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Note

THERMODYNAMICS OF TERNARY SALTS IN DIOXANE—WATER MIXTURES FROM CONDUCTANCE MEASUREMENTS

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Studies of electrolytic conductance in dioxane—water mixtures of varying dioxane content were initiated in 1978 [1]. In the present communication, an attempt has been made to evaluate the thermodynamic function ΔG_t^0 for the transfer of $Mg(ClO_4)^+$, $Mg(NO_3)^+$, $BaCl^+$, $BaBr^+$, $Ba(ClO_4)^+$, $Ba(NO_3)^+$, $SrCl^+$, $Sr(NO_3)^+$, $CaCl^+$ and $Ca(NO_3)^+$ from water to dioxane—water media, which would give some information regarding ionic solvation.

MATERIALS AND METHODS

The salts $Mg(NO_3)_2$, $BaCl_2$, $BaBr_2$, $Ba(NO_3)_2$, $SrCl_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$ used were Merck extra-pure grade. The solutions of $Mg(ClO_4)_2$, $Ba(ClO_4)_2$ and $CaCl_2$ were prepared by the method used by Nanda and Aditya [2]. The purification of dioxane, the preparation of solvents and solutions, and the measurement of conductance have been described previously [1]. The conductance measurements were of an accuracy of ±2 in 1000 and the concentration range was from 0.02 to 0.002 mole l^{-1}. The temperature of investigation was $35 \pm 0.01°C$.

RESULTS AND DISCUSSION

The plot of Λ^0 vs. $C^{1/2}$ was linear but the observed slope(S) was found to be different from the calculated slope (S_T), indicating ion pair formation. The dissociation constants of the ion pairs were calculated and reported earlier [3] and the ΔG^0 values of the ion pairs were calculated from the equation

$$\Delta G^0 = -RT\ln K$$

The standard thermodynamic quantities (ΔG_t^0) for the transfer process from water to 10, 20 and 30% dioxane—water mixtures were determined by the Feakins and Turner method [4]. These values are tabulated in Table 1. The probable uncertainty in ΔG_t^0 is ±15 J $mole^{-1}$.

The ΔG_t^0 values are observed to be negative at all solvent compositions. The negative value indicates that the ion pairs are in a lower free energy state

TABLE 1

Values of ΔG^0_t (kJ mole^{-1}) for the transfer from water to dioxane—water mixtures

Salt	Mass fraction of dioxane in solvent		
	10%	20%	30%
$Mg(ClO_4)^+$	−4.10	−9.10	−13.02
$Mg(NO_3)^+$	−3.21	−5.11	−9.91
$BaCl^+$	−3.23	−6.17	−10.05
$BaBr^+$	−2.06	−6.68	−8.07
$Ba(ClO_4)^+$	−4.98	−10.09	−15.38
$Ba(NO_3)^+$	−2.66	−3.55	−5.66
$SrCl^+$	−2.64	−9.11	−11.62
$Sr(NO_3)^+$	−2.17	−3.12	−5.17
$CaCl^+$	−2.43	−5.14	−7.94
$Ca(NO_3)^+$	−1.97	−3.36	−5.36

in dioxane—water mixtures than water, suggesting that their formation is favoured by increase in the dioxane content, i.e. by decrease in the dielectric constant, of the medium.

Knowing the ΔG^0_t values and the ionic radii of the ion pairs [3], ΔG^0_t has been split into two parts by Roy et al. [5], an electrostatic part, $\Delta G^0_{t(el)}$, corresponding to a change in the dielectric constant of the medium, and non-electrostatic part, $\Delta G^0_{t(Ch)}$, corresponding to chemical contributions, arising from the specific chemical interaction between the ion pairs and the solvent. $\Delta G^0_{t(el)}$ has been calculated from the Born equation [6] and $\Delta G^0_{t(Ch)}$ was then determined. These are tabulated in Table 2. It is evident that $\Delta G^0_{t(Ch)}$ values are negative in all cases and increase with the increase in dioxane content. This indicates that the transfer of ion pairs from water to dioxane—water mixtures is favoured as far as chemical interaction is concerned and is in the order $BaBr^+ > BaCl^+ > Ba(ClO_4)^+ > Ba(NO_3)^+$, $Mg(NO_3)^+ >$

TABLE 2

Values of $\Delta G^0_{t(el)}$ and $\Delta G^0_{t(Ch)}$ for the transfer from water to dioxane—water mixtures

Salt	$\Delta G^0_{t(el)}$ (kJ mole^{-1})			$\Delta G^0_{t(Ch)}$ (kJ mole^{-1})		
	10% dioxane	20% dioxane	30% dioxane	10% dioxane	20% dioxane	30% dioxane
$Mg(ClO_4)^+$	32.66	72.59	127.04	−36.76	−81.59	−136.95
$Mg(NO_3)^+$	61.56	136.81	239.41	−64.77	−141.92	−249.32
$BaCl^+$	69.10	153.56	268.73	−72.33	−159.73	−278.78
$BaBr^+$	130.80	206.60	361.56	−132.86	−213.28	−369.63
$Ba(ClO_4)^+$	30.15	67.01	117.24	−35.98	−77.10	−132.62
$Ba(NO_3)^+$	28.90	64.22	112.38	−31.56	−67.77	−118.04
$SrCl^+$	38.95	86.55	151.47	−41.12	−95.66	−163.09
$Sr(NO_3)^+$	36.44	80.97	141.69	−38.61	−84.09	−146.86
$CaCl^+$	45.23	100.51	175.90	−47.66	−105.55	−183.84
$Ca(NO_3)^+$	42.71	94.93	166.12	−44.68	−98.29	−171.48

$Mg(ClO_4)^+$, $SrCl^+ > Sr(NO_3)^+$ and $CaCl^+ > Ca(NO_3)^+$ and $Ba^{2+} > Ca^{2+} > Sr^{2+}$.

The $\Delta G^0_{t(el)}$ values are positive in all cases and are in the order $BaBr^+ > BaCl^+ > Ba(ClO_4)^+ > Ba(NO_3)^+$, $Mg(NO_3)^+ > Mg(ClO_4)^+$, $SrCl^+ > Sr(NO_3)^+$ and $CaCl^+ > Ca(NO_3)^+$ and hence ionic solvation is in the reverse order.

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