

Effect of Dimethyl Sulphoxide on the Conductance and Solvation Behaviour of Pyridinium Dichromate in Water

V. Radhika¹, N. Srinivas and P. Manikyamba*

Department of Chemistry, Kakatiya University, Warangal 506009.
E-mail: mani_prerepa@yahoo.co.in

Article history:

Received: 17 June 2010

Accepted: 23 July 2010

ABSTRACT

Conductance of pyridinium dichromate has been measured in dimethyl sulphoxide-water mixtures of different compositions in the temperature range 283-313K. The limiting molar conductance, Λ° and the association constant of the ion pair, K_A have been computed using Shedlovsky equation. Λ° increases with increase in the proportion of water in the solvent mixture. K_A values increases with increase in temperature. The effective ionic radii (r_i) of $(C_5H_5NH^+)_2 Cr_2O_7^{2-}$ have been determined from Λ_i° values using Gill's modification of the Stokes law. Walden product and thermodynamic parameters are also reported. The results of the study have been interpreted in terms of ion-solvent interactions and solvent properties.

Keywords: Association constant, ion-pair, Walden product, Thermodynamic parameter, ion-solvent

© 2010 ijCEPr. All rights reserved

INTRODUCTION

Literature survey on behavior of different electrolytes in mixed solvent systems indicates that their conductance is 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. Such studies 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[6-9, 12-13,15-18,20-22,24], similar information on pyridinium dichromate is not available. Recently pyridinium dichromate has emerged as a very useful and versatile oxidant[1,3,11,14]. This is a stable oxidant which was prepared and analyzed by Corey E J and Schmidt[2]. In the present communication the authors report their observations on the conductance behaviour of pyridinium dichromate in aqueous mixtures of dimethyl sulphoxide.

MATERIALS AND METHODS

Deionised water was distilled and used. Dimethyl sulphoxide (s.d. fine-chem) was used as such. Pyridinium dichromate was prepared as reported in the literature[2]. A stock solution of this reagent was prepared by dissolving a known weight of the sample in water and standardized 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 electrodes was used to measure the conductance of the solution. The conductance measurements were reproducible within $\pm 5\%$. The conductivity values of the solvent systems used in the present study were less than $5 \mu\text{S cm}^{-1}$. The temperature was maintained constant using a thermostat (INSREF make) with an accuracy of $\pm 0.2^\circ\text{C}$. To maintain the temperature below room temperature an ice bath equipped with a stirrer was used. At each temperature the solution of pyridinium dichromate and the solvent mixture were thermally equilibrated. Conductance values of pyridinium 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 283-313K. After making the solvent corrections the molar conductance values, Λ_m of pyridinium dichromate were evaluated at different compositions of dimethyl sulphoxide-water mixtures in the range 0-100% (v/v) of dimethyl sulphoxide.

The molar conductance (Λ_m) values determined are analysed using Kraus-Bray equation [10] Eqn.(1) and Shedlovsky equation[10] Eqn.(2).

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

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

Λ_m is molar conductance at concentration C, Λ^0 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

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

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

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

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

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

$$R = q = \frac{e^2}{2\epsilon kT} \quad (7)$$

k is the Boltzmann's constant and T is the temperature in degrees kelvin. S is calculated using Λ^0 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 0.92-0.97. Dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ in the aqueous solution in the concentration range used in the present study exists in the monomeric form[23] as CrO_4^{2-} and ionizes as HCrO_4^- . Therefore the conductivity equations applicable to 1:1 electrolytes are used.

