



**EVALUATION OF ION ASSOCIATION AND THERMODYNAMIC
PARAMETERS OF METHYL BIS-1-AMIDINO-O-MEHTYLUREA NICKEL
(II) HALIDES IN WATER AT DIFFERENT TEMPERATURES**

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Abstract

Electrical conductivity measurements of methyl bis-1-amidino-O-mehtylurea nickel (II) bromide and methyl bis-1-amidino-O-mehtylurea nickel (II) iodide have been measured in aqueous solution at 288.15-318.15K. The limiting molar conductance (λ_0) and the association constant (K_A) have been analyzed by Shedlovsky technique for the electrolytes. For both salts, limiting equivalent conductances have been increased with raise in temperature. The K_A values decrease with rise in temperature until the $K_{A(\min)}$ is reached at a particular temperature (t_{\min}). Before t_{\min} , the K_A values for both salts decrease gradually and after t_{\min} , the K_A values increase gradually. The thermodynamic parameters viz., changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) have been evaluated to understand the change of the association constants with aqueous medium. The results have been discussed in terms of ion-ion, ion-solvent and solvent-solvent interactions.

Key words: Electrical conductivity, methyl bis-1-amidino-O-mehtylurea nickel (II) halides, Shedlovsky technique, thermodynamic parameters

Introducion

The knowledge of the state of association of electrolytes in solution and their interactions with the solvent molecules is essential for a proper understanding of their behaviour in solution. Ion pairing describes the association of oppositely charged ions in electrolyte solutions to form distinct chemical species are called ion pairs¹. Then, Bjerrum² had first introduced the concept of ion pairs into the evaluation of the enter-ionic



forces in electrolytic solutions. The tendency of ions to associate into ion pair depends on the balance between the electrostatic forces and thermal energy. Ion pair formation refers to the association of cations and anions in solution. The significance influence of dielectric constants on the ion-pairing process of an electrolyte has been revealed by many workers³⁻⁵. The theories of conductance have revealed one feature in common that the solvent is assumed as a continuum of permittivity D and viscosity. This assumption is hardly valid when discussing strong ion-solvent interaction, since the size of solvent molecules are comparable to those of solute molecules, since the size of solvent molecules are also considered as rigid uniformity charged unpolarizable sphere. Concerning ion solvent interactions this model is at best a doubtful approximation. Fous^{6,7} has developed a model which permits treatment of long and short range interionic effects.

Review

Mukhopadhyay and his co-workers⁸ had studied further addition of acetonitrile results in progressive disruption of water structure and the ions become solvated with the other component of the solvent mixture. Das⁹ had studied electrical conductivities and laser Raman spectra of solutions of lithium chloride, LiBr, LiBF₄ and LiClO₄ in tetrahydrofuran and he found that all of the electrolytes formed symmetrical triple ions in solutions along with ion pairs by using Fouss-Krauss theories. Mohondas *et al*¹⁰⁻¹⁶ had evaluated the thermodynamic parameters, Walden Products of different complexes and the comparison of transition metal complexes like Co^{III}, Ni^{II} and Cu^{II} among the halide groups in aqueous and methanol-water mixed solutions at different temperatures for ion-ion, ion-solvent and solvent-solvent interactions.

Method

Electrical conductivity measurements of methyl bis-1-amidino-O-mehtylurea nickel (II) bromide and bis-1-amidino-O-mehtylurea nickel



(II) iodide were prepared by following the reported procedure¹⁷. The purity of the sample was determined by conventional chemical analysis and spectral measurements. The values were in good agreement with the literature values. Water of specific conductance of the order $< 2 \times 10^{-6}$ S cm⁻¹ was used. All the solutions were prepared by dissolving weighed samples of the electrolyte in solvent mixtures. All the viscosity, dielectric constant and density values were interpolated from literature values¹⁸. The electric conductivities were measured by Orion Star A112 Conductivity Benchtop meter with Epoxy 2 cell (K=1.0) digital conductivity bridges with a dip type immersion conductivity cell were used.. The observed conductivities were connected for the conductivity solvent. The experiment was performed between 10-40 °C. The temperature was controlled in a thermostatic bath- Model D-G of HAAKE Mess-technik.

