THERMODYNAMICS OF Sr(NO$_3$)$_2$ AND Cd(NO$_3$)$_2$ IN MIXED SOLVENTS FROM VISCOSITY DATA

D.K. DASH

Department of Chemistry, S.C.S. College, Puri (India)

P.B. DAS *

*Department of Chemistry, Ravenshaw College, Cuttack 753003 (India)*

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ABSTRACT

The viscosities of Sr(NO$_3$)$_2$ and Cd(NO$_3$)$_2$ have been determined in dioxane, glycol and methyl alcohol+water mixtures at 10, 20 and 30% by weight. The B values have been computed at different temperatures both from the Jones–Dole and Das's equation. From the B values, the effective rigid molar volume, its change with % of organic solvent, temperature and the ion–solvent interaction have been inferred. Activation parameters have also been calculated and the structure breaking effect has been deduced.

INTRODUCTION

Water at ordinary temperature has a quasicrystalline structure. A dynamic equilibrium seems to exist between the three-dimensional hydrogen bonded clusters and the denser monomers

$$(H_2O)_c \rightleftharpoons (H_2O)_d$$
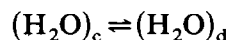
Electrolytes which dissolve in water have been classified as structure makers or breakers, depending on whether the above equilibrium shifts to the left or the right. Ions with a lower charge density have a smaller width of region A which is surrounded by a concentric region of water molecules, analogous to a kind of freezing, and a larger width of region B which has the tendency to resist the normal three-dimensional water structure called region C, and balance between the two competing forces, are net structure breakers. On the other hand, ions with a high charge density show an opposite behaviour and are net structure makers [1].

Organic solvents like dioxane, glycol and methyl alcohol are miscible with

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* To whom all correspondence should be addressed.

water at all solvent compositions and their dielectric constants and dipole moments are very different. Dioxane, glycol and methyl alcohol are aprotic solvents, whereas water is both an electron donor and an acceptor. Hence studies of their aqueous mixtures become an interesting field to explore, particularly the ionic processes accompanying the solutions of the strong electrolytes. It becomes relevant to enquire whether a given mixed solvent will resist the centrosymmetric ordering of the ion more or less than pure water.

From this point of view, the viscosities of the solutions of $Sr(NO_3)_2$ and $Cd(NO_3)_2$ at weight % of dioxane, glycol and methyl alcohol, 10, 20 and 30% have been measured at concentration $C \leqslant 0.1$ mole 1^{-1} at 30–45°C for dioxane + water and glycol + water, and at $30-40 \pm 0.01$°C for methyl alcohol + water mixtures.

MATERIALS AND METHOD

All the salts used were of E. Merck, 'Extra pure' varieties. The contents were estimated in the usual manner. The preparations of the solvents solutions and viscometric technique were the same as those used by Misra and Das [2]. The densities of the solutions and the solvents were determined by pycnometry with bouyancy correction and is the same as that of Das and Das [3]. All sorts of precautions were taken to check the evaporation of the solvent [4]. The time of flow for each concentration did not exceed 0.2 s in about 15 min. Density readings were precise up to 0.0002 g cm^{-3}, i.e., an error of 4 in 10^6. The concentration range was from 0.1 to 0.001 mole 1^{-1}.

RESULTS AND DISCUSSION

The viscosities of the mixed solvents as well as those of the salt solutions under study were measured and the results were analyzed. The Jones–Dole [5] equation

$$\eta_r = 1 + A\sqrt{C} + BC$$

is found to be valid as the plot of $\eta_r - 1/C^{1/2}$ vs. $C^{1/2}$ is linear. The intercept and the slope gave coefficients A and B, respectively.