RESULTS AND DISCUSSIONS

The limiting molar conductance values Λ_0 thus obtained using both Kraus-Bray and Shedlovsky equations are presented in Table 1. The Λ^0 values obtained from these two models are in good agreement (within 0-3% variation). These Λ_0 values at each temperature, depend on the composition of the solvent system. Addition of dimethyl sulphoxide to water decreases the Λ^0 values. This may be due to the change in the solvent molecular size and their viscosity of the medium and ion-solvent interactions. A decrease in mobility of the ion due to increases in solvation is also expected. Increase in the proportion of dimethyl sulphoxide in the solvent system increases the viscosity of the medium thus the mobilities of the ions decrease. The Λ^0 values increase with increase in temperature. This variation may be due to increase in the mobility of the ions with increase in temperature. It is supposed that this variation has to follow Arrhenius relation, i.e

$$\Lambda_0 = A e^{-E_a/RT}$$

where A is a constant, E_a is 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 plot obtained when $\log \Lambda_0$ is plotted against $1/T$. are presented in Table 2. E_a values are lower in pure water than in other solvent systems i.e aq DMSO. In solution the ions are in equilibrium with the ion-pairs. 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. These values increase with temperature. In general the association constant K_A or dissociation constant K_C depend on the viscosity, dielectric constant and temperature of the medium. At any given temperature the association constant, K_A values are higher in binary solvent mixtures than in pure solvents. Change in enthalpy (ΔH) determined from the slopes of the linear plots of $\log K_A$ against T^{-1} are presented in Table 3. The free energy change accompanied by the ion-pair formation (ΔG_A^0) is computed using the

relation $\Delta G_A^\circ = -RT \ln K_A$. These values calculated at all temperatures are tabulated in Table 4. The differential free energy change in different solvents is computed, using the equations,

$$\Delta G_i^\circ = -RT \ln(wK_A/sK_A) \quad (8)$$

and

$$\Delta G_i^\circ = \Delta G^\circ (s) - \Delta G^\circ (w) \quad (9)$$

Where wK_A , sK_A are association constant of the ion-pair in water and in solvent mixture respectively. ΔG_i° is the free energy change accompanied by the addition of different amounts of dimethyl sulphoxide to water. The magnitude of ΔG_i° depends on the relative magnitude of stabilization of the ion-pair and are presented in Table 4. Change in entropy ΔS_A° are presented in Table 5. These are all negative and are in the range 0.072-0.154.

As suggested by Hammamy and coworkers[4] the ionic conductance Λ_+^0 of the anion HCrO_4^- is calculated from the intercept ($\Lambda_+^0 \eta_0$) of the straight line obtained when the Walden product ($\Lambda^\circ \eta_0$) of different salts with common anion is correlated with reciprocal of the molecular weights of the salts. Using this Λ_-^0 the Λ_+^0 of the pyridinium ion is calculated applying Kohlrausch's law. These ionic conductances computed in all the solvent systems used at 293K and 303K are presented in Table 6. Λ_-^0 attains minimum value in 20%(v/v) DMSO-water mixture, while Λ_+^0 gradually increases due to the addition of water to DMSO and attains a maximum value at this composition. This variation in the ionic conductances suggests that the specific solvation of the anion is by water while DMSO from the solvent mixture solvates the cation.

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[5]-

$$r_i = \frac{0.820|Z|}{\Lambda_+ \eta_0} + 0.0103\epsilon + r_y \quad (8)$$

where r_y is a parameter equal to 0.85 \AA^0 for non associated solvents and 1.13 \AA^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° , the limiting molar conductance values recorded in Table 1 indicate that these values decrease continuously due to the addition of DMSO to water.

The Walden product $\Lambda^\circ \eta_0$, 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 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 composition 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 $\log \Lambda_0$ against $1/\epsilon$ according to the equation

$$\log \Lambda^0 = \log \Lambda^{0l} - \frac{Z_A Z_B e^2}{\epsilon d_{AB} k_B T} \quad (9)$$

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. This value is 11.32 and 11.77 \AA^0 at 293 and 303K respectively which is higher than the sum of the ionic radii. This suggests the formation of a solvent separated ion-pair (SSIP). The solvation number is calculated using the relation

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

in each solvent, and are recorded in Table 8. These values increase as the proportion of water in the solvent mixture increases. This observation indicates that the ions are selectively solvated with the water molecules.

