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Thermodynamics of Extraction Equilibria. Part 5.* Correction of the Method for the Determination of Equilibrium Constants of Extraction Processes

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A previously established method for the determination of extraction constants has been verified for extraction processes in which a 1 : 1 solvate is formed. In the case of formation of a higher solvate, the method has to be corrected so that the extraction equilibria are represented in terms of chemical equivalents. Published distribution data on the extraction of nitric acid and uranyl nitrate with tributyl phosphate are used to illustrate the validity of the method.

IN previous Parts [1-4] of this series a method was reported for the determination of thermodynamic extraction constants and its application to various extraction systems. In Part 2 the method was described starting from the general extraction equilibrium (1), where M is

$$M^{z+} + zA^- + nS_{org.} \rightleftharpoons MA_z{\cdot}nS_{org.} \qquad (1)$$

the metal ion, A the anion, S the solvent molecule, and z the positive charge. The subscript org. denotes the organic phase, whereas for the aqueous phase the subscript is omitted. The expression (2) for the thermodynamic equilibrium constant of reaction (1) was

$$K = \frac{a_{MAS(org.)}}{a_M a_A{}^z a^n{}_{S(org.)}} \qquad (2)$$

transformed into (3) where a represents the chemical activity. Charges and solvation numbers are omitted

$$\log \frac{1}{a_M a_A{}^z} = \log K + \log \frac{a^n{}_{S(org.)}}{a_{MAS(org.)}} \qquad (3)$$

from the subscript to simplify the notation. The method is based on the fact that equation (3), when plotted as the function $\log(1/a_M a_A{}^z) = f[a_{MAS(org.)}]$, has an inflexion point at $a^n{}_{S(org.)} = a_{MAS(org.)}$ and reduces to $\log(1/a_M a_A{}^z) = \log K$. It was later found that consideration of the second derivative of equation (3) could lead to ambiguities. Namely, the differentiation of the additional condition, $a^n{}_{S(org.)} = a_{MAS(org.)}$, which has to be fulfilled at one point, is questioned. In order to avoid this problem it was decided to consider equation (3) in another way.

THEORY

For simplicity, equation (3) may be restated in the general form (4). Due to the presence of two unknown variables,

$$y = \log K + \log (z^n/x) \qquad (4)$$

z and x, and their unknown inter-relation, it is not possible to find a condition for an inflexion point if equation (4) is plotted as $y = f(x)$. It is known, however, that in extraction equilibria, if the total concentration of extractant is kept constant, z increases with decreasing x and *vice versa*. Furthermore, in the case of an ideal organic phase, where the activities of the free extractant and solvate approach their concentrations, the relation between z and x can be described by equation (5). Here, the total concen-

$$z + nx = c \qquad (5)$$

tration of extractant, c, is kept constant. Equation (5) can be introduced into (4) to obtain (6).

The second derivative of equation (6), *i.e.* (7), when set

$$y = \log K + \log[(c - nx)^n/x] \qquad (6)$$

$$\frac{d^2y}{dx^2} = -\frac{2.3n^3}{(c - nx)^2} + \frac{2.3}{x^2} \qquad (7)$$

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* Part 4 is ref. 4.

[1] Part 1, Dj. M. Petković, B. A. Kezele, and A. Lj. Ruvarac, in ' Contribution to Co-ordination Chemistry in the Solution,' ed. Erik Högfeldt, Swedish Natural Science Research Council, Stockholm, 1972, p. 435.

[2] Part 2, Dj. M. Petković, A. Lj. Ruvarac, J. M. Konstantinović, and V. K. Trujić, *J.C.S. Dalton*, 1973, 1649.

[3] Part 3, A. Lj. Ruvarac, Z. B. Maksimović, and R. M. Halaši, *J. Radioanalyt. Chem.*, 1974, **21**, 39.

[4] Part 4, Dj. M. Petković and G. J. Laurence, *Bull. Soc. chim. France*, 1975, 949.

equal to zero, is used to determine the value of the quotient on the right-hand side of equation (6) at the inflexion point [equation (8)]. Apparently, the quotient is equal to unity

$$(c - nx)^n/x = x^{n-1}{}_n3^{n/2} \qquad (8)$$

at the inflexion point only if $n = 1$, whereby equation (6) reduces to $y = \log K$. The third derivative of equation (6), for $n = 1$, is not equal to zero for $x = 0.5c$. The validity of the method, when a monosolvate is formed in extraction equilibria, can be also numerically illustrated for different K values and $0 < x < c$.

