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Note

THERMODYNAMICS OF SALTS IN DIOXANE—WATER MIXTURES FROM VISCOSITY, APPARENT MOLAR VOLUME AND CONDUCTANCE DATA AT 35°C

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Dioxane and water are miscible at all solvent compositions and some of their physical properties, such as boiling point, vapour pressure and density, are identical but their dielectric constants and dipole moments are very different. Dioxane is an aprotic solvent, whereas water is both an electron donor and acceptor. These and several other properties make a study of their aqueous mixtures an interesting field to explore; particularly of the ionic processes accompanying the solutions of strong electrolytes.

In the present communication, the viscosity, apparent molar volume and conductivity of chlorides, bromides, nitrates, bromates, iodates and sulphates of potassium and sodium solutions at mass fraction of dioxane (10, 20 and 30%)—water mixtures have been studied at 35 ± 0.01°C and an attempt has been made to investigate the structure-breaking or structure-making effect in dioxane + water mixtures.

MATERIALS AND METHODS

All the salts used were of "extra pure" varieties. The preparation of solvents, solutions and the measurement techniques were the same as reported earlier [1]. The concentration range was 0.1—0.001 mole l^{-1} for viscosity and apparent molar volume and 0.01—0.001 mole l^{-1} for conductivity studies. The accuracy of the period of flow is 0.2 s in 20 min for viscosity measurements. The density data are accurate up to ±4 in 10^6. Conductance measurements were of an accuracy of ±2 in 1000.

RESULTS AND DISCUSSION

Viscosity

The viscosity data were analysed in terms of the Jones—Dole equation [2], as the plot of $(\eta - 1)/C^{1/2}$ vs. $C^{1/2}$ is linear. The intercept and the slope gave the values of the constants A, a measure of ion—ion interaction and B, a

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TABLE 1

B (l mole^{-1})

	Mass fraction of dioxane (%)			
	0	10	20	30
KCl	−0.0014	0.020	0.040	0.052
KBr	0.002	0.034	0.051	0.062
KNO_3	−0.004	0.015	0.39	0.050
$KBrO_3$	0.040	0.043	0.059	0.078
KIO_3	0.133	0.152	0.164	0.175
K_2SO_4	0.194	0.280	0.300	0.380
NaCl	0.079	0.091	0.112	0.166
NaBr	0.065	0.115	0.124	0.170
$NaNO_3$	0.044	0.085	0.109	0.142
$NaBrO_3$	0.090	0.089	0.109	0.119
$NaIO_3$	0.220	0.210	0.235	0.264
Na_2SO_4	0.238	0.300	0.325	0.410

manifestation of ion—solvent interaction. The B values are tabulated in Table 1.

The positive B values indicate strong alignment of the solvent molecules with the ions which undoubtedly promotes the structure of the solvent molecules in their immediate vicinity. The B values of K^+ and Na^+ salts containing the same anions different, which indicates that the B values are also dependent both on the cations and the anions with which they are paired.

Apparent molar volume (ϕ)

The apparent molar volumes are calculated in the usual manner [3]. The data obtained have been found to agree with that of Masson's equation [4],

TABLE 2

ϕ^0 (cm^3 mole^{-1})

	Mass fraction of dioxane (%)			
	0	10	20	30
KCl	26.52	25.4	24.3	22.3
KBr	33.73	32.1	33.1	33.4
KNO_3	38.18	35.7	37.5	40.9
$KBrO_3$		135.3	140.4	147.0
KIO_3		170.0	173.4	178.0
K_2SO_4		125.0	125.5	127.0
NaCl	16.40	17.30	16.40	14.40
NaBr	23.51	22.20	23.9	24.9
$NaNO_3$	27.50	27.20	29.8	31.3
$NaBrO_3$		112.0	116.5	121.2
$NaIO_3$		132.2	135.3	139.0
Na_2SO_4		74.5	76.0	79.5

TABLE 3

$\Lambda^0\eta$ (Ω^{-1} cm^2 equiv.$^{-1}$ Poise)

	Mass fraction of dioxane (%)				Mass fraction of dioxane(%)		
	10	20	30		10	20	30
KCl	1.348	1.349	1.341	NaCl	1.240	1.239	1.234
KBr	1.296	1.298	1.295	NaBr	1.188	1.187	1.188
KNO_3	1.244	1.247	1.244	$NaNO_3$	1.137	1.157	1.137
$KBrO_3$	1.162	1.551	1.097	$NaBrO_3$	1.055	1.041	1.037
KIO_3	1.259	1.254	1.244	$NaIO_3$	1.149	1.154	1.138
K_2SO_4	1.522	1.510	1.389	Na_2SO_4	1.423	1.400	1.264

as the plot of ϕ vs. $C^{1/2}$ is linear. The limiting apparent molar volumes (ϕ^0) obtained from the intercept are tabulated in Table 2. The ϕ^0 values of all the salts are found to be linear with $1/\epsilon$, the reciprocal of the dielectric constant. The slope is found to be positive for all the salts except KCl and NaCl. The slopes of the Na^+ salts are different from those of the K^+ salts, which indicates that ϕ^0 is also dependent both on the anions and cations with which they are paired.