The limiting equivalent conductances (Λ_0) and ion association constants (K_A) have been computed using Shedlovsky method¹⁹. Shedlovsky method involves the linear extrapolation using equation (1):

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0^2}\right) (C\Lambda \int_{\pm}^2 S(z)) \quad (1)$$

where Λ is equivalent conductance at a concentration c (g.mol.dm⁻³), Λ_0 the limiting equivalent conductance and K_A the observed association constant. The other symbols are given by

$$S(z) = \left(\frac{z}{2} \sqrt{1 + \left(\frac{z}{2}\right)^2}\right)^2 ; \quad Z = \left[\frac{\alpha\Lambda_0 + \beta}{\Lambda_0^{s/z}}\right] (C\Lambda)^{1/2} ; \quad \alpha = \frac{17.147 \times 105W}{(DT)^{3/2}}$$

$$w = z_+ z_- \frac{2q}{1+q^{1/2}} ; \quad q = \frac{z_+ z_-}{z_+ + z_-} \times \frac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+} ; \quad \beta = \frac{151.47}{\eta(DT)^{1/2}}$$

Z and λ are the valence and conductance of the ions respectively, excluding their signs. D is the dielectric constant of the medium, η the



viscosity (c.p). The degree of dissociation (τ) is related to $S(z)$ by the equation, $\tau = \Lambda S(z)/\Lambda_0$

f_{\pm} is the activity coefficient of the free ions and was calculated using equation (2)

$$-\log f_{\pm} = \frac{Az+z-\mu^{1/2}}{1+BR\mu^{1/2}} \quad (2)$$

where, $A = \frac{1.8247 \times 10^6}{(DT)^{s/z}}$; $B = \frac{0.5029 \times 10^{10}}{(DT)^{1/2}}$; $\mu = \frac{1}{2} \sum_i (c_i v_i) z_i^2$

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no method of determining the value of R precisely [13]. In order to treat the data in our system the R value is assumed to be $R = a + d$, where a , the sum of crystallographic radii of the ions, is approximately equal to $5A^0$ and d (A^0) is given by ⁷

$$d = 1.183(M/\rho)^{1/3} \quad (3)$$

where M is the molecular weight of the solvent and ρ is the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{avg} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1}$$

X_1 is the mole fraction of methanol of molecular weight M_1 and X_2 that of water of molecular weight M_2 .

As per Shedlovsky method, an initial value of λ^0 was obtained from the intercept of the linear Onsager plot of Λ versus $c^{1/2}$, λ^0 is obtained from the literature at 25°C and at other temperatures it was obtained by using the following equation ²⁰:

$$\lambda_t^0 = \lambda_{25}^0 [1 + \alpha'(t - 25)] \quad (4)$$



α' is constant. Using these values of Λ_0 , $\lambda^{\circ-}$, $\lambda^{\circ+}$, z , $s(z)$ and r values were calculated. The mean activity coefficient f was determined by equation (2) for the above chosen complex salts. From the linear plot of $1/\Lambda S(Z)$ versus $C \Lambda f_{\pm}^2 S(Z)$; Λ_{\pm} and K_A was evaluated from the intercept $1/\Lambda_{\pm}$ and the slope K_A/Λ_0^2 respectively. The procedure was repeated using these new values of Λ_0 and K_A . All calculations were carried out by IBM-PC-AT/386.

Results and Discussions

As observed from Table 1 and Fig.1, the Λ_0 values for the electrolytes increase with rise in temperature in aqueous solutions. These are due to the fact that increased thermal energy results in bond breaking and vibration in vibrational, rotational and translational energies in the molecule that leads to higher frequency and higher mobility of ions. The values of Λ_0 for $[\text{Ni}(\text{Me-AMUH})_2]\text{Br}_2$ is always greater than those of $[\text{Ni}(\text{Me-AMUH})_2]\text{I}_2$. This shows that first salt is more prone to the above explanations than later salt.

