Ion-solvation behaviour of Nicotinium dichromate in water-N,N-dimethyl formamide mixtures at 293K

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ABSTRACT

Molar conductivities of dilute solutions of Nicotinium dichromate, ($c < 0.0021$ eq·dm−3) were measured in binary aqueous mixtures containing up to 100 % cosolvent (N, N- dimethyl formamide) at 293 K ± 0.1. Data were treated by the Shedlovsky equation, and its parameters, the limiting equivalent conductivity, Λ_0, and the association constants, K_A, were evaluated. Variations in Walden products and K_A were interpreted in terms of ionic properties as well as solvent structure and dielectric constant. The distances of closest approach which were determined were compared with those found using the Kraus-Bray equation. The effective ionic radii (r_i) of Nicotinium dichromate have been determined from Λ_i^o values using Gill's modification of the Stokes law. The influence of the mixed solvent composition on the solvation of ions has been discussed with the help of 'R'-factor. Thermodynamic parameters are evaluated and reported. The results of the study have been interpreted in terms of ion-solvent interactions and solvent properties.

Key words: Limiting molar conductance, Ionic Walden product, Ionic radius, Association constant.

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INTRODUCTION

The conductance behavior of many electrolytes in mixed solvent systems is reported to be influenced by number of factors like density, viscosity, dielectric constant of the medium, ion-solvent interactions and solvent-solvent interactions. Ion-solvent interactions stabilize the ion by solvating it. The solvation of dissolved ions determines many of the properties of electrolyte solutions [22-24], including their redox, complexation, and kinetic behavior.

Conductance studies in binary solvent mixtures not only give an idea about ion-solvent and solvent-solvent interactions but also the preferential solvation of an ion. Though literature is replete with such type of information [1-15]. Similar studies have not been reported on Nicotinium dichromate. It is a new Chromium (IV) complex of heterocyclic base. It has emerged as a very useful and versatile oxidant and finds wide spread application for selective oxidation [16-20]. This is a stable oxidant which was prepared and analyzed by Lopez C and coworkers

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[21]. In the present communication the authors report their observations on the conductance behavior of Nicotinium dichromate in aqueous mixtures of N,N-dimethyl formamide.

MATERIALS AND METHODS

Deionised water was distilled and used. N,N-Dimethyl formamide (sd. fine) was used as such. Nicotinium dichromate was prepared as reported in the literature [21]. A stock solution of this reagent was prepared by dissolving a known weight of the sample in water and standardizing by iodometric method. A conductivity bridge (model M.180,ELICO) equipped with a glass conductivity cell of cell constant, 1.103 cm^{-1} with smooth platinised platinum electrodes was used to measure the conductance of the solution. The conductance measurements were reproducible within ±0.2%. The conductivity values of the solvent systems used in the present study were less than 5 µS cm^{-1}. The conductances of the electrolyte solutions were always corrected for the contribution of the solvent conductance. The temperature was maintained constant using a thermostat (INSREF-India make) with an accuracy of ±0.1K. To maintain the temperature below room temperature an ice bath equipped with a stirrer was used. At 293K temperature the solution of Nicitinium dichromate and the solvent mixture were thermally equilibrated before measuring the conductance. These conductance values of Nicotinium dichromate at different concentrations were measured by diluting this solution using the thermally equilibrated solvent. After making the solvent corrections the molar conductance values, Λ_m of Nicotinium dichromate were evaluated at different compositions of N,N-dimethyl formamide-water mixtures in the range 0-100% (v/v) of N,N-dimethyl formamide.

The molar conductance (Λ_m) values determined are analyzed using Kraus-Bray equation [25], Eqn.(1) and Shedlovsky equation [25] Eqn.(2).

$$\frac{1}{\Lambda_m} = \frac{\Lambda_m C}{K_c \Lambda^{0^2}} + \frac{1}{\Lambda^0} \qquad \dots \qquad (1)$$

$$\frac{1}{S\Lambda_m} = \frac{S f_\pm^2 K_A C \Lambda_m}{\Lambda^{0^2}} + \frac{1}{\Lambda^0} \qquad \dots \qquad (2)$$

