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Gas chromatographic study of complexing in the system hydrazoic acid–tributyl phosphate–nitric acid–uranyl nitrate

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Abstract

Elution gas chromatography has been used to study complexing of hydrazoic acid with tributyl phosphate (TBP) in hexadecane solution in the presence of nitric acid and/or uranyl nitrate. The study covered the temperature range 298–338 K, with concentrations of either additive up to 0.41 mol dm^{-3}. The results for hydrazoic acid elution at infinite dilution establish (a) that stoichiometry of the TBP–HNO_3 complex is 1:1 and (b) that both 2:1 and 1:1 TBP–$UO_2(NO_3)_2$ complexes co-exist in the system, the latter increasing in amount as the temperature is raised. Both HNO_3 and $UO_2(NO_3)_2$ act simply to reduce the amount of TBP free to form the 1:1 TBP–HN_3 complex. Stability constants for the equilibrium $UO_2(NO_3)_2 \cdot$ TBP+TBP$\rightleftarrows UO_2(NO_3)_2 \cdot$2TBP are presented.   © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solvent extraction is an extremely versatile analytical technique, with a wide range of applications and invoking many of the physical chemical principles underlying separation science. One of the most powerful applications of the process is its use in the extraction and analysis of metals, with phosphorus-based compounds providing one of the largest families of extractants. Tributyl phosphate (TBP) was shown early to be a powerful and versatile extractant and, by today, has many commercial uses, not only as a primary extractant, but also as a synergist and phase modifier [1–6]. It has been particularly widely utilized to extract metals from both chloride and nitrate media and, although some basic work has involved transition or other metals, for reasons that are self-evident most reported effort has centered on the mechanism and thermodynamics of extraction in the $UO_2(NO_3)_2$–HNO_3–TBP system [7] We have previously reported chromatographically based quantitative measurements of the strength of complexation of the hydracids HCl, HCN, and HN_3 with TBP in hexadecane solution [8–10]. We now report a study of the complexation of HN_3 with TBP in hexadecane solutions containing varying added amounts of the competitive complexers HNO_3 and $UO_2(NO_3)_2$.

2. Experimental

Gas chromatographic measurements were carried

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out using the purpose-built high precision instrument previously described [8]. The eluent was scrubbed of hydracid by employing an alkali trap, which was replaced at regular intervals. Column packings of 7% (w/w) of liquid phase on Chromosorb G AW DMCS (Jones Chromatography, Llanbradach, UK) were prepared by the rotary evaporator technique with dichloromethane as the slurry solvent. The dried, free-flowing powders were then packed into pre-coiled columns with the aid of aspiration and gentle tapping. The all stainless steel system allowed HN_3 to be eluted quantitatively with minimal corrosion problems. The small amounts of impurities and surface corrosion which appeared after extended use were conveniently eliminated by periodically flushing the system out with dilute nitric acid and acetone.

All chemicals and solvents used were purchased in the highest purity available and used without further purification. Ethereal hydrazoic acid was prepared by adding an excess molar amount of finely powdered sodium azide to sulfuric acid in diethyl ether. Samples of these acid–ether solutions were injected as ether solutions through a PTFE-coated silicon septum, with sample sizes ranging from 1 to 100 µl, a range previously shown to be suitable for the elution by characteristic point technique used here.

Since the addition of nitric acid and particularly of uranyl nitrate affect the density of the liquid phase, an important variable in our calculations, we required accurate solution density determinations as a function of temperature. These were made with a Lipkin-type bicapillary pyknometer (5 cm^3). Densities for the TBP–hexadecane systems, calculated from literature values for each component [11,12] (assuming negligible volume change on mixing) agreed favorably with measured values with deviations well within 0.5% in all cases. The experimentally determined change in density of the medium with added uranyl nitrate and nitric acid was well described by the following equation:

$$\rho = 0.9964 - 0.000807 T') \varphi_{TBP}$$
$$+ (0.7878 - 0.000688 T') \varphi_{C16}$$
$$+ (0.0274 - 0.000047 T') M_{HNO_3}$$
$$+ (0.001353 - 8.2 \cdot 10^{-7} T') C_U$$

where ρ = density of the solution in g cm^{-3}, φ =

volume fraction, M_{HNO_3} = molarity of nitric acid, C_U = uranium concentration in g dm^{-3} and T' is temperature in °C. (In our earlier publication [8], the coefficients of T' for TBP and hexadecane were erroneously reported as 0.00807 and 0.00688, respectively.)

