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Partial Molar Volumes and Viscosities of Monochloroacetic acid in Acetone-Water Mixtures

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Viscosity data of monochloroacetic acid solutions in aqueous acetone at 25, 30 and 35°C are analysed with the help of modified Jones-Dole and Vand's equations, and the density data are analysed with the help of Masson's equation. The activation parameters of viscous flow are obtained by the application of transition state theory. Results show that monochloroacetic acid acts as structure promoter in water-acetone mixtures.

INTRODUCTION

Dependence of viscosity and apparent molar volume (ϕ_v) on concentration (C) of solute and temperature (T) of solutions has been employed as a tool to study ion-ion and ion-solvent interactions in aqueous and mixed solvents. Ion-solvent interactions in water-acetone mixtures have been reported earlier by other workers[1–4]. In these mixtures the thermodynamic properties of transfer of electrolytes between the pure solvents are very large[5, 6], which are attributed partly to the very strong interactions between water and acetone molecules and partly to the transmission of the Lewis basicity of the acetone molecules in water-acetone mixtures through hydrogen bonds[7–9]

A survey of literature showed that there is a lack of such study of monochloroacetic acid in water-acetone mixtures. Moreover, acetone-water solvent system has been extensively used in the study of organic reactions[10, 11], hence a detailed study of thermodynamics of ion-solvent interactions in this system is of considerable importance. These interactions have already been reported[12] from ultrasonic study of this system. In order to supplement the above study, density and viscosity measurements of this system are reported here.

EXPERIMENTAL

Monochloroacetic acid (MCAA) and acetone were purified as decribed earlier[13, 14]. Triply distilled water was mixed with acetone by weight to give mixtures of different dielectric constants[15]. The densities of molar solutions of MCAA in different solvents with an accuracy of 5 in 10^5 g/ml and viscosities,

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with an accuracy of 3 in 10^4 cP were measured by using a bicapillary pycnometer and Ubbelhode viscometer respectively at 25, 30 and 35°C, as has been done previously[16, 17]

RESULTS AND DISCUSSION

In the present investigation the variation of relative viscosity (η_r) of monochloroacetic acid (MCAA) solutions in 10, 30, 50, 70, 90 and 100 wt % acetone at 25, 30 and 35°C with concentration (C) is expressed by modified Jones-Dole equation[18] and Vand's equation[19]. Figures 1 and 2 show the validity of the modified Jones-Dole and Vand's equation respectively, and the viscosity B coefficients calculated from these equations are listed in Table 1.

