CONDUCTANCE BEHAVIOUR OF DIFFERENT DICHROMATES IN WATER-BENZYL ALCOHOL SOLVENT MIXTURES

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ABSTRACT: The paper explores conductance behaviour of Nicotinium, Pyridinium, Quinolinium dichromates at 288K – 318K in Benzyl alcohol, water and varying compositions of Water-Benzyl alcohol (v/v). Analysis of conductance data to obtain Λ_o is on the lines of Kraus-Bray and Shedlovsky models. Λ_o, the limiting molar conductance increased with increase in the proportion of water in the solvent mixture. This is used in the interpretation of the favored / discerning solvation of cations by Benzyl alcohol. The influence of mixed solvent composition on the solvation of ions is discussed in tune with the composition dependence of Walden product. The influence of the mixed solvent composition on the solvation of ions has been discussed with the help of 'R'-factor.

Key words: ion-pair association constant / ion-pair dissociation constant / solvation number / R-factor/ limiting molar conductance/ thermodynamic parameter.

INTRODUCTION

Quinolinium dichromate is a suitable oxidant which was prepared by reported method[1]. This was used as an oxidant in the kinetic studies of oxidation of different functional groups [2-4], Solvation behavior of this oxidant in Aqueous-DMF was presented in our previous paper [5]. Pyridinium dichromate is a steady oxidant which was primed and analyze by Corey E J and Schmidt G[6], Pyridinium dichromate has emerged as a very useful and versatile oxidant which can be used in many applications[7-9]. Nicotinium dichromate is stable oxidant, which was prepared and analyzed by Lopez C and coworkers[10]. Though a large body of literature is available on kinetic aspects of these three oxidants, no information on the conductance behavior of these dichromate's is available. Density, viscosity and dielectric constant of the medium, ion-solvent and solvent-solvent interactions influence conductance behavior of electrolytes in binary solvent mixtures. Ion solvent interactions stabilize the ion by solvating it which is substantiated through information . The present paper details the observations on conductance behavior of Quinolinium, Pyridinium and Nicotinium dichromate's in dual solvent mixtures of aqueous-Benzyl alcohol.

MATERIALS AND METHODS

Quinolinium, Pyridinium and Nicotinium dichromates are prepared on the lines of the literature methods [1-10]. A stock solution of the reagent is prepared by dissolving a known weight of the sample in water and standardized by iodometric method. A conductivity bridge (ELICO model-180) equipped with a glass conductivity cell of cell constant 1.103 cm^{-1} is used to measure the conductance of the solution. Conductivity cell is calibrated using 0.1M KCl solution. Deionised water is distilled and used for the preparation of the solution. The precision of the conductivity bridge used is ±0.05mS. Temperature is kept constant during the experiment using a thermostat with an accuracy of ±0.05^{0}C. To maintain the temperature lower room temperature an ice bath equipped with a mechanical stirrer is used. Spectroscopic grade sample of Benzyl alcohol is procured from Sd-fine Chemicals Ltd., Bombay, India.

The solutions of Quinolinium, Pyridinium and Nicotinium dichromates are diluted to different concentrations in the range 0.1M to 5.0×10^{-3} M Using different volumes of solvent / solvent mixture and their conductance is measured at 283-313K. The solvent systems used in this study have conductance values between 0.029 - 0.0315mS. The values are found to be reproducible with ±0.1% error. The solvent conductance values are deducted from the conductance of the solution to get the conductance of the solute. The molar conductance is calculated using the relation $\Lambda = 1000\times k/C$ where k is the specific conductance and C is the molarity of the solute. The same procedure is followed at different compositions of solvent mixtures and at different temperatures.

The limiting molar conductance (Λ_m) values resolute are analyzed via Kraus-Bray model equation, Eqn.(1) and Shedlovsky model equation [1] Eqn.(2).

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

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

Λ_m is limiting molar conductance on 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

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

$$\log f_\pm = \left[\frac{-1.8246\times10^6 (C\alpha)^{1/2}/(\varepsilon T)^{3/2}}{1+50.24\times10^8 R(C\alpha)^{1/2}(\varepsilon T)^{1/2}}\right]^2 \quad \dots (4)$$

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

$$\beta = \frac{8.20\times10^5 \Lambda^0}{(\varepsilon T)^{3/2}} + \frac{82.5}{\eta(\varepsilon T)^{1/2}} \quad \dots \quad (6)$$

where R is ion-size factor which is identical to the Bjerrum's critical distance q specified by

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

k is the Boltzmann's constant and T is the temperature in degrees Kelvin. S is deliberate by Λ^0 obtained from the Onsager model using the plot of Λ_m against √c. The least four-sided figure analysis of the statistics (Λ_m and C) using the higher than two equations (1,2) is appropriate with linear association coefficients in the range 0.96-0.98.

RESULTS DISCUSSION

Limiting molar conductance

The limiting molar conductance values Λ^o thus obtained with the two models (eq. 1 and eq. 2) are presented in Table 1. These values amplify with boost in the temperature as expected. This is attributed to increase in the mobility of the ions due to increase in the temperature. The Λ^o values also depend on the composition of the binary solvent mixture. Adding up of Benzyl alcohol to water decreases Λ^0 worth. This can be due to reduce in the dielectric constant of the medium.

It is observed that the conductivity of the solution in each solvent system is increased with increase in the temperature.

