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THERMODYNAMIC STUDY OF STRONG ELECTROLYTE IN MIXED SOLVENT SYSTEM FROM CONDUCTANCE AND VISCOSITY METHODS

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The viscosity and ionic conductivity of nickel chloride in 50% (v/v) methanol water mixture at different temperatures have been studied. The conductivity data have been analysed by various equations to evaluate molar conductivity at infinite dilution λ^o_m, Walden constant, equilibrium constant and dissociation constant at different temperatures. The viscosity data have been found to fit in the Jones-Dole equation and the additive character 'B' has been found to depend on the composition of solvent and temperature. Activation parameters have also been evaluated.

Key words: Viscosity, conductivity, Jones-Dole coefficients, Walden constant, Equilibrium constant.

Introduction

The study of variation of conductivity with concentrations and viscosity provides statisfactory information about the behaviour of solutions. Different equations for conductivities and viscosities of 1:1 and 2:1 electrolytes in solutions have been deduced and subjected to test using the data available in the literature (Ibuki and Nakahara 1991, Jenkins *et al.* 1993, Donald and jenkins 1995, Fahimuddin *et al* 1995 a &b, Khan *et al* 1996, Dhanaragu *et al* 1997, Kapadi *et al* 1997).

The present investigation has been undertaken with a view to test the applicability of conductivity and viscosity data for the evaluation of different parameters. Molar conductivities at infinite dilution λ^o_m have been determined by the Ostwald dilution law (Bhat and Bindu 1994).

$$\lambda_m = \lambda^o_m - [A + B\lambda^o_m]\sqrt{C} \quad \text{.......} \quad (1)$$

where λ_m is the polar conductivity, λ^o_m is the molar conductivity at infinite dilution,

$$A = \frac{82.4}{(DT)^{1/2}\eta} \quad \text{.......} \quad (2)$$

$$B = \frac{8.20\text{x}10^5}{(DT)^{3/2}} \quad \text{.......} \quad (3)$$

where D is the dielectric constant, η is vicosity and T is the absolute temperature. C represents molar concentration of solution. Walden product relates molar conductivity at infinite dilution to the vicosity of that solvent as:

$$\lambda^o_m \eta_0 = \text{Constant}/r \quad \text{.......} \quad (4)$$

where r is the radius of the ion and η_0 is the viscosity of the solvent in poise.

Walden product of the ion is inversely proportional to the effective radius of the ion in a given solvent (Bockris and Reddy 1970). Viscosity is one of the most appreciated technique to study various types of interaction occurring in solutions. The viscosity data are computed using the Jones-Dole equation (Jones and Dole 1929):

$$\eta_{sp}/\sqrt{C} = A + B\sqrt{C} \quad \text{.......} \quad (5)$$

where n_{sp} is the specific viscosity and 'A' and 'B' are coefficients which represent ion-ion and ion-solvent interactions respectively.

Experimental

$NiC1_2$ (E.Merck), methanol (CH_3OH) (BDH) of analar grade extra pure was used without further purification. Double distilled water of 0.06 μ S cm^{-1} was used for preparation of different percentages (v/v) of mixed solvent system.

Conductivities were measured by digital direct reading conductivity meter model 103, range 0-20.00 Kμ S/cm manufactured by jenco Electronic Ltd. A dip type conductivity cell with platinised electrode was calibrated having cell constant 0.999 cm^{-1}.

Viscosities were measured by Ostwald viscometer type, Techniconominal constant 0.01 Cs/s, capillary ASTMAD 445 USA, having glass jacketted water tube with constant circulation of water. Densities were determined by specific gravity bottle with capacity of 10 ml by volume. Temperature was kept constant throughout the experiment by a thermostatic water

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bath type Haak-13, manufactured by Haak, Karlshuhe, Germany.

Results and Discussion

To study the behaviour and nature of electrolytes in mixed solvent system, the nature of solvent must be taken under consideration. The physical properties such as dielectric constant, dipole moment, attraction forces, ionic interactions of mixed solvents are quite differnet from that of water. The organic solvents are more or less aprotic, this and other properties make a study of their aqueous mixtures an interesting thing to explore, particularly of the ionic processes accompanying the solution of strong electrolyte (Das and Hazra 1995).

