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Ultrasonic Velocity and Apparent Molar Compressibility of Trichloroacetic Acid in Aqueous Ethanol

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Ultrasonic velocities of solutions of trichloroacetic acid in aqueous ethanol have been measured at 25, 30, 35 and 40°C, using a single crystal interferometer at frequency of 1.5 MHz. The ultrasonic velocity (U), density (ρ) and concentration (C) are used to calculate adiabatic compressibility (β_{ad}), intermolecular free length (L_f) and apparent molar compressibility (ϕ_k). Bachem's relation and Gucker's limiting law have been found to obey and constants A, B and ϕ_k^0 and S_k of these relations in various solvents have also been reported.

INTRODUCTION

Accurate thermodynamic data on dilute electrolyte solutions are frequently needed. The sound velocity is a purely thermodynamic function. Many other thermodynamic properties of electrolyte solutions are determined from sound velocity[1]. As these properties are a more accurate measure of ion-ion and ion-solvent interactions, an ultrasonic study on solutions of trichloroacetic acid in aqueous ethanol of varying dielectric constants has been made at different temperatures.

EXPERIMENTAL

Trichloroacetic acid (TCAA) has been recrystallized from distilled chloroform and dried under vacuum over calcium chloride[2]. Ethanol and water, purfied by standard methods[3] were mixed by weight to give mixtures of different dielectric constants[4]. The solutions of different molarities were prepared by dissolving accurately weighed amounts of electrolyte. The experimental set up and methods used for measuring densities and ultrasonic velocities were similar to those decribed elsewhere[5–7]. The reproducibilities in densities and ultrasonic velocities were ±0.001 g/ml and ±0.03% m/s respectively.

RESULTS AND DISCUSSION

Eyring and Kincaid[8] showed that ultrasonic velocity should increase if the intermolecular free length (L_f) decreases as a result of mixing of components. In the present investigation it has been observed that intermolecular free length, calculated from an equation

$$L_f = K \times \sqrt{\beta_{ad}} \quad (1)$$

where K is Jacobson's constant, decreases with increase in concentration of TCAA in 0, 8 and 16.4 wt. % ethanol, suggesting a structure promoting tendency of the added electrolyte. However, intermolecular free length increases on increasing the concentration of TCAA which results in a decrease of ultrasonic velocity in solutions in 25.3, 34.4 and 54.1 wt. % ethanol implying the presence of ion–ion interactions in lower dielectric constant media.

Adiabatic compressibilities of solutions are found to obey Bachem's[9] relation

$$\beta_{ad} = \beta^0_{ad} + AC + BC^{3/2} \quad (2)$$

where C is the molar concentration, A, B are constants, β_{ad} and β^o_{ad} are adiabatic compressibilities of solution and solvent respectively. The slopes, B of the linear plots of $\frac{\beta_{ad} - \beta^o_{ad}}{C}$ versus $\sqrt{C}$ have positive sign in the systems studied. However, the intercepts, A, have positive as well as negative signs. The constants A and B are given in Table 1.

From the sound velocity and density values the apparent molar compressibility, ϕ_k, is calculated using the equation

$$\phi_k = \frac{1000(\beta_{ad} \times \rho_0 - \beta^0_{ad} \times \rho)}{C \times \rho_0} + \frac{\beta^0_{ad} \times M_2}{\rho_0} \quad (3)$$

where ρ_0 and ρ are the densities of solvent and solution respectively and M_2 is the molecular weight of TCAA. The apparent molar compressibility varies linearly with square root of concentration in accordance with Gucker's[10] limiting law

$$\phi_k = \phi^0_k + S_k\sqrt{C} \quad (4)$$

The limiting apparent molar compressibilities, ϕ^0_k, are negative in sign (Table 1) for 0, 8 and 16.4 wt. % ethanol. This can be explained by postulating that electrostriction at the anionic end makes the solvent near the charges considerably less compressible than the bulk solvent due to the formation of rigid structures of solvent molecules around ions of solute, while ϕ^0_k are positive in sign for solutions in 25.3, 34.4 and and 54.1 wt % ethanol indicating decrease in ion-solvent interactions with increase of ethanol content in the solvent mixture. ϕ^0_K, irrespective of the sign does not change appreciably with temperature. The near constancy of ϕ^0_k (T) values could be explained on the basis of Frank and Wen[11] model for interactions with solvent molecules. The slopes, S_k, are positive in all the solvents. The value of S_k depends on the dielectric constant of the medium. Since low dielectric constant enhances electrostatic attraction, it is quite reasonable to obtain positive slopes.

TABLE 1
A, B OF BACHEM'S EQUATION AND ϕ_k^0 AND S_k VALUES OF GUCKER'S RELATION

Wt % of ethanol	$A \times 10^{12}$	$B \times 10^{12}$	$\phi_k^0 \times 10^9$	$S_k \times 10^9$	$A \times 10^{12}$	$B \times 10^{12}$	$\phi_k^0 \times 10^9$	$S_k \times 10^9$
	25°C				30°C			
0	–8.0	3.41	–6.4	4.12	–7.8	2.40	–6.1	3.04
8	–6.8	1.72	–4.6	4.22	–6.8	2.30	–4.7	3.83
16.4	–7.0	5.40	–3.0	5.70	–6.8	6.72	–3.5	6.55
25.3	0.2	3.33	–4.0	2.59	0.2	3.26	3.5	4.19
34.4	–0.6	4.50	3.1	4.74	–0.5	4.16	3.4	4.30
54.1	0.0	3.28	4.4	3.95	–0.2	2.99	4.8	3.00
	35°C				40°C			
0	–7.6	1.80	–6.2	3.29	–7.6	1.98	–5.8	1.86
8	–8.0	3.54	–5.2	4.76	–7.2	3.33	–4.6	5.28
16.6	–6.6	4.19	–3.0	4.39	–6.8	5.38	–2.8	4.76
25.3	0.4	2.97	4.3	2.70	0.1	2.67	3.8	2.62
34.4	–0.5	4.26	3.3	4.67	0.0	3.03	4.1	3.37
54.1	–0.2	2.90	5.0	3.24	–0.3	3.38	5.0	4.06

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