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THERMODYNAMICS OF THE CHLORIDES OF POTASSIUM, SODIUM, RUBIDIUM AND CAESIUM IN TETRAMETHYLUREA–WATER MIXTURES FROM CONDUCTANCE DATA AT 30°C

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ABSTRACT

Studies of electrolyte conductance in tetramethylurea–water mixtures were initiated previously [1] In the present communication an attempt is made to evaluate the thermodynamic function ΔG_t^0 for the transfer of NaCl, KCl, RbCl and CsCl from water to the respective tetramethylurea–water mixtures, which would give some information regarding ionic solvation

MATERIALS AND METHODS

The salts were of "Aristar" varieties. Tetramethylurea was from Sigma Company. Purification of tetramethylurea, preparation of solvents, solutions and measurements have been reported previously [1]. The concentration range was 0.01–0.001 mole l^{-1} for all the salts and the investigation temperature was 30 ± 0.001°C.

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. Λ_0 and K were also obtained using the method of Fuoss and Krauss [2] and Shedlovsky [3], which gave the same results.

The ΔG^0 values were calculated by the equation

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

The standard thermodynamic quantities (ΔG_t^0) for the transfer process (from water to 5 and 14 mole % tetramethylurea–water) were calculated by Feakins and Turner's method [4], and are tabulated in Table 1. The probable uncertainty in ΔG_t^0 is ± 20 J mole^{-1}.

The ΔG_t^0 values are observed to be positive at all solvent compositions. This indicates that the salts are in a higher free energy state in tetramethylurea–water mixtures than in water, suggesting that water has more affinity for the salts than for the tetramethylurea–water mixtures.

TABLE 1

Free energy of transfer of salts from water to tetramethylurea–water mixtures

Salt	ΔG_t^0 (kJ mole^{-1})	
	5 mole % Tetramethylurea	14 mole % Tetramethylurea
NaCl	2.451	0.768
KCl	1.940	0.986
RbCl	1.861	1.089
CsCl	1.120	1.390

ΔG_t^0 has been divided into two parts according to Roy et al. [5]:

(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. Knowing the values of the ionic radii of the cations and anions [1], $\Delta G_{t(el)}^0$ has been calculated from the Born equation [6]

$$\Delta G_{t(el)}^0 = \frac{Ne^2}{2}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

where r_+ and r_- are the crystallographic radii of the cation and anion, respectively, and ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and water, respectively. The results obtained are given in Table 2. $\Delta G_{t(ch)}^0$ was then evaluated. The values are given in Table 2.

It was evident that the $\Delta G_{t(ch)}^0$ values are negative in all cases, which indicates that the transfer of salts from water to tetramethylurea–water is favoured as far as chemical interaction is concerned. $\Delta G_{t(el)}^0$ is positive in all cases and the lower the value, the greater is the ion–solvent interaction. It is of the order Cs > Rb > K > Na. As far as ion–solvent interaction is considered, it is also of the order Cs > Rb > K > Na, which is in accord with viscosity results [1].

TABLE 2

Electrical and Chemical parts of the free energy change accompanying the transfer of salts from water to tetramethylurea

Salt	$\Delta G_{t(el)}^0$ (kJ mole^{-1})		$-\Delta G_{t(ch)}^0$ (kJ mole^{-1})	
	5 mole % Tetramethyl-urea	14 mole % Tetramethyl-urea	5 mole % Tetramethyl-urea	14 mole % Tetramethyl-urea
NaCl	17.7060	41.9254	+15.2550	+41.1574
KCl	14.4644	34.2489	+12.5244	+33.2629
RbCl	13.6065	32.2176	+11.7465	+31.1286
CsCl	12.8306	30.3805	+11.7106	+28.9905

TABLE 3

The Walden product $\Lambda^0\eta_0(\Omega^{-1}\ cm^2\ p)$ of the four salts at different solvent compositions

Salt	5 mole % Tetramethylurea	14 mole % Tetramethylurea
NaCl	0 568	0 850
KCl	0.650	0 903
RbCl	0 681	0 941
CsCl	0.703	0.943

Using conductance data [1], the Walden product $\Lambda^0\eta_0$ has also been employed to study the ion–solvent interaction in a solution. $\Lambda^0\eta_0$ values of the four salts at different solvent compositions are recorded in Table 3. The plot of $\Lambda^0\eta_0$ vs. solvent compositions is linear and the slope is of the order Cs > Rb > K > Na which indicates the order of ionic solvation [7] which is in agreement with the $\Delta G^0_{t(ch)}$ values.

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