SOLUBILITY OF THALLIUM PERTECHNATE IN NITRATE SOLUTIONS

Vladimír MIKULAJ[a], Eva MIŠIANIKOVÁ[b] and Fedor MACÁŠEK[a]

[a] *Department of Nuclear Chemistry,*
Comenius University, 816 31 Bratislava, and
[b] *Price Research Institute, 801 00 Bratislava*

Received August 7th, 1980

Solubility of $TlTcO_4$ was determined in water and in HNO_3, $NaNO_3$, NH_4NO_3, $Ca(NO_3)_2$, and $LiNO_3$ aqueous solutions in concentrations 5—8 mol l^{-1}. The solubility increases with increasing concentration of the electrolyte; the values measured were used for a calculation of the stoichiometric molar activity coefficients of the Tl^+ and TcO_4^- ions. The activity coefficient values corrected for the fraction of the nonassociated Tl^+ ions approach those of the base electrolytes up to their concentrations of 4—5 mol l^{-1}.

Thallium pertechnate is one of the lowest soluble technetium inorganic salts (0·072 g/100 g H_2O at 20°C, ref.[1]). In view of the fact that fission products effluents from irradiated nuclear fuel treatment, which represent sources of technetium, contain considerable quantities of nitrates, it was of interest to determine the solubility of $TlTcO_4$ in nitrate solutions. As is well known, solubility measurements of a low soluble salt can serve to determine the corresponding activity coefficients and their variations in dependence on the solution composition. Such data are of use for a quantitative characterization of various separation methods, such as extraction. The activity coefficients of sodium pertechnate and pertechnic acid in aqueous solutions have been, in fact, determined by Boyd[2,3], but the data are not directly applicable to multicomponent systems where technetium only represents a minor component in a base electrolyte solution. It was therefore the purpose of the present work to determine the solubility of $TlTcO_4$ in nitric acid and nitrate salts solutions over wide regions of their concentrations.

EXPERIMENTAL

Technetium as $NH_4{}^{99}TcO_4$ was a product of Radiochemical Centre Amersham, the other chemicals used were reagent grade preparations of Lachema, Brno. $TlTcO_4$ was prepared by neutralization reaction of $HTcO_4$ with TlOH in concentrations 0·2 mol l^{-1}. $HTcO_4$ was prepared by allowing an NH_4TcO_4 solution to pass through a cation exchanger column in the H-form (Dowex 50 WX-4), TlOH was obtained analogously from $TlNO_3$ by using an anion exchanger in the OH-form (Amberlite IRA-400). $TlTcO_4$ crystals were washed with distilled water, dried to constant weight at 100°C, and stored in a dessicator.

The solubility of $TlTcO_4$ was determined radiometrically. A suspension of the salt in the base electrolyte solution under study was stirred in a thermostat at 25°C until the equilibrium established (50 min). The crystals were collected on a frit and the filtrate was measured for the volume activity. The solubility was determined based on the established specific activity of $TlTcO_4$. The sample activity was measured after evaporating the sample, using a scintillation probe with a plastic scintillator in conjunction with a VA-M-160 measuring kit (RTF Vakutronik, GDR). The self-absorption effect was eliminated by diluting the solutions prior to the measurements. The overall error of solubility determination did not exceed 2%.

RESULTS AND DISCUSSION

For all of the electrolytes under study, the solubility of $TlTcO_4$ increases with increasing ionic strength of the solution (Table I). The solubility in the low ionic strength region ($I < 0{\cdot}05$ for HNO_3 and $NaNO_3$) was extrapolated to zero ionic strength to obtain the value $(c_s)_0 = 2{\cdot}01 \text{ mmol l}^{-1}$; hence, the true solubility product of $TlTcO_4$ is $P = 4{\cdot}04 \,.\, 10^{-6} \text{ mol}^2 \text{ l}^{-2}$ at 25°C. Consistent with the Debye–Hueckel limiting relation, the dependence of log c_s on $\sqrt{I}$ in the above region is linear, with the expected slope of 0·5 for 1-1 type binary electrolytes.

The stoichiometric mean molar activity coefficients were calculated as

$$y_{\pm s} = (c_s)_0/c_s\,, \tag{1}$$

where c_s is the solubility of the salt in the electrolyte solution in question (Fig. 1). The specific effect of the electrolytes is pronounced notably for concentrations above 1 mol l^{-1}, increasing in the order $LiNO_3 \sim HNO_3 < NaNO_3 < NH_4NO_3 \sim \sim Ca(NO_3)_2$. It should be mentioned that there are available data on the formation of weak complexes or ion pairs of thallium cations with nitrate anions. The association constant values for the $TlNO_3$ complex (K_{as}) fall within the region of 2·1 to 3·2 (ref.[4]). Knowing the K_{as} value, the stoichiometric activity coefficients can be corrected for the fraction of the nonassociated Tl^+ ions (α) by using the relation

$$P = \alpha \,.\, y_{\pm}^2 c_s^2 = y_{\pm s}^2 c_s^2 \tag{2}$$

following from the definition of the solubility product.

Rearranging we obtain

$$y_{\pm} = y_{\pm s}\{\tfrac{1}{2}K_{as}y_{\pm s}a_{NO_3} + [(\tfrac{1}{2}K_{as}y_{\pm s}a_{NO_3})^2 + 1]^{1/2}\}\,. \tag{3}$$

In application of this relation, the value of 2·7 was used for K_{as}; a_{NO_3} was the activity of nitrate ions for the base electrolyte used[5,6].