3. Results and discussion

In situations where small samples provided adequate peak size for direct measurement, the stoichiometric liquid–gas partition coefficient, K_R, can be evaluated via $K_R = V_N/V_L$, where V_N is the fully corrected net retention volume and V_L is the solvent volume. For skewed peaks, an adequate estimate of V_N is derived, following Littlewood et al. [13] from

$$t_R = t_T + t_F - t_{max} \tag{1}$$

where t_T is the time of intersection of the baseline of a tangent to the leading edge, t_F that for the trailing edge, and t_{max} is the peak maximum retention time. In many of the experiments, the long retention times of the hydracid, and consequent peak broadening, required use of injected sample sizes which exceeded those appropriate to the linear partition isotherm. In these situations, the infinite dilution retention time was estimated by extrapolating to baseline the diffuse side of the elution boundary, which had a common envelope independent of solute concentration, as we have illustrated previously [10]. The vertical, self-sharpening side of the peaks, and common envelope on the diffuse side, when the chromatograms are superimposed, affords an excellent example of a diffuse elution boundary.

We have previously established [9,10] that hydrazoic acid forms a 1:1 complex with TBP and that the infinite dilution partition coefficient for the elution of the acid at infinite dilution (K_R^∞) is related to the concentration of TBP (C_{TBP}^0) via the familiar equation:

$$K_R^\infty = K_R^0[1 + K_1 C_{TBP}^0] \tag{1}$$

where K_R^0 is the infinite dilution partition coefficient for the hydracid in hexadecane alone and K_1 is the stability constant of the complex. The theoretical significance of this equation is detailed elsewhere

[10,14] and only holds for complexes of class A (one of five classes) where only one molecule of additive is involved in each complex and the solute reacts only with the additive and not the solvent or itself [14]. Statistical processing of all of the data obtained [9,10] over the range of conditions (T/K, 298–338; C_{TBP}^0, 0–1.1 mol dm^{-3}) yielded the equation for HN$_3$:

$$K_R^\infty = \exp[(2502/T) - 4.980]$$
$$+ C_{TBP} \exp[(4813/T) - 8.145] \qquad (2)$$

Whence, we see that K_1 ranges between about 100 dm^3 mol^{-1} and 40 dm^3 mol^{-1} over the temperature range cited.

Given this precise information HN$_3$ may be used as a probe in TBP–hexadecane systems containing other possibly complexing species.

The most extensive information on the extraction of mineral acids by TBP relates to nitric acid. Studies of partition between water and TBP–kerosene have established [15,16] that the extracted species is the 1:1 complex HNO$_3$·TBP with only low concentrations of free acid or water in the organic phase. Addition of HNO$_3$ to TBP–hexadecane solutions leads to a linear decrease of the partition coefficient for HN$_3$ (K_R^{exp}) with increasing C_{HNO_3}, as seen in Fig. 1, which illustrates the data of Table 1. The effect diminishes with increasing temperature and is well represented quantitatively by a simple Van 't Hoff equation which, when subtracted from Eq. (2) above provides the general partition equation:

$$K_R^\infty = \exp[(2502/T) - 4.980]$$
$$+ C_{TBP} \exp[(4813/T) - 8.145]$$
$$- C_{HNO_3} \exp[(4837/T) - 8.218] \qquad (3)$$

where C is solution concentration in mol dm^{-3} and T is temperature in K (°C + 273.15) and $\exp = e^x$.

Partition coefficients calculated via Eq. (3) compare extremely favorably with the experimental values, as shown in Table 1. The data plotted in Fig. 1 generally show excellent linearity with correlation coefficients squared (r^2) of 0.995, 0.999, 0.999, 0.999 and 0.981 for 25, 35, 45, 55 and 65°C respectively. The data at 65°C shows a small deviation from linearity with the curve slightly convex upwards and greater than average positive deviations

