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# Ultrasonic, Volumetric and Viscometric Studies of Trichloroacetic acid-Nitrobenzene-Ethanol Solutions at Different Temperatures

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Ultrasonic velocity, density and viscosity of trichloroacetic acid (TCAA) solutions in 0, 20, 40, 60, 80 and 100 wt% ethanol-nitrobenzene have been determined at 298.15, 303.15, 308.15 and 313.15 K. The viscosity B coefficient, limiting partial molar volume ($\bar{V}_2^0$) and limiting apparent molar compressibility ($\phi_K^0$) throw light on the type of solute-solvent interaction in solution.

Measurement of viscosities, apparent molar volumes and ultrasonic velocities in solutions provide an excellent method of obtaining data on solute-solute and solute-solvent interactions. These interactions have been studied in aqueous and nonaqueous solutions by many workers, but such investigations in mixed solvents are scanty. Whenever studies in mixed solvents are reported attention has never been given to the mutual interactions of the solvent molecules[1]. Ultrasonic velocity measurements through nitrobenzene-ethanol mixtures at various temperatures showed that addition of nitrobenzene (non-associated) to strongly associated ethanol, dissociated alcohol molecules[2], forming clusters of varying compositions and sizes which are present in the critical solution region[3]. No attempt has been made to study the effect of the addition of electrolyte on inter-molecular interaction leading to hydrogen bond formation between nitrobenzene and ethanol molecules. In order to investigate the effect of addition of chloroacetic acids[4–6] on the structure of ethanol-nitrobenzene, ultrasonic, volumetric and viscometric studies of trichloroacetic acid solutions in ethanol-nitrobenzene have been undertaken at different temperatures.

Trichloroacetic acid[7], ethanol[8] and nitrobenzene[9] were purified by standard methods. Solutions of different molarities were prepared by dissolving accurately known weight of the acid in 0, 20, 40, 60, 80 and 100 wt% ethanol mixtures.

Ultrasonic velocity, viscosity and density of these solutions have been measured in a thermostated water bath having thermal stability of $\pm 0.01$°C, using M–82 interferometer having frequency of 3.5 MHz, Ostwald viscometer and bicapillary pycnometer with an accuracy of 0.03%, $\pm 0.0003$ Cp and $\pm 0.0001$ g/ml respectively. The efflux times were measured with a stop watch correct to 0.01 second.

The variation of relative viscosity ($\eta_r$) in the concentration range studied is analysed with the help of equation (1).

$$\eta_r = 1 + BC,\ 0.002M < C < ca.\ 0.1M \quad (1)$$

The values of viscosity B coefficients obtained from slopes of the plots of $\eta_r$ versus C are given in Table 1. The negative values of dB/dT in solutions in 0, 20, 40 and 60 wt% ethanol and positive values of dB/dT for solutions in 80 and 100 wt% ethanol suggest structure-promoting and structure-breaking effects of TCAA respectively[10].

TABLE 1

B COEFFICIENTS OF TRICHLORO-ACETIC ACID AT DIFFERENT TEMPERATURES

| wt% Ethanol | B coefficient | | | |
|---|---|---|---|---|
| | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0 | 0.155 | 0.146 | 0.145 | 0.135 |
| 20 | 0.246 | 0.229 | 0.215 | 0.186 |
| 40 | 0.209 | 0.205 | 0.204 | 0.197 |
| 60 | 0.280 | 0.263 | 0.249 | 0.243 |
| 80 | 0.237 | 0.239 | 0.240 | 0.243 |
| 100 | 0.217 | 0.218 | 0.222 | 0.223 |

The apparent molar volume ($\phi_v$) was calculated from density data[11]. The limiting apparent molar volume ($\phi_v^0$) which are also equal to partial molar volume ($\bar{V}_2^0$) at infinite dilution are obtained from linear plots of $\phi_v$ versus C and are listed in Table 2. The negative values of $d(\phi_v^0)dT$ in solutions in 0, 20 and 40 wt% ethanol and positive values of $d(\phi_v^0)/dT$ in 60, 80 and 100 wt% ethanol indicate the structure-promoting and structure-breaking effect of TCAA respectively.

The apparent molar compressibility ($\phi_k$) obeys Gucker's limiting law[12]. The apparent molar compressibilities at infinite dilution ($\phi_k^0$) are obtained as intercepts of linear plots of $\phi_k$ versus $C^{1/2}$ and are listed in Table 2. The positive values of $\phi_k^0$ in solutions in 0 and 20 wt% ethanol and negative values of $\phi_k^0$ in 40, 60 and 100 wt% ethanol suggest structure-promoting and structure-breaking effects of TCAA respectively. Negative $\phi_k^0$ values can be explained on Frank and Wen model[13] for the interaction of ions with solvent molecules.

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TABLE 2

LIMITING PARTIAL MOLAR VOLUMES AND LIMITING APPARENT MOLAR COMPRESSIBILITIES AT DIFFERENT TEMPERATURES

| wt% Ethanol | $\phi_v^0 = \bar{V}_2^0$ (cm³ mol⁻¹) | | | |
|---|---|---|---|---|
| | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0 | 90.00 | 89.45 | 86.20 | 84.10 |
| 20 | 93.33 | 91.67 | 90.33 | 90.00 |
| 40 | 91.70 | 88.20 | 86.00 | 84.50 |
| 60 | 88.40 | 88.60 | 88.67 | 88.70 |
| 80 | 93.48 | 93.80 | 94.00 | 95.60 |
| 100 | 64.50 | 68.50 | 73.09 | 75.25 |
| | $\phi_K^0 \times 10^9$ (cm² dyne⁻¹) | | | |
| 0 | 20.6 | 11.2 | 7.8 | 5.5 |
| 20 | 24.9 | 28.6 | 32.7 | 16.4 |
| 40 | −36.8 | −22.3 | −35.5 | −28.1 |
| 60 | −65.0 | −43.9 | −67.8 | −58.4 |
| 80 | −2.7 | −1.9 | −1.6 | 3.9 |
| 100 | −28.9 | −6.5 | −5.0 | 5.2 |

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