ACTIVITY COEFFICIENTS OF TETRAALKYLAMMONIUM REINECKATES IN WATER AND WATER–METHANOL SOLUTIONS

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The solubilities of tetraalkylammonium diaminetetraisothiocyanatochromates(III) in water and water–methanol solutions were measured at 25 °C as function of ionic strength. The results have been used to evaluate the activity coefficients of the saturating salts. For tetra-1-butylammonium salt the Gibbs free energy of transfer has been determined, and with the use of known ionic transfer function of tetrabutylammonium ion, based on TATB assumption, the Gibbs free energy of transfer of Reineckate anion has been obtained.

Tetraalkylammonium Reineckates, i.e. $R_4N[Cr(NH_3)_2(NCS)_4]$ (R = CH_3, C_2H_5, 1-C_3H_7, and 1-C_4H_9) are only sparingly soluble in water and in water–methanol solvent mixtures. The anion $[Cr(NH_3)_2(NCS)_4]^-$ strongly absorbs in near ultraviolet region because of the NCS-intraligand transition. These properties enable to use solubility measurements of examined salts as a simple and accurate method of determining of activity coefficients. The investigated compounds belong to the class of kinetically inert complexes[1], nevertheless, their kinetic stability is rather limited with regard to the aquation and/or base hydrolysis of Reineckate anion[2] . This instability was the main reason that a special experimental procedure has been used in the present investigation. The above-mentioned compounds dissociate in a solution as uni-univalent electrolytes, so the absence of specific interaction effects can be assumed.

It seemed to be interesting to measure a sequence of quaternary ammonium salts with the large complex anion. The aim of the measurements in water–methanol mixed solvents was to gain the experimental data for the evaluation of Gibbs free energy of transfer from water to these media.

EXPERIMENTAL

Tetraalkylammoniumdiaminetetraisothiocyanatochromates(III) have been prepared by precipitation of the saturated solution of $NH_4[Cr(NH_3)_2(NCS)_4]$ (Reinecke salt, USB Bruxelles, r. g.) with the solutions of tetraalkylammonium bromides (Lachema, Brno).

For $(CH_3)_4N[Cr(NH_3)_2(NCS)_4]$ (392.4) calculated: 24.46% C, 4.61% H, 24.98% N; found: 23.92% C, 4.60% H, 25.1% N.

For $(C_2H_5)_4N[Cr(NH_3)_2(NCS)_4]$ (448.5) calculated: 32.11% C, 5.83% H, 21.86% N; found: 31.77% C, 5.88% H, 22.10% N.

For $(1\text{-}C_3H_7)_4N[Cr(NH_3)_2(NCS)_4]$ (504.6) calculated: 38.05% C, 6.79% H, 19.43% N; found: 38.10% C, 7.00% H, 19.81% N.

For $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ (560.63) calculated: 42.81% C, 7.55% H, 17.49% N; found: 42.61% C, 7.65% H, 17.34% N.

Reinecke salt (Merck, r. g.) has been used for measurements of the extinction coefficients. Its value at 33 000 cm^{-1} (303 nm) is 16 640 ± 525 kg mol^{-1} cm^{-1} in water, the same value within the experimental error was found in the water–methanol mixtures. All the other chemicals used were products of analytical purity (Lachema, Brno). Double distilled water was used throughout.

Measuring procedure. An excess of solid sample was added to an approx. 25 ml of solvent in a stoppered bottle and plunged into the water bath of an ultrasound generator (UC 005, Tesla Vrable, Czechoslovakia), with the output of 45 W at 38 kHz frequency. The duration of ultrasonic agitation, necessary for preparation of a saturated solution, was ascertained experimentally. The evaluation of the concentration dependence of the saturating salt on the duration of ultrasonic operation showed that no further changes took place after 360 s of agitation for all measured salts in all investigated media. After attainment of equilibrium between the solid phase and its saturated solution, the system were still equilibrated in an ultrathermostat (20 min at 25 ± 0.05 °C), then filtered through a sintered glass and diluted, if necessary. The absorbance of solutions was measured by means of a spectrophotometer SPECORD UV-VIS (Carl Zeiss, Jena). This procedure was controlled occasionaly by measurements of the concentration of saturating salts in the mixtures stirred 2 – 3 h in a Jacketted vessel, thermostatted at 25 °C. The results were the same as in the ultrasound experiments, however, the Reinecke anion began to decompose after 3 h of stirring. With regard to this fact, the ultrasonic agitation was prefered.

