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Note

Thermodynamics of KCl, KBr and KNO_3 in dioxane–water mixtures from conductance measurements

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Studies of electrolytic conductance in dioxane–water mixtures of varying compositions and at 30, 35, 40 and 45°C were initiated in which the variations in the Walden product with solvent composition and temperature were reported and discussed with respect to theories concerning solvent structure and ion–solvent interaction[11]. In the present communication, attempts have been made to evaluate the thermodynamic functions for the transfer of KCl, KBr and KNO_3 from water to the respective dioxane–water media, which would give some information regarding the ionic solvation.

MATERIALS AND METHODS

The salts and dioxane used were of E. Merck "Extra-pure" varieties. Purification of dioxane, preparation of solvents, solutions and conductance measurements have been reported earlier[1]. The conductance measurement was of an accuracy of ± 2 in 1000. The concentration range was from 0.01 to 0.001 mole l^{-1}.

RESULTS AND DISCUSSION

The plot of Λ vs. $C^{1/2}$ was found to be linear and Λ^0 has been obtained from the extrapolated values at zero concentration. The Walden product is almost constant at all temperatures and at all solvent compositions[1]. This constancy is presumably due to the contribution of the positive temperature coefficient of the conductivity with the negative temperature coefficient of the viscosity of the solvent. Hence, it is extremely difficult to make predictions about the breaking or promoting structure of the solvent within the temperature range studied here (i.e. from 30 to 45°C).

Since the dielectric constant of the medium is less, the dissociation constant, K, has been calculated by the method Fuoss and Krauss[2] and that of Shedlovsky[3]

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TABLE 1

FREE ENERGY, ENTHALPY AND ENTROPY OF KCl, KBr AND KNO_3 FOR THE TRANSFER FROM WATER TO DIOXANE–WATER AT DIFFERENT TEMPERATURES

Temp. (°C)	ΔG_t^0 (*J mole*$^{-1}$)			$-\Delta H^0$ (*J mole*$^{-1}$)			$-\Delta S^0$ (*J K*$^{-1}$ *mole*$^{-1}$)		
	10% dioxane	*20% dioxane*	*30% dioxane*	*10% dioxane*	*20% dioxane*	*30% dioxane*	*10% dioxane*	*20% dioxane*	*30% dioxane*
KCl									
30	524	1072	1443	302	851	1050	2.73	6.85	8.23
35	513	1014	1614	204	720	1243	2.33	5.64	9.29
40	622	1498	1772	476	788	1556	3.50	7.29	10.62
45	782	1594	2101	704	1121	1937	4.56	8.52	12.68
KBr									
30	513	1013	1445	311	912	1214	2.72	6.35	8.77
35	504	1123	1505	512	913	1612	3.30	6.61	10.13
40	901	1248	1863	580	1236	1900	4.72	7.92	12.00
45	918	1582	2083	813	1514	2510	5.44	9.92	14.42
KNO_3									
30	563	1103	1467	403	912	1115	3.19	6.65	8.52
35	608	1162	1673	403	1313	1516	3.29	7.46	10.36
40	978	1680	1864	506	1094	1766	4.73	8.85	11.58
45	972	1672	243	904	1715	2317	5.71	10.64	14.86

which were found to be the same. The standard thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0, have been calculated[4]. The plots of ΔG^0, ΔH^0 and ΔS^0 vs. solvent compositions were found to be linear. The extrapolated values give the thermodynamic parameters for water. The standard thermodynamic quantities (ΔG_t^0, ΔH_t^0 and ΔS_t^0) for the transfer process, from water to 10, 20 and 30% dioxane–water mixtures, could be calculated from the values of water and different percentages of dioxane–water mixtures[4] by using the method of Feakins and Turner[5]. These values are tabulated in Table 1. The probable uncertainties in ΔG_t^0, ΔH_t^0 and ΔS_t^0 are ± 16 J mole^{-1}, ± 18 J mole^{-1} and ± 0.5 JK^{-1} mole^{-1}, respectively, in 10, 20 and 30% solvent compositions.

The standard Gibbs free energy of transfer, ΔG_t^0, is observed to be positive at all solvent compositions and at all temperatures. The positive value indicates that the salts KCl, KBr and KNO_3 are in a higher free energy state in dioxane + water mixtures than in water, suggesting that water has more affinity for the salts than for dioxane + water mixtures. The values of ΔH_t^0 and ΔS_t^0 are negative for all the solvent mixtures, so the enthalpy in dioxane + water mixtures is less than in pure water and hence the net amount of order created by the salts in dioxane + water mixtures is more than in pure water.

Since single ion values of free energy are not available for the solvent mixture studied, the method adopted by Khoo and Chan[6] was followed to study ion–solvent interaction. Since $\Delta G^0_{t(Cl^-)}$-$\Delta G^0_{t(Br^-)}$ and $\Delta G^0_{t(Br^-)}$-$\Delta G^0_{t(NO_3^-)}$ are mostly positive, there is qualitative agreement with the Born theory. Therefore, a better fit of the Born equation may be expected as the dioxane content of the mixture is increased. The same observations were made by Feakins and Turner[5]. It may be possible to split the ΔG^0_t values into two parts, as done Roy et al.[7]: a nonelectrostatic or chemical contribution, denoted in their terminology by $\Delta G^0_{t(Ch)}$, and an electrostatic contribution $G^0_{t(el)}$ which has been calculated from the Born equation