The change in the free energy accompanied by the solvation process of the ion ΔG_{i-s} is calculated using Born[19] equation at each composition of the solvent mixture at 293K and 303K. These values are shown in Table 9. 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 suggests that the solvated species is more stable in 100% DMSO system at which ion-solvent interactions are stronger than at other compositions.

CONCLUSIONS

The presence of molecular interaction is further supported by the solvation number. Solvation is higher in water system compare to other organic solvent systems. Due to high polarity of water, solvent-solute interactions take place to greater extent there by increasing the solvation number at lower concentration of solute. Solvation number of PDC in water-dimethyl sulphoxide is better then compare to solvation number in BDC (Benzimidazolium dichromate)[15] in our earlier work.

More polarity more-solvation number. The decrease in Solvation number might be due to disruption of solvent structure. The resultant values of Solvation number decided on the basis of dipole-dipole interactions.

ACKNOWLEDGEMETS

The authors are thankful to the authorities of kakatiya University, Warangal for laboratory and instrumentation facilities respectively.

REFERENCES

1. Coates, W. M. and Corrigan, Chem.and Ind., (1969),1594.
2. Corey, E. J. , Schmidt, G., Tetrahedron Letters, **20** (1979) 399.
3. Czerncki, S., Georgoulis, C., Stevens, C.L. and Vijayakumaran, Tetrahedron Letters, **26**(1985),1699
4. El-Hammamy, N. H. , Amira, M F. , Abou El Enien, S. A. , El Halim, F. M. , Indian Journal Chem, **23**(1984), 43.
5. Gill, D. S. , Kumari, N., Chauhan, M. S. , Journal of Chem Soc Faraday Trans **1**, **81**(1985),687.
6. Gill, D.S. , Rana, D., Gupta, R. , Journal of Thermochemica Acta ,**478**(2008)1.
7. Gupta, R. , Chandra, A. , J. Chem. Phys,**127** (2007)2043.
8. Ishwara Bhat, J. , Sreelatha, T. N. , Indian Journal Chem., **45A** (2006) 1165.
9. Jalalif, A., Shaeghi Rad, Journal of the Iranian Society, **5(2)** (2009)309.
10. John, O. M., Bockris , Reddy, A. K. N. , Modern Electro Chemistry, 1970, Plenum, New York.
11. Kabilan, S., et. al, J.Chem.Soc. Perkin Transactions, **2**(2002) 1151.
12. Kondo, K. , The Journal of Physical Chemistry B, **113 (35)** (2009) 11988.
13. Morteza, Jabbari, Farrokh, Gharib, Journal of Acta Chim. Slov, **57** (2010) 325.
14. Parish, E. J. and Wei, T. Y., Synthetic Communications,**17(10)**(1987),1227.
15. Radhika, V. , Manikyamba, P. , Indian Journal Chem, **47A**(2008)1814.
16. Radhika, V. , Manikyamba, P., , J Chem Eng Data, **53(12)** (2008) 2766.
17. Radhika, V. , Manikyamba, P., Proc. Nat. Acad. Sci.India , **79A,Pt.II**(2009) 167.
18. Rezaei Behbehani, G. , Waghorne, W. E. , Journal of Thermochemica Acta, **478**(2008)1.
19. Robinson , R. A., Stokes., R. H., 1959. Electrolyte Solutions, Butter worth's Scientific, London.
20. Sanjib, B. A. Maitra, Journal of Molecular Liquids, **137** (2008) 131.
21. Senem, A. , Ksel Altun, Y., Nurullah, A. , Alsancak, G. L. , Beltran, L. , J. Chem. Eng. Data, **54 (11)** (2009)3014.
22. Victor, P. J. , Journal of Chemical & Engineering Data, **54 (10)** (2008) 2902.
23. Wiberg, K. B. Oxidations in Organic Chemistry ,1965. AP, New York.
24. Yang, L. J. , Qing, X. , Yang, Huang, K. M. , Jia, G. Z. , Shang, H. , Int. J. Mol. Sci., **10(3)** (2009) 1261.

