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Ion association and solvation behavior of nicotinium dichromate in water-*N*,*N*-dimethyl formamide mixtures by a conductometric study

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ABSTRACT

The electrical conductance of nicoitinium dichromate has been measured in water-*N*,*N*-dimethyl formamide mixtures of different compositions in the temperature range 283-313 K. The limiting molar conductance, Λ_o and the association constant of the ion-pair, K_A have been calculated using Shedlovsky equation. The effective ionic radii (r_i) of $(C_6H_6O_2)^+$ and $(C_6H_6O_2NCr_2O_7)^-$ ions 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.

1. Introduction

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 chromium (IV) complex of heterocyclic base. It has emerged as a very useful and versatile oxidant and finds wide spread applications for selective oxidation [16-20]. This is a stable oxidant which was prepared and analyzed by Lopez and coworkers [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 (DMF).

2. Experimental

Deionised water was distilled and used. DMF (S.D. Fine Chem.) was used as such after checking its boiling point. 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 CM185, 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. This conductivity cell was calibrated using standard KCl solution. The conductance measurements were reproducible within ±0.05%. The conductivity values of the solvent systems used in the present study were less than 0.1 µS/cm. 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 ±0.01 °C. To maintain the temperature below room temperature an ice bath equipped with a stirrer was used. At each temperature the solution of nicotinium 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. The same procedure was followed at different temperatures in the range 283-313 K. After making the solvent corrections the molar conductance values, Λ_m of nicotinium dichromate were evaluated at different compositions of DMF-water mixtures in the range 0-100% (v/v) of DMF.

3. Theory and calculation

The molar conductance (Λ_m) values determined are analyzed using Shedlovsky equation [22].

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

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, $f_{\pm}$ is the mean ionic activity coefficient, S is a factor given by

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

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Table 1. Limiting molar conductance (Λ^o) values in S cm^2/mol and ion-pair association constant K_A of nicotinium dichromate in aqueous mixtures of DMF at different temperatures [a,b].

T (K)	Water / DMF, % (v/v)											
	0%		20%		40%		60%		80%		100%	
	Λ^o	K_A	Λ^o	K_A	Λ^o	K_A	Λ^o	K_A	Λ^o	K_A	Λ^o	K_A
283	186.86	11.98	104.73	11.95	72.06	12.81	55.09	18.13	40.03	19.21	47.62	24.53
293	222.80	10.18	125.23	11.09	92.66	19.17	75.62	17.80	60.21	18.31	68.87	29.59
303	243.86	7.79	148.37	10.95	115.70	15.69	98.73	18.69	83.06	23.61	91.26	26.96
313	263.82	5.79	173.37	14.69	140.08	15.48	123.84	17.69	108.69	26.25	116.40	35.62

[a] Λ^o = Limiting molar conductance from Shedlovsky model.

[b] K_A = Association constant from Shedlovsky equation.

Table 2. Computed change in free energy (ΔG_a) and transfer (ΔG_t) of ion-pair association for nicotinium dichromate in aqueous-DMF mixtures in kJ/mol.

T (K)	Water / DMF, % (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
283	-11.25	-	-5.84	5.41	-8.82	2.43	-8.16	3.09	-6.06	5.19	-6.28	4. 98
293	-11.26	-	-7.25	4.01	-8.21	3.05	-10.75	0.51	-7.00	4.26	-8.23	3.03
303	-10.95	-	-8.40	2.55	-7.47	3.48	-10.08	0.87	-10.19	0.76	-11.24	-0.29
313	-10.53	-	-9.12	1.32	-7.12	3.41	-8.50	2.04	-11.07	0.54	-11.79	-1.26

$$\log f_{\pm} = \left[\frac{-1.8246\times10^{6}(C\alpha)^{1/2}/(\varepsilon T)^{3/2}}{1+50.24\times10^{8}q(C\alpha)^{1/2}(\varepsilon T)^{1/2}}\right]^{2} \qquad (3)$$

$$\alpha = \frac{S\Lambda}{\Lambda^{0}} \qquad (4)$$

$$\beta = \frac{8.20\times10^{5}\Lambda^{0}}{(\varepsilon T)^{3/2}} + \frac{82.5}{\eta(\varepsilon T)^{1/2}} \qquad (5)$$

where q is Bjerrum's critical distance given by

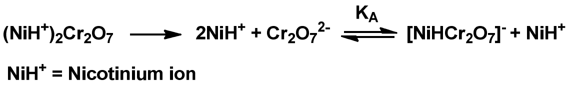
$$q = \frac{e^{2}}{2\varepsilon kT} \qquad (6)$$

k is the Boltzmann 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 Equation 1 is satisfactory with linear correlation coefficients in the range 0.95-0.97.

