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Note

THERMODYNAMICS OF $CdCl_2$ AND $CdBr_2$ IN MIXED SOLVENTS FROM VISCOSITY DATA

S.C. RATH
Department of Chemistry, S.C.S. College, Puri (India)
P.B. DAS *
Department of Chemistry, G.M. College, Sambalpur, Orissa (India)

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Water at room 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 structure breakers, depending on whether the above equilibrium shifts to the left or right. Ions with a low charge density have a smaller width of region A in which they are surrounded by a concentric region of water molecules, analogous to a kind of freezing, and a larger width of region B which tends to resist the normal three-dimensional water structure called region C, and balanced between the two competing forces are net structure breakers. On the other band, 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 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 electron acceptor. Hence studies of their aqueous mixtures become an interesting field of study, particularly with regard to 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 $CdCl_2$ and $CdBr_2$ at 10, 20 and 30 weight % of dioxane, glycol and methyl alcohol have been measured at concentration $C \leqslant 0.1$ mole l^{-1} at 30–45°C for dioxane + water and glycol + water and at 30–40 ± 0.01°C for methyl alcohol + water mixtures.

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* To whom correspondence should be addressed.

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MATERIALS AND METHOD

All the salts used were of E. Merck, 'Extra pure' varieties. The contents were estimated in the usual manner. The preparation of the solvents, solutions and viscometric technique were the same as described by Misra and Das [2]. The densities of the solutions and solvents were determined using a pycnometer with bouyancy correction as used by 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 0.1–0.001 mole l^{-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 analyzed. The Jones–Dole [5] equation

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

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

From conductance results it is seen that 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

TABLE 1

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

Temp. (°C)	Dioxane (wt.%)			Glycol (wt.%)			CH_3OH (wt. %)		
	10	20	30	10	20	30	10	20	30
$CdCl_2$									
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			
$CdBr_2$									
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[l mole^{-1} (J–D method)]

Temp. (°C)	Dioxane (wt.%)			Glycol (wt.%)			CH_3OH (wt.%)		
	10	20	30	10	20	30	10	20	30
$CdCl_2$									
30	0.170	0.340	0.452	0.310	0.430	0.510	0.161	0.232	0.370
35	0.194	0.412	0.484	0.320	0.521	0.612	0.152	0.264	0.402
40	0.253	0.478	0.535	0.392	0.543	0.662	0.142	0.283	0.434
45	0.318	0.545	0.578	0.483	0.594	0.713			
$CdBr_2$									
30	0.160	0.320	0.422	0.300	0.411	0.498	0.154	0.221	0.352
35	0.182	0.398	0.461	0.305	0.505	0.594	0.146	0.251	0.394
40	0.238	0.457	0.519	0.376	0.531	0.640	0.132	0.270	0.418
45	0.297	0.522	0.554	0.454	0.565	0.698			

the ion association effect. 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

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

TABLE 3

B[l mole^{-1}(Das's equation)]

Temp. (°C)	Dioxane (wt.%)			Glycol (wt.%)			CH_3OH (wt.%)		
	10	20	30	10	20	30	10	20	30
$CdCl_2$									
30	0.151	0.320	0.428	0.298	0.406	0.494	0.150	0.219	0.354
35	0.184	0.402	0.466	0.302	0.504	0.601	0.139	0.248	0.382
40	0.238	0.461	0.521	0.371	0.523	0.643	0.131	0.272	0.420
45	0.304	0.528	0.554	0.460	0.554	0.691			
$CdBr_2$									
30	0.150	0.310	0.421	0.288	0.399	0.481	0.141	0.205	0.344
35	0.164	0.374	0.448	0.294	0.488	0.579	0.131	0.240	0.368
40	0.224	0.435	0.502	0.364	0.514	0.621	0.119	0.252	0.392
45	0.284	0.502	0.531	0.431	0.542	0.672			

where I is the ionic strength. Therefore a plot of $(\eta_r - 1 - A\sqrt{I})/C$ vs. 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 those of the former, which is quite obvious as ion association has been taken into account in the latter method.