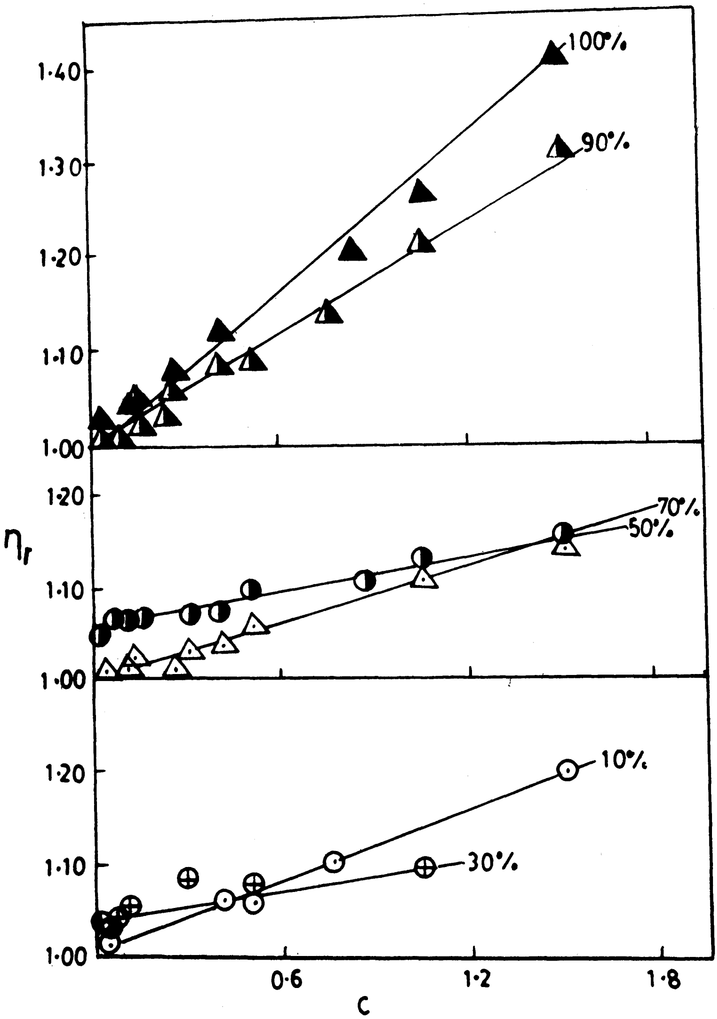

Fig. 1 Plots of η_r versus concentration (C) in different compositions of acetone-water at 25°C.

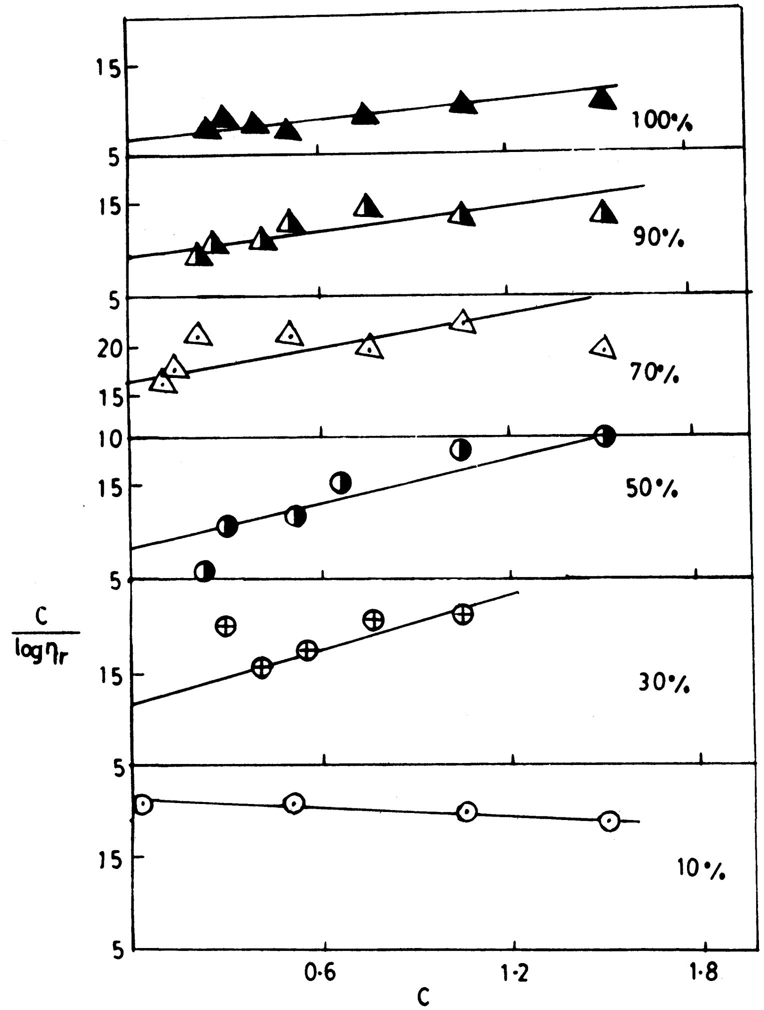

Fig. 2 Plots of C/log η_r versus concentration (C) in different compositions of acetone-water at 25°C.

TABLE 1
VALUES OF B FROM DIFFERENT EQUATIONS

Wt % Acetone	25°C		30°C		35°C	
	B_1	B_2	B_1	B_2	B_1	B_2
10	0.1275	0.1047	0.1250	0.0980	0.1226	0.1001
30	0.0943	0.1151	0.0932	0.1123	0.0921	0.1316
50	0.1000	0.2094	0.0968	0.1919	0.0938	0.1706
70	0.1060	0.1096	0.0968	0.0940	0.0938	0.0850
90	0.2000	0.2093	0.1905	0.1919	0.1818	0.1771
100	0.2667	0.2709	0.2500	0.2558	0.2353	0.2424

B_1: from $\eta_r = 1 + BC$ B_2: from Vand's equation

Close examination of Table 1 shows that 'B' values are positive and decrease with increase in temperature (negative dB/dT) suggesting structure promoting tendency of MCAA. The positive B values and negative dB/dT indicate the absence of a fixed layer of solvent molecules around the ions in their cosphere (*i.e.* absence of electrostrictive ion solvation).