In real extraction systems the sum of the activities of species in the organic phase is not a constant value. In this case an equilibrium-constant expression, for $n = 1$, has to be written as in (9) where z is a function of x. Although the

$$y = \log K + \log(z/x) \qquad (9)$$

value of the quotient z/x cannot be determined at the inflexion point, one may expect, on the basis of conclusions made from equations (6)—(8), that this quotient could also be equal to unity at the inflexion point. The property of equation (6) for $n = 1$ may be similar to that of equation (9) because the relation between the activities of species in the organic phase has the same trend as that between the concentrations of the same species. This is supported by the treatment of experimental data on the extraction of nitric acid with tributyl phosphate (see below).

In order to extend the validity of the method to the extraction equilibria where $n > 1$, equation (1) must be written in another form giving an equilibrium-constant expression similar to (9). This can be achieved by expressing the chemical equilibria in terms of chemical equivalents. Thus, equation (1) is written as (10). Equations (1) and

$$z(\frac{1}{z}\mathrm{M}^{z+}) + z\mathrm{A}^- + z(\frac{n}{z}\mathrm{S}_{\mathrm{org.}}) \rightleftharpoons z\left[(\frac{1}{z}\mathrm{M})\mathrm{A}\cdot\frac{n}{z}\mathrm{S}\right]_{\mathrm{org.}} \qquad (10)$$

(10) are given for univalent anions and are slightly different in the case of polyvalent anions. The equilibrium constant (11) of reaction (10) may also be written in logarithmic form, (12), in which, however, the numerator and the

$$K = \frac{[a^{\mathrm{E}}{}_{\mathrm{MAS(org.)}}]^z}{(a_{\mathrm{M}}{}^{\mathrm{E}})^z(a_{\mathrm{A}}{}^{\mathrm{E}})^z[a^{\mathrm{E}}{}_{\mathrm{S(org.)}}]^z} \qquad (11)$$

$$\log\frac{1}{a_{\mathrm{M}}{}^{\mathrm{E}}a_{\mathrm{A}}{}^{\mathrm{E}}} = \frac{1}{z}\log K + \log\frac{a^{\mathrm{E}}{}_{\mathrm{S(org.)}}}{a^{\mathrm{E}}{}_{\mathrm{MAS(org.)}}} \qquad (12)$$

denominator of the quotient on the right-hand side have the same power, although $n > 1$. The superscript E denotes activities on the scale of chemical equivalents. It is evident that equation (12) belongs to the general case of (9). As in equation (9), one can expect that equation (12) will be reduced, at the inflexion point, to $\log(1/a_{\mathrm{M}}{}^{\mathrm{E}}a_{\mathrm{A}}{}^{\mathrm{E}}) = \frac{1}{z}\log K$. This is supported by the treatment of distribution data on the extraction of uranyl nitrate with tributyl phosphate (see below).

The value of the equilibrium constant obtained does not change within the range of total concentration of extractant where the stoicheiometry $n = 2$ is valid. Therefore, the distribution data on systems where $n > 1$ may be plotted as (13). However, the values of the activities on the

$$\log(1/a_{\mathrm{M}}{}^{\mathrm{E}}a_{\mathrm{A}}{}^{\mathrm{E}}) = f[a^{\mathrm{E}}{}_{\mathrm{S(org.)}}] = f[a^{\mathrm{E}}{}_{\mathrm{MAS(org.)}}] \qquad (13)$$

chemical-equivalent scale represents another problem. For this purpose one can use the relations between the equivaent and molar activities given by Högfeldt[5] for ion-exchange equilibria. In the case of the extraction processes considered in this work they can be written as in equations (14)—(17). Högfeldt[5] also derived the indentity of the

$$a_{\mathrm{M}}{}^{\mathrm{E}} = a_{\mathrm{M}}{}^{1/z} \qquad (14)$$

$$a_{\mathrm{A}}{}^{\mathrm{E}} = a_{\mathrm{A}} \qquad (15)$$

$$a^{\mathrm{E}}{}_{\mathrm{S(org.)}} = a^{n/z}{}_{\mathrm{S(org.)}} \qquad (16)$$

$$a^{\mathrm{E}}{}_{\mathrm{MAS(org.)}} = a^{1/z}{}_{\mathrm{MAS(org.)}} \qquad (17)$$

equilibrium constants when the molar or equivalent scale is used.