4. Results and discussion

The limiting molar conductance values Λ^o thus obtained are presented in Table 1. These Λ^o values at each temperature depend on the composition of the solvent system. Addition of DMF 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 DMF in the solvent system increases the viscosity of the medium thus the mobilities of the ions decrease. A glance at Λ^o values determined at different temperatures indicates that these values increase with increase in the temperature. This variation may be due to increase in the mobility of the ions with increase in temperature.

In solution, the free ions are always in equilibrium with the ion-pairs. This is indicated as given in Scheme 1.


$$(\mathrm{NiH^{+}})_2\mathrm{Cr_2O_7} \longrightarrow 2\mathrm{NiH^{+}} + \mathrm{Cr_2O_7^{2-}} \xrightleftharpoons{K_A} [\mathrm{NiHCr_2O_7}]^{-} + \mathrm{NiH^{+}}$$

$\mathrm{NiH^{+}}$ = Nicotinium ion

Scheme 1

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 $(KCr_2O_7)^-$ [23].

From the slopes of the linear least square analysis of the conductance data using Shedlovsky model, the values of association constant K_A of the ion-pair also have been evaluated and presented in Table 1. In general the association constant, K_A depends 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 values are observed to be higher in organic solvent than in aqueous solvent mixtures. The free energy change accompanied by the ion-pair formation (ΔG_a^o) is computed using the relation ($\Delta G_a^o = -R.T.\ln K_A$). These values calculated at all temperatures are tabulated in Table 2. 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+DMF, ΔG_t°, is calculated and presented in Table 2. The magnitude of ΔG_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,

$$\Delta G_t^o = -RT \ln (wK_A/sK_A) \qquad (7)$$

and

$$\Delta G_t^o = \Delta G^o(s) - \Delta G^o(w) \qquad (8)$$

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 DMF to water. The magnitude of ΔG_t^o depends on the relative magnitude of stabilization of the ion-pair and are presented in Table 2. The change in entropy values accompanied by the ion association process are evaluated and presented in Table 3.

As suggested by Hammamy [24] the ionic conductances $\Lambda_{\pm}^{0}$ of the nicotinium ion and the dichromate ion are computed in all the solvent systems used and presented in Table 4. 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.

Table 3. Computed change in entropy (ΔS_a) and transfer (ΔS_t) of ion-pair association for nicotinium dichromate in aqueous-DMF mixtures in kJ/mol.

T (K)	Water / DMF, % (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
283	-0.140	-	-0.040	0.113	0.002	0.141	0.009	0.142	-0.019	-0.113	-0.074	0.067
293	-0.135	-	-0.030	0.117	0.004	0.147	0.002	0.147	-0.018	-0.117	-0.071	0.059
303	-0.112	-	-0.029	0.091	0.005	0.121	0.003	0.121	-0.016	-0.091	-0.069	0.030
313	-0.108	-	-0.026	0.094	0.006	0.125	0.004	0.125	-0.013	-0.094	-0.064	0.032

Table 4. Ionic conductances, 'R'-factor and radii of solvated ions of nicotinium dichromate in aqueous-DMF mixtures at 303 K.

***N,N*-dimethyl formamide**	Λ^0_+ **(S cm²/mol)**	Λ^0_- **(S cm²/mol)**	r^+ **(Å)**	r^- **(Å)**	**'R' factor of cation**	**'R' factor of anion**
0%	79.45	34.98	3.53	3.85	-	-
20%	32.72	28.34	4.03	3.30	0.58	1.38
40%	19.74	27.91	4.26	2.77	0.51	1.84
60%	26.46	21.09	3.27	3.26	0.79	1.29
80%	21.83	20.10	3.71	3.64	0.60	1.03
100%	29.13	11.50	4.90	7.54	-	-

Table 5. Walden product ($\Lambda_0\eta_0$, S cm²/mol. cP) and Solvation number (S_n) values of the conducting molecular species of nicotinium dichromate in aqueous-DMF mixtures at different temperatures.

