3/2}$	Φ_v^0 cm^3mol^{-1}	Sv cm^3 $L^{1/2}mol^{-3/2}$
	0 wt. % *i*-PrOH		10 wt. % *i*-PrOH		20 wt. % *i*-PrOH	
25	60.50	1.88	55.00	38.15	40.00	40.15
30	60.66	1.92	56.25	38.46	40.50	32.00
35	62.67	1.98	59.00	29.41	42.05	31.65
	30 wt. % i-PrOH		40 wt. % i-PrOH		50 wt. % i-PrOH	
25	33.00	52.63	37.00	58.00	50.00	12.22
30	36.00	48.00	38.01	6.60	60.00	10.60
35	46.50	32.70	39.05	18.85	66.00	5.00
	60 wt. % i-PrOH		70 wt. % i-PrOH		80 wt. % i-PrOH	
25	8.00	12.33	6.50	12.50	58.00	36.00
30	43.00	15.00	44.75	25.00	58.09	18.27
35	50.00	29.50	54.00	15.00	59.00	10.33
	90 wt.% i-PrOH					
25	59.00	46.43				
30	60.75	11.54				
35	63.50	5.67				

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

Where V_{vw} is the intrinsic or the Vander Wall'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 the identical in aqueous isopropanol and in water, the expected changes (V_s + V_h) should explain the observed trains in Φ_v^0. The (V_s + V_h) for MCAA in water–isopropanol can be given as;

$$(V_s + V_h) \text{ in water isopropanol} = Vss - Vsw + V_{iPrOH\ iPrOH} - Vs_{\ iPrOH} + Vww \qquad (3)$$

Where s stands for solute MCAA, w for water, *i*-PrOH for isopropanol. Enlarge in Φ_v^0 with raise of temperature can be recognized to decline in –Vsw and $-Vs_{iPrOH}$ due to preferential salt – salt (Vss) interactions. Input from changes in Vww and $V_{iPrOH\ iPrOH}$ can be taken as comparatively small[8].

The option of positive Sv value is accounted for strong electrostatic ion–ion interactions due to bulky size of acetate ion which end result in interionic penetration[9] foremost to ion – ion interaction. The applicability of John`s - Dole equation is discovered by linear plot.

ηr $-1/\sqrt{C}\ vs.\sqrt{C}$ at all temperatures the values of constant A and B precise by the intercept and slope of the plots respectively are given in Table 2. "A' values are minute but positive in solutions in 10, 20, 60, 70, 80 and 90 wt.% isopropanol representing in significant solute–solute interactions. However unexpected negative values of "A" in MCAA solution in 30, 40, 50 and 100 wt.% isopropanol can not give details Falkenhagen theory. This uncharacteristic performance of MCAA in these solution as regards the symbol of "A' is comparable to that obtained for MCAA in additional mixed solvents[10,11].

Table 2. A and B Parameters of Jone`s-Dole equation at different compositions and diffrent 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
20	0.029	–0.032	0.041	–0.052	0.057	–0.790
30	– 0.142	0.136	–0.112	0.100	–0.130	0.025
40	– 0.150	0.087	–0.121	0.105	–0.122	0.027
50	– 0.0044	0.038	–0.047	0.037	–0.048	0.035
60	0.052	–0.059	–0.051	0.039	–0.041	0.038
70	0.057	– 0.061	0.065	–0.064	0.059	–0.052
80	0.013	–0.010	0.015	–0.007	0.014	–0.001
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 $\frac{dB}{dT}$ values for MCAA in solution in 30, 40 and 50 wt.% isoprpanol indicate strong solute– solvent interaction making MCAA as structure promoter[12] in these solvent mixtures however negative 'B' and positive $\frac{dB}{dT}$ values for MCAA in solution 10, 20, 60, 70, 80 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 solute is given by

$$\frac{dU}{dC} = -\frac{U}{2}\left[\frac{1}{\beta ad} x \frac{d\beta ad}{dc} + \frac{d\beta ad}{dc} + \frac{1}{\rho} x \frac{d\rho}{dC}\right] \qquad (4)$$