From conductance results it is seen that the dissociation of the salts is incomplete. Hence the modified Davies–Molpaus equation proposed by the author [6] is more suitable as it was specifically formulated to account for the effect of ion association. For ternary salts which dissociate in two stages

$$MA_2 \rightleftharpoons MA^+ + A^-$$

$$MA^+ \rightleftharpoons M^{2+} + A^-$$

If α is the degree of ionization of the ion pair then

$$\eta_r = 1 + A\sqrt{I} + B_A - (1 + \alpha C) + B_{M^{2+}}\alpha C + B_{MA} + (1 - \alpha)\,C$$

or

$$\frac{\eta_r - 1 - A\sqrt{I}}{C} + (B_{MA^+} + B_{A^-}) + \alpha(B_{M^{2+}} + B_{A^-} - B_{MA^+})$$

Therefore a plot of $(\eta_r - 1 - A\sqrt{I})/C$ against α should have a slope of $(B_{M^{2+}} + B_{A^-} - B_{MA^+})$ and an intercept at $\alpha = 0$, $(B_{MA^+} + B_{A^-})$, and at $\alpha = 1$ the intercept is $(B_{M^{2+}} + 2B_{A^-})$ since there would be no ion pair formation. Hence B is computed. The values of A are recorded in Table 1 and B values obtained from both the methods are given in Tables 2 and 3, respectively. The B values obtained by the latter method are slightly less than that of the former, which is quite obvious as ion association has been taken into account in the latter method.

A Values

The differences in A values (Table 1) indicate the dependence of ionic interaction on the nature of the electrolyte; all values are positive. The electrostatic ion–ion interaction and hence the value of A is found to increase with decrease in dielectric constant when the concentration of the organic solvent increases. From Table 1, it is seen that the ion–ion interaction is of the order $Cd^{2+} > Sr^{2+}$. Further, the value of A decreases with increase in temperature, which one should expect (excepting glycol) in view of more thermal agitation at higher temperatures and a reduction in the

TABLE 1

$A \times 10^3$ ($l^{1/2}$ mole$^{-1/2}$)

Temp. (°C)	wt.% dioxane			wt.% glycol			wt.% CH$_3$OH		
	10	20	30	10	20	30	10	20	30
Sr(NO$_3$)$_2$									
30	10.4	10.9	11.0	14.4	15.2	16.3	9.3	10.1	10.6
35	10.6	10.7	11.8	14.5	15.1	16.2	9.1	9.9	10.4
40	10.4	10.5	11.6	14.6	15.4	16.3	8.8	9.7	10.1
45	10.8	10.3	11.4	14.5	15.6	16.4			
Cd(NO$_3$)$_2$									
30	12.1	12.6	13.2	16.2	17.2	18.4	10.4	11.2	11.6
35	12.0	12.4	13.0	16.1	17.0	18.3	10.2	10.9	11.4
40	11.8	12.2	12.8	16.0	17.1	18.1	10.0	10.7	11.2
45	11.6	12.0	12.0	16.2	17.2	18.2			

TABLE 2

B (1 mole^{-1})

Temp. (°C)	wt.% dioxane			wt.% glycol			wt.% CH$_3$OH		
	10	20	30	10	20	30	10	20	30
Sr(NO$_3$)$_2$									
30	0.265	0.270	0.500	0.355	0.390	0.530	0.245	0.260	0.320
35	0.270	0.380	0.555	0.360	0.480	0.550	0.235	0.265	0.340
40	0.280	0.430	0.605	0.420	0.500	0.620	0.240	0.280	0.360
45	0.290	0.480	0.680	0.520	0.610	0.695			
Cd(NO$_3$)$_2$									
30	0.170	0.340	0.450	0.305	0.420	0.500	0.160	0.230	0.370
35	0.195	0.410	0.485	0.330	0.520	0.610	0.150	0.265	0.400
40	0.250	0.475	0.530	0.390	0.540	0.660	0.140	0.280	0.430
45	0.315	0.545	0.580	0.420	0.590	0.710			

attractive forces. In the case of glycol + water this does not occur as it is more viscous.

