Ion-solvent interaction: Viscosity, apparent molar volume and conductivity of univalent electrolytes in dioxane-water mixtures at different temperatures

N.C. Das and P.B. Das

Department of Chemistry, Ravenshaw College, Cuttack-753003 (India), 10 August 1977

Summary. The viscosity, apparent molar volume and conductivity of NaCl, KCl, NaBr, KBr, $NaNO_3$ and KNO_3 solutions at mass fraction of dioxane (10, 20 and 30%)-water mixtures at 30-45 °C±0.01 °C have been measured. The ions appear to interact appreciably, and the ion-solvent interaction is of the order $NO_3^- > Br^- > Cl^-$.

Many approaches like viscosity[1-3], apparent and partial molar volumes[4-8], electrolytic conductance[9-12], activity coefficient[13-15] have been utilized to study ion-solvent interaction of various common cations, anions and symmetrical tetraalkyl ammonium ions in aqueous and nonaqueous solutions. In the present communication, viscosity, apparent molar volume and conductivity of NaCl, KCl, NaBr, KBr, $NaNO_3$ and KNO_3 solutions at mass fraction of dioxane (10, 20 and 30%)-water mixtures at 30, 35, 40 and 45 °C±0.01 °C have been studied and an attempt has been made to deal with the nature of ion-solvent interaction and to see the effect of the dielectric constant, temperature and hydrogen bonding on the above properties.

Materials and methods. All the salts used were of E. Merck 'extra pure' varieties. The apparatus, technique, preparation of solvents, and solutions were as used by Das et al.[16,17]. The concentration range for viscosity and apparent molar volume was from 0.1 to 0.001 moles $\cdot$ l^{-1} and from 0.01 to 0.001 moles $\cdot$ l^{-1} for conductance measurements. The accuracy of the period of flow is 0.2 sec in 20 min. The density data are accurate upto 4 in 10^6. Conductance measured was of an accuracy of ±2 in 1000.

Results and discussion. Viscosity. The viscosity data were analysed in terms of the Jones-Dole equation as the plot of φ_π-$1/C^{1/2}$ vs $C^{1/2}$ is linear. The B values obtained from the slope are tabulated in table 1. According to Stokes and Mills[18], the viscosity of dilute electrolytic solution incorporates of the solvent plus the contribution from other sources, which are φ^E, positive increase due to the shape and size of an ion; φ^A, the increase due to the alignment or orientation of the polar molecules by the ionic field and φ^D, the decrease in viscosity due to the distortion of the solvent structure by the ions. Therefore the B coefficient can also be discussed in terms of these viscosity effects at different temperatures.

The B coefficients of the salts containing Cl^- and NO_3^- increases with increase in temperature and φ^D is small and $\varphi^E + \varphi^A > \varphi^D$. In case of Br^-, φ^D (except at 35 °C) increases and hence B coefficient decreases with increase in temperature. The lesser the value of the B coefficient the greater is the ion-solvent interaction. Hence the ion-solvent interaction is of the order $Br^- > NO_3^- > Cl^-$ and is in agreement with that of Kay[19].

The increase in B coefficient with increase in dioxane content in the solvent mixtures may be attributed to the large size of the solvent molecules and also to the strong association between water and dioxane hydrogen bonding[20] and for dissolved ions it would lead to larger values of φ^E and φ^A. Consequently B coefficient becomes larger and larger with the increase in dioxane content in the medium.

Apparent molar volume (Φ). The Φ values calculated from equation[21] were found to vary linearly with $C^{1/2}$. The values of the limiting apparent molar volume (Φ^0) obtained from the extrapolation of the above plot are reported in table 2. The Φ^0 increases with the increase in temperature. This can be explained as follows: the ion-dipole interaction energy in case of dioxane-water mixtures is appreciable[22], and the attachment of the solvent molecules to the ions may not be loose and at the same time no structure formation would occur around the ion[3]. The net result will be stronger solvency.