$$\Delta G^0_{t(el)} = \left(\frac{Ne^2}{2}\right)\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{1}$$

where r_+ and r_- are the crystallographic radii of the cation and anion, respectively, ε_s and ε_w are the dielectric constants of the mixed solvent and water, respectively. To calculate the electrostatic part of the entropy of transfers after differentiation and algebraic manipulation, eqn. (1) yields

$$\Delta S^0_{t(el)} = -\left(\frac{Ne^2}{2}\right)\left[\frac{1}{\varepsilon_w}\cdot\frac{\mathrm{d}\ln\varepsilon_w}{\mathrm{d}T} - \frac{1}{\varepsilon_s}\frac{\mathrm{d}\ln\varepsilon_s}{\mathrm{d}T}\right]\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{2}$$

where the values of $\mathrm{d}\ln\varepsilon_w/\mathrm{d}T$ and $\mathrm{d}\ln\varepsilon_s/\mathrm{d}T$ can be evaluated from the simple empirical equation

$$\frac{\mathrm{d}\ln\varepsilon}{\mathrm{d}T} = -\frac{1}{\theta} \tag{3}$$

where θ is a constant, characteristic of the medium, so eqn. (2) may be written as

$$\Delta S^0_{t(el)} = -\left(\frac{Ne^2}{2}\right)\left(\frac{1}{\varepsilon_s\,\theta_s} - \frac{1}{\varepsilon_w\,\theta_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{4}$$

From a knowledge of $\Delta G^0_{t(el)}$ and $\Delta S^0_{t(el)}$, the electrostatic part of the enthalpy change has been computed. The chemical contribution of the free energy of transfer ($\Delta G^0_{t(Ch)}$), entropy of transfer ($\Delta S^0_{t(Ch)}$) and enthalpy of transfer ($\Delta H^0_{t(Ch)}$) can then be obtained by subtracting the respective electrostatic contribution values from the molar quantities. These values are presented in Table 2.

It is evident from examination of Table 2 that the chemical contribution of the free energy of transfer is negative in almost all cases and hence is thermodynamically favourable. Since $\Delta G^0_{t(el)}$ is positive, the lesser the value the greater is the ion–solvent interaction. Hence, from Table 2 it can be said that the ion–solvent interaction is of the order: $NO_3^- > Br^- > Cl^-$ and is in accordance with our viscosity and apparent molar volume results[8]. $\Delta H^0_{t(el)}$ is negative, whereas $\Delta H^0_{t(Ch)}$ is positive, and both increase with increase in dioxane content. $\Delta S^0_{t(el)}$ is negative in all cases and becomes more and more negative with increase in dioxane content, indicating the orderliness in the solvent structure. $\Delta S^0_{t(Ch)}$ is always positive (except in a few cases) and decreases with increase in temperature and increases with increase in dioxane content, indicating the disorderliness of chemical interaction.

TABLE 2

ELECTRICAL AND CHEMICAL PARTS OF THE THERMODYNAMIC QUANTITIES ACCOMPANYING THE TRANSFER OF SALTS FROM WATER TO DIOXANE-WATER MIXTURES

Temp. (°C)	$\Delta G_{t(el)}^0$ (J mole^{-1})			$\Delta G_{t(ch)}^0$ (J mole^{-1})			$-\Delta H_{t(el)}^0$ (J mole^{-1})			$+\Delta H_{t(ch)}^0$ (J mole^{-1})			$-\Delta S_{t(el)}^0$ (J K^{-1} mole^{-1})			$S_{t(ch)}^0$ (J K^{-1} mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
KCl																		
30	1023	1764	2916	−499	−692	−1573	1053	1809	2886	851	957	2035	6.85	11.77	19.15	4.12	5.42	10.92
35	787	1642	2810	−274	−628	−1196	1018	1866	3008	814	1147	1755	5.86	11.39	18.89	3.53	6.75	9.60
40	739	1806	3004	−317	−308	−1230	407	2019	3228	69	1231	1672	4.30	12.22	19.91	0.80	4.93	8.29
45	662	1616	2832	+120	−22	−731	1107	1971	3212	403	850	1275	5.56	11.46	19.31	0.90	2.94	6.63
KBr																		
30	992	1711	2829	−479	−698	−1384	1020	1740	2792	709	828	1578	6.64	11.39	18.55	3.92	4.94	9.78
35	763	1593	2725	−259	−470	−1220	986	1804	2908	474	891	1396	5.68	11.03	18.29	2.38	4.42	8.16
40	911	1752	2914	−199	−504	−1051	394	1954	3124	−186	718	1224	4.17	11.84	19.29	−0.55	3.92	7.29
45	642	1567	2748	+276	+115	−665	1069	1962	3199	246	448	1116	5.38	11.10	18.70	−0.06	1.18	4.28
KNO$_3$																		
30	935	1715	2758	−372	−612	−1318	1025	1651	2723	622	739	1608	6.47	11.11	18.09	3.28	4.46	9.57
35	744	1553	2657	−136	−371	−1291	959	1758	2837	556	445	1321	5.53	10.75	17.84	2.24	3.29	7.48
40	888	1708	2841	+90	−28	−977	383	1904	3047	−123	810	1281	4.06	11.54	18.81	−0.67	3.29	6.63
45	626	1530	2667	+346	+144	−314	1044	1912	3030	140	197	713	5.25	10.82	18.23	−0.46	0.18	3.37

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