The viscosity data of the present systems are also analysed on the basis of the transition state treatment of relative viscosity of the electrolyte solutions as suggested by Feakins *et al.*[20] The B parameter in terms of this theory is given by

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left[\frac{\Delta\mu_2^{0\pm} - \Delta\mu_1^{0\pm}}{RT}\right] \tag{1}$$

where $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molar volumes of the solvent and solute (at infinite dilution) respectively. The free energies of activation per mole of the pure solvent ($\Delta\mu_1^{0\pm}$) and the solute ($\Delta\mu_2^{0\pm}$) are calculated with the help[20] of equations (2) and (3) respectively.

$$\Delta\mu_1^{0\pm} = RT \ln (\eta_0 \bar{V}_1^0/hN) \tag{2}$$

$$\Delta\mu_2^{0\pm} = \Delta\mu_1^{0\pm} + \frac{RT}{\bar{V}_1^0}[1000B - (\bar{V}_1^0 - \bar{V}_2^0)] \tag{3}$$

where h is the Planck constant, N the Avogadro's number and η_0 is the viscosity of the solvent.

The partial molar volumes at infinite dilution ($\bar{V}_1^0$) of acetone at 25, 30, 35°C were 66.22, 66.60 and 66.98 ml respectively. The values of $\bar{V}_2^0$, $\Delta\mu_1^{0\pm}$ and $\Delta\mu_2^{0\pm}$ in different compositions of acetone-water mixtures at 25, 30 and 35°C are listed in Table 2. The B values used to calculate $\Delta\mu_2^{0\pm}$ were obtained from the modified Jones-Dole equation.

A perusal of Table 2 shows that $\Delta\mu_1^{0\pm}$ values are practically constant irrespective of temperature and solvent composition. According to Feakins *et al.*[20], $\Delta\mu_2^{0\pm} > \Delta\mu_1^{0\pm}$ for the solutes having positive B values. In the present investigation $\Delta\mu_2^{0\pm}$ values are positive and greater than $\Delta\mu_1^{0\pm}$. This suggests that the formation of the transition state is less favoured in presence of the MCAA meaning that formation of transition state is accompanied by the breaking and distortion of the intermolecular bonds. Moreover, greater the values of $\Delta\mu_2^{0\pm}$ than those of $\Delta\mu_1^{0\pm}$, the greater is the structure making ability of the solute. On the basis of this viewpoint MCAA is an efficient structure maker in 100 wt % acetone. According to Feakins' model, $\Delta\mu_2^{0\pm}$ decreases with increase of temperature for solutes having negative values of $\frac{dB}{dT}$. This is nicely shown in the present investigation where MCAA acts as a structure promoter in all solvent mixtures.

TABLE 2

VALUES OF $\bar{V}_2^0$, $\Delta\mu_1^{0\pm}$ AND $\Delta\mu_2^{0\pm}$ AT VARIOUS TEMPERATURES

Wt % acetone	$\bar{V}_2^0$ ml mol^{-1}	$\Delta\mu_1^{0\pm}$ (KJ mol^{-1})	$\Delta\mu_2^{0\pm}$ (KJ mol^{-1})
25°C			
10	58.00	11.69	16.75
30	43.50	11.96	14.65
50	27.00	11.81	14.09
70	69.00	11.14	15.22
90	57.00	10.66	17.82
100	51.00	9.80	31.47
30°C			
10	57.50	11.65	16.04
30	43.00	11.90	14.53
50	27.00	11.78	13.99
70	68.50	11.16	14.89
90	57.00	10.78	17.62
100	51.00	9.95	30.37
35°C			
10	58.00	11.71	15.91
30	43.00	11.84	14.45
50	27.00	11.81	13.86
70	69.50	11.12	14.80
90	56.50	10.92	16.02
100	51.00	10.10	29.41