TABLE I

Solubility of thallium pertechnate (c_s) in nitrate solutions

Electrolyte concentration mol l^{-1}	c_s mmol l^{-1}	Electrolyte concentration mol l^{-1}	c_s mmol l^{-1}	Electrolyte concentration mol l^{-1}	c_s mmol l^{-1}
H_2O		$LiNO_3$		NH_4NO_3	
—	2·116	1·0	3·881	0·1	2·664
		2·0	4·464	0·5	3·567
HNO_3		3·0	5·294	1·0	4·218
0·10	2·665	4·0	6·436	2·0	5·495
0·30	3·147	6·0	7·551	2·5	7·218
0·50	3·494			3·0	8·057
1·0	4·215	$NaNO_3$		3·5	9·313
2·0	5·178	0·10	2·404	4·0	10·97
3·0	6·044	0·50	3·193	5·0	12·21
4·0	6·494	2·0	4·292		
5·0	6·944	2·5	5·954	$Ca(NO_3)_2$	
6·0	7·310	1·0	6·482	0·1	2·911
7·0	7·820	3·0	7·153	0·3	3·475
8·0	7·753	3·5	7·666	0·5	3·948
		4·0	8·612	1·0	4·902
		5·0	8·445	2·0	5·733
				3·0	8·219
				4·0	10·07

TABLE II

Ratios of the corrected activity coefficients $y_{\pm}$ of thallium pertechnate to the mean activity coefficients of the base electrolytes[a]

Electrolyte	Activity coefficient ratios for the electrolyte concentrations, mol l^{-1}									
	1	2	2·5	3	3·5	4	5	6	7	8
HNO_3	1·01	1·15	—	0·99	—	1·08	1·15	1·24	1·26	1·46
$LiNO_3$	1·13	1·25	—	1·20	—	1·09	—	1·16	—	—
$NaNO_3$	1·18	1·05	1·04	0·99	0·98	0·89	1·04	—	—	—
NH_4NO_3	0·97	1·25	0·86	0·91	—	0·70	0·68	—	—	—

[a] Values see ref.[5].

The $y_{\pm}$ values corrected for the association of thallium ions according to Eq. (*3*) are even more susceptible to the individual effect of the electrolyte (Fig. 2); the latter is due, to a first approximation, to two phenomena: different hydration of the cations of 1-1 type electrolytes, and specific interaction within the M^+-TcO_4^- ion pairs (formation of ionic associates). Indeed, the hydration of the H^+, Li^+, Na^+, and NH_4^+ ions decreases in the order of their effect on the $y_{\pm}$ values. The possibility of formation of pertechnate associates with alkali metal cations is indicated by the data[7] on incomplete dissociation of the $KTcO_4$ and $CsTcO_4$ salts in aqueous solutions.

On the other hand, unlike the stoichiometric $y_{\pm s}$ values, the $y_{\pm}$ values approach the mean activity coefficients of the base electrolytes (Table II) even for rather high concentrations of the latter. For practical purposes, the activity coefficients of TcO_4^- in very low and trace concentrations in solutions of HNO_3, $LiNO_3$, $NaNO_3$ (in concentrations up to 5 mol l^{-1}) and NH_4NO_3 (up to 3 mol l^{-1}) can be equated with the mean activity coefficients of the electrolytes, the resulting error being below 15%.

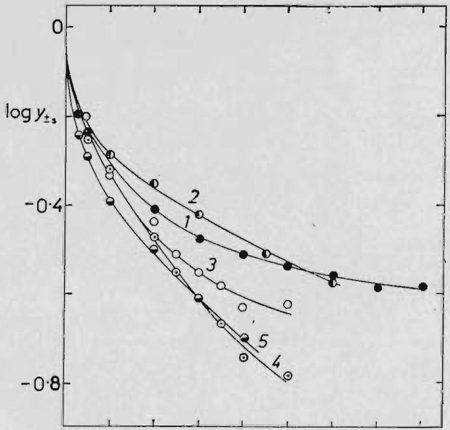

FIG. 1

Stoichiometric mean molar activity coefficients $y_{\pm s}$ of thallium pertechnate in dependence on the base electrolyte concentration. *1* HNO_3, *2* $LiNO_3$, *3* $NaNO_3$, *4* NH_4NO_3, *5* $Ca(NO_3)_2$

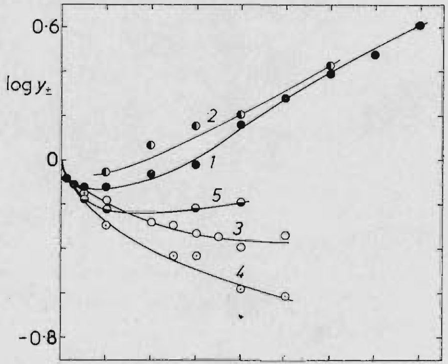

FIG. 2

Corrected mean molar activity coefficients $y_{\pm}$ of thallium pertechnate in dependence on the base electrolyte concentration. *1* HNO_3, *2* $LiNO_3$, *3* $NaNO_3$, *4* NH_4NO_3, *5* $Ca(NO_3)_2$

REFERENCES

1. Keller C., Kanellakopulos B.: Radiochim. Acta *1*, 107 (1963).
2. Boyd G. E.: J. Solut. Chem. *7*, 229 (1977).
3. Boyd G. E.: Inorg. Chem. *17*, 1808 (1978).
4. Sillén L. G., Martell A. E.: *Stability Constants of Metal-Ion Complexes*, p. 174. The Chemical Society, London 1964.
5. Marcus Y., Kertes A. S.: *Ion Exchange and Solvent Extraction of Metal Complexes*, p. 921. Wiley-Interscience, London 1969.
6. Robinson R. A., Stokes R. H.: *Electrolyte Solutions* (Russian translation), p. 576. Izd. Inostr. Lit., Moscow 1963.
7. Shvedov V. P., Lotegov K. V.: Radiokhimiya *5*, 374 (1963).

Translated by P. Adámek.