RESULTS AND DISCUSSION

The solubilities S of investigated tetraalkylammonium Reineckes in aqueous solutions of sodium perchlorate are reported in Table I. It can be seen from the table that for all measured saturating salts the dependence of the logarithm of solubility on ionic strength according to the relationship (*1*) gives a straight line with the experimental slope C, which includes the charge product and the Debye–Hückel constant.

$$\log (S/S_0) = C\sqrt{I}/(1+\sqrt{I}) \qquad (1)$$

The numerical values of the experimental slopes C for tetramethyl-, tetraethyl-, tetra-1-propyl-, and tetra-1-butylammonium Reineckates are 0.575 ± 0.018, 0.653 ± 0.062, 0.592 ± 0.026, and 0.678 ± 0.047, respectively. With the aid of Eq. (*1*) the measured solubilities can be extrapolated to zero-ionic strength. Using these extrapolated values, S_0, the mean activity coefficients $\gamma_\pm$ have been evaluated according to

$$\gamma_\pm = S_0/S\,. \qquad (2)$$

The solubilities of $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ were also measured in the solutions of $NaNO_3$, KCl and K_2SO_4 as supporting electrolytes. The results of these measurements are reported in Table II. For all these electrolytes the dependence

$\log S = f\ \{\sqrt{I}/(1+\sqrt{I})\}$ was linear and enabled the extrapolation to zero-ionic strength, the extrapolated value of solubility being $S_0 = (2.069 \pm 0.032) \cdot 10^{-5}$ mol kg^{-1} in all cases. On the other hand, however, from the experimental values in Tables I and II three straight lines can be constructed in the coordinates $-\log \gamma_{\pm}$ vs $\sqrt{I}/(1+\sqrt{I})$ with different slopes (Fig. 1). These slopes are 0.622 ± 0.034 for $NaClO_4$ and $NaNO_3$, respectively, 0.387 ± 0.021 for KCl, and 0.256 ± 0.009 for K_2SO_4. The theoretical value for the saturating salt as uni-univalent electrolyte, $A\ z_+z_-$ (A being the Debye–

TABLE I
Solubility S (mol kg^{-1}) of different tetraalkylammonium Reineckates in aqueous solutions of $NaClO_4$ of various molality m (mol kg^{-1}) at 298.1 K

m_{NaClO_4}	$S \cdot 10^5$	m_{NaClO_4}	$S \cdot 10^5$
Tetramethylammonium[a]		Tetraethylammonium[b]	
0	7.139 ± 0.09	0	13.00 ± 0.06
0.0020	7.572 ± 0.090	0.0030	13.57 ± 0.05
0.0050	7.811 ± 0.030	0.0050	14.27 ± 0.06
0.0100	8.089 ± 0.144	0.0100	14.57 ± 0.15
0.0201	8.377 ± 0.030	0.0201	15.37 ± 0.28
0.0403	8.936 ± 0.361	–	–
Tetrapropylammonium[c]		Tetrabutylammonium[d]	
0	22.56 ± 0.42	0	2.080 ± 0.044
0.0050	24.70 ± 0.72	0.0100	2.289 ± 0.083
0.0100	25.18 ± 0.99	0.0201	2.404 ± 0.089
0.0201	25.93 ± 0.90	0.0403	2.662 ± 0.049
0.0352	27.49 ± 0.15	0.0606	2.706 ± 0.010
0.0504	28.70 ± 1.05	0.1016	2.971 ± 0.040

All extrapolated values in mol kg^{-1}: [a] $S_0 = (7.102 \pm 0.026) \cdot 10^{-5}$; [b] $S_0 = (12.73 \pm 0.14) \cdot 10^{-5}$; [c] $S_0 = (22.20 \pm 0.18) \cdot 10^{-5}$; [d] $S_0 = (2.069 \pm 0.032) \cdot 10^{-5}$.

TABLE II
Solubility S (mol kg^{-1}) of $(C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ in solutions of different supporting electrolytes of various molality m (mol kg^{-1}) at 298.1 K

m_{KCl}	$S \cdot 10^5$	m_{NaNO_3}	$S \cdot 10^5$	$m_{K_2SO_4}$	$S \cdot 10^5$
0.0100	2.278 ± 0.042	0.0100	2.314 ± 0.066	0.0050	2.241 ± 0.060
0.0201	2.338 ± 0.030	0.0201	2.422 ± 0.036	0.0100	2.320 ± 0.015
0.1002	2.572 ± 0.012	0.0140	2.596 ± 0.006	0.0201	2.419 ± 0.002

Hückel constant), is 0.5115 at 25 °C. The experimental value most similar to the theoretical one, is that for $NaClO_4$ and $NaNO_3$. The observed differences can be explained using the idea on the effect of supporting electrolytes on the cluster structure of water. Both $NaClO_4$ and $NaNO_3$ are structure breakers[3,4], i.e. they increase the number of free H_2O molecules. The larger the number of water molecules available to act as solvent, the larger the increase in solubility[5]. This interpretation is stressed by the fact that $NaClO_4$, which is the most powerful structure breaker shows the highest value of the experimental slope. KCl and K_2SO_4 in contrast with $NaClO_4$ enhance the cluster structure of water. However, the differences between theoretical and experimental slopes are too large in these solutions, that the explanation, based exclusively on the effect of these salts on cluster structure of water, seems to be improbable.