The values of $\log K_A$ are plotted against temperature (t) in Fig. 1 which has given smooth curve with particular temperature minima (t_{\min}) generally at 30°C for both the complexes. The relative order of magnitude of $\log K_A$ for the chosen complexes depends on the temperature which can be reproduced by a quadratic equation (5)²¹.

$$\log K_A = p((t-t_{\min})^2 + \log k_{A(\min)}) \quad (5)$$

where t_{\min} , $\log k_{A(\min)}$ are constant and p corresponds to the curvature of the parabola. The following expressions for the standard entropies change and enthalpies change of ion association in salt solutions ΔS^0 and ΔH^0 can be derive from eqn. (5),

$$\Delta S^0 = 2.303 R \{ \log k_{A(\min)} + p(3t-t_{\min} + 546.3) (t-t_{\min})$$

$$\Delta H^0 = 4.605 pR(t+273.15)^2 (t-t_{\min})$$



and standard association free energies change (ΔG^0) was calculated from the following equation (6),

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

The values of the K_{AS} for these salts at different temperatures in aqueous solutions increase with rise in temperature and are summarized in Table 1. As expected the order of K_A values are $Br^- > I^-$. The K_A values in the case of $[Ni(Me-AMUH)_2]Br_2$ may be ascribed to the more coulombic type of interaction between nickel(II) complex ion and bromide ion. This is because the charge density of $[Ni(Me-AMUH)_2]Br_2$ is greater than that of charge density of $[Ni(Me-AMUH)_2]I_2$. The values of the K_{AS} for these salts decrease with rise in temperature until the $K_{A(min)}$ s are reached at 30°C, which is characteristics of the anion¹⁰⁻¹². This decrease in K_A is due to the fact that the increased thermal energy results in greater bond breaking and vibration in vibrational, rotational and translational energies in the molecules leads to dissociations. The presence of t_{min} was explained due to the weak hydration of the anion related to their structure breaking properties.

Beyond t_{min} , the K_A values for both salts increase gradually which supported by the positive values of entropy change (table 2). A positive ΔS^0 has been explained on the assumption that the 'iceberg' structure around the cation and anion are broken when association takes place leading to increase in the degree of the disorderliness. After t_{min} , the positive values of ΔH^0 indicated that ion-association processes are endothermic in nature. Between these salts, the negative values of ΔG^0 (Table 2) become more in $[Ni(Me-AMUH)_2]Br_2$ salt, indicating that the ion pair association is favoured with lowering size of the complexes anion.

Conclusion

The limiting molar conductance (Λ_0) values for both electrolytes increase with rise in temperature in aqueous solutions. The K_A values decrease with rise in temperature until the $K_{A(\min)}$ s are reached at 30°C (t_{\min}). Beyond t_{\min} , the K_A values for both salts increase gradually which is supported by the positive ΔS^0 . After t_{\min} , the positive values of ΔH^0 indicated that ion-association processes are endothermic in nature. The negative values of ΔG^0 show that both the salts are favoured in ion pair association at different temperatures in aqueous solutions. The association constants are found in order $[\text{Ni}(\text{Me-AMUH})_2]\text{Br}_2 > [\text{Ni}(\text{Me-AMUH})_2]\text{I}_2$.

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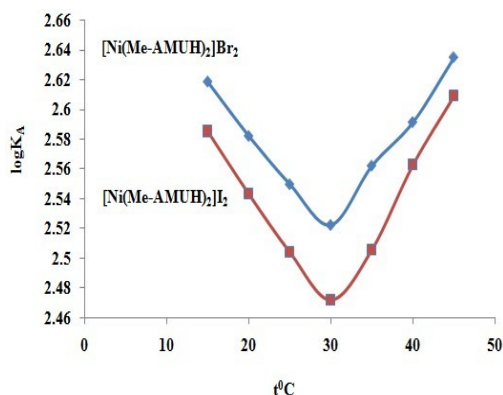