Conductivity

The equivalent conductivities of all the salts are found to be linear with $C^{1/2}$, and Λ^0 is obtained from the intercept. The theoretical slopes were obtained from the Λ^0 values. There is some difference between the experimental and theoretical slopes. The Walden product, $\Lambda^0\eta$, where η is the viscosity of the solvent, which can be employed for the study of ion—solvent interaction [5] is recorded in Table 3. $\Lambda^0\eta$ is almost constant with the change in dioxane content. The smaller the value of $\Lambda^0\eta$, the greater the electrostatic ion—solvent interaction. The electrostatic charged density plays an important role in inducing ion—solvent interaction and solvation. It also appears that during migration these common ions are covered with a sheath of solvent molecules, resulting in a larger size of the solvodynamic unit and hence

TABLE 4

Dissociation constant ($K \times 10^2$)

	Mass fraction of dioxane (%)				Mass fraction of dioxane (%)		
	10	20	30		10	20	30
KCl	12.06	9.17	8.54	NaCl	20.89	13.51	10.72
KBr	10.50	8.94	7.78	NaBr	17.38	16.22	12.88
KNO_3	8.34	6.62	6.18	$NaNO_3$	13.80	12.30	10.23
$KBrO_3$	16.60	9.77	7.59	$NaBrO_3$	13.80	11.75	9.33
KIO_3	10.77	8.51	6.76	$NaIO_3$	12.02	9.33	7.24
K_2SO_4	18.2	14.7	9.8	Na_2SO_4	13.60	10.40	7.40

TABLE 5

ΔG^0 (J mole^{-1})

	Mass fraction of dioxane (%)				Mass fraction of dioxane (%)		
	10	20	30		10	20	30
KCl	1131	1181	1241	NaCl	1004	1103	1167
KBr	1150	1212	1251	NaBr	1015	1047	1128
KNO_3	1221	1278	1327	$NaNO_3$	1080	1125	1187
$KBrO_3$	1051	1171	1284	$NaBrO_3$	1089	1141	1191
KIO_3	1151	1202	1275	$NaIO_3$	1151	1193	1281
K_2SO_4	1236	1299	1425	Na_2SO_4	1167	1376	1486

a decrease in $\Delta^0\eta$, so that the ion—solvent interaction in dioxane—water mixtures is of the order: $BrO_3^- > NO_3^- > IO_3^- > Br^- > Cl^- > SO_4^{2-}$.

Since the dielectric constant of the medium is low, the dissociation constant K, has been calculated by the methods of Fuoss and Krauss [6] and Shedlovsky [7] (for uniunivalent salts), which were found to be same. The K values for K_2SO_4 and Na_2SO_4 have been calculated by the method of Davies [8]. These K values are given in Table 4. The ΔG^0 values were calculated from the K values and are recorded in Table 5. From ΔG^0, the ion—solvent interaction is found to be of the order: $BrO_3^- > Br^- > Cl^- > IO_3^- > NO_3^- > SO_4^{2-}$. It is observed that the order of ion—solvent interaction from $\Lambda^0\eta$ and ΔG^0 are different to some extent. The difference arises because of the reason assigned below.

Dioxane is more basic and less acidic than water, because of the electron-releasing tendency of the methylene group in the molecule. A water molecule which is hydrogen bonded to the oxygen atom of a dioxane molecule also becomes more basic and less acidic than pure water. A cation will interact more strongly with the oxygen atoms of dioxane—water mixtures. An anion will react more strongly with hydrogen atoms. This type of ion—solvent interaction is in the primary solvation sheath.

Addition of small amounts of dioxane to water may give rise to two effects: if the dioxane is accommodated in the solvent structure it may strengthen the water structure because dioxane is a better proton acceptor. If it cannot be accommodated because of its bulky size, then it may cause a breakdown in the three-dimensional water structure. It is seen from viscosity and apparent molar volume data that the B coefficients are greater in dioxane—water mixtures where ϕ^0 values are smaller than those found in water [9,10]. These values also increase with an increase in dioxane content, but the difference in B and, for example, for KCl—NaCl, KBr—NaBr, etc., do not remain the same. This indicates that due to the bulkiness, the dioxane is not accommodated in the solvent structure and breaks down the three-dimensional water structure; hence the additivity law is not expected to hold good.

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