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SOLUBILITY OF 1:1 ELECTROLYTES IN 1,1,3,3-TETRAMETHYLUREA–WATER MIXTURES

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ABSTRACT

The solubilities of five 1:1 electrolytes in 1,1,3,3-tetramethylurea (TMU)–water mixtures have been determined. Combination of these data and ion pair association for the electrolytes in TMU–water mixtures yield solubility (ion-activity) products from which free energies of solution of the ionic species $M^+ + X^-$ have been calculated. Using the corresponding data in water, the free energies of transfer of $M^+ + Y^-$ from water to TMU–water mixtures are obtained. The changes in free energy that accompany the transfer of electrolytes from water to mixed aqueous solvents will be discussed.

INTRODUCTION

Several papers [1–3] from our laboratory have been concerned with the effect of water on tetramethylurea. As a continuation of these investigations, the present paper reports the solubilities of the alkali halides in the various mixtures of water and tetramethylurea.

In spite of the practical interest of 1,1,3,3-tetramethylurea (TMU), little information is found in the literature regarding the solubilities of 1:1 electrolytes in this solvent and its aqueous solutions.

The aim of the present study is to measure the solubilities of 1:1 electrolytes in TMU–water mixtures in order to derive the free energies of transfer of these electrolytes from water to the TMU mixtures.

EXPERIMENTAL

The alkali-metal halides were AR grade reagents. The solvent TMU was purified as described elsewhere [1]. Triply distilled, conductivity water was used in the preparation of all mixtures. Blank determinations for chloride were done on each batch of water used in the preparation of the mixtures.

Saturated solutions were obtained by adding an excess amount of the salt

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to the solvent mixtures. The mixtures were stirred and left for several days in a thermostat at $25 \pm 0.02°C$. Three methods were used to determine the solubilities.

(a) Titration method using fluorescein as an indicator.

(b) Weighing method: aliquots of the saturated solutions were removed and the solvent evaporated until the weight was constant.

(c) Electroanalytical method using an Orion chloride electrode as suggested by Orion Research Inc. through correspondence.

All measurements were done in triplicate. Blank experiments showed that the solvent mixtures contained no impurities.

RESULTS AND DISCUSSION

There are no solubility data with which to compare our results in the various TMU–water mixtures. However, the values for the molar solubility of the various 1:1 electrolytes in pure water agree quite well with the literature values [4]. The values obtained by the three methods agree with one another within $\pm 2\%$. Since the agreement is excellent, the values for the solubility given in Table 1 are average values.

The solubilities of 1:1 electrolytes in TMU–water mixtures are shown in Table 2. From the solubility data, the solubility (ion-activity) product, reported as pK_s^0 (Table 2), was calculated from $K_s = (C_i f_\pm)^2$, where C_i is the ionic molar concentration in TMU–water and $f_\pm$ the mean ionic activity coefficient of $M^+ + X^-$ in the given mixture of TMU–water. $f_\pm$ were calculated from the complete form of the Debye–Huckel equation.

The standard Gibbs free energy of solution ΔG^0 $(M^+ = X^-)$ is obtained from the relationship $\Delta G_s^0 = -RT \ln K_s^0 = -RT \ln(C_i f_\pm)^2$. The free energy of transfer, ΔG_t^0 $(M^+ + X^-)$ from water to TMU–water mixtures was obtained by combining ΔG_s^0 $(M^+ + X^-)$ in TMU–water mixtures and in water.

For the alkali metals, the halides ΔG_t values increase with the increase in the mole percent of TMU, which clearly indicates that as the dielectric

TABLE 1

Comparison of the three methods for determining the solubilities of 1:1 electrolytes in pure water

	Titration (solubility wt.%)	Weighing (solubility wt.%)	Electroanalytical (solubility wt.%)	Literature [4] (wt.%)
NaCl	26.40	26.41	26.41	26.43
KCl	26.33	26.32	26.31	26.34
RbCl	48.83	48.82	48.84	48.85
CsCl	65.92	65.93	65.93	69.95

TABLE 2

Calculation of free energies of transfer from water to TMU–water mixtures at 298 K