from predicted partition coefficients as seen in Table 1 perhaps due to competitive complexation beginning to occur at the highest temperature. The precision of triplicate measurements at identical concentrations was excellent with less than 1% RSDs and the accuracy of this chromatographic technique has been evaluated elsewhere with Henry's law constants calculated using this method comparing favorably to conventional techniques with overall less than 3% relative average deviation per measurement [17]. The exponential terms involving TBP and HNO$_3$ are clearly essentially identical; equating these and solving for the ratio C_{TBP}/C_{HNO_3} for each experimental temperature yields values in the range 1.008 (25°C) to 0.998 (65°C). These results agree with those of previous workers in aqueous extraction systems [15,18], that a simple 1:1 complex is formed between HNO$_3$ and TBP and there is little doubt that the reduction in K_R^∞ for HN$_3$ (reduction due to solubility) on addition of HNO$_3$ to the system is thus simply due to loss of TBP available (free) for complexation with HN$_3$ in amount equal to added acid since, with TBP in excess, the concentration of free nitric acid is extremely low. This is made apparent by re-writing Eq. (3), with little approximation, as

$$K_R^\infty = \exp[(2502/T) - 4.980]$$
$$+ [C_{TBP} - C_{HNO_3}] \exp[(4813/T) - 8.145]$$
$$\qquad (4)$$

Partition coefficients for HN$_3$ in TBP–hexadecane solutions containing 0.1 mol dm^{-3} HNO$_3$ and concentrations of uranium ranging from 0 to 0.4 mol dm^{-3} are listed in Table 2 and the linear decrease in the partition coefficient with increasing additive concentration is illustrated in Fig. 2. The data plotted in Fig. 2 showed excellent linearity with correlation coefficients squared (r^2) of 0.999 for all temperatures. The temperature dependence of this decrease is, as before, logarithmic so that an additional term derived from the data can be added to Eq. (4) to give, again, a general equation valid over the range of conditions employed:

$$K_R^\infty = \exp[(2502/T) - 4.980]$$
$$+ [C_{TBP} - C_{HNO_3}] \exp[(4813/T) - 8.145]$$
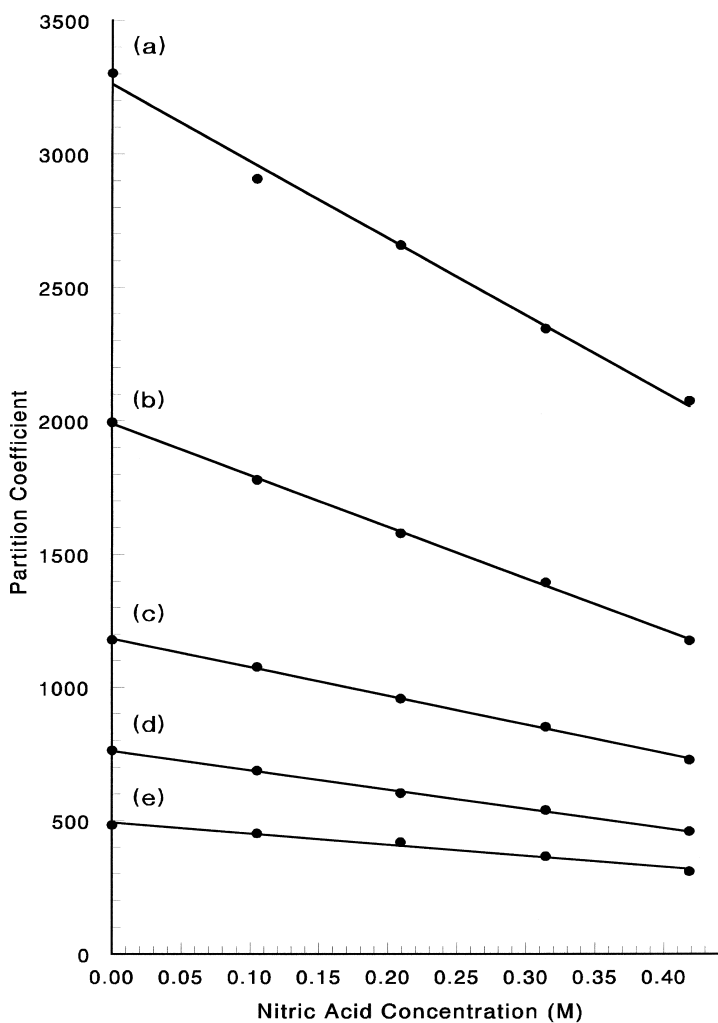$$- C_U \exp[(5236/T) - 8.886] \qquad (5)$$

Fig. 1. Plots of infinite dilution liquid–gas partition coefficients (K_R^∞) for HN_3 eluted from TBP–hexadecane (30:70, v/v)–HNO_3 solutions as a function of HNO_3 concentration for elution at temperatures in the range 298–338 K.

where all of the concentrations are in mol dm^{-3}.

