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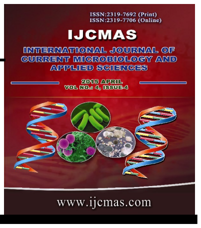

Original Research Article

Viscosity studies of Ni $(NO_3)_2.6H_2O$ in Propan-2-ol + Water at 303.15 K

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ABSTRACT

Keywords

Viscosity,
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Ion-solvent interaction

The present work deals with the measurement of viscosity of Ni(NO3).6H2O at 10%, 20% and 30% (w/w) in Propan -2-ol + Water mixture at 30º, 35º and 40ºC. The ions appear to interact and the ion-solvent interaction or structure-breaking effect of the anions changes with the change in Propan-2-ol content.

Introduction

Liquid water retains the tetrahedral bonding and the resulting network structure characteristic of the crystalline structure of ice i.e. quasi-crystalline structure at ordinary temperature (Bernal et al, 1933, Popple, 1951, Frank & Wen, Pauling, 1969, Nemetty et al, 1962). A dynamic equilibrium seems to exist between the three dimensional hydrogen bonded clusters and the denser monomers (Nemetty et al, 1962).

$[H_2O]_c \rightarrow [H_2O]_d$

Electrolytes when dissolved in water have been classified as the structure makers or structure breakers depending on whether the above equilibrium is shifted to left or right. In the light of Frank and Wen model, the width of inner most region (Region A) is smaller for ions with low charge density and next region (Region B) is larger, such ions are structure breakers. The behavior of ions with high charge density is opposite and these ions are net structure makers.

Propan-2-ol and water though miscible with each other at all proportions differ in their dielectrics, dipole moment values and electron accepting tendencies. Propan-2-ol is an electron acceptor but water is both an electron acceptor and donor. These properties generate interest for studies of ionic processes in aqueous mixtures of Propan-2-ol.

A key concept in classical electro-kinetic theories is that the viscosity of interfacial fluids is much higher than that of bulk fluids (Peng et al, 2011). Ion-ion interaction is found in low molecular mass organo-gelators which can assemble in organic solvent to form three dimensional fibrillar networks (Gangopadhyay et al, 2011). Ion-solvent interaction exists resulting in attractive forces which promote the structure making tendency (Smrutiprava et al, 2012).

In the present communication, viscosity of $Ni(NO_3)_2$ solutions at 10%, 20% and 30% (w/w) in Propan -2-ol +

Water mixture at 30º, 35º and 40ºC have been studied and an attempt has been made to enquire about net structure breaking or net structure making effect in Propan-2-ol + Water mixtures.

Materials and Methods

Nickel nitrate [$Ni(NO_3).6H_2O$] used is of 'Extra pure' variety. The solvents used were purified by appropriate method. Propan -2-ol (E-Merck) and water were triple distilled. The preparation of the solvents, solutions and the measurement techniques were the same as that of Das et al, 1977, the concentration ranges were from 0.1 to 0.001 mol L^{-1}. The accuracy of the period of flow is ± 0.2 second in 20 minutes and the density data are accurate upto 0.0002 g in 60 ml.

Results and Discussion

The viscosity data are analyzed in terms of Jones-Dole equation as the plot of $\eta_r - 1 / \sqrt{C}$ versus $\sqrt{C}$ is linear. The intercept of the slope gave the value of A i.e. a measure of ion-ion interaction and B i.e. a manifestation of ion-solvent interaction and are tabulated in Table 1 and Table 2 respectively.

A-values

These are the measure of ion-ion interactions, which are positive for all electrolytes studied and increase with decrease in dielectric constant, when the concentration of Propan-2-ol increases (Table-1). These values decreases with increase in temperature for all the salts, which one should expect in view of more thermal agitation at higher temperatures and reduction of attractive forces.

Dependence of B on temperature

According to Stokes and Mills, the viscosity of a dilute electrolytic solution incorporates that of the solvent in addition to the contribution from other sources. They are η^E, the positive increase due to shape and size of the ion; η^A, the increase due to alignment or orientation of the polar molecules by ionic field and η^D, the decrease in viscosity arising due to the distortion of the solvent structure by the ions. Therefore, B coefficient can be discussed in terms of these viscosity effects at different temperatures.

The B coefficient of salts increases with increase in temperature. This indicates that the viscosity decreases due to solvent structure, i.e. η^D is small and hence, $\eta^E + \eta^A > \eta^D$ and B is positive (Table 2). The lesser the value of B, lesser is the distortion and hence the ion-solvent interaction. So, the ion-solvent interaction is of the order :

$$Br^- < NO_3^- < F^- < Cl^- < I^- < SO_4^{--} .$$

Also, according to Stokes and Mills, the lesser the value of dB / dt , greater is the ion-solvent interaction. In the present case , the plot of B vs t is linear and
dB / dt is of the order:

$$Br^- < NO_3^- < F^- < Cl^- < I^- < SO_4^{--} .$$

This indicates that the order of the ion solvent interaction is:

$Br^{-} < NO_3^{-} < F^{-} < Cl^{-} < I^{-} < SO_4^{--}$ and confirms the above interpretations.

Dependance of B on Propan-2-ol content

The increase in B coefficient with increase in Propan-2-ol content in the solvent mixture (Table 2) may be attributed due to the large size of the solvent molecules and also to the strong association between water and propan-2-ol through hydrogen bonding (Assarsons et al, 1968) and for solvated ions it would lead to larger values of η^{E} and η^{A}. Consequently, the B coefficient becomes

Larger with increase in Propan-2-ol content in the molecules.

Propan-2-ol is more basic and less acidic than water. A water molecule is hydrogen bonded with OH of

Propan-2-ol molecule. A cation will react more strongly with oxygen atom of Propan-2-ol + Water mixture and anion will interact less strongly with hydrogen atoms. This type of ion-solvent interaction is in the primary sheath.

Addition of even small amount of Propan-2-ol to water may give rise to one of these two effects.

If Propan-2-ol is accommodated in the solvent structure, it may strengthen the water structure. If it cannot be accommodated, then it may cause a break down in the three dimensional water structure. It is seen from the viscosity data that B coefficient are positive in Propan-2-ol + Water mixtures. The values also increase with increase in Propan-2-ol content, but the difference in B do not remain the same, which shows that the salvation sphere of the ion differs. This indicates that Propan-2-ol is not accommodated in the solvent structure. Hence, it breaks down the three dimensional water structures and the additivity law does not hold good.

Table.1 A × 10^{2} ($L^{½}$ $mol^{-½}$)

Solvent	**Temperature in ºC**	**$Ni(NO_3)_2.6H_2O$**		
		10%	**20%**	**30%**
Propan-2-ol + water	**30**	3.03	3.07	3.16
	35	2.99	3.02	3.09
	40	2.94	2.98	3.02
Dioxane + water	**30**	3.14	3.19	3.27
	35	3.08	3.14	3.21
	40	3.02	3.10	3.15
Glycol + water	**30**	3.19	3.27	3.34
	35	3.15	3.23	3.29
	40	3.09	3.16	3.24

Table.2 B (L mol^{-1})

Solvent	**Temperature in ºC**	**$Ni(NO_3)_2.6H_2O$**		
		10%	**20%**	**30%**
Propan-2-ol + water	**30**	0.492	0.589	0.679
	35	0.483	0.576	0.658
	40	0.475	0.568	0.635
Dioxane + water	**30**	0.593	0.635	0.779
	35	0.585	0.614	0.756
	40	0.568	0.603	0.739
Glycol + water	**30**	0.623	0.698	0.893
	35	0.607	0.673	0.879
	40	0.589	0.654	0.868

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