Dependence of B *on temperature*

According to Stokes and Mills [7], the viscosity of dilute electrolytic solutions incorporates that of the solvent plus the contribution from the other sources. They are η^E, the positive increase due to the shape and size of

TABLE 3

B (1 mole^{-1})

Temp. (°C)	wt.% dioxane			wt.% glycol			wt.% CH$_3$OH		
	10	20	30	10	20	30	10	20	30
Sr(NO$_3$)$_2$									
30	0.254	0.259	0.429	0.323	0.354	0.472	0.233	0.248	0.284
35	0.259	0.340	0.505	0.329	0.423	0.484	0.239	0.255	0.299
40	0.262	0.380	0.535	0.363	0.443	0.534	0.239	0.260	0.309
45	0.269	0.418	0.582	0.445	0.524	0.584			
Cd(NO$_3$)$_2$									
30	0.154	0.312	0.408	0.280	0.373	0.462	0.151	0.208	0.318
35	0.162	0.364	0.432	0.293	0.438	0.524	0.156	0.212	0.328
40	0.208	0.394	0.480	0.313	0.456	0.553	0.138	0.234	0.342
45	0.256	0.438	0.498	0.361	0.499	0.604			

the ion; η^A, the increase due to the alignment or orientation of the polar molar molecules by the ionic field; and η^D, the decrease in the viscosity arising due to the distortion of the solvent structure. Therefore, B coefficients can be discussed in terms of these viscosity effects at different temperatures.

The B coefficient of both the salts increases with increase in temperature. This indicates that the viscosity decreases due to the solvent structure, η^D, is small and $\eta^E + \eta^A > \eta^D$, and B is positive. The B value is found to be of the order $Sr^{2+} > Cd^{2+}$ and glycol + water > dioxane + water > methyl alcohol + water for both the salts. The smaller the value of B, the greater is the ion–solvent interaction; so the ion–solvent interaction is of the order $Cd^{2+} > Sr^{2+}$.

Also according to Stokes and Mills [7], the smaller the value of dB/dt, the greater is the ion–solvent interaction. In the present case, the plot of B vs. t is linear and the slope dB/dt is found to be of the order glycol + water > dioxane + water > methyl alcohol + water, so the ion–solvent interaction is of the average order methyl alcohol + water > dioxane + water > glycol + water.

Effective rigid molar volume

Breslau and Miller [8] have calculated the effective rigid molar volume, V_e, from the B coefficient. V_e is that volume which a mole of solute particle behaves like when considered, for purely hydrodynamic reasons, as a rigid macroscopic sphere. A particle which has a measurable effect on neighbouring solvent molecules, from physical considerations alone, would be expected

TABLE 4

V_e (l mole^{-1})

Temp. (°C)	wt.% dioxane			wt.% glycol			wt.% CH$_3$OH		
	10	20	30	10	20	30	10	20	30
Sr(NO$_3$)$_2$									
30	0.208	0.282	0.415	0.202	0.281	0.414	0.158	0.198	0.290
35	0.200	0.270	0.400	0.180	0.264	0.400	0.150	0.188	0.258
40	0.191	0.261	0.392	0.171	0.252	0.387	0.143	0.180	0.250
45	0.183	0.251	0.380	0.162	0.241	0.370			
Cd(NO$_3$)$_2$									
30	0.212	0.302	0.442	0.221	0.308	0.484	0.178	0.218	0.300
35	0.231	0.286	0.403	0.241	0.291	0.421	0.166	0.210	0.292
40	0.201	0.248	0.382	0.251	0.288	0.411	0.154	0.199	0.287
45	0.216	0.287	0.389	0.257	0.292	0.403			

to have a higher V_e than one which has a lesser effect. Since the B coefficient is a measure of the ion–solvent interaction, a relation should therefore exist with the slope, when B is plotted vs. V_e. The above-mentioned authors have obtained a relationship for monovalent and bivalent salts. This has been extended to mixed solvents, such as dioxane + water, glycol + water and methyl alcohol + water mixtures. The B coefficient from Table 3 has been utilized to calculate V_e for both the salts. The value V_e thus obtained is recorded in Table 4.