Λ_m is molar conductance at concentration C, Λ^o is the limiting molar conductance, K_A is the association constant of the ion-pair, K_C is the dissociation constant, $f_\pm$ is the mean ionic activity coefficient, S is a factor given by

$$S = \left[\frac{\beta\sqrt{C\Lambda}}{4\Lambda^{0^{3/2}}} + \sqrt{1 + \frac{\beta^2 C\Lambda}{4\Lambda^{0^3}}} \right]^2 \qquad \dots \qquad (3)$$

$$\log f_\pm = \left[\frac{-1.8246 \times 10^6 (C\alpha)^{1/2} / (\varepsilon T)^{3/2}}{1 + 50.24 \times 10^8 R(C\alpha)^{1/2} (\varepsilon T)^{1/2}} \right]^2 \qquad \dots (4)$$

$$\alpha = \frac{S\Lambda}{\Lambda^0} \qquad \dots (5)$$

$$\beta = \frac{8.20 \times 10^5 \Lambda^0}{(\varepsilon T)^{3/2}} + \frac{82.5}{\eta(\varepsilon T)^{1/2}} \qquad \dots (6)$$

where R is ion-size parameter which is equal to the Bjerrum's critical distance q given by

$$R = q = \frac{e^2}{2\varepsilon\,kT} \qquad\qquad \ldots \quad (7)$$

k is the Boltzmann's constant and T is the temperature in degrees Kelvin. S is calculated using Λ^o obtained from the Onsager model using the plot of Λ_m against $\sqrt{c}$. The least square analysis of the data (Λ_m and C) using the above two equations (1,2) is satisfactory with linear correlation coefficients in the range 0.95-0.97.

RESULTS AND DISCUSSION

The limiting molar conductance values Λ^o thus obtained using both Kraus-Bray and Shedlovsky equations are presented in Table 1. The Λ^o values obtained from these two models are in good agreement (within 0-3% variation). These Λ^o values at each temperature depend on the composition of the solvent system. Addition of N,N-dimethyl formamide to water decreases the Λ^o values. This may be due to the change in the dielectric constant and the viscosity of the medium .These factors influence ion-solvent interactions which in turn affect the extent of solvation. A decrease in conductance is an indication of increase in the extent of solvation. Increase in the proportion of N,N-dimethyl formamide in the solvent system increases the viscosity of the medium thus the mobilities of the ions decrease. It is supposed that this variation has to follow Arrhenius relation, i.e

$$\Lambda^0 = Ae^{-Ea/RT}$$

where A is a constant, E_a is the activation energy of the conducting process, R is gas constant and T is the temperature on absolute scale. E_a values obtained from the slopes of the linear plots obtained when $\log \Lambda^0$ is plotted against $1/T$ are presented in Table 2. E_a values are lower in water than in other solvent systems in the range 0.95-0.97.

In solution the free ions are always in equilibrium with the ion-pairs. This is indicated as

$$NiH^+ + Cr_2O_7^{2-} \overset{K_A}{\rightleftharpoons} [NiHCr_2O_7]^-$$
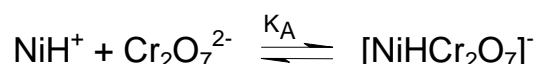
The formation of negatively changed ion-pair has been proposed by Swamy and coworkers in $(NH_4)_2Cr_2O_7$ and $K_2Cr_2O_7$ that is $(NH_4Cr_2O_7)^-$ and $(KCr_2O_7)^-$[26].

From the slopes of the linear least square analysis of the conductance data using Kraus-Bray and Shedlovsky models, the dissociation constant K_C and the association constant K_A of the ion-pair have been evaluated and presented in Table 3. In general the association constant K_A or dissociation constant K_C depend on the viscosity, dielectric constant and temperature of the medium. The data given in the above table indicates that at a given temperature the association constant, K_A is higher in binary solvent mixtures than in pure solvents. The free energy change accompanied by the ion-pair formation (ΔG_A^0) is computed using the relation $\Delta G_A^0 = -RT \ln K_A$. These values calculated at all temperatures are tabulated in Table 4.These are all negative indicating a spontaneous ion-pair formation. Using these values the differential free energy change i.e the free energy change accompanied by the transfer of the ion-pair from water to water + N,N-dimethylformamide, $\Delta G_t°$, is calculated and presented in Table 4. The magnitude of $\Delta G_t°$ is a measure of the overall change in the solvation (energy) of an ion upon its transfer from

