Thermochimica Acta, 38 (1980) 245—248

Note

THERMODYNAMICS OF THE CHLORIDES, BROMIDES, NITRATES, BROMATES, IODATES AND SULPHATES OF POTASSIUM AND SODIUM IN DIOXANE—WATER MIXTURES FROM CONDUCTANCE DATA AT DIFFERENT TEMPERATURES

N.C. DAS, P.P. MISRA and P.B. DAS

Department of Chemistry, Ravenshaw College, Cuttack 753003 (India)

(Received 13 November 1979)

Studies on electrolytic conductance in dioxane—water mixtures of varying compositions 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 interactions. In the present communication, attempts have been made to evaluate the thermodynamic function (ΔG_t^0) for the transfer of KCl, KBr, KNO_3, $KBrO_3$, KIO_3, K_2SO_4, NaCl, NaBr, $NaNO_3$, $NaBrO_3$, $NaIO_3$ and Na_2SO_4 from water to respective dioxane + water media, which would give some information regarding 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 measurements have been reported previously [1]. The conductance measurement was of an accuracy of ±2 in 1000. The concentration range was 0.01—0.001 mole l^{-1} for uniunivalent salts and 0.02—0.002 mole l^{-1} for K_2SO_4 and Na_2SO_4.

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. 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 predict the breaking and promoting structure of the solvent within the temperature range studied (i.e., 30—45°C).

Since the dielectric constant of the medium is low, the dissocation constant K has been calculated by the method of Fuoss and Krauss [2] and also by the method of Shedlovsky [3], both methods giving the same results. The K values for K_2SO_4 and Na_2SO_4 have been calculated from Davies' method [4]. The ΔG^0 values have been calculated and the plot of ΔG^0 vs. mass fraction of dioxane was found to be linear. The extrapolated values gave ΔG^0 for

TABLE 1

Free energy transfer of salts from water to dioxane + water mixtures at different temperatures [ΔG_t^0 (J mole^{-1})]

Salt	Temp. (°C)	ΔG: 10% dioxane	20% dioxane	30% dioxane	Salt	Temp. (°C)	ΔG: 10% dioxane	20% dioxane	30% dioxane
KCl	30	524	1072	1443	NaCl	30	614	1313	2073
	35	513	1014	1614		35	743	1723	2373
	40	622	1498	1772		40	749	2074	2618
	45	782	1594	2101		45	1211	2019	3181
KBr	30	513	1013	1445	NaBr	30	442	832	1414
	35	504	1123	1505		35	552	871	1681
	40	901	1248	1863		40	1030	1109	2083
	45	918	1582	2083		45	808	1672	2287
KNO_3	30	563	1103	1467	$NaNO_3$	30	446	900	1403
	35	608	1162	1673		35	504	952	1573
	40	978	1680	1864		40	702	1455	2099
	45	972	1672	2113		45	903	1507	2309
$KBrO_3$	30	1012	2012	3043	$NaBrO_3$	30	541	923	1461
	35	1113	2313	3443		35	591	1144	1611
	40	1265	2756	3354		40	702	1455	2099
	45	1313	2754	3603		45	623	1622	2229
KIO_3	30	612	1152	1853	$NaIO_3$	30	807	1178	1868
	35	714	1215	1954		35	808	1228	2114
	40	1080	1356	2134		40	954	1577	2417
	45	1016	1646	2754		45	1318	2178	3467
K_2SO_4	30	−1560	−2670	−4150	Na_2SO_4	30	−1480	−2670	−4660
	35	−2080	−3450	−5190		35	−1760	−2860	−4950
	40	−2820	−4250	−6060		40	−1860	−3060	−4350
	45	−1450	−3080	−5260		45	−2210	−3710	−5810

water. The standard thermodynamic quantities (ΔG_t^0) for the transfer process (from water to 10, 20 and 30% dioxane + water mixtures) were calculated by Feakins' method [5], and are tabulated in Table 1. The probable uncertainty in ΔG_t^0 is ±15 J mole^{-1}.

The ΔG_t^0 values are seen to be positive at all solvent compositions and at all temperatures for the uniunivalent salts, whereas they are negative for K_2SO_4 and Na_2SO_4. The positive values indicate that the uniunivalent salts are in a higher free energy state in dioxane + water mixtures than in water, so suggesting that water has more affinity for the salts than for dioxane + water mixtures, whereas the reverse occurs in the case of unibivalent salts, i.e. K_2SO_4 and Na_2SO_4.

The plot of ΔG_t^0 vs. r_-^{-1} for KCl, KBr and KNO_3 in dioxane + water mixtures is found to be linear. Knowing the ΔG_t^0 values of the salts $KBrO_3$,

KIO_3 and K_2SO_4, the ionic radii of BrO_3^-, IO_3^- and SO_4^{2-} could be estimated. Utilising these values ΔG_t^0 has been divided into two parts according to Roy et al. [6]:

(1) an electrostatic part, $\Delta G_{t(el)}^0$, corresponding to a change in the dielectric constant of the medium, and

(2) a nonelectrostatic part or chemical contribution, $\Delta G_{t(Ch)}^0$, arising from the specific chemical interactions between the ions and the solvent, and therefore solvent dependent.