In the present communication, the conductivities and viscosities of nickel chloride in aqueous methanol mixtures were studied. The specific conductance after correction for solvent conductance at each concentration is used for determining molar conductivity λ_m at different temperatures. The molar conductivity values of nickel chloride in (50%, v/v) aqueous methanol mixtures at different temperatures are tabulated in Table 1. Results show that molar conductivity values λ_m increase with decrease in concentration of salt at all temperatures and at a fixed concentration, and increase with rise of temperature. Molar conductivity at infinite dilution λ^o_m were computed by Debye-Huckel-Onsager limiting law (Fahimuddin *et al* 1995b). These results are shown in Table-2, and representative plot of λ_m vs $\sqrt{c}$ at 50°C is shown in Fig 1. The plot of λ_m vs $\sqrt{c}$ is linear and intercept gave the molar conductivity at infinite dilution. The increase in values of λ^o_m with increase in temperature indicates increase in ionic mobility or decrease in viscosity. λ^o_m values have been regarded as a measure of solute-solvent interaction (Robinson and Stoked 1959). Greater the magnitude of λ^o_m, greater would be the solute-solvent interaction.

Table 1

Molar conductivity of $NiCl_2$ in 50% (v/v) aqueous methanol solution at different temperatures

10^2 (Salt) (mol.dm^{-3})	Molar conductivity(S.cm^2.mol.$^{-1}$)at temperature°C				
	30°	35°	40°	45°	50°
1.0	160.0	163.0	185.0	204.0	225.0
2.0	169.5	179.5	183.0	191.5	201.5
3.0	122.0	127.0	141.6	142.3	153.0
4.0	114.5	121.2	128.5	136.0	143.2
5.0	112.4	114.0	122.4	124.2	136.0
6.0	111.8	115.1	120.8	125.6	128.0
7.0	106.4	110.7	116.1	121.5	124.5
8.0	121.2	125.8	128.3	134.3	129.0
9.0	112.1	115.8	118.8	121.4	122.5

Table 2

Values of Molar conductivity at infinite dilution (λ^o_m) equilibrium constant (K_c), dissociation constant (K_d) and Walden constant of $NiCl_2$ in aqueous methanoal solution at different temperatures

Temperature (°C)	λ^o_m	K_c	K_d	Walden constantx10^2
30	184.1	0.15	0.05	4.86
35	191.3	0.15	0.04	4.32
40	214.5	0.09	0.04	4.23
45	231.9	0.08	0.03	3.98
50	260.5	0.04	0.04	3.88

The equilibrium constant K_c of the nickel chloride in aqueous-methanol mixture is determined by the following equation (Glasstone 1965, and Samanta *et al.*1996):

$$\frac{1}{\lambda_m} = \frac{1}{\lambda^o_m} + \frac{1}{\lambda^{o2}_m . Kc} . C . \lambda_m \text{ .... } (6)$$

An electrolyte which forms ion-pair in equilibrium with ions shows a linear relationship for the plot of $1/\lambda_m$, against $C.\lambda_m$. A

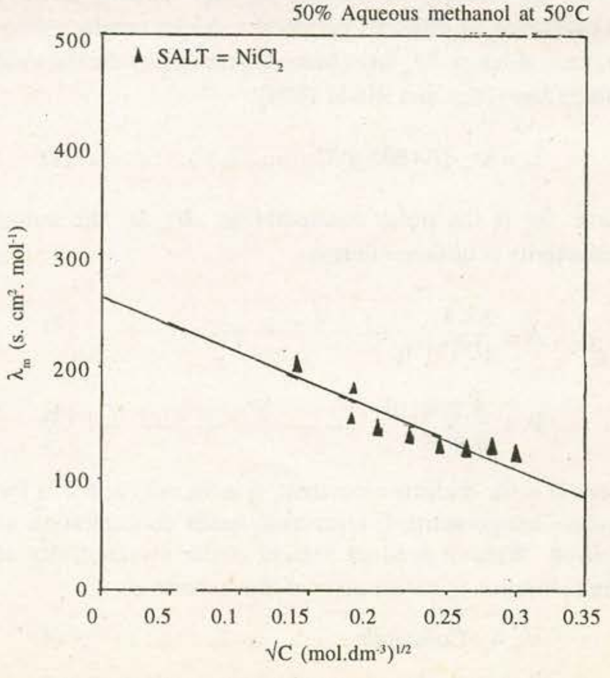

Fig 1. Plot of λ_m versus ($\sqrt{C}$) for nickel chloride in 50% aqueous methanol at 50°C.

representative straight line plot of $1/\lambda_m$, vs $C.\lambda_m$, at 45°C is shown in Fig 2 and equilibrium constant (K_c) values were calculated from the slope of the plot.