The position of the inflexion point can be localized graphically by calculating values of the gradient, $\Delta y/\Delta x$, of the curve $y = f(x)$ and plotting them against x on the same graph. The value of the abscissa at the minimum which appears is also that of the inflexion point.

RESULTS AND DISCUSSION

Treatment of Experimental Data.—Extraction of nitric acid with tributyl phosphate (*tbp*). The chemical reaction (18) is considered to occur and the corresponding

$$\mathrm{H}^+ + [\mathrm{NO_3}]^- + \mathrm{tbp}_{\mathrm{org.}} \rightleftharpoons \mathrm{HNO_3{\cdot}tbp}_{\mathrm{org.}} \qquad (18)$$

equilibrium-constant expression is the same as equation (2) but with $n = 1$. The standard state of the activities of the species involved in equilibrium (18) is their infinite dilution in the aqueous or in the organic phase, and their concentrations are expressed in mol dm^{-3}. The distribution data[6] have been treated by use of the function $\log(l/a_{\pm}{}^2) = f[c_{\mathrm{hnt(org.)}}]$ and the activities of nitric acid in the aqueous phase have been taken from the literature.[7] The equilibrium constant has been calculated directly from the ordinate of the inflexion point obtained. Figure 1 shows that the value of this constant, $\log K = -0.59$, is independent of the total concentration of

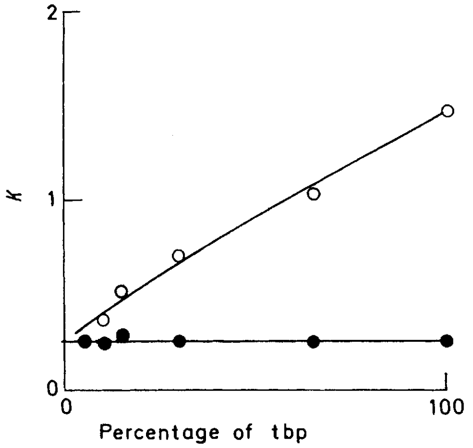

FIGURE 1 Values of equilibrium constant of the extraction of $\mathrm{HNO_3}$ with tbp, calculated by the present method (●) from Davis' data[6] for different concentrations of tbp. The values of Kf_{T} (○), calculated by Davis,[6] are also included

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[5] E. Högfeldt, *Arkiv. Kemi*, 1952, **5**, 147.

[6] W. Davis, jun., *Nuclear Sci. Eng.*, 1962, **14**, 159.

[7] Y. Marcus and A. S. Kertes, 'Ion Exchange and Solvent Extraction of Metal Complexes,' Wiley–Interscience, New York, 1969, pp. 922—926.

tbp, an exceptional case in solvent-extraction chemistry. The value is in very good agreement with that obtained by extrapolation of the product Kf_T, determined by Davis[6] for various tbp concentrations, to infinite dilution of tbp (*cf.* Figure 1, open circles). In the present method, however, only one isotherm of the distribution data is required for the determination of the thermodynamic equilibrium constant, so that the often uncertain extrapolation of the effective constants to infinite dilution can be avoided. The use of stoicheiometric concentrations instead of the activities of the nitric acid solvate in the organic phase leads to the good value of thermodynamic constant. This can be explained provided the total concentration of extractant, $c_{S(tot.)}$, is kept constant throughout. Under these conditions $c_{S(org.)}$ is a function of $c_{MAS(org.)}$ and $a_{S(org.)}$ is also a function of $a_{MAS(org.)}$. Therefore, it is convenient to replace the quotient $a_{S(org.)}/a_{MAS(org.)}$ by the often more accessible concentrations of the species involved.

Extraction of uranyl nitrate with tbp. This has been considered in terms of the chemical reaction (19) and

$$[UO_2]^{2+} + 2[NO_3]^- + 2tbp_{org.} \rightleftharpoons [UO_2][NO_3]_2{\cdot}2tbp \qquad (19)$$

the corresponding equilibrium constant is defined by equation (2) with $n = 2$. The standard state of the activities and the concentration scale of the species involved are the same as in the case of the extraction of HNO_3 with tbp.