For the salts containing Br^- and NO_3^-, Φ^0 increases with increase in dioxane content where as the reverse is true for NaCl and KCl. This is ascribed due to low surface charge density of Br^- and NO_3^- as compared to that of Cl^-, as a result of which electrostatic attraction is more in a medium

Table 1. $B \cdot 10^2/l \cdot mole^{-1}$

Mass fraction of dioxane temperature in °C	10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%
	NaCl			KCl			NaBr			KBr			$NaNO_3$			KNO_3		
30	8.1	10.0	15.5	1.9	3.4	4.8	9.7	12.0	15.1	2.8	4.7	5.1	7.1	9.6	13.0	1.1	3.2	4.2
35	9.1	11.2	16.6	2.0	4.0	5.2	11.4	12.4	17.0	3.4	5.1	6.1	8.5	10.9	14.2	1.5	3.9	5.0
40	14.0	15.0	20.0	3.3	5.0	6.6	6.6	11.2	14.5	2.2	6.2	5.8	10.2	11.5	15.3	1.8	4.3	5.7
45	15.0	16.2	22.0	3.6	5.8	6.9	6.5	10.8	13.7	2.2	5.2	5.6	11.2	12.5	16.0	1.9	4.7	6.1

Table 2. $\phi^0/cm^3 \cdot mole^{-1}$

Mass fraction of dioxane temperature in °C	10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%
	NaCl			KCl			NaBr			KBr			$NaNO_3$			KNO_3		
30	17.2	15.8	13.8	25.2	24.1	22.1	21.2	23.5	24.1	31.5	32.0	33.3	24.5	25.8	28.9	30.7	32.6	35.9
35	17.3	16.4	14.4	25.4	24.3	22.4	23.2	23.9	24.3	32.2	33.1	33.4	27.2	29.8	31.3	35.7	37.5	40.9
40	17.4	16.6	14.6	25.5	24.4	23.6	23.5	24.4	24.6	32.9	33.3	34.7	32.5	34.4	35.2	40.6	41.5	45.5
45	17.9	16.8	14.6	25.9	24.5	22.7	23.3	24.8	25.0	33.0	33.5	35.6	36.8	38.0	40.4	41.8	43.4	42.1

of low dielectric constant and ion-solvent interaction would be more and consequently Φ^0 will be larger.

The plot of o^0 vs $1/\varepsilon$ (ε = dielectric constant) is found to be linear, indicating the dependence of Φ^0 on dielectric constant and the slope is of the order $NO_3 > Br^- > Cl^-$.

Conductance. The equivalent conductance of all the 6 salts are found to be linear with $C^{1/2}$, which indicates that the Debye-Huckel-Onsager theory of electrolytic conductivity is applicable to these ions. The Walden product $\Lambda^0\zeta$, which can be employed to study ion-solvent interaction (table 3) is almost constant. The constancy of $\Lambda^0\zeta$ is most presumably due to the compensating contribution of positive temperature coefficient of the conductance to the negative temperature coefficient of the viscosity of the solvent. Hence it appears that the temperature dependence of $\Lambda^0\zeta$ is not very helpful in the study of ion-solvent interaction in dioxane-water mixtures.

Table 3. $\Lambda^0\zeta \cdot 10^2/\Omega^{-1} \cdot cm^2 \cdot$ poise

Mass fraction of fraction temperature in °C	10%	20%	30%	10%	20%	30%
	NaCl			KCl		
30	124.88	123.82	123.26	136.23	134.50	134.06
35	124.00	123.85	123.35	134.77	134.89	134.05
40	124.87	124.55	123.23	136.24	135.49	134.19
45	123.35	123.36	123.56	135.66	135.59	134.74
	NaBr			KBr		
30	118.67	118.58	118.40	130.02	129.27	129.21
35	118.83	118.74	118.77	129.60	129.78	129.47
40	118.85	119.72	118.41	130.31	130.07	129.30
45	118.17	117.73	118.41	129.65	129.85	129.58
	$NaNO_3$			KNO_3		
30	114.24	113.76	113.54	125.59	124.45	124.33
35	113.66	115.68	113.71	124.43	124.65	124.41
40	113.90	112.15	113.60	125.36	124.94	124.49
45	113.67	112.08	113.36	125.30	125.15	124.43

The size of the anions studied are almost of the same order[22] and the $\Lambda^0\zeta$ values are of the order $Cl^- > Br^- > NO_3^-$. The lesser the value of $\Lambda^0\zeta$, the greater is the ion-solvent interaction. During migration, these common ions which are fairly small, are covered with a sheath of solvent molecules resulting in a larger size of the solvedynamic unit, so that the size of the dissolved ions and ion-solvent interaction in dioxane-water mixtures is of the order $NO_3^- > Br^- > Cl^-$.

