

VISCOSITY OF CdSO₄ AND MgSO₄ IN MIXED SOLVENTS

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The viscosities of CdSO₄ and MgSO₄ have been determined in glycerol, glycol and isopropanol + water mixtures at 10, 20 and 30% by weight at different temperatures. The B coefficients have been determined by two methods. Activation parameters have also been calculated and ion-solvent interaction has been inferred.

INTRODUCTION

The viscosity of CdSO₄ and MgSO₄ at wt % of glycerol, glycol and isopropanol, at 10, 20 and 30% have been measured at concentration $C < 0.1 \text{ mol dm}^{-3}$ at $30 \text{ to } 45 \pm 0.01^\circ$. This study was undertaken in order to find out whether the given mixed solvent will resist the centro-symmetric ordering of the ion more or less than that of water, since the latter has been classified as structure breakers of makers [1].

EXPERIMENTAL

All the salts used were of E. Merck, 'extra pure' grade. The preparation of the solvents and solutions and viscometric and pycnometric techniques were the same as Das [2]. The buoyancy correction has been considered for the calculation of densities [3]. All precautions were taken to check evaporation of the solvent [4]. Time of flow of each concentration did not exceed 0.20 in 15 min. Density readings were precise up to $0.000.2 \text{ g cm}^{-3}$. The concentration range was $0.1 - 0.001 \text{ mol dm}^{-3}$.

RESULTS AND DISCUSSION

Viscosity has been analysed in terms of the Jones-Dole equation,

$$\eta_r = 1 + A \sqrt{\alpha C} + BC \quad \dots(1)$$

since the plot of $\eta_r = 1/\sqrt{c}$ Vrs \sqrt{C} is almost linear. From conductance results, it is found that the dissociation of the salts are incomplete and so the modified Davies-Malpauss equation proposed by Das [6] is more suitable as it was specifically formulated to account for the effect of ion-association. Hence, the equation could be written as

$$\eta_r = 1 + A\sqrt{\alpha C} + B_1 \alpha C + (1 - \alpha) B_1 PC$$

or, $\frac{\eta_r - 1 - \sqrt{\alpha C}}{C}$ vs α was found to be linear and the intercept at $\alpha = 1$ gave the value of B_1 , since there will be no ion-pair formation. The α values have been obtained from the

conductance data [7]. The B values calculated by both the methods are given in Table 1 and the B values obtained by the modified equation is slightly less which is quite obvious.

Table - 1

St. % Temp. (°C)	Glycerol			Glycol			Isopropanol		
	10%	20%	30%	10%	20%	30%	10%	20%	30%
Values of B (dm³ mol⁻¹) (J - D equation)									
CdSO₄									
30	0.847	0.898	0.954	0.798	0.793	0.833	0.660	0.696	0.724
35	0.864	0.909	0.969	0.780	0.804	0.853	0.675	0.708	0.784
40	0.880	0.983	0.989	0.755	0.829	0.874	0.683	0.719	0.753
45	0.905	0.948	0.999	0.785	0.849	0.898	0.693	0.738	0.774
MgSO₄									
30	0.757	0.782	0.829	0.709	0.728	0.764	0.647	0.680	0.734
35	0.742	0.774	0.810	0.684	0.717	0.749	0.697	0.667	0.724
40	0.734	0.760	0.797	0.672	0.704	0.749	0.629	0.655	0.698
45	0.720	0.748	0.785	0.664	0.693	0.728	0.625	0.635	0.685
Values of B (dm³ mol⁻¹) (Das's equation)									
CdSO₄									
30	0.833	0.845	0.908	0.698	0.725	0.765	0.613	0.645	0.695
35	0.836	0.849	0.916	0.707	0.733	0.773	0.617	0.650	0.699
40	0.841	0.855	0.827	0.715	0.740	0.778	0.628	0.665	0.707
45	0.849	0.864	0.936	0.723	0.740	0.787	0.640	0.668	0.715
MgSO₄									
30	0.708	0.734	0.784	0.665	0.696	0.715	0.609	0.624	0.689
35	0.703	0.730	0.770	0.664	0.690	0.708	0.594	0.623	0.674
40	0.697	0.727	0.771	0.653	0.682	0.704	0.587	0.619	0.669
45	0.680	0.729	0.765	0.643	0.628	0.709	0.589	0.615	0.689

Dependence of B on temperature : The B coefficient of CdSO₄ increases with the increase in temperature whereas it decreases in case of MgSO₄. This indicates that the viscosity decrease due to distortion of solvent [8], η^D is small and $\eta^E + \eta^A > \eta^D$, where η^E is the viscosity increase due to the shape and size of an ion and η^A , due to the alignment or orientation of the polar molecules by the ionic field and hence B increases in case of CdSO₄. In case of M₂SO₄, η^D is fairly large and hence B decreases with the decrease of temperature.

In general B coefficient of MgSO₄ is less than that of CdSO₄ and when comparison is made amongst the non-aqueous+water mixture, which is of the order : glycerol + water > glycol + water > isopropanol + water, and the ion-solvent interaction is of the reverse order since distortion is more.

Dependence of B on organic solvent : The increase in B coefficient with increase in organic contents in the mixture (Table 1) may be attributed due to the large size of the solvent

molecules and also to be due to strong association between water and organic solvent through hydrogen bonding and for solvated ions, which would lead to a large value of η^E and η^A . Consequently, the B coefficients become larger and larger with the increase in organic solvent of the medium.

Activation parameters :

Eyring [9] applied the theory of absolute reaction rate' to interpret the viscosity of liquids by calculating the energy, free energy and energy of activation. Nightingale and Benck [10] and Feakins [11] have shown that the theory of reaction rate can be successfully applied to electrolyte solutions. Proceeding in the similar lines ΔE (which does not differ very much ΔH), ΔG , and ΔS for the solvents and salts at different weight percent have been calculated (results not given). It is observed that the ΔE , ΔG , and ΔS values for viscous flows of the salts are less than that of the solvent, indicating a structure breaking effect and is of the order $Mg^{11} > Cd^{11}$.

Glycerol has got three OH groups, glycol got two OH groups and isopropanol only one OH group, whereas water is both an electron donor and acceptor. Isopropanol accepts a proton and hence the three-dimensional water structure is easily broken. Glycol and glycerol though contain more number of OH groups are not able to break the hydrogen bond of water so easily as they are linked with each other. So the ion-solvent interaction found to be is of the order : isopropanol + water > glycol + water > glycerol + water.

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