Since in this case the numerator and the denominator of the quotient on the right-hand side of equation (3) have not the same power, equilibrium (19) has been expressed in terms of chemical equivalents [equation (20)]. Consequently the equilibrium constant of reaction (20) is represented by the general equation (11).

$$2(\tfrac{1}{2}[UO_2]^{2+}) + 2[NO_3]^- + 2tbp_{org.} \rightleftharpoons 2\{(\tfrac{1}{2}[UO_2])[NO_3]{\cdot}tbp\}_{org.} \qquad (20)$$

Therefore, the distribution data for the $[UO_2][NO_3]_2$–tbp–amsco system[8] have been plotted according to equation (21), derived from equations (13)—(17). The

$$\log(1/a_N a_U^{1/2}) = f[a_{T(org.)}] \qquad (21)$$

activities of $[UO_2][NO_3]_2$ in the aqueous phase have been taken from the literature.[7]

The activity of free tbp has been used because activity-coefficient data for tbp in the system tbp-diluant are more certain than the activity coefficients of the uranyl nitrate solvate in the system $[UO_2][NO_3]_2{\cdot}2tbp$–diluant. The activity coefficients of free tbp, f_T, for the system presented by equation (19), have been calculated according to Ryazanov[9] by graphical integration of equation (22). A similar method for the calculation of activity coefficients was suggested earlier by Högfeldt[5] for ion-exchange equilibria.

The activity coefficients of tbp when $[UO_2][NO_3]_2$ is not present in the organic phase, f_T^0, have been taken from Pushlenkov and Shuvalov[10] and converted from

$$\ln f_T(c_{unt}, c_T^{tot}) = \ln f_T^0(0, c_T^{tot}) - \int_0^{c_{unt}} \ln K_{eff.} dc_{unt} \qquad (22)$$

$$\text{where } K_{eff.} = c_{unt}(org.)/a_U a_N^2 c^2_{T(org.)} \qquad (23)$$

the mol fraction to the molarity scale[11] using the densities of tbp–hexane solutions determined in our laboratory. Hexane has been assumed to simulate the amsco diluant used by Davis *et al.*[8] The standard state of f_T, as calculated from equation (22), is the pure component. It has not been changed to infinite dilution because of very uncertain extrapolation of f_T to zero tbp concentration. Practically, this change in the standard state is not necessary since we require the ordinate of the inflexion point, and the abscissa, $a_{T(org.)}$ can be varied by a constant factor without influencing the value of the ordinate. Figure 2 shows the treatment of Davis' data on 15% tbp by use of function (23) (open circles), and the case in which stoicheiometric concentrations have been used instead of the activities of free tbp (full circles). The same value of the ordinate of the inflexion point is obtained regardless of whether the stoicheiometric concentration or the activity of the free extractant is used.

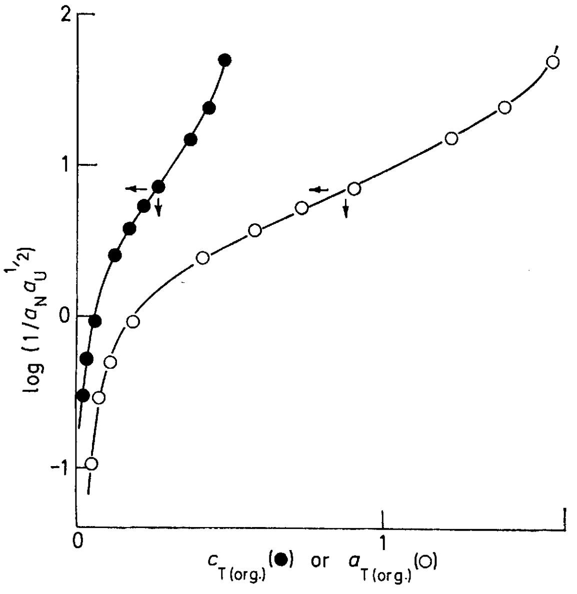

FIGURE 2 Distribution data on the system $[UO_2][NO_3]_2$–15% tbp–amsco as calculated from equation (21), using the stoicheiometric concentrations (●) or the activities (○) of free tbp. The arrows show the positions of the inflexion points

Values of the equilibrium constant of reaction (19), determined from function (21) for different constant total concentrations of tbp, are shown in Figure 3. In addition to Davis' data, unpublished data on the system $[UO_2][NO_3]_2$–tbp–hexane are also included. The value

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[8] W. Davis, jun., J. Mrochek, and R. R. Judkins, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1689.

