PHYSICOCHEMICAL STUDIES OF Ca(NO₃)₂ IN GLYCOL+WATER AND GLYCEROL+WATER MIXTURES FROM VISCOSITY MEASUREMENT AT 30⁰, 35⁰ AND 40⁰C

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"The ion solvent interaction of the electrolyte Ca(NO₃)₂ in glycerol+water and glycerol+water at temperatures 30°, 35° and 30°C has been studied. The results indicate strong alignment of solvent molecule with the ions which promotes the structure of solvent molecule. These are studied from viscosity measurements".

INTRODUCTION

The ion solvent interaction of $Ca(NO_3)_2$ in glycol+water and glycol+water mixtures at 10, 20 and 30% (w/w) within the temperature range of 30-40^{0}C have been inferred from viscosity measurements. The order is Glycol+water > Glycerol+water.

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

$$(H_2O)_c \;\; = \;\; (H_2O)_d$$
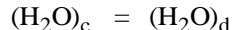
Electrolytes which dissolve in water have been classified as structure makers or structure breakers, depending on whether the above equilibrium is shifted to left or right. Frank and Wen gave a picture in which an ion is surrounded by concentric region of water molecules polarized, immobilized and electrostricted by the ion, analogous to a kind of freezing. They called this as region-A. The water molecules in the region-C has the normal three dimensional network as stated above. The centro symmetric structures imposed by the ion in the region – A is incompatiable with the normal structure in the region – C and there is a tendency to resist such order and balance between the two competing forces gives rise to a region-B. Ions with low charge density has a smaller width of region-A and larger width of region-B are net structure breakers. On the other hand, ions with a high charge density show in opposite behaviour and are net structure makers.

The organic solvents like glycol and glycerol are miscible with water at all solvent compositions and their dielectric constant and dipole moments are very different. Glycol and glycerol are aprotic solvents, whereas, water is both an electron donor and an acceptor. Hence studies of their aqueous mixtures became an interesting field to explore, particularly of the ionic processes accompanying the solutions of strong electrolytes. It becomes relevant to acquire whether a given mixed solvent will resist the centro-symmetric ordering of the ion more or less than pure water.

From this point of view, the viscosity of $Ca(NO_3)_2$ in glycol and glycerol 10%, 20% and 30% have been measured at $C \leq 0.1$ mol.L^{-1} at 30°, 35° and 40°C.

$\mathcal{E}$XPERIMENTAL

$\boxed{T}$he change in viscosity with concentrations for aqueous solution and nonaqueous solution of electrolyte is represented satisfactorily by Jone-Dole equation.

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

where η_r is the relative viscosity and A & B are constants. The constant A is long range inter ionic attraction coefficient and can be calculated theoretically by Falkenhagen and Vernon's expression. B is a measure of solute-solvent interaction and C is the concentration of solution in mol.L^{-1}. The procedure to see the validity of the above equation is to first see that a straight line is obtained by plotting $(\eta_r-1)/\sqrt{C}$ Vs. $\sqrt{C}$. The above plots are found to be linear. The intercept and the slope of the above plot gave respectively the value of A and B. In the present investigation the viscosity of $Ca(NO_3)_2$ in 10%, 20% and 30% (v/v) of glycol+water and glycerol+water mixtures are taken at 30°, 35° and 40°C.

Table – 1 : η_r at 30°C of $Ca(NO_3)_2$

Concentration	Glycol+water			Glycerol+water		
	10%	20%	30%	10%	20%	30%
0.1000	1.0462	1.0501	1.0553	1.0594	1.0639	1.0719
0.0750	1.0356	1.0386	1.0424	1.0459	1.0494	1.0555
0.0500	1.0247	1.0269	0.0296	1.0322	1.0345	1.0387
0.0250	0.0135	1.0147	0.0162	1.0178	1.0191	1.0214
0.0100	1.0063	1.0069	1.0076	1.0085	1.0091	1.0101
0.0075	1.0051	1.0055	1.0061	1.0068	1.0073	1.0081
0.0050	1.0037	1.0040	1.0045	1.0050	1.0054	1.0059
0.0025	1.0022	1.0024	1.0027	1.0031	1.0033	1.0036
0.0010	1.0012	1.0013	1.0014	1.0017	1.0018	1.0019

