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Note

THERMODYNAMICS OF NaCl, NaBr AND $NaNO_3$ IN DIOXANE—WATER MIXTURES FROM CONDUCTANCE MEASUREMENTS

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Studies of electrolytic conductance in dioxane—water mixtures containing 10, 20 and 30% dioxane have been reported [1]. The variation in the Walden product with solvent composition and temperature was described and discussed with respect to theories concerning solvent structure and ion—solvent interaction. In the present work, attempts have been made to evaluate the thermodynamic functions for the transfer of NaCl, NaBr and $NaNO_3$ from water to the respective dioxane—water media, which would give some information regarding solute—solvent interaction.

MATERIALS AND METHODS

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

RESULTS AND DISCUSSIONS

The plot of Λ vs. $C^{1/2}$ was found to be linear and Λ° 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 very difficult to predict whether the solvent will have a positive or negative effect within the temperature range studied presently (i.e. from 30 to 45° C).

Since the dielectric constant of the medium is less, the dissociation constants, K were calculated by both the Fuoss and Krauss [2] and the Shed-

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TABLE 1

Free energy, enthalpy and entropy of transfer of NaCl, NaBr and $NaNO_3$ from water to dioxane—water mixtures at different temperatures

Temp. (°C)	ΔG_t° (J mole^{-1})			$-\Delta H_t^\circ$ (J mole^{-1})			$-\Delta S_t^\circ$ (J K^{-1} mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
NaCl									
30	614	1313	2073	312	512	1022	3.06	6.02	10.21
35	743	1723	2373	310	713	1225	3.39	7.94	11.67
40	749	2074	2618	520	788	1302	4.09	9.13	12.51
45	1211	2019	3181	870	1342	2223	6.54	10.57	16.99
NaBr									
30	442	832	1414	113	312	640	1.96	3.78	6.78
35	552	871	1681	314	413	873	2.81	4.17	8.38
40	1030	1109	2083	408	452	1050	4.59	5.30	9.83
45	808	1672	2287	613	814	1614	4.46	7.99	12.23
$NaNO_3$									
30	446	900	1403	7.0	572	614	1.49	4.86	6.66
35	504	952	1573	314	513	873	2.66	4.77	7.95
40	702	1455	2099	742	628	1050	3.97	6.65	8.70
45	903	1507	2309	112	1280	1614	3.19	9.57	12.32

lovsky [3] methods. The results obtained by the two methods 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 composition 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 in water and the different dioxane—water mixtures [4] by using the Feakins and Turner method [5]. These are tabulated in Table 1. The probable uncertainties in ΔG_t^0 are ±15 J mole^{-1}, in ΔH_t^0 are ±18 J mole^{-1} and in ΔS_t^0 are ±0.5 J K^{-1} mole^{-1} in all solvent compositions.

The standard Gibb's free energy of transfer, ΔG_t^0, is observed to be positive at all solvent compositions and at all temperatures. The positive values indicate that the salts NaCl, NaBr and $NaNO_3$ 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 entropies 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 energies are not available presently for the solvent mixtures studied, the method adopted by Khoo and Chan [6] was followed to study ion—solvent interaction. Considering that $\Delta G^0_{t(Cl^-)} - \Delta G^0_{t(Br^-)}$ and $\Delta G^0_{t(Br^-)} - \Delta G^0_{t(NO_3^-)}$ are mostly positive, this is qualitatively in agreement with the Born theory, which predicts that bromide ion should be in a lower free energy state than the chloride ion and nitrate lower than bromide in mixed solvents of lower dielectric constant than water. Therefore, the Born equation may be expected to fit increasingly better 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_t^0 values into two parts as Roy et al. [7] have done, i.e. a "non-electrostatic" or "chemical" contribution, denoted in their terminology by $\Delta G^0_{t(Ch)}$, and an electrostatic contribution, $\Delta G^0_{t(el)}$, which has been calculated from the Born equation.

$$\Delta G^\circ_{t(el)} = \frac{Ne^2}{2}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{1}$$

where r_+ and r_- are the crystallographic radii of the cation and anion, and 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 transfer, eqn. (1) on differentiation and algebraic manipulation yields

$$\Delta S^\circ_{t(el)} = -\frac{Ne^2}{2}\left[\frac{1}{\epsilon_w}\frac{d\ln\epsilon_w}{dT} - \frac{1}{\epsilon_s}\frac{d\ln\epsilon_s}{dT}\right]\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{2}$$

where the values of $d\ln\epsilon_s/dT$ and $d\ln\epsilon_w/dT$ can be evaluated from the simple