A comparison of the measured partition coefficients with those predicted by Eq. (5) is given in Table 2 and the equation is seen to reproduce the experimental data well.

Equating the appropriate terms in Eq. (5), as before, gives

$$C'_{TBP}/C_U = \exp[(423/T) - 0.741] \qquad (6)$$

where $C'_{TBP} = (C_{TBP} - C_{HNO_3})$ is the concentration of

TBP free to complex with other species. For elution of HN_3 at 25°C this yields $C'_{TBP}/C_U = 1.97$, a very acceptable result since the existence of the $UO_2(NO_3)_2 \cdot 2TBP$ complex in comparable conditions is well documented [19]. The agreement indicates that effects of the activity coefficient of HN_3 due to the added uranyl nitrate are small at 25°C. However, the temperature dependence is such that, over the range of this study, the ratio progressively diminishes to 1.66 at 65°C.

The results for HN_3 elution from TBP–hexade-

Table 1
Comparison of actual and calculated [Eq. (3)] infinite−dilution partition coefficients (K_R^∞) for HN_3 eluted from TBP–hexadecane (30:70, v/v) containing indicated concentrations of HNO_3 (C_{HNO_3})

C_{TBP} (mol dm^{-3})	C_{HNO_3} (mol dm^{-3})	T/K	K_R^{exp}	K_R^{calc} (Eq. (4))	Relative deviation (%)
1.10	0.000	298	3300	3330	−0.91
1.09	0.000	308	1990	1960	+1.51
1.08	0.000	318	1180	1190	−0.85
1.07	0.000	328	763	747	+2.10
1.06	0.000	338	483	482	+0.2
1.10	0.106	298	2910	3010	−3.44
1.09	0.105	308	1780	1770	+0.56
1.08	0.105	318	1080	1080	0.00
1.07	0.104	328	687	676	+1.60
1.06	0.103	338	452	436	+3.54
1.10	0.213	298	2660	2690	−1.13
1.09	0.211	308	1580	1580	0.00
1.08	0.209	318	956	964	−0.84
1.07	0.207	328	602	605	−0.50
1.06	0.205	338	418	391	+6.46
1.10	0.319	298	2350	2370	−0.85
1.09	0.316	308	1390	1400	−0.72
1.08	0.314	318	851	850	+0.12
1.07	0.311	328	538	534	+0.74
1.06	0.308	338	364	345	+5.22
1.10	0.425	298	2070	2050	+0.97
1.09	0.422	308	1170	1210	−3.42
1.08	0.418	318	726	737	−1.52
1.07	0.414	328	458	464	−1.31
1.06	0.411	338	308	300	+2.60

cane–HNO_3 solutions are simply explained in terms of formation of the anticipated 1:1 complex TBP·HNO_3 in the organic phase with consequent corresponding depletion of the TBP available for complexing of the HN_3. This established too that formation of TBP·HN_3 is unaffected by the presence of TBP·HNO_3 and that HN_3 does not interact with this complex. The stoichiometry 2:1 established for the complexing of TBP with $UO_2(NO_3)$·2TBP at 25°C compares well with the results of Healy and McKay [19] for partition of the salt between saturated aqueous $UO_2(NO_3)_2$ and TBP–hydrocarbon solutions in the temperature range 25–50°C. Other workers, however, found that in dilute solution, with 1,2-dichloromethane as organic solvent, in contact with solid $UO_2(NO_3)_2$·$2H_2O$ the stoichiometry corresponded to 1.4 (TBP·$UO_2(NO_3)_2$, which could be indicative of the concurrent existence in the

organic phase of the alternative complexes, 2TBP·$UO_2(NO_3)_2$ and TBP·$UO_2(NO_3)_2$. We believe this to be the explanation of the changes in apparent stoichiometry of the uranium complex found in the study, a view supported by the observation earlier that the changes are accommodated by a single Van 't Hoff expression (Eq. (6)) as would arise where successive stepwise complexing steps were involved. If this is true we conclude that, whereas the 2:1 complex predominates at around 25°C, the 1:1 complex moves into excess around 95°C. In addition, we can now carry out further analysis of the results.