Fig.2 Temperature Dependence of $\log K_A$ for $[\text{Ni}(\text{Me-AMUH})_2]\text{Br}_2$ and $[\text{Ni}(\text{Me-AMUH})_2]\text{I}_2$

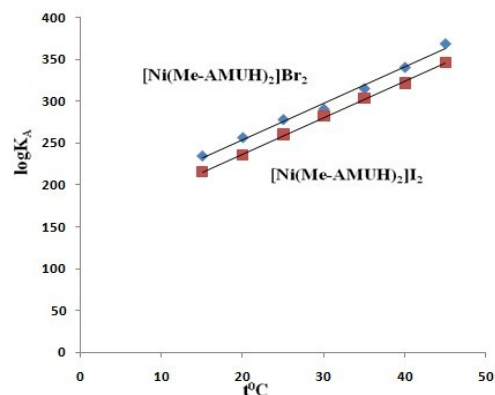


Fig.2 Temperature Dependence of $\log K_A$ for $[\text{Ni}(\text{Me-AMUH})_2]\text{Br}_2$ and $[\text{Ni}(\text{Me-AMUH})_2]\text{I}_2$



Table 1. Values of limiting molar conductances λ_0 ($S\ cm^2\ mol^{-1}$), Association constant K_A ($dm^3\ mol^{-1}$) by Shedlovsky Technique for $[Ni(Me-AMUH)_2]Br_2$ and $[Ni(Me-AMUH)_2]I_2$ in aqueous solution at different temperature.

	288.15K		293.15K		298.15K		303.15K	
	λ_0	K_A	λ_0	K_A	λ_0	K_A	λ_0	K_A
$[Ni(Me-AMUH)_2]Br_2$	234.10	415.62	256.21	381.99	277.85	354.51	290.32	332.84
$[Ni(Me-AMUH)_2]I_2$	215.52	384.75	235.53	349.26	260.01	319.19	282.31	296.51
	308.15K		313.15K		318.15K			
	λ_0	K_A	λ_0	K_A	λ_0	K_A	λ_0	K_A
$[Ni(Me-AMUH)_2]Br_2$	314.96	364.85	340.51	390.32	368.88			431.57
$[Ni(Me-AMUH)_2]I_2$	303.92	320.45	321.71	365.39	346.34			406.42

Table 3. p values of $[Ni(Me-AMUH)_2]Br_2$ and $[Ni(Me-AMUH)_2]I_2$ in aqueous solution at different temperature.

Temperature	P values	
	$[Ni(Me-AMUH)_2]Br_2$	$[Ni(Me-AMUH)_2]I_2$
288.15K	4.29×10^{-4}	5.03×10^{-4}
293.15K	5.99×10^{-4}	7.12×10^{-4}
298.15K	1.10×10^{-3}	1.28×10^{-3}
308.15K	1.60×10^{-3}	1.35×10^{-3}
313.15K	6.92×10^{-4}	9.08×10^{-4}
318.15K	5.02×10^{-4}	6.09×10^{-4}

Table 2. Thermodynamic parameters ΔG^0 ($kJ\ mol^{-1}$), ΔH^0 ($kJ\ mol^{-1}$) and ΔS^0 ($kJ\ K^{-1}\ mol^{-1}$) of $[Ni(Me-AMUH)_2]Br_2$ and $[Ni(Me-AMUH)_2]I_2$ in aqueous solution at different temperature.

		288.15K	293.15K	298.15K	308.15K	313.15K	318.15K
		$[Ni(Me-AMUH)_2]Br_2$	$10^3\Delta S^0$	-20.87	-17.81	-13.97	143.48
	ΔH^0	-20.46	-19.71	-18.72	29.08	25.98	29.18
	ΔG^0	-14.45	-14.49	-14.55	-15.13	-15.55	-16.07
$[Ni(Me-AMUH)_2]I_2$	$10^3\Delta S^0$	-33.76	-31.24	-25.13	127.65	157.98	161.27
	ΔH^0	-23.98	-23.43	-21.78	24.54	34.08	35.40
	ΔG^0	-14.25	-14.27	-14.29	-14.80	-15.39	-15.91



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