water to an aqueous-organic mixture. The differential free energy change in different solvents is computed, using the equations,

$$\Delta G_t^o = -RT \ln(wK_A/sK_A) \qquad \text{…...(8)}$$

and

$$\Delta G_t^o = \Delta G^o (s) - \Delta G^o (w) \qquad \text{……(9)}$$

where wK_A, sK_A are the association constants of the ion-pair in water and in solvent mixture respectively. ΔG_t^o is the free energy accompanied by the addition of different amounts of N,N - dimethyl formamide to water. The magnitude of ΔG_t^o depends on the relative magnitude of stabilization of the ion-pair and are presented in Table 4. The change in entropy values accompanied by the ion association process are evaluated and presented in Table 5.

As suggested by Hammamy [27] the ionic conductances Λ_+^0 and Λ_-^0 of the Nicotinium ion and the dichromate ion are computed in all the solvent systems used and presented in Table 6. Λ_+^0 is maximum in 100% water and decreases due to the addition of DMF and then slightly increases in 100% DMF. The anionic conductance slightly increases due to the initial addition of DMF and gradually decreases attaining a minimum value in 100% DMF. This variation in the ionic conductance suggests that the specific solvation of the anion is by water while DMF from the solvent mixture solvates the cation. According to Morinaga and coworkers [28] the ratio (R), $R = \dfrac{\eta \Lambda_\pm^0(solvent)}{\eta \Lambda_\pm^0(water)}$ can be used to obtain information on the nature of solvation of an electrolyte and its constituent ions in aqueous solvent mixtures. Computed values of 'R' are presented in Table 6. This ratio for the cation is less than one in the case of aqueou*s*-N,N-dimethyl formamide and decreases sharply with the increase in the proportion of organic component. The 'R' values of anions are greater than 1 indicating that the anion is more solvated by water. That is the anion is selectively hydrated from the aqueous solvent mixture. The addition of organic solvent breaks the structure of water and makes the water molecules available for hydration of the anion. This type of behavior is observed by Morinaga [28] and Petrella [29] for alkali metal ions in water rich regions of water-acetonitrile and water-DMSO mixtures. The anionic Walden product becomes less than one in 60 and 80% (v/v) solvent mixtures. Such behavior is observed in zinc and copper perchlorates [29] in aqueous-DMF medium.

The effective ionic radii(r_i) of the cation and anion in each solvent system used are calculated by using Stoke's radius equation modified by Gill [30]

$$r_i = \frac{0.820|Z|}{\Lambda_+ \eta_o} + 0.0103\epsilon + r_y \qquad \dots \qquad (8)$$

where r_y is a parameter equal to $0.85\,A^0$ for non associated solvents and $1.13\,A^0$ for associated solvents. These values are tabulated in table 6. These values which are radii of solvated ions vary with the solvent composition suggesting the operation of ion-solvent interactions. Λ^o, the limiting molar conductance values recorded in Table 1 indicate that these values decrease continuously due to the addition of DMF to water.

The Walden product $\Lambda^0\eta_0$, which is the limiting molar conductance of the electrolyte and viscosity of the solvent is calculated in each solvent system and presented in Table 7. At a given

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temperature this is expected to be constant if the sum of the effective radii of ions is same in all the solvent systems used. The variation in the Walden product as a function of the solvent is generally regarded as an index of specific ion-solvent interaction including structural effects. In the present study the variable Walden product observed may be interpreted as due to variable ion-solvent interactions as the solvent composition is changed.