The present results, and previous experience, leave no doubt that the 'free' concentrations of uranyl nitrate and of nitric acid in the organic phase are, with excess TBP, are extremely low. Thus, for convenience in presentation, using the symbolism U for uranyl nitrate, T for TBP and UT and UT_2 for the

Table 2
Comparison of actual and calculated [Eq. (5)] infinite-dilution partition coefficients (K_R^∞) for HN_3 eluted from TBP–hexadecane (30:70, v/v)–HNO_3 (0.1 M) containing indicated concentrations of uranium (C_u)

C_U (mol dm^{-3})	T/K	K_R^{exp}	K_R^{calc} (Eq. (5))	Relative deviation (%)
0.000	298	2910	3010	0.00
0.000	308	1790	1770	+1.12
0.000	318	1080	1080	0.00
0.000	328	687	676	+1.60
0.000	338	452	436	+3.54
0.105	298	2380	2390	−0.42
0.104	308	1430	1420	+0.70
0.103	318	876	876	0.00
0.102	328	562	555	+1.25
0.101	338	386	362	+6.22
0.209	298	1720	1770	−2.91
0.208	308	1050	1080	−2.86
0.206	318	656	674	−2.74
0.204	328	434	434	0.00
0.203	338	302	286	+5.30
0.3 14	298	1160	1150	+0.86
0.311	308	700	732	−4.57
0.309	318	458	472	−3.06
0.307	328	316	312	+1.27
0.304	338	226	212	+6.19
0.418	298	558	539	+3.4 1
0.4 15	308	390	385	+1.28
0.412	318	267	271	−1.50
0.409	328	193	191	+1.04
0.406	338	145	136	+6.21

complexes, we can write the material balance equation

$$[U]_0 = [UT] + [UT_2] \tag{7}$$

$$[T]_0 - [HNO_3] = [T]_0' = [T] + [UT] + 2[UT_2] \tag{8}$$

where the zero subscript designates the initial values. Correspondingly, the apparent stoichiometry S is defined by

$$S = 1 + [UT_2]/[U]_0 \tag{9}$$

Via Eq. (6) we can evaluate S for each experimental temperature and so, via Eq. (9), the relevant value of $[UT_2]$. Eqs. (7) and (8) allow us to calculate the corresponding values of $[UT]$ and $[T]$. Finally, from these values we can calculate values of the quantity

$$K' = [UT_2]/[UT][T] \tag{10}$$

Recognizing that the K' is the stoichiometric stability constant for the equilibrium

$$UT + T \rightleftarrows UT_2$$
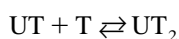
The relevant data are listed in Table 3. The value of K' for 298 K is liable to significant error due to the high value of S and the method of calculation. The other values provide a good linear Van 't Hoff plot of slope corresponding to $\Delta H = -41$ kJ mol^{-1}.

The work presented provides a further example of the utility of the gas chromatographic technique in the study of complexing systems which are difficult to study by conventional techniques. The method is technically straightforward and provides highly accurate data for reactive species over a range of temperature range while requiring only small amounts of the probe material, which need not be particularly pure.
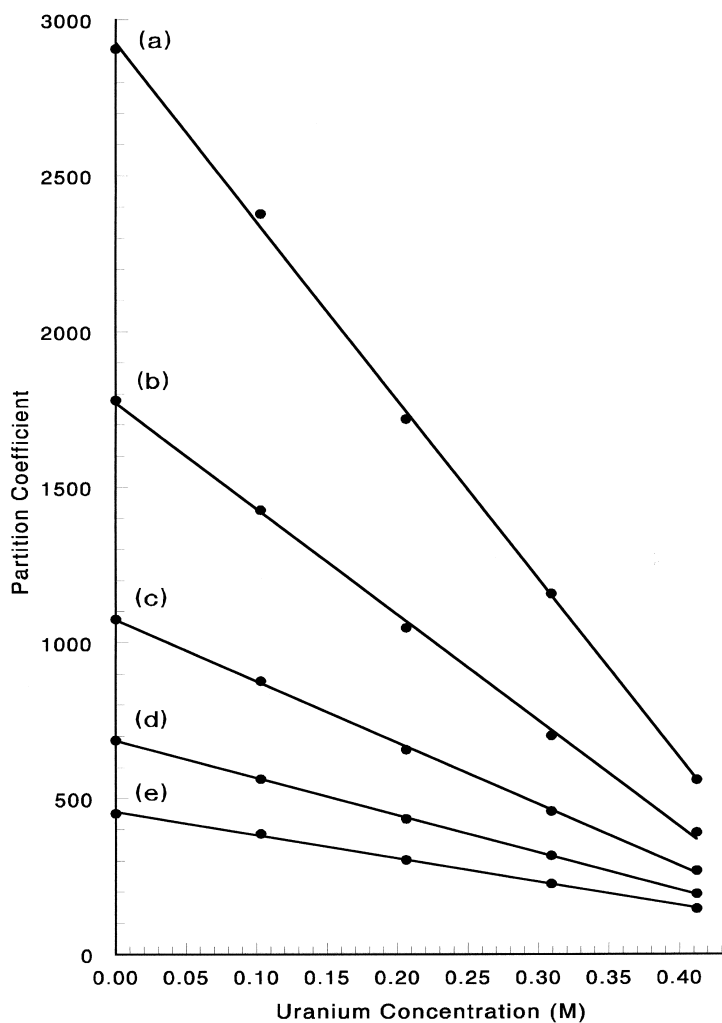
Fig. 2. Plots of infinite dilution liquid–gas partition coefficients (K_R^∞) for HN$_3$ eluted from TBP–hexadecane (30:70, v/v)–HNO$_3$ (0. 1 M)–UO$_2$(NO$_3$)$_2$ solutions as a function of uranyl nitrate concentration for elution at temperatures in the range 298–338 K.