Conclusions

Amongst the three dichromates studied Pyridinium dichromate the solvation number is observed to be higher compared to Quinolinium and Nicotinium dichromates. This may be attributed to small size of the Pyridinium ion which increases the charge density.

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Table 1 – Limiting molar conductance (Λ^o) values in S cm^2 mol^{-1} of Quinolinium , Pyridinium and Nicotinium dichromates in aqueous mixtures of Benzyl alcohol at different temperatures.

Quinolinium dichromate

T (K)	0% Benzyl alcohol		20% Benzyl alcohol		40% Benzyl alcohol		60% Benzyl alcohol		80% Benzyl alcohol		100% Benzyl alcohol	
	1	2	1	2	1	2	1	2	1	2	1	2
288	121.66	122.27	101.03	10.614	80.45	80.24	64.19	64.17	76.91	77.32	45.73	44.53
298	143.89	138.02	128.21	126.94	109.15	108.83	98.06	98.31	92.66	93.07	46.96	48.74
308	154.66	154.93	146.91	139.55	125.52	139.30	115.94	116.93	98.54	98.62	49.49	49.33
318	196.67	196.40	159.95	160.66	167.67	154.71	156.67	147.51	124.84	123.57	55.38	55.04

Pyridinium dichromate

T(K)	0% Benzyl alcohol		20% Benzyl alcohol		40% Benzyl alcohol		60% Benzyl alcohol		80% Benzyl alcohol		100% Benzyl alcohol	
	1	2	1	2	1	2	1	2	1	2	1	2
288	205.55	205.67	126.06	132.50	108.5	108.41	95.50	95.35	75.05	78.58	69.61	69.85
298	221.58	222.80	176.98	175.56	140.35	137.35	112.05	112.25	95.80	90.65	72.08	71.73
308	253.42	259.61	225.41	226.76	159.62	158.32	122.84	123.24	104.34	98.09	76.24	76.61
318	303.43	307.27	252.61	254.71	219.88	219.19	158.29	159.57	128.85	121.30	85.42	84.81

T(K)	Nicotinium dichromate 0% Benzyl alcohol		20% Benzyl alcohol		40% Benzyl alcohol		60% Benzyl alcohol		80% Benzyl alcohol		100% Benzyl alcohol	
	1	2	1	2	1	2	1	2	1	2	1	2
288	127.77	127.27	115.03	113.14	98.45	97.24	84.19	84.17	79.91	79.32	48.31	47.86
298	154.66	154.93	138.21	136.94	119.15	118.83	108.06	108.31	99.66	97.07	55.56	55.75
308	173.71	179.40	156.76	155.53	145.52	139.30	123.94	123.93	104.76	104.56	60.24	60.25
318	199.66	198.50	169.49	169.57	158.67	158.51	151.51	154.84	124.42	132.56	67.11	67.24

1 = Kraus-Bray Model 2 = Shedlovsky model

Table 2. K_A and K_C values of Quinolinium, Pyridinium and Nicotinium dichromates in aqueous-Benzyl alcohol mixtures

Quinolinium dichromate

T (K)	0% Benzyl alcohol		20% Benzyl alcohol		40% Benzyl alcohol		60% Benzyl alcohol		80% Benzyl alcohol		100% Benzyl alcohol	
	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
288	54.67	0.02	31.60	0.03	21.12	0.05	35.33	0.04	35.57	0.03	61.65	0.02
298	70.07	0.01	22.03	0.06	20.55	0.04	21.39	0.09	29.69	0.03	54.90	0.02
308	28.24	0.02	13.56	0.04	19.90	0.05	16.20	0.13	29.86	0.05	45.61	0.02
318	21.89	0.05	45.14	0.23	19.41	0.05	18.70	0.16	29.10	0.04	44.91	0.02

Pyridinium dichromate

T (K)	0% Benzyl alcohol		20% Benzyl alcohol		40% Benzyl alcohol		60% Benzyl alcohol		80% Benzyl alcohol		100% Benzyl alcohol	
	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
288	7.58	0.13	4.07	0.21	19.10	0.05	7.00	0.14	8.76	0.13	13.89	0.03
298	15.20	0.11	6.73	0.15	19.88	0.05	6.59	0.16	10.29	0.12	7.73	0.03
308	37.65	0.28	8.91	0.11	12.66	0.08	38.09	0.26	8.40	0.15	31.08	0.03
318	38.61	0.27	4.77	0.21	19.23	0.08	50.00	0.19	10.64	0.12	36.11	0.03

Nicotinium dichromate

T (K)	0% Benzyl alcohol		20% Benzyl alcohol		40% Benzyl alcohol		60% Benzyl alcohol		80% Benzyl alcohol		100% Benzyl alcohol	
	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
288	11.95	0.059	10.98	0.091	11.33	0.077	9.09	0.11	10.98	0.092	17.30	0.057
298	10.78	0.091	11.24	0.081	12.00	0.088	8.89	0.12	15.87	0.082	32.80	0.031
308	12.77	0.077	12.55	0.079	8.75	0.113	15.43	0.066	12.55	0.079	30.19	0.033
318	5.76	0.174	6.34	0.15	12.01	0.084	11.33	0.088	13.16	0.075	33.82	0.030

K_A = Association constant from Shedlovsky equation. K_C = Dissociation constant from Kraus-Bray equation

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