The apparent molar volumes were calculated using the density data of solutions. The limiting apparent molar volume (ϕ_v^0) which is equal to the partial molar volume at infinite dilution ($\bar{V}_2^0$) is obtained by extrapolating ϕ_v versus $\sqrt{C}$ curves (Fig. 3) to zero concentration, neglecting the points at low concentrations, which deviated considerably from linearity. The same procedure was adopted by us[16] because of the possibility of systematic error at low concentrations due to the dissolved air in solution. $\bar{V}_2^0$ of MCAA in water, acetone and acetone-water mixtures at 25, 30 and 35°C are listed in Table 2. $\bar{V}_2^0$ of MCAA is the sum of its ionic partial molar volumes[16], $\bar{V}_H^0$ and $\bar{V}_{CH_2ClCOOH}^0$ as

$$\bar{V}_{CH_2ClCOOH}^0 = V_{H^+(int)} + V_{CH_2ClCOO^-(int)} + \Delta V \tag{4}$$

where $V_{H^+(int)}$ and $V_{CH_2ClCOO^-(int)}$ are *intrisic* volumes of the ions and ΔV is the change in volume of the system due to ion-solvent interactions. Due to its larger size, monochloroacetate ion is less solvated in comparison to H^+ Therefore ΔV term in equation (4) is mainly due to proton solvation. It has been observed that $\bar{V}_2^0$ of MCAA has minimum and maximum values at 50 and 70 wt % acetone

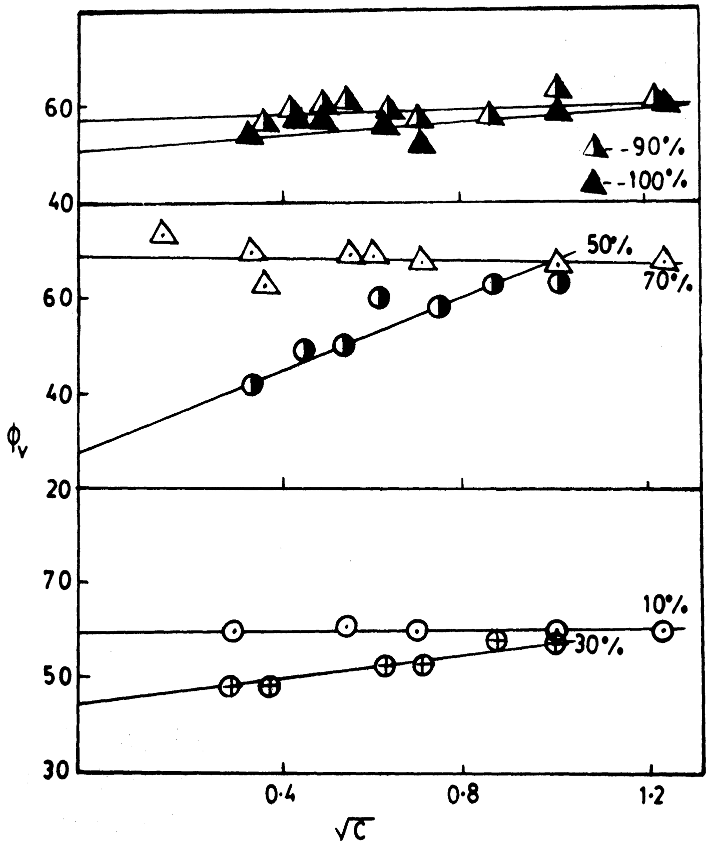

Fig. 3 Plots of apparent molar volume (ϕ_V) versus C in different compositions of acetone-water at 25°C.

respectively. It is suggested that around 50 wt % acetone the structure formation between the two kinds of the solvent molecules is the most enhanced, and in this solvent mixture due to the preformed holes into which the anion CH_2ClCOO^- may fit without the prerequisite of hole formation prior to dissolution, $\bar{V}_2^0$ becomes minimum. At 70 wt % acetone, where $\bar{V}_2^0$ becomes maximum, the competition between the pure water and pure acetone structure results in the mixture having essentially a close packed structure, with consequent minimum free volume. Thus there are no preformed holes in the binary solvent and dissolution of the third component solute required maximum expansion of the solvent to accommodate the solute.

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