% w/w	Solubility ($mol\ l^{-1} \times 10^{-3}$)	pK_s^0	ΔG_s^0 ($kJ\ mol^{-1}$)	$\Delta G_{H_2O}^0$ ($kJ\ mol^{-1}$)	ΔG_t^0 obs.
(a) NaCl in TMU–H_2O mixtures					
5	4.770	4.715	26.903	−8.995	35.898
10	4.400	4.785	27.302		36.297
15	4.041	4.858	27.719		36.714
20	3.720	4.9291	28.125		37.120
25	3.430	4.9988	28.522		37.517
30	3.120	5.0793	28.981		37.976
35	2.730	5.1930	29.630		38.625
40	2.382	5.3099	30.297		39.292
45	2.051	5.4383	31.030		40.025
50	1.710	5.5941	31.919		40.914
55	1.330	5.8093	33.147		42.142
60	1.022	6.0353	34.436		43.431
65	0.780	6.2698	35.774		44.769
70	0.541	6.5797	37.543		46.538
75	0.400	7.0301	40.113		48.702
80	0.140	7.5235	42.928		53.001
(b) KCl in TMU–H_2O mixtures					
5	3.582	4.954	28.267	−5.104	33.371
10	3.220	5.046	28.791		33.895
15	2.890	5.138	29.317		34.421
20	2.581	5.235	29.870		34.974
25	2.301	5.333	30.429		35.533
30	2.070	5.423	30.943		36.047
35	1.760	5.561	31.730		36.834
40	1.502	5.697	32.506		37.610
45	1.242	5.860	33.436		38.540
50	0.994	6.051	34.526		39.630
55	0.703	6.348	36.426		41.530
60	0.462	6.706	38.263		43.367
65	0.272	7.163	40.871		45.975
70	0.131	7.788	44.437		49.541
75	0.033	8.976	51.216		56.320
80	0.015	9.658	55.107		60.211
(c) RbCl in TMU–H_2O mixtures					
5	5.200	4.644	26.498	−8.368	34.865
10	4.781	4.716	26.909		35.277
15	4.400	4.787	27.314		35.682
20	4.002	4.868	27.776		36.144
25	3.670	4.943	28.204		36.572
30	3.320	5.028	28.689		37.057
35	2.821	5.165	29.471		37.839
40	2.480	5.276	30.104		38.472
45	2.030	5.447	31.080		39.448
50	1.680	5.609	32.004		40.372

TABLE 2 (continued)

% w/w	Solubility (mol $l^{-1} \times 10^{-3}$)	pK_s^0	ΔG_s^0 (kJ mol^{-1})	$\Delta G_{H_2O}^0$ (kJ mol^{-1})	ΔG_t^0 obs.
55	1.281	5.841	33.328		41.696
60	0.972	6.078	34.680		43.048
65	0.701	6.360	36.289		44.657
70	0.480	6.681	38.121		46.489
75	0.200	7.430	42.394		50.762
80	0.102	8.008	45.692		54.060
(d) CsCl in TMU – H_2O mixtures					
5	6.940	2.405	13.722	−8.996	22.718
10	6.420	2.472	14.105		23.101
15	6.002	2.530	14.436		23.432
20	5.610	2.588	14.767		23.763
25	5.202	2.653	15.138		24.134
30	4.860	2.711	15.469		24.464
35	4.380	2.799	15.971		24.967
40	3.930	2.893	16.507		25.503
45	3.404	3.016	17.209		26.205
50	2.904	3.152	17.985		26.981
55	2.402	3.316	18.921		27.917
60	1.900	3.516	20.062		29.058
65	1.440	3.756	21.431		30.427
70	1.100	3.983	22.726		31.722
75	0.650	4.432	25.288		34.284
80	0.385	4.879	27.839		36.835

constant of the mixture decreases, the stability of the ions in the mixture decreases. The positive values of ΔG_t^0 indicate that the ions are more stable in water than in TMU.

In order to explain the ΔG_t^0 behaviour, we have first to divide the interaction of an ion with the solvent mixture into two classes. Firstly, the introduction of an ion into the solvent mixture, a solvent will result in a system with a structure different from that of the "pure" solvent mixture, in that the arrangement of the solvent molecules around an ion, perhaps for a few molecular diameters, will differ from that in the pure solvent. In this process hydrogen bonds will also be made or broken, strengthened or weakened. It is easy to visualize the changes in entropy, for example, which accompany this process, and we may expect that there will be a structural contribution to the free energy of transfer.

Secondly, there will be an interaction between the charge on the ion and the total charges on the solvent molecules and one could, in principle, calculate an electrostatic interaction energy between the ion and the solvent molecules.

Although the structural contribution may be the resultant of quite large

enthalpic and entropic contributions, it is itself small, and may be neglected in comparison with the electrostatic contribution in determining the overall free energy of transfer.

For the alkali chlorides, as the TMU content of the mixture increases, ΔG_t^0 increases monotonically. There is an electrostatic enthalpy of transfer, which, apart from a small entropic correction, probably follows the electrostatic free energy of transfer, and hence the overall free energy of transfer fairly closely, increasing as the cationic radius increases.

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