Table-1: Limiting molar conductance (Λ°) values in $S\text{ cm}^2\text{ mol}^{-1}$ of pyridinium dichromate in aqueous mixtures of dimethyl sulphoxide at different temperatures.

Dimethyl sulphoxide (%v/v) → T (K) ↓	0%		20%		40%		60%		80%		100%	
	1	2	1	2	1	2	1	2	1	2	1	2
283	205.55	205.67	131.46	130.81	78.05	78.21	54.43	53.75	39.38	39.34	42.97	42.85
293	221.58	222.80	142.61	141.78	100.15	100.54	63.94	62.81	45.09	45.36	52.46	51.50
303	253.42	259.61	185.49	186.86	129.10	128.84	84.60	85.86	59.92	60.85	69.056	68.06
313	303.49	307.27	202.84	199.47	154.85	155.49	99.74	103.85	65.97	66.92	71.122	81.86

1 = Kraus-Bray Model 2 = Shedlovsky model

Table-2: Computed Values of E_a and ΔH_A (kJ mol^{-1}) for pyridinium dichromate under varying compositions(v/v) of aqueous dimethyl sulphoxide mixtures .

	0% dimethyl sulphoxide	20% dimethyl sulphoxide	40% dimethyl sulphoxide	60% dimethyl sulphoxide	80% dimethyl sulphoxide	100% dimethyl sulphoxide
E_a	9.59	11.40	17.14	15.75	13.65	11.31
ΔH_A	-31.43	-16.82	-18.72	-9.56	-46.26	-48.36

Table-3: K_A and K_C values of pyridinium dichromate in aqueous dimethyl sulphoxide mixtures

T (K)	0% dimethyl sulphoxide		20% dimethyl sulphoxide		40% dimethyl sulphoxide		60% dimethyl sulphoxide		80% dimethyl sulphoxide		100% dimethyl sulphoxide	
	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
283	7.58	0.133	10.4	0.10	32.02	0.21	22.35	0.23	33.39	0.30	10.63	0.25
293	15.20	0.21	42.2	0.23	37.37	0.17	33.98	0.26	35.75	0.31	11.16	0.18
303	37.65	0.28	59.2	0.17	40.53	0.19	40.71	0.25	50.74	0.33	20.59	0.20
313	37.65	0.27	60.55	0.24	53.3	0.20	44.88	0.31	56.81	0.35	30.88	0.32

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 dimethyl sulphoxide mixtures at all temperatures in kJ mol^{-1}

T (K)	0% dimethyl sulphoxide		20% dimethyl sulphoxide		40% dimethyl sulphoxide		60% dimethyl sulphoxide		80% dimethyl sulphoxide		100% dimethyl sulphoxide	
	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	-4.760	-	-5.52	-0.758	-8.17	-2.65	-8.24	-2.54	-8.24	-3.48	-5.57	-0.81
293	-4.032	-	-9.13	-5.10	-8.59	-4.56	-8.51	-3.27	-8.51	-4.48	-5.88	-1.85
303	-9.151	-	-10.25	-1.10	-8.57	+0.58	-9.33	-0.18	-9.90	-0.75	-5.91	+3.24
313	-9.513	-	-9.63	-0.12	-6.70	+2.81	-9.21	+0.30	-8.91	+0.60	-8.91	+0.60

Table-5: Computed change in entropy (ΔS_a) and transfer(ΔS_t) for pyridinium dichromate in aqueous dimethyl sulphoxide mixtures at all temperatures in kJ mol^{-1}