TABLE 2

Electrical and chemical part of the thermodynamic quantities accompanying the transfer of salts from water to dioxane—water mixtures

Temp. (°C)	$\Delta G^{\circ}_{t(el)}$ (J mole^{-1})			$\Delta G^{\circ}_{t(Ch)}$ (J mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
NaCl						
30	1260	2173	3593	—646	—860	—1520
35	970	2023	3462	—227	—290	—1089
40	1157	2225	3704	—408	—151	—1086
45	315	1991	3490	396	28	—309
NaBr						
30	1228	2118	3501	—786	—1286	—2087
35	945	1972	3373	—393	—1109	—1692
40	1127	2169	3606	—97	—1059	—1523
45	794	1940	3400	14	—368	—1113
$NaNO_3$						
30	1211	2089	3454	—765	—1189	—2051
35	932	1945	3328	—438	—993	—1755
40	1112	2139	3557	—410	—684	—1458
45	784	2139	3355	119	—632	—1046
Temp. (°C)	$-\Delta H^{\circ}_{t(el)}$ (J mole^{-1})			$\Delta H^{\circ}_{t(Ch)}$ (J mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
NaCl						
30	1294	2211	3546	982	1699	2524
35	1215	2219	3577	905	1506	2352
40	499	2479	3521	—21	1691	2428
45	1258	2493	4063	388	1151	1840
NaBr						
30	1263	2155	3317	1150	1843	2677
35	1220	2233	3600	906	1820	2722
40	488	2418	3478	78	1976	2478
45	1324	2430	3958	711	1616	2349
$NaNO_3$						
30	1243	2125	3409	1236	1553	2795
35	1202	2200	550	888	1687	2677
40	481	2384	3814	—261	1756	2764
45	1306	2170	4808	1194	888	3194
Temp. (°C)	$-\Delta S^{\circ}_{t(el)}$ (J K mole^{-1})			$\Delta S^{\circ}_{t(Ch)}$ (J K^{-1} mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
NaCl						
30	8.43	14.47	23.56	5.37	8.45	13.35
35	7.21	14.00	23.23	3.82	6.06	11.56
40	5.29	15.03	24.50	1.24	5.90	11.99
45	6.84	14.10	23.75	0.34	3.53	6.76

TABLE 2 (continued)

Temp. (°C)	$-\Delta S^{\circ}_{t(el)}$ (J K mole^{-1})			$\Delta S^{\circ}_{t(Ch)}$ (J K^{-1} mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
NaBr						
30	8.22	14.10	22.95	6.26	10.32	16.17
35	7.03	13.65	22.64	4.22	8.48	14.26
40	5.16	14.65	22.63	—0.57	9.35	12.80
45	6.66	13.74	23.34	2.20	5.75	10.91
$NaNO_3$						
30	8.10	13.91	22.65	6.69	9.05	15.99
35	6.93	13.46	22.33	4.27	8.69	14.38
40	5.09	14.45	23.55	2.12	8.80	14.75
45	6.57	13.55	25.67	3.38	3.98	13.35

empirical equation

$$\frac{d \ln \epsilon}{dT} = -\frac{1}{\theta} \tag{3}$$

in which θ is a constant characteristic of the medium. So eqn. (2) may be written as

$$S^{\circ}_{t(el)} = -\frac{Ne^2}{2}\left(\frac{1}{\epsilon_s \theta_s} - \frac{1}{\epsilon_w \theta_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{4}$$

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 an examination of the Table 2 that the chemical contribution of the free energy of transfer is negative in almost all cases and hence is thermodynamically favourable as far as the chemical interactions are concerned. Since $\Delta G^{0}_{t(el)}$ is positive, the lower the value, the greater is the ion—solvent interaction. Hence, from Table 2 it can be said that the ion—solvent interaction is in the order $NO_3^- > Br^- > Cl^-$, which 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 negative with increase in dioxane content, indicating the order in the solvent structure. With a few exceptions, $\Delta S^{0}_{t(Ch)}$ is positive and is almost independent of temperature. It increases with increase in dioxane content, indicating the chemical interaction.

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