$\Delta G_{t(el)}^0$ has been calculated from the Born equation [7] utilising the values of ionic radii; the results obtained are given in Table 2. $\Delta G_{t(Ch)}^0$ was then evaluated; the values are recorded in Table 3. It is evident that the $\Delta G_{t(Ch)}^0$ values are negative in all cases except $KBrO_3$, which indicates that the transfer of salts from water to dioxane + water is favoured as far as chemical interaction is concerned (except $KBrO_3$). $\Delta G_{t(el)}^0$ is positive in all cases and is of the order $Cl^- > Br^- > NO_3^- > BrO_3^- > IO_3^- > SO_4^{2-}$. As far as ion solvent

TABLE 2

Electrical part of ΔG_t^0 accompanying the transfer of salts from water to dioxane + water mixtures [$\Delta G_{t(el)}^0$ (J $mole^{-1}$)]

Salt	Temp. (°C)	Electrical part of ΔG_t^0			Salt	Temp. (°C)	Electrical part of ΔG_t^0		
		10% dioxane	20% dioxane	30% dioxane			10% dioxane	20% dioxane	30% dioxane
KCl	30	1022	1764	2916	NaCl	30	1260	2173	3593
	35	787	1642	2810		35	970	2024	3461
	40	939	1806	3004		40	1157	2225	3704
	45	662	1616	2832		45	815	1991	3489
KBr	30	992	1711	2829	NaBr	30	1228	2118	3501
	35	763	1593	2725		35	945	1972	3373
	40	911	1792	2914		40	1127	2168	3606
	45	642	1567	2748		45	794	1940	3400
KNO_3	30	935	1715	2758	$NaNO_3$	30	1211	2089	3454
	35	744	1553	2657		35	932	1945	3328
	40	888	1708	2841		40	1112	2139	3557
	45	626	1528	2767		45	784	2139	3356
$KBrO_3$	30	904	1560	2578	$NaBrO_3$	30	1446	2494	4123
	35	696	1452	2484		35	1113	2322	3972
	40	830	1597	2656		40	1328	2553	4246
	45	577	1428	2504		45	935	2442	4004
KIO_3	30	836	1442	2384	$NaIO_3$	30	1063	1833	3031
	35	643	1343	2297		35	818	1707	2920
	40	768	1476	2455		40	976	1877	3122
	45	541	1321	2315		45	688	1679	2944
K_2SO_4	30	108	235	415	Na_2SO_4	30	266	579	1032
	35	114	254	445		35	281	625	1994
	40	121	254	464		40	297	657	1141
	45	121	273	483		45	297	672	1186

TABLE 3

Chemical part of ΔG_t^0 accompanying the transfer of salts from water to dioxane + water mixtures [$\Delta G_{t(Ch)}^0$ (J mole^{-1})]

Salt	Temp. (°C)	Chemical part of ΔG_t^0			Salt	Temp. (°C)	Chemical part of ΔG_t^0		
		10% diox-ane	20% diox-ane	30% diox-ane			10% diox-ane	20% diox-ane	30% diox-ane
KCl	30	−498	−692	−1573	NaCl	30	−646	−860	−1520
	35	−274	−628	−1196		35	−227	−291	−1088
	40	−317	−308	−1230		40	−408	−151	−1085
	45	120	−22	−731		45	396	28	−309
KBr	30	−479	−698	−1384	NaBr	30	−786	−1286	−2087
	35	−259	−470	−1220		35	−393	−1101	−1692
	40	−10	−504	−1051		40	−97	−1059	−1523
	45	27	15	−665		45	14	−368	−1118
KNO_3	30	−372	−612	−1318	$NaNO_3$	30	−765	−1189	−2051
	35	−136	−371	−1291		35	−438	−993	−1755
	40	90	−28	−977		40	−410	−684	−1458
	45	346	144	−314		45	119	−632	−1046
$KBrO_3$	30	198	452	465	$NaBrO_3$	30	−895	−1551	−2662
	35	417	961	959		35	−502	−1208	−2361
	40	435	1159	1688		40	−636	−1098	−2165
	45	736	1296	1099		45	−310	−622	−1775
KIO_3	30	−224	−290	−531	$NaIO_3$	30	−750	−918	−1103
	35	71	−127	−342		35	−112	−479	−806
	40	312	−120	−321		40	−84	−193	−705
	45	575	322	439		45	224	744	523
K_2SO_4	30	−1668	−3249	−4569	Na_2SO_4	30	−1746	−3249	−5962
	35	−2194	−3485	−5635		35	−2041	−3485	−6044
	40	−2941	−3717	−6524		40	−2157	−3717	−5471
	45	−1571	−4382	−5743		45	−2507	−4382	−7096

interaction is considered, it is of the order: $SO_4^{2-} > BrO_3^- > IO_3^- > Br^- > NO_3^- > Cl^-$ in the case of the Na^+ salt, whereas it is of the order $SO_4^{2-} > Cl^- > Br^- > NO_3^- > IO_3^- > BrO_3^-$ in the case of the K^+ salts (Table 3). These differences arise because of the difference in the solvation spheres of Na^+ and K^+.

REFERENCES

1 N.C. Das, P.P. Misra and P.B. Das, Experentia, 35 (1979) 457.
2 R.M. Fuoss and C.A. Krauss, J. Am. Chem. Soc., 33 (1933) 476.
3 T. Shedlovsky, J. Franklin Inst., 225 (1938) 439.
4 C.W. Davies, J. Chem. Soc., 140 (1938) 2093.
5 D. Feakins and D.J. Turner, J. Chem. Soc., (1965) 4786.
6 R.N. Roy, W. Vernon and A.L.M. Bothwell, Electrochim. Acta, 17 (1972) 5.
7 H.P. Bernets and M.M. Spetzer, J. Chem. Soc., Faraday Trans. 1 (1973) 1492.