The correlation of log Λ^o against $1/\varepsilon$ according to the equation

$$\log \Lambda^0 = \log \Lambda^{0^1} - \frac{Z_A Z_B e^2}{\in d_{AB} k_B T} \qquad \ldots \qquad (9)$$

resulted in a linear plot, from the slope of which d_{AB} the distance between the centres of the two ions in the ion-pair is calculated. These values are 8.73 A^0 at 293K respectively. These values are larger than the sum of the ionic radii suggesting the formation of solvent separated ion-pair (SSIP). Further these values recorded at different temperatures suggest that the number of solvent molecules around the ions increase with increase in the temperature. This suggests the formation of a solvent separated ion-pair (SSIP).

$$M^+ S + A^{2-} S \rightleftharpoons M^+ S S A^{2-}$$
Free ions   Solvent separated ion pair

$$S [M^+ A^{2-}] S$$
Contact ion pair
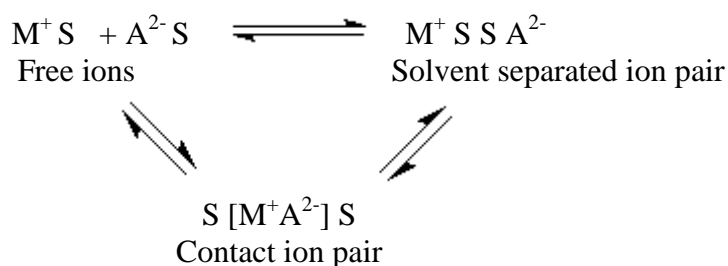
The solvation number is calculated using the relation

$$S_n = \frac{d_{AB} - (r_+ + r_-)}{r_{solvent}} \qquad \ldots \qquad (10)$$

where r_i is the Stokes radius of the ion calculated using Stoke's equation

$$r_i = \frac{0.820|Z|}{\Lambda_o \eta_o} + 0.0103 \in + r_y \qquad \ldots \qquad (11)$$

Where r_y = 0.85A^o for dipolar unassociated solvents and 1.13A^o for protic and associated solvents. These r_i values are tabulated in Table 6.
In order to understand molecular interactions occurring in the solutions, solvation number was calculated.

Solvation numbers thus determined are presented in Table 8. These values are determined at 293K which indicate that at each temperature addition of water to N,N-dimethyl formamide slightly increases the solvation number due to increase in viscosity and then decrease in pure water because of less viscosity and more dielectric constant.

The change in the free energy accompanied by the solvation process of the ion ΔG_{i-s} in each solvent calculated using Born [31] equation at each composition of the solvent mixture at 283-313K and recorded in Table 9. These values increase with increase in proportion of water. These are all negative and change due to change in composition of the solvent mixture. ΔG_{i-s} is a measure of the stability of the solvated system and larger the negative value higher will be its stability.

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Table 1 – Limiting molar conductance (Λ^o) values in s cm^2 mol^{-1} of Nicotinium dichromate in aqueous mixtures of N,N-dimethyl formamide at 293K.

T (K)	N,N-dimethyl formamide (%v/v)											
	0%		20%		40%		60%		80%		100%	
	1	2	1	2	1	2	1	2	1	2	1	2
293	205.55	205.67	114.43	114.73	82.69	82.00	65.50	60.61	45.46	45.01	69.40	68.40

1 = Kraus-Bray Model   2 = Shedlovsky model

Table 2. Computed Values of E$_a$ and ΔH (kJ mol^{-1}) for Nicotinium dichromate under varying compositions(v/v) of aqueous N,N-dimethyl formamide mixtures .

	N,N-dimethyl formamide.(%v/v)					
	0%	20%	40%	60%	80%	100%
E$_a$	9.52	18.38	19.19	20.11	21.45	11.31
ΔH	43.18	14.05	5.21	4.68	9.98	26.35

Table 3. K$_A$ and K$_C$ values of pyridinium dichromate in aqueous N,N-dimethyl formamide mixtures at 293K.

T (K)	N,N-dimethyl formamide.(%v/v)											
	0%		20%		40%		60%		80%		100%	
	K$_A$	K$_C$	K$_A$	K$_C$	K$_A$	K$_C$	K$_A$	K$_C$	K$_A$	K$_C$	K$_A$	K$_C$
293	7.58	0.13	5.30	0.19	11.40	0.09	8.08	0.13	6.81	0.15	9.69	0.10

K$_A$ = Association constant from Shedlovsky equation   K$_C$ = Dissociation constant from Kraus-Bray equation

Table 4. Computed change in free energy (ΔG$_a$) and transfer (ΔG$_t$) for pyridinium dichromate in aqueous-N,N-dimethyl formamide mixtures at 293K in kJ mol^{-1}