Table 3
Evaluated component concentrations and stability constants[a]

T/K	$[U]_0$	$[T]_0'$	S	$[UT_2]$	$[UT]$	$[T]$	K' (dm^3 mol^{-1})
298	0.418	1.000	1.97	0.405	0.013	0.177	176
308	0.415	0.990	1.88	0.365	0.050	0.210	34.7
318	0.412	0.980	1.80	0.330	0.082	0.229	17.6
328	0.409	0.971	1.73	0.298	0.110	0.265	10.2
338	0.406	0.961	1.66	0.268	0.138	0.287	6.77

[a] All concentrations in mol dm^{-3}.

Acknowledgements

References

[1] B. Johnston, Chem. Ind. 17 (1988) 656.
[2] A.J. Britz, F.L.D. Cloete, Hydrometallurgy 25 (1990) 213.
[3] J.N. Mathur, M.S. Murali, P.R. Natarajan, Waste Manag. 13 (1993) 317.
[4] K.G. Furton, L. Chen, R. Jaffe, Analyt. Chim. Acta 304 (1995) 203.
[5] M. Rajan, V. M Shinde, J. Radioanalyt. Nucl. Chem. 203 (1996) 169.
[6] W.A. Abbasi, M. Streat, Solvent Extr. Ion Exch. 16 (1998) 1303.
[7] A.K. De, S.M. Khopkar, R.A. Chalmers, in: Solvent Extraction of Metals, Van Nostrand, New York, 1970, p. 172.
[8] K.G. Furton, J.H. Purnell, G. Stedman, J. Chromatogr. 468 (1989) 73.
[9] K.G. Furton, J.H. Purnell, G. Stedman, Anal. Proc. 27 (1990) 42.
[10] K.G. Furton, J.H. Purnell, G. Stedman, J. Chem. Soc. Farad. Trans. 86 (1990) 3561.
[11] J.A. Riddick, W.B. Bunger (Eds.), Organic Solvents: Physical Properties and Methods of Purification, Wiley, New York, 1970, p. 323.
[12] E.W. Washburn (Ed.), International Critical Tables of Numerical Data: Physics, Chemistry and Technology, Vol. III, McGraw-Hill, New York, 1928, p. 30.
[13] A.B. Littlewood, C.S.G. Phillips, D.T.J. Price, Chem. Soc. (1955) 1480.
[14] J.R. Conder, C.L. Young, in: Physicochemical Measurement by Gas Chromatography, Wiley, New York, 1979, pp. 222–272, Chapter 6: Complexes.
[15] K. Alcock, S.S. Grimley, T.V. Healy, J. Kennedy, H.A.C. McKay, Trans. Faraday Soc. 52 (1956) 39.
[16] V.V. Fomin, E.P. Maiorova, Neorgan. Kihim. 1 (1956) 1703.
[17] K.G. Furton, J.H. Purnell, G. Stedman, J. Radioanalyt. Nucl. Chem., in press.
[18] W. Davis Jr., Nucl. Sci. Eng. 14 (1962) 162.
[19] T.V. Healy, H.A.C. McKay, Trans. Far. Soc. 52 (1956) 633.