Magnitudes of positive values of $\left[\frac{1}{\rho}x\frac{d\rho}{dc}\right]$ are smaller than negative magnitude of $\left[\frac{1}{\beta ad}x\frac{d\beta ad}{dc}\right]$ making $\frac{dU}{dC}$ positive in solution in 10, 20, 30, 40 and 100 wt.% isopropanol. However in solution in 50, 60, 70, 80 and 90 wt.% isopropanol $\frac{1}{\rho}x\frac{d\rho}{dC}$ as well as $\frac{1}{\beta ad}x\frac{d\beta ad}{dC}$ are positive making $\frac{dU}{dC}$ negative. Thus the fact that increase of velocity (U), decrease of adiabatic compressibility, decrease of inter molecular free length (L_f), increase of specific acoustic impendence (Z) and decrease of salvation numbers (S_n) with increase of molar concentration of MCAA in 10, 20, 30, 40 and 100 wt.% isopropanol at all temperature 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 impendence (Z) and increase of salvation number (S_n) with increase of MCAA concentration in 50, 60. 70. 80 and 90 wt.% isopropanol at all temperatures supports the existence of solute-solute interactions in these solutions. Similar behavior is observed at other temperature.

Apparent molar compressibility value (Φ_k) vary linearly with $\sqrt{C}$ all temperatures obeying Gucker's limiting law.

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

The intercept (Φ_k^0) and slopes (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 in solution in 10, 20, 30, 40 and 100 wt.% isopropanol indicates strong electrostatic solute-solvent interaction ,while the positive. Φ_k^0 and negative S_k values in solution in 50, 60, 70, 80 and 90 wt.% isopropanol suggest that solvent molecules are loosely attached to solute. The adiabatic compressibility of MCAA solution are found to obey Bachem's relation.

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

β_{ad}, β_{ad}^0 and C have their usual meanings[15]. Constant `A' and `B' are intercepts and slopes of linear plots of $\beta_{ad} - \beta_{ad}^0$ *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	Ax10^{12}	Bx10^{12}	Φ_k^0x 10^9	S_kx10^9
		25 °C		
10	–17.4	0.33	–13.0	0.04
20	–11.45	0.25	–10.8	0.08
30	5.5	0.16	–3.7	0.12
40	0.1	0.8	–0.09	–0.36
50	4.5	–0.20	6.6	–0.40
60	8.5	–0.15	9.6	–0.54
70	11.8	–0.10	15.7	–0.08
80	10.6	–0.008	16.09	-0.06
90	12.5	–0.06	16.4	–0.1

Contd…

100	15.1	0.01	–8.9	8.80
		30 ^{0}C		
10	–16.1	0.12	–11.5	0.05
20	–10.4	0.118	–9.3	0.07
30	–6.3	0.11	–5.1	0.11
40	–3.2	0.09	–4.6	0.13
50	11.7	–0.07	15.7	–0.68
60	10.6	0.06	14.3	–0.078
70	9.8	–0.09	11.5	–0.11
80	6.8	–0.05	10.2	–0.12
90	5.9	–0.06	11.1	–0.14
100	–20.1	–0.03	–12.7	17.86
		35 ^{0}C		
10	-15.3	0.50	–8.5	0.04
20	-10.4	0.40	–5.4	0.1
30	-7.7	0.1	–3.2	0.15
40	-5.3	0.07	18.2	0.16
50	14.0	–0.06	16.8	–.007
60	15.2	–.003	18.2	–0.06
70	17.3	–.004	19.1	–0.52
80	8.5	–.007	15.6	–0.08
90	7.5	–.005	13.1	–0.09
100	–6.5	0.2	–10.2	18.00

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