Degree of dissociation was calculated by the relationship:

$$\alpha = \lambda_m / \lambda^o_m \qquad (7)$$

Results tabulated in Table 3 show that the degree of dissociation α decreases both with increase in concentration and also with rise of temperature. The values of dissociation contant (K_d) of nickel chloride in 50% aqueous methanol solvent at different temperatures were calculated by:

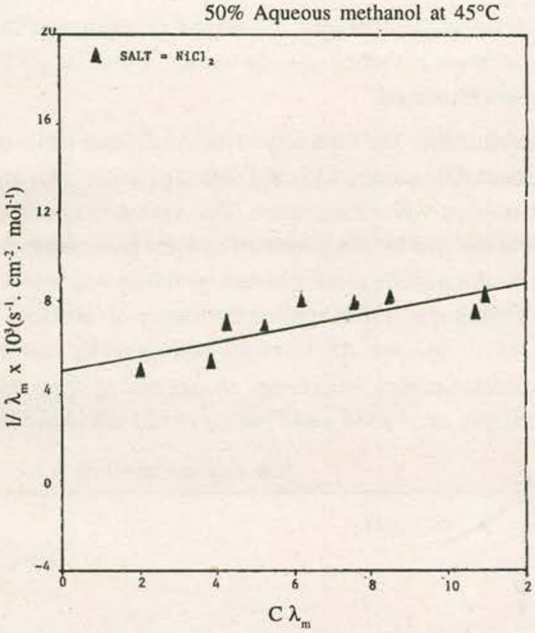

Fig 2. Plot of $1/\lambda_m$ versus $c\lambda_m$ for nickel chloride in 50% aqueous methanol at 45°C.

Table 3

Degree of dissociation of NiC1$_2$ in 50% aqueous methanol at different temperatures

10^2 (Salt) (mol.dm^{-3})	Degreeof dissociation (a)at temperatures °C				
	30°	35°	40°	45°	50°
1.0	0.87	0.85	0.86	0.88	0.86
2.0	0.92	0.94	0.85	0.82	0.77
3.0	0.66	0.66	0.66	0.61	0.58
4.0	0.62	0.63	0.60	0.59	0.55
5.0	0.61	0.59	0.57	0.54	0.52
6.0	0.61	0.60	0.56	0.54	0.49
7.0	0.58	0.58	0.54	0.52	0.48
8.0	0.66	0.66	0.60	0.58	0.50
9.0	0.61	0.61	0.55	0.52	0.47

$$K_d = [\alpha^2/1-\alpha]\,C \qquad (8)$$

The results for K_c and K_d tabulated in Table 2, show a slight decrease in value with rise of temperature. The decrease in dissociation constant show that the nickel chloride causes a reduction in the thickness of ionic atmosphere surrounding the polar species and reduces repulsion between them thus resulting in an increase in aggregation number and formation of micelles. In mixed solvent system decrease in hydration of ions also lead to decrease in value of dissociation constant. Walden constant, as a function of temperature, show a direct relationship with temperature. Results tabulated in Table 2, show that the ions solvated at different temperatures, attach themselves by physical or chemical forces or both to a number of molecules of solvent. Therefore, the size of solvating molecule varies with nature of solvent and the effective radius will not be constant. Reppresentative plot of λ°_m, vs$1/\eta$ is shown in Fig 3.

The values of viscosities of the nickel chloride in 50% aqueous methanol solutions are summarized in Table 4 and interactions of ions and solutions ar computed by means of Jones-Dole equation.

$$\eta/\eta_o = 1 + A\sqrt{C} + BC \qquad (9)$$

where η/η_o is the relative viscosity i.e. viscosity of salt solu-

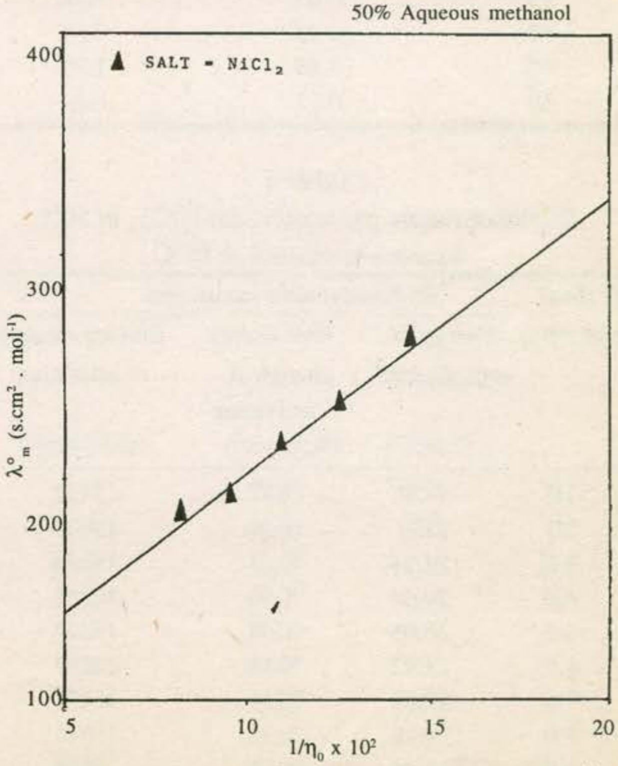

Fig 3. Plot of λ°_m versus $1/\eta^{\circ}$ for nickel chloride in 50% aqueous methanol.