A *value*

The different A values (Table 1) indicate the dependence of ionic interaction on the nature of the electrolytes, and are all positive. The electrostatic ion–ion interaction, and hence the value of A, is found to increase with decrease in dielectric constant with an increase in the concentration of the organic solvent. Table 1 shows that the ion–ion interaction is of the order $Br^- > Cl^-$. Further the value of A decreases with increase in temperature, which is to be expected (excepting glycol) in view of an increase in thermal agitation at higher temperatures and a reduction of attractive forces. In the case of glycol + water this is not the case as the mixture 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 other sources, which are η^E, the positive increase due to the shape and size of 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 due to the distortion of the solvent structure. 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, $\eta^E + \eta^A > \eta^D$, and B is positive. The B value is found to be of the order $Cl^- > Br^-$ and is of the order glycol + water > dioxane + water > methyl alcohol + water for both the salts. The smaller the value of B, the greater the ion–solvent interaction. So the ion–solvent interaction is of the order $Br^- > Cl$.

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 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 1 mole of solute particle behaves like when considered, from a purely hydrodynamic point of view, as a rigid macroscopic sphere. A particle which has a measured effect on neighbouring solvent molecules, from physical considerations alone, would be expected 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 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. The B coefficients from Table 3 have been utilized to calculate V_e for both the salts. The V_e values thus obtained are 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 the 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 et al. [9] applied the theory of absolute reaction rate to interpret the viscosity of liquids by calculating the energy, free energy and entropy of

TABLE 4

V_e(l mole^{-1})

Temp. (°C)	Dioxane (wt.%)			Glycol (wt.%)			CH_3OH (wt.%)		
	10	20	30	10	20	30	10	20	30
$CdCl_2$									
30	0.210	0.285	0.417	0.287	0.292	0.417	0.160	0.200	0.293
35	0.204	0.274	0.405	0.182	0.268	0.404	0.152	0.190	0.260
40	0.193	0.264	0.394	0.174	0.255	0.390	0.145	0.182	0.252
45	0.185	0.253	0.387	0.164	0.244	0.373			
$CdBr_2$									
30	0.212	0.304	0.445	0.225	0.310	0.486	0.178	0.220	0.302
35	0.234	0.288	0.405	0.245	0.294	0.424	0.169	0.214	0.296
40	0.204	0.250	0.386	0.256	0.292	0.414	0.156	0.201	0.290
45	0.218	0.288	0.392	0.259	0.294	0.405			

TABLE 5

Activation parameter

Wt.% of organic solvent	Dioxane + water			Glycol + water			CH_3OH + water		
	ΔG (kJ $mole^{-1}$)	ΔE (kJ $mole^{-1}$)	ΔS (J K^{-1} $mole^{-1}$)	ΔG (kJ $mole^{-1}$)	ΔE (kJ $mole^{-1}$)	ΔS (J K^{-1} $mole^{-1}$)	ΔG (kJ $mole^{-1}$)	ΔE (kJ $mole^{-1}$)	ΔS (kJ $mole^{-1}$)
10% Solvent	9.57	17.07	24.33	10.52	18.22	24.67	10.33	18.71	24.41
$CdCl_2$	9.48	16.98	24.12	10.32	18.12	24.51	10.21	18.52	24.23
$CdBr_2$	9.28	16.78	23.81	10.04	17.84	24.13	9.95	18.23	24.03
20% Solvent	10.41	17.38	22.61	11.42	19.31	24.98	10.62	19.22	24.22
$CdCl_2$	10.22	17.12	22.44	11.14	19.07	24.64	10.34	19.01	23.01
$CdBr_2$	10.01	16.94	22.10	10.91	18.91	24.42	10.12	18.78	22.78
30% Solvent	10.78	16.81	19.56	12.22	19.63	23.57	10.98	19.99	25.07
$CdCl_2$	10.58	16.57	19.41	12.00	19.42	23.33	10.72	19.78	24.91
$CdBr_2$	10.18	16.21	19.08	11.81	19.11	23.02	10.48	19.59	24.68

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 weight % 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 $Br^- > Cl^-$.

Dioxane is more basic and less acidic than water because of the electron releasing tendency of the methylene group in the molecule. A water molecule where hydrogen is 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: (i) if the dioxane is accommodated in the solvent structure it may strengthen the water structure because dioxane is a better proton acceptor; (ii) if it cannot be accommodated because of its bulky size, then it may cause a breakdown in the three-dimensional water structure, and 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, whereas water is both an electron donor and an electron acceptor. Methyl alcohol 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. Therefore the ion–solvent interaction order is MeOH + water > dioxane + water > glycol + water.

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