With regard to the fact that both cation and anion of the investigated salts are relatively large ions, the effect of a non-electrostatic activity coefficient contribution, which causes positive deviations from the Debye–Hückel law, can arise[6]. It can be seen from Table I, that the theoretical values of the mean activity coefficients, evaluated with the aid of Eq. (*3*) for aqueous solutions ($z_+z_- = -1$), are larger than the experimental ones for tetramethyl-, tetraethyl-, and tetra-1-propylammonium Reineckates, on the contrary, for tetra-1-butylammonium salt having largest cation, $(\gamma_\pm)_{theor} < (\gamma_\pm)_{exp}$.

$$-\log \gamma_\pm = A\,|z_+ z_-|\,\sqrt{I}/(1+\sqrt{I}) \qquad (3)$$

The solubility of $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ has been measured as a function of sodium perchlorate concentration in the mixture H_2O–CH_3OH 20 vol.%. The dependence $\log S = f\,\{\sqrt{I}\,/\,(1+\sqrt{I})\}$ was linear with the experimental slope 0.754 ± 0.043, whereas the theoretical slope according to the Eq. (*1*) in this solvent mixture with relative permittivity 71.05 (see ref.[7]) is 0.592. We see that the experimental slope is shifted

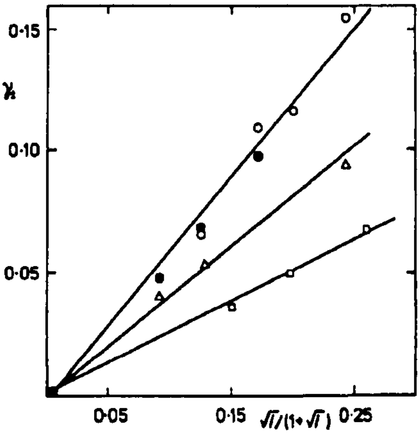

FIG. 1

Dependence of logarithm of the mean activity coefficient of $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ on the function of ionic stength adjusted by: ○ $NaClO_4$, ● $NaNO_3$, Δ KCl, □ K_2SO_4

to a larger value, similar as in the aqueous solution. The solubility in the pure H_2O–CH_3OH mixture is $(4.994 \pm 0.066) \,.\, 10^{-5}$ mol kg^{-1}, and the solubility extrapolated to zero-ionic strength, $S_0 = (4.983 \pm 0.069) \,.\, 10^{-5}$ mol kg^{-1}. These data, together with the data in Table I for $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ enable the evaluation of Gibbs free energy of transfer, ΔG_t^0, of this salt from water to the mixture water–methanol 20 vol.%. According to the basic thermodynamic relationship between Gibbs free energy of solvation in water and in a mixed solvent, and the solubility products in these media, K_S^W and K_S^{Mix}, the Eq. (*4*) can be written for ΔG_t^0 in the form

$$\Delta G_t^0 = 2RT \ln (K_S^{Mix}/K_S^W) \,. \tag{4}$$

Using the solubilities in water and in the solvent mixture, S^W, S^{Mix}, we obtain for uni-univalent electrolyte

$$\Delta G_t^0 = 2RT \ln \{(S^W/S^{Mix})(\gamma_\pm^W/\gamma_\pm^{Mix})\} \,, \tag{5}$$

where $\gamma_\pm^W$, $\gamma_\pm^{Mix}$ are the corresponding activity coefficients which can be evaluated from the above-mentioned data. For the ratio of the activity coefficients in the absence of supporting electrolytes the value of 0.975 has been obtained, and the Gibbs free energy of transfer of the measured salt, ΔG_t^0 is -4.47 kJ mol^{-1}. We can see that the ratio of activity coefficients in Eq. (*5*) differs only little from unity. When merely the approximate values of ΔG_t^0 are required, this difference can be neglected. Under this condition the values of ΔG_t^0, corresponding to the transfer of $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ from water to the other investigated water–methanol mixtures have been evaluated and are summarized in Table III. Together with ΔG_t^0 the Gibbs free energies of transfer of $[Cr(NH_3)_2(NCS)_4]^-$ anion, $\Delta G_t^{R^-}$, are reported. They were obtained combining the transfer functions of the salt, ΔG_t^0, with the transfer functions of tetrabutylammonium cation, ΔG_t^{Cat}, i.e.

$$\Delta G_t^0 = \Delta G_t^{Cat} + \Delta G_t^{R^-} \,. \tag{6}$$

The transfer functions of ΔG_t^{Cat} based on TATB assumption[8] were taken from ref.[9].

TABLE III

Gibbs free energies of transfer, ΔG_t^0 (kJ mol^{-1}), of $(1\text{-}C_4H_9)_4N[Cr(NH_3)_2(NCS)_4]$ from water to the water–methanol mixtures, and the transfer function ΔG_t^R (kJ mol^{-1}) of the Reineckate anion at 298.1 K

Methanol, vol.%	ΔG_t^0	ΔG_t^R
10	-1.99	-0.53
20	-4.47	-1.33
30	-7.02	-2.21

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