T (K)	0% dimethyl sulphoxide		20% dimethyl sulphoxide		40% dimethyl sulphoxide		60% dimethyl sulphoxide		80% dimethyl sulphoxide		100% dimethyl sulphoxide	
	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	-0.154	-	-0.144	-0.168	-0.005	-0.151	-0.041	-0.025	-0.030	-0.057	-0.091	-0.570
293	-0.151	-	-0.127	-0.159	-0.003	-0.143	-0.033	-0.022	-0.028	-0.048	-0.087	-0.400
303	-0.129	-	-0.119	-0.170	-0.003	-0.150	-0.031	-0.031	-0.023	-0.064	-0.084	-0.052
313	-0.124	-	-0.117	-0.156	-0.009	-0.150	-0.030	-0.032	-0.025	-0.069	-0.072	-0.053

Table-6: Ionic conductances and stoke's radius of solvated ions of pyridinium dichromate in aqueous dimethyl sulphoxide mixtures at 293 and at 303K.

At 293K %DMSO.(%v/v)	Λ_+^0 ($\text{S cm}^2\text{mol}^{-1}$)	Λ_-^0 ($\text{S cm}^2\text{mol}^{-1}$)	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	174.35	48.54	2.42	3.60	6.02
20%	114.90	26.88	2.31	4.55	6.86
40%	61.32	39.22	2.09	3.50	5.59
60%	23.70	40.29	4.66	3.35	8.01
80%	23.27	21.0	4.61	1.58	6.19
100%	10.37	31.63	5.37	2.66	8.03

At 303K %DMSO(%v/v)	Λ_+^0 (S cm ² mol ⁻¹)	Λ_-^0 (S cm ² mol ⁻¹)	$r_+(A^0)$	$r_-(A^0)$	$r_+ + r_-(A^0)$
0%	169.15	84.27	2.50	3.05	5.55
20%	107.56	77.93	2.14	4.56	6.7
40%	50.11	78.10	3.12	2.55	5.67
60%	35.64	49.03	3.69	3.09	6.78
80%	20.84	39.09	5.12	3.39	8.51
100%	19.8	29.26	5.14	3.91	9.05

Table-7: Walden product($\Lambda^0 \eta_0$), S cm² m⁻¹ poise of the conducting molecular species of pyridinium dichromate in aqueous dimethyl sulphoxide mixtures at 293,303K.

T (K)	0% dimethyl sulphoxide	20% dimethyl sulphoxide	40% dimethyl sulphoxide	60% dimethyl sulphoxide	80% dimethyl sulphoxide	100% dimethyl sulphoxide
293	1.44	1.34	1.11	0.85	0.55	0.85
303	1.24	1.47	1.33	1.08	0.62	0.90

Table-8: Solvation number values for ion pair formation of pyridinium dichromate in aqueous dimethyl sulphoxide mixtures at 293,303K.

T (K)	0% dimethyl sulphoxide	20% dimethyl sulphoxide	40% dimethyl sulphoxide	60% dimethyl sulphoxide	80% dimethyl sulphoxide	100% dimethyl sulphoxide
293	4.08	2.05	2.48	1.41	1.97	1.08
303	3.22	2.49	2.64	1.92	1.25	0.89

Table-9: Computed change in free energy of solvation (ΔG_{i-s}^+) and (ΔG_{i-s}^-) for pyridinium dichromate in aqueous dimethyl sulphoxide mixtures at 293,303K in kJ mol⁻¹.

T (K)	0% dimethyl sulphoxide		20% dimethyl sulphoxide		40% dimethyl sulphoxide		60% dimethyl sulphoxide		80% dimethyl sulphoxide		100% dimethyl sulphoxide	
	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}^-
293	1.64	3.97	2.61	5.67	5.41	5.05	6.28	5.13	6.46	2.09	12.45	8.24
303	1.60	2.70	2.10	5.44	4.43	3.48	5.27	4.58	6.48	5.23	6.80	6.06