T (K)	N,N-dimethyl formamide.(%v/v)											
	0%		20%		40%		60%		80%		100%	
	ΔG$_a$	ΔG$_t$	ΔG$_a$	ΔG$_t$	ΔG$_a$	ΔG$_t$	ΔG$_a$	ΔG$_t$	ΔG$_a$	ΔG$_t$	ΔG$_a$	ΔG$_t$
293	-4.76	-	-3.89	0.87	-5.73	-0.18	-4.92	-0.030	-4.51	0.05	-5.34	0.58

Table 5. Computed change in entropy (ΔS$_a$) and transfer(ΔS$_t$) for Nicotinium dichromate in aqueous-N,N-dimethyl formamide mixtures at 293 in kJ mol^{-1}

T (K)	N,N-dimethyl formamide.(%v/v)											
	0%		20%		40%		60%		80%		100%	
	ΔS$_a$	ΔS$_t$	ΔS$_a$	ΔS$_t$	ΔS$_a$	ΔS$_t$	ΔS$_a$	ΔS$_t$	ΔS$_a$	ΔS$_t$	ΔS$_a$	ΔS$_t$
293	-0.140	-	-0.040	0.113	0.002	0.141	0.009	0.142	-0.019	-0.113	-0.074	0.067

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Table 6. Ionic conductances, 'R'factor and radii of solvated ions of pyridinium dichromate in aqueous-N,N-dimethyl formamide mixtures at 293K.

N,N-dimethyl formamide.(%v/v) at 293K

Composition	Λ_+^0 (s cm²mol⁻¹)	Λ_-^0 (s cm²mol⁻¹)	$r_+(A^0)$	$r_-(A^0)$	'R'factor of(cation)	'R'factor of(anion)
0%	84.86	53.14	3.36	3.53	-	-
20%	31.38	78.43	4.16	3.28	0.49	1.95
40%	24.22	63.08	3.82	3.34	0.55	2.28
60%	16.39	44.22	4.29	3.61	0.43	1.86
80%	12.09	42.92	5.46	3.76	0.29	1.65
100%	11.11	36.46	7.77	7.04	-	-

Table 7 – Walden product($\Lambda_0\eta_0$, s cm² mol⁻¹cp) of the conducting molecular species of Nicotinium dichromate in aqueous-N,N-dimethyl formamide mixtures at 293K.

N,N-dimethyl formamide.(%v/v)

T (K)	0%	20%	40%	60%	80%	100%
293	2.80	2.48	2.67	2.69	1.66	0.77

Table 8 – Solvation number values for ion - pair formation of Nicotinium dichromate in aqueous N,N-dimethyl formamide mixtures at 293K.

N,N-dimethyl formamide.(%v/v)

T (K)	0%	20%	40%	60%	80%	100%
293	1.23	1.55	1.60	1.43	0.88	0.46

Table 9. Computed change in free energy of solvation ($\Delta G_{i\text{-}s}^+$) and ($\Delta G_{i\text{-}s}^-$) for Nicotinium dichromate in aqueous-N, N-dimethyl formamide mixtures at 293K in kJ mol⁻¹.

N,N-dimethyl formamide.(%v/v)

T (K)	0%		20%		40%		60%		80%		100%	
	$\Delta G_{i\text{-}s}^+$	$\Delta G_{i\text{-}s}^-$	$\Delta G_{i\text{-}s}^+$	$\Delta G_{i\text{-}s}^-$	$\Delta G_{i\text{-}s}^+$	$\Delta G_{i\text{-}s}^-$	$\Delta G_{i\text{-}s}^+$	$\Delta G_{i\text{-}s}^-$	$\Delta G_{i\text{-}s}^+$	$\Delta G_{i\text{-}s}^-$	$\Delta G_{i\text{-}s}^+$	$\Delta G_{i\text{-}s}^-$
293	3.96	2.44	4.25	3.77	4.92	4.86	4.93	4.56	5.79	6.03	4.15	8.84

CONCLUSION

The ΔG_{i-s}^{+} and ΔG_{i-s}^{-} computed in the present system suggest that the solvated species is more stable in 80% DMF system at which ion-solvent interactions are stronger than at other compositions. That is the anion is selectively hydrated from the aqueous solvent mixture.
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