Table – 2 : η_r at 35°C of $Ca(NO_3)_2$

Concentration	Glycol+water			Glycerol+water		
	10%	20%	30%	10%	20%	30%
0.1000	1.0450	1.0487	1.0520	1.0575	1.0616	1.0699
0.0750	1.0346	1.0375	1.0401	1.0445	1.0475	1.0539
0.0500	1.0241	1.0261	1.0279	1.0311	1.0332	1.0376
0.0250	1.0131	1.0142	1.0153	1.0172	1.0183	1.0207
0.0100	1.0061	1.0067	1.0072	1.0082	1.0087	1.0098
0.0075	1.0049	1.0053	1.0057	1.0066	1.0069	1.0078
0.0050	1.0036	1.0039	1.0042	1.0048	1.0051	1.0057
0.0025	1.0021	1.0023	1.0025	1.0029	1.0031	1.0035
0.0010	1.0011	1.0012	1.0013	1.0016	1.0017	1.0019

Table – 3 : η_r at 40°C of Ca(NO$_3$)$_2$

Concentration	Glycol+water			Glycerol+water		
	10%	20%	30%	10%	20%	30%
0.1000	1.0433	1.0467	1.0498	1.0560	1.0605	1.0684
0.0750	1.0332	1.0359	1.0384	1.0433	1.0466	1.0527
0.0500	1.0230	1.0249	1.0267	1.0303	1.0325	1.0367
0.0250	1.0125	1.0135	1.0146	1.0167	1.0179	1.0202
0.0100	1.0058	1.0063	1.0069	1.0079	1.0085	1.0095
0.0075	1.0046	1.0050	1.0055	1.0064	1.0068	1.0076
0.0050	1.0033	1.0036	1.0040	1.0047	1.0050	1.0055
0.0025	1.0020	1.0022	1.0024	1.0028	1.0030	1.0033
0.0010	1.0010	1.0011	1.0013	1.0015	1.0016	1.0017

Table – 4 : $A \times 10^2$ ($l^{1/2}.mol^{-1/2}$)

Electrolyte	Temp. °C	Glycol+water			Glycerol+water		
		10%	20%	30%	10%	20%	30%
Ca(NO$_3$)$_2$	30°C	3.74	3.79	3.84	3.42	3.54	3.68
	35°C	3.69	3.75	3.80	3.38	3.50	3.61
	40°C	3.64	3.71	3.78	3.34	3.46	3.56

Table – 5 : B (L.mol^{-1})

Electrolyte	Temp. °C	Glycol+water			Glycerol+water		
		10%	20%	30%	10%	20%	30%
Ca(NO$_3$)$_2$	30°C	0.775	0.849	0.893	0.719	0.738	0.774
	35°C	0.759	0.824	0.872	0.694	0.727	0.759
	40°C	0.748	0.812	0.853	0.682	0.714	0.750

DISCUSSION

The different 'A' values (Table-4) indicate the different ionic interactions on the nature of the electrolyte. It is also seen that the 'A' values also increase with the increase in organic solvent of the solutions. This may be attributed due to the change in the mobility of the ions with a change in the dielectric constant of the medium. Positive 'A' values suggest ion-ion interaction, possibility due to cation-cation and cation-anion penetration. It may also be noted that 'A' decreases with rise in temp for the salt in all the solvents, which one would expect in view of the thermal agitation at higher temperature and reduction of attractive forces.

The positive 'B' values indicate strong alignment of the solvent molecules with the ions which undoubtedly promote the structure of the solvent molecules in its immediate vicinity.

The interaction due to non-aqueous solvents and water is such that the basic geometric structure of both the components will be distorted and then the individual Glycol, Glycerol and water molecules will be loosely associated through hydrogen bonding. This loose association of the molecules would give rise to an apparent slight positive deviation in ΔE and ΔS values as observed. It is of the order Glycol+water > Glycerol+water. The addition of a small amount of organic solvents to water may give rise to two effects. If the Glycol and Glycerol are accommodated ion the solvent structure, it may strengthen the water structure because organic solvent molecule is a proton acceptor. If it can not be accommodated because of its bulky size then it may cause a breakdown in three dimensional water structure. Several authors have observed that Glycol or Glycerol is less ordered than pure water. It is observed that ΔE and ΔG increase with increase in organic solvent content and hence the three dimensional water structure is broken down though the quanta is less than that of solvent+water mixture. Again between Glycol and Glycerol the extent of hydrogen bonding is more in Glycerol. So far as the solvents are concerned the ion solvent interaction is found to be of the order Glycerol+water > Glycol+water.

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