Table 4

Viscosities of $NiCl_2$ in 50% (v/v) aqueous methanol at different temperatures

10^2 (Salt)	Viscosities (millipoise)				
($mol.dm^{-3}$)	30°C	35°C	40°C	45°C	50°C
1.0	12.36	10.57	9.30	8.04	7.02
2.0	12.52	10.69	9.45	8.14	7.23
3.0	12.63	10.89	9.56	8.24	7.48
4.0	12.75	10.95	9.60	8.29	7.77
5.0	12.80	11.06	9.72	8.38	7.86
6.0	12.86	11.12	9.78	8.48	7.91
7.0	12.93	11.27	9.84	8.65	8.00
8.00	13.05	11.39	9.90	8.75	7.48
9.0	12.83	11.49	10.18	8.93	8.22

Table 5

Values of Jones-Dole coefficient 'A' and 'B' for $NiCl_2$ at different temperatures in 50% aqueous methanol

Temperature	The values of Jones-Dole parameters Aand B	
(°C)	A ($dm^3.mol^{-1}$)$^{1/2}$	B ($dm^3.mol^{-1}$)
30	0.13	0.33
35	0.03	1.02
40	0.15	0.64
45	-0.03	1.36
50	0.17	1.48

Table 6

Thermodynamic parameters for $NiCl_2$ in 50% aqueous-methanol at 35°C

10^2 [Salt]	Thermodynamic parameters		
($mol.dm^{-3}$)	Energy of activation(E^*_η) ($J.mol^{-1}$)	Free energy change of activation ($K.J.mol^{-1}$)	Entropy change of activation ($J.k^{-1}.mol^{-1}$)
1.0	22.46	69.97	-154.22
2.0	21.91	69.99	-156.11
3.0	21.24	70.04	-158.44
4.0	20.04	70.06	-162.38
5.0	20.05	70.08	-162.44
6.0	19.92	70.10	-162.92
7.0	19.62	70.14	-164.01
8.0	21.98	70.16	-156.41
9.0	18.26	70.19	-168.58

tion relative to that of aqueous-methanol solvent, C is molar concentration, A and B are constant of characteristic of electrolyte. The A-coefficient represents the contribution from interionic electrostatic forces, the B-coefficient measure the order or disorder introduced by the ions into the solvent structure. B-coefficient is specific and an additive property of the ions of strong electrolyte at a given temperature. A representative plot of $\eta_{sp}/\sqrt{C}$ vs $\sqrt{C}$ at 35°C is shown is Fig 4. The results of A and B coefficient are tabulated in Table 5. The increase in values of B-coefficient with rise of temperature led to the conclusion that nickel chloride behaves as structure breaker in 50% aqueous methanol mixture. The nickel ion strongly orders the solvent in the cosphere about the ion, with increasing temperature the solvent ordering is perturbed by the increase in thermal energy and the B-coefficient for the nickel ion increased.

The conductance and viscosity of an ion depend on its rate of movement (Glasstone 1965) and dielectric constant, variation of the solvent with temperature. The viscosity is one of the valuable method for evaluation of activity parameters for the process taking place at difinite rate with increase in temperature. (Erying *et al* 1980) applied the theory of 'absolute reaction rate' to interpret the viscosity of liquids by calculating the activation energy, free energy change and entropy change. (Nightingale *et al* 1959 and Feakins *et al* 1974) have shown