1 R.W. Gurney, in: Ionic Processes in Solutions, p. 159. McGraw Hill Co, New York 1953.
2 R.L. Kay, T. Vituccio and D.F. Evans, J. phys. Chem. *70*, 2336 (1966).
3 P. Rastogi and R. Gopal, Z. phys. Chem. *69*, 1 (1970).
4 W.Y. Wen and S. Saito, J. phys. Chem. *68*, 2639 (1964).
5 J. Padova and I. Abrahamer, J. phys. Chem. *71*, 2112 (1967).
6 D.F. Frank and T. Smith, Trans. Faraday Soc. *63*, 2586 (1967).
7 R.G. Gopal, K. Singh and A. Siddique, Z. phys. Chem. *75*, 7 (1971).
8 R. Gopal and K. Singh, Z. phys. Chem. *69*, 81 (1970).
9 J.R. Ernesto and J.E. Lind, Jr, J. chem. Soc. *1966*, 2876.
10 R.L. Kay and D.F. Evans, J. phys. Chem. *70*, 2974 (1968).
11 R.D. Singh and R. Gopal, Bull. chem. Soc. Jap., *45*, 2088 (1972).
12 W.A. Adams and K.J. Laidler, Can. J. Chem. *46*, 1977 (1968).
13 M.A.V. Devanathan and M.J. Fernada, Trans. Faraday. Soc. *56*, 1409 (1960).
14 R.M. Diamond, J. phys. Chem. *67*, 2513 (1967).
15 W.Y. Wen, S. Saito and W.H. Lee, J. phys. Chem. *70*, 1254 (1970).
16 P.B. Das, Electro Chim. Acta, in press (1977).
17 P.B. Das, P.K. Das and D. Patnaik, J. Ind. chem. Soc. *36*, 411 (1959).
18 R.H. Stokes and R. Mills, in: Viscosity and Related Properties, p. 124. Pergamon Press, New York 1965.
19 R.L. Kay, in: Adv. Chem. Series, p. 1, No. 73. R.F. Gould, American Chemical Society, Washington D.C. 1968.
20 P. Assarson and F.R. Eirich, J. phys. Chem. *72*, 2710 (1968).
21 R.L. Blokhra and Y.P. Sehgal, Ind. J. Chem. *14A*, 162 (1976).
22 D.K. Aggrawal and K. Singh, J. Ind. chem. Soc. *53*, 482 (1976).

Biochemical studies of pigments from a pathogenic fungus *Microsporum cookei*. V. Evidence for the transmembrane permeability of xanthomegnin across phospholipid bilayer membranes

K. Kawai, T. Akita and Y. Nozawa

Department of Biochemistry, Gifu University School of Medicine, Tsukasamachi 40, Gifu (Japan), 21 November 1977

Summary. Direct evidence is provided for the transmembrane permeation of xanthomegnin across phospholipid bilayer mebranes using ascorbate-loaded liposomes. This process may be associated with an uncoupling effect on the oxidative phosphorylation of mitochondria.

Xanthomegnin, a binaphthoquinone pigment isolated from a pathogenic fungus *Microsporum cookei*, has been shown to uncouple the oxidative phosphorylation of rat liver mitochondria[1-3] and to lose its uncoupling effect by the O-methylation of the phenolic hydroxyl groups of the pigment[3]. In general, it has been well documented by many experiments using liposomes and reconstituted membrane vesicles that compounds which uncouple mitochondrial respiration discharge the electrochemical potential by acting as proton conductors on mitochondrial inner membranes[4-12]. We have investigated the transmembrane permeability and proton conductivity of xanthomegnin across phospholipid bilayer membranes to study the molecular mechanism for the uncoupling effect on mitochondrial respiration. This communication deals with spectroscopic evidence for the transmembrane permeability of xanthomegnin.

Materials and methods. Xanthomegnin was isolated from dried mycelium of *M. cookei* by a procedure previously described[2]. Cytochrome c (bovine heart muscle) and Tris were purchased from Sigma Chemical Co. Bio-Gel P-150 was a product of Bio-Rad Laboratories. Egg lecithin (the product of Sigma Chemical Co.) was used after further purification by means of silicic column chromatography. Other reagents were of the purest form commercially available. The ascorbate-loaded liposomes were prepared by ultrasonic oscillation of egg lecithin suspension (20 mg egg lecithin in 2 ml of 0.1 M ascorbate). The ascorbate in