T (K)	Water / DMF, % (v/v)											
	0%		20%		40%		60%		80%		100%	
	$\Lambda_0\eta_0$	S_n	$\Lambda_0\eta_0$	S_n	$\Lambda_0\eta_0$	S_n	$\Lambda_0\eta_0$	S_n	$\Lambda_0\eta_0$	S_n	$\Lambda_0\eta_0$	S_n
283	2.80	1.23	2.48	1.55	2.67	1.60	2.69	1.43	1.66	0.88	0.77	0.46
293	2.35	1.70	2.45	2.12	2.39	2.01	2.12	1.73	1.43	1.02	0.77	0.54
303	1.90	2.28	2.11	2.55	2.24	2.38	1.62	2.02	1.30	1.37	0.67	0.61
313	2.00	2.56	2.37	2.84	2.31	2.83	1.70	2.32	1.12	1.70	0.62	0.97

Table 6. Computed change in free energy of solvation ($-\Delta G_{i-s^+}$) and ($-\Delta G_{i-s^-}$) for nicotinium dichromate in aqueous-DMF mixtures at 283-313 K in kJ/mol.

T (K)	Water / DMF, % (v/v)											
	0%		20%		40%		60%		80%		100%	
	ΔG_{i-s^+}	ΔG_{i-s^-}	ΔG_{i-s^+}	ΔG_{i-s^-}	ΔG_{i-s^+}	ΔG_{i-s^-}	ΔG_{i-s^+}	ΔG_{i-s^-}	ΔG_{i-s^+}	ΔG_{i-s^-}	ΔG_{i-s^+}	ΔG_{i-s^-}
283	3.96	2.44	4.25	3.77	4.92	4.86	4.93	5.09	5.79	6.03	4.15	7.84
293	4.05	2.59	4.26	4.46	4.85	5.27	5.14	6.03	4.73	7.20	5.70	5.12
303	4.58	3.36	4.39	3.89	5.09	5.50	5.35	5.75	5.99	6.45	5.93	4.36
313	3.91	3.83	5.34	3.72	6.21	5.28	5.07	5.98	7.00	7.26	4.54	6.80

According to Morinaga and coworkers [25] the ratio (R),

$$R = \frac{\eta\Lambda^0_\pm(solvent)}{\eta\Lambda^0_\pm(water)} \qquad (9)$$

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 4. This ratio for the cation is less than one in the case of water-DMF and decreases sharply with the increase in the proportion of organic component. The 'R' values of anions are greater than one 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 [25] and Petrella [26] for alkali metal ions in water rich regions of water-acetonitrile and water-DMSO mixtures.

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 [27]

$$r_i = \frac{0.820|Z|}{\Lambda_+\eta_o} + 0.0103\epsilon + r_y \qquad (10)$$

where r_y is a parameter equal to 0.85 Å for non-associated solvents and 1.13 Å for associated solvents. These values are tabulated in Table 4. These values which are radii of solvated ions vary with the solvent composition suggesting the operation of ion-solvent interactions.

The Walden product $\Lambda^0\eta_0$, which is the product of limiting molar conductance of the electrolyte and viscosity of the solvent is calculated in each solvent system and presented in Table 5. At a given 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/ε according to Equation 11.

$$\log\Lambda^0 = \log\Lambda^{0'} - \frac{Z_A Z_B e^2}{\epsilon d_{AB} k_B T} \qquad (11)$$

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 6.72, 7.93, 9.56 and 10.95 Å at 283, 293, 303 and 313 K, respectively.

The solvation number is calculated using the relation

$$S_n = \frac{d_{AB} - (r_+ + r_-)}{r_{solvent}} \qquad (12)$$

These values are recorded in Table 5. The change in the free energy accompanied by the solvation process of the ion ΔG_{i-s} in each solvent calculated using Born [28] equation are recorded in Table 6. 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. 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.

5. Conclusion

The calculated 'R' value which is the ratio of the ionic Walden product in the binary solvent to that in pure water for the cation is less than one and decreases sharply with the proportion of organic component. The 'R' values of anions are greater than one indicating that the anion is more solvated by water. This indicates a hetero selective solvation of the ions in the present system.

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