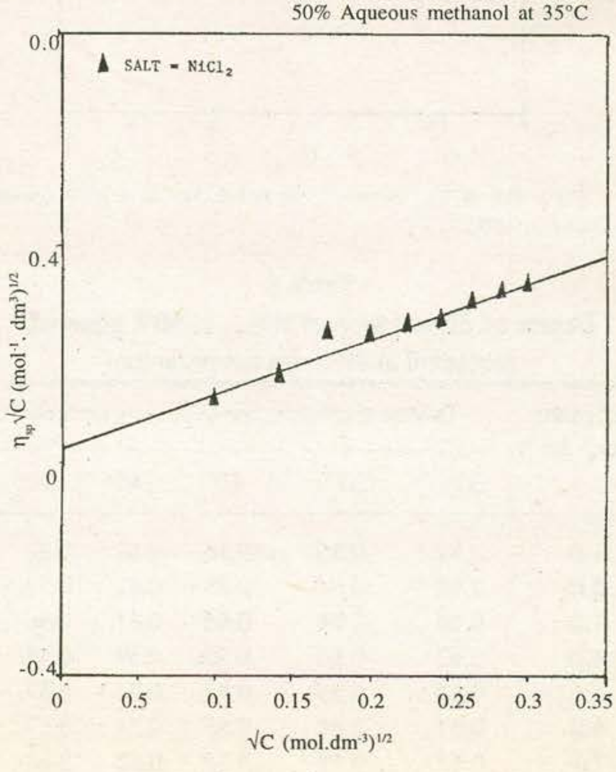

Fig 4. Plot for $\eta_{sp}/\sqrt{C}$ versus$\sqrt{C}$ for nickel chloride in 50% aqueous methanol at 35°C.

that the theory of reaction rate can be successfully applied to electrolyte solutions. Energy of activation (E^{*}_{η}) with the effect of temperature is expressed as:

$$\eta = A \, . \, e^{E\eta/RT} \quad \ldots\ldots\ldots\ldots \quad (10)$$

where A is frequency factor, R is a gas constant and T is absolute temperature. Values of energy of activation have been determined from the slope of the plot of log η vs 1/T.

Representative plot of log η vs 1/T in 50% aqueous methanol at 6.0×10^{-2} mol.dm^{-3} is shown in Fig 5.

Values of free energy change of activation ΔG*and entropy change of activation ΔS* for viscous flow are expressed as:

$$\Delta G^{*} = RT \ln \frac{\eta V}{hN} \quad \ldots\ldots\ldots\ldots \quad (11)$$

and

$$\Delta G^{*} = \frac{E^{*}\eta - \Delta G^{*}}{T} \quad \ldots\ldots\ldots\ldots \quad (12)$$

where h is planck's constant, N is Avogadro number and V is the volume of one mole of solution particles.

Values of activation parameters for nickel chloride in 50% aqueous methanol mixtures at 35°C are tabulated in Table 6. Results show that change in free energy increase with increase in concentration of salt and also with rise of temperature (Fahimuddin *et al* 1997a&b). Change in entropy of activation is increased with increase in concentration of electrolyte while a decrease was observed with the rise of temperature. This suggests that as water is both electron acceptor and donor, the hydroxyl group of methanol accepts a proton and hence the three dimensional water structure is easily broken, thus the ion-solvent interactions increase and nickel chloride behaves as structure breaker in aqueous methanol solvent.

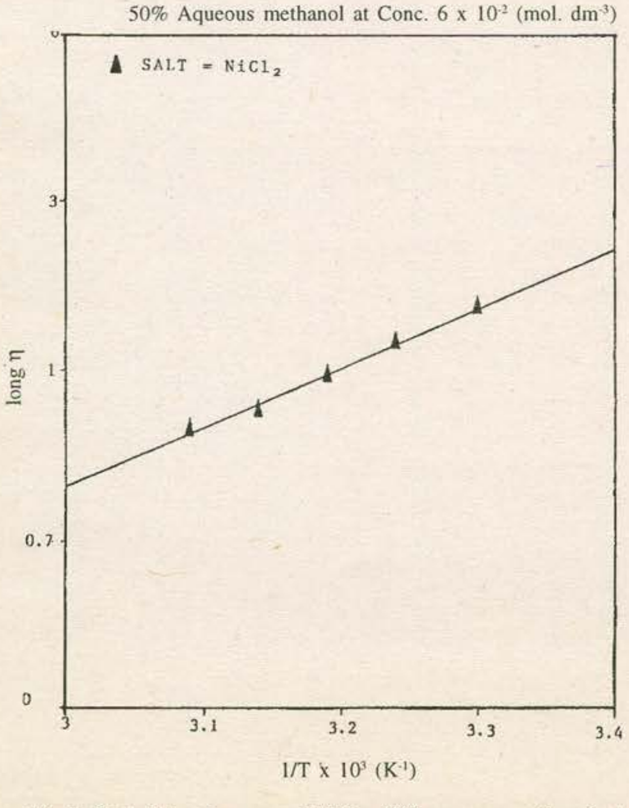

Fig 5. Plot of log η versus 1/T for 50% aqueous methanol at concentration 6.0×10^{-2} (mol.dm^{-3}).

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