[9] M. A. Ryazanov, *Zhur. fiz. Khim.*, 1971, **45**, 1812.

[10] M. F. Pushlenkov and O. N. Shuvalov, *Radiokhimiya*, 1963, **5**, 536.

[11] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' Butterworths, London, 1968, p. 32.

of K remains unchanged almost up to 0.3 mol dm^{-3} tbp in the organic phase, while the change in value at higher concentrations of tbp could be due to a change in the stoicheiometry of the uranyl nitrate extraction process. McKay[12] found that the solvation number of $[UO_2][NO_3]_2$ is two when the proportion of tbp in a diluant is <5% (*ca.* 0.2 mol dm^{-3} tbp). Some papers dealing with the nature of the extracted species of $[UO_2][NO_3]_2$ were reviewed by Poczynailo *et al.*[13]

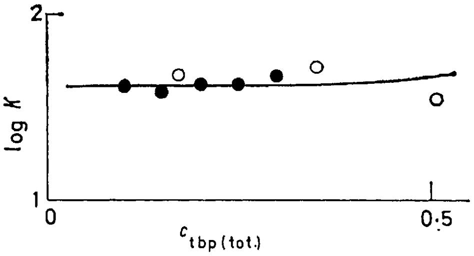

FIGURE 3 Uranyl nitrate extraction constants, determined from equation (21), in hexane (●) and amsco (○) [8]

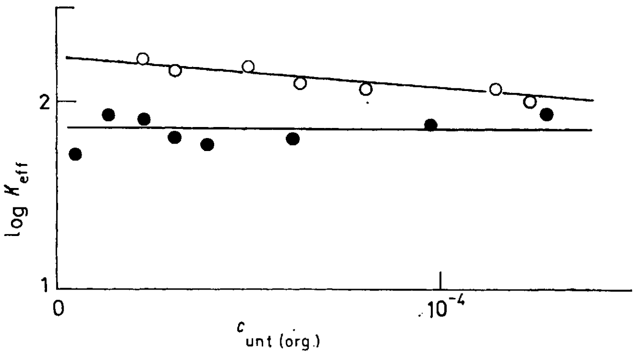

FIGURE 4 Extrapolation of the effective constants, equation (23), to infinite dilution of uranium in the organic phase for 0.05 mol dm^{-3} tbp (●) and 0.10 mol dm^{-3} tbp (○) in hexane

The present value of the constant of the extraction of $[UO_2][NO_3]_2$ with tbp, log K 1.6, differs from that obtained by Marcus,[14] log K 2.25. Marcus evaluated the equilibrium constant of reaction (19) by extrapolating literature values of the product Kf_{T}, determined in paraffin hydrocarbons, to infinite dilution of tbp. An explanation for the difference between these two values can, perhaps, be found by considering the extrapolation of $K_{\text{eff.}}$ values to infinite dilution. According to the present experimental data for a very low loading of the organic phase and for c_{tbp} <0.1 mol dm^{-3} (Figure 4), the extrapolation of $K_{\text{eff.}}$ values to infinite dilution leads to the K value obtained by the method given. It seems that the product Kf_{T} is very sensitive to changes in the total concentration of tbp below 0.1 mol dm^{-3}. This can result from the large changes in the tbp activity coefficients, f_{T}, at low concentrations of tbp.[10]

The data presented in Figures 3 and 4 support the value of the extraction constant obtained by the present method and justify the expression of the distribution data in terms of chemical equivalents. Whereas the value of K is not changed in the region of $c_{\text{tbp(tot.)}}$ up to *ca.* 0.3 mol dm^{-3}, on the other hand the product Kf_{T}, as a function of the total concentration of tbp below 0.1 mol dm^{-3}, approaches the value of K at infinite dilution of tbp.

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[12] H. A. C. McKay, *Proc. Internat. Conf. Peaceful Uses of Atomic Energy*, Geneva, 1955, vol. 7, p. 314.

[13] A. Poczynailo, P. R. Danesi, and G. Scibona, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3249.

[14] Y. Marcus, 'Critical Evaluation of Some Equilibrium Constants Involving Organophosphorus Extractants,' Butterworths, London, 1974, p. 61.