The plot of B vs. V_e is found to be linear and the equations that fit the data are different for the different solvent compositions and for different temperatures. The value of V_e decreases with decrease in nonaqueous solvent. This may be due to the hydrogen bond between water and the nonaqueous solvent. As the nonaqueous solvent is increased dioxane + water, glycol + water and methyl alcohol + water molecules are formed, resulting in an increase in V_e.

Activation parameters

Eyring [9] applied the theory of absolute reaction rate to interpret the viscosity of liquids by calculating the energy, free energy and entropy of activation. Nightingale and Benck [10] and Feakins et al. [11] have shown that the theory of reaction rate can be successfully applied to electrolyte solutions. Proceeding along similar lines, ΔE (which does not differ very much from ΔH), ΔG and ΔS for the solvents and the salts at different wt.% have been calculated at 35°C and are tabulated in Table 5. It is observed that ΔE, ΔG and ΔS values for viscous flows are less than that of the solvent, indicating a structure breaking effect, and is of the order $Cd^{2+} > Sr^{2+}$.

Dioxane is more basic and less acidic than that of water because of the electron releasing tendency of the methylene group in the molecule. A water molecule which is hydrogen bonded with the oxygen atom of a dioxane molecule also becomes more basic and less acidic than pure water. A cation will interact more strongly with the oxygen atoms of dioxane + water mixtures and an anion will react more strongly with hydrogen atoms. This type of ion–solvent interaction is in the primary solvation sheath.

The addition of small amounts of dioxane may give rise to two effects: if the dioxane is accommodated in the solvent structure, it may strengthen the water structure, because dioxane is a better proton acceptor; if it cannot be accommodated because of its bulky size, then it may cause a breakdown in the three-dimensional water structure. The B value is seen to be less than that of glycol + water mixtures. This indicates that dioxane is not accommodated in the solvent structure and hence it breaks down the three-dimensional water structure.

Glycol has two –OH groups and methyl alcohol has one –OH group, whereas water is both an electron donor and an acceptor. Methyl alcohol

TABLE 5

Activation parameters

wt.% organic solvent		Dioxane+water			Glycol+water			Methyl alcohol+water		
		ΔG(kJ mole^{-1})	ΔE(kJ mole^{-1})	ΔS(JK^{-1} mole^{-1})	ΔG(kJ mole^{-1})	ΔE(kJ mole^{-1})	ΔS(JK^{-1} mole^{-1})	ΔG(kJ mole^{-1})	ΔE(kJ mole^{-1})	ΔS(JK^{-1} mole^{-1})
10%	Solvent	9.57	17.07	24.33	10.52	18.22	24.67	10.33	18.71	24.41
	$Cd(NO_3)_2$	9.12	16.44	23.88	10.32	17.81	23.76	9.72	18.11	23.31
	$Sr(NO_3)_2$	9.24	16.76	24.08	10.41	18.08	23.71	9.88	18.22	24.41
20%	Solvent	10.41	17.38	22.61	11.42	19.31	24.98	10.62	19.22	24.82
	$Cd(NO_3)_2$	9.92	16.94	22.42	11.21	18.21	23.94	9.81	18.63	23.42
	$Sr(NO_3)_2$	10.08	17.12	23.51	11.28	18.29	23.88	9.99	18.74	23.51
30%	Solvent	10.78	16.81	19.56	12.22	19.63	23.57	10.98	19.99	25.07
	$Cd(NO_3)_2$	9.84	15.94	19.82	11.84	19.40	23.82	10.24	19.25	24.81
	$Sr(NO_3)_2$	10.41	16.32	19.56	11.95	19.47	23.77	10.38	19.39	24.89

accepts a proton and hence the three-dimensional water structure is very easily broken. Although glycol contains two –OH groups it is not able to break the hydrogen bond of water so easily, as CH_2OH groups are linked with each other; so the ion–solvent interaction order is MeOH + water > dioxane + water > glycol + water.

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