Thermodynamics of Extraction Equilibria. Part 6.* A Further Study of the Method for Determination of Equilibrium Constants of Extraction Processes

Djordje M. Petkovic
Chemical Dynamics Laboratory, The Boris Kidrič Institute of Nuclear Sciences, P.O. Box 522, 11001 Beograd, Yugoslavia

The equilibrium constant (K) expression of the extraction of an inorganic compound (M) from the aqueous phase by an organic solvent (S) forming a solvate ($M{\cdot}nS$), rearranged in the form $-\log a_M = y = \log K + \log a_S{}^n/a_{MS}$ (a = chemical activity of species), has been used to determine K. The method is based on the appearance of an inflexion point in a plot of the experimental data as $y = f(c_{MS})$, where c denotes analytical concentration. The quotient $a_S{}^n/a_{MS}$ at the inflexion point can be substituted by an expression containing the total concentrations of the solvent and the compound extracted.

An inorganic compound (M) is usually extracted from the aqueous phase by an organic solvent (S) forming a solvate ($M{\cdot}nS$) in the organic phase. Such an extraction process is presented by equation (1). In order to simplify the writing of chemical formulae an extra notation of the existence of species in the aqueous or organic phase is avoided; M is always related to the aqueous phase and S and $M{\cdot}nS$ to the organic phase. M is also used to denote ions of an inorganic compound as well as the compound itself; the distinction is unimportant here.

$$M + nS \rightleftharpoons M{\cdot}nS \qquad (1)$$

In Parts 1 and 2 of this series [1,2] the equilibrium constant expression (2), rearranged in the form (3), was the starting point of a method for experimental determination of K. Here a is the chemical activity of the species which are marked with appropriate subscripts (the subscript $M{\cdot}nS$ is simplified to MS). The method is based on the use of an inflexion point in the sigmoid curve, obtained by plotting equation (3) as $y = f(c_{MS})$ where c is the analytical concentration of the various species, to evaluate the quotient $a_S{}^n/a_{MS}$. Not having found a mathematical solution for the quotient at the inflexion point in previous work, it was assumed that $a_S{}^n/a_{MS} = c_S{}^n/c_{MS}$ and mass balance equation (4) could be introduced.[3] Equation (3) then becomes equation (5). The second derivative of equation (5), equalized to zero, shows [3] that the inflexion point exists where $c_S = c_{MS} = \frac{1}{2}c_{S(tot.)}$ when $n = 1$ and the system approaches ideality in the organic phase. Only in this case, equation (5) is reduced to $\ln(1/a_M) = \ln K$ at the inflexion point. In the case when n differs from unity we suggest that the extraction equilibrium (1) is presented in the form of chemical equivalents.[3]

$$K = a_{MS}/a_M a_S{}^n \qquad (2)$$

$$\ln(1/a_M) = y = \ln K + \ln(a_S{}^n/a_{MS}) \qquad (3)$$

$$c_{S(tot.)} = c_S + nc_{MS} \qquad (4)$$

$$\ln(1/a_M) = \ln K + \ln[c_{S(tot.)} - nc_{MS}]^n/c_{MS} \qquad (5)$$

The experimental data on the extraction of nitric acid [4] and uranyl nitrate [5] with tri-n-butyl phosphate, as well as on dissociation of strong acids,[6] have shown that the ordinate values of inflexion points approach the values of equilibrium constants determined by other methods. However, the conclusion drawn from the mathematical treatment of ideal extraction systems and the assumption that it could be extended to real extraction systems [3] was an over-simplification.

In this paper a mathematical procedure using the appearance of an inflexion point to evaluate the quotient $a_S{}^n/a_{MS}$ is reported. Therefore, the previous findings [3] have to be understood as a special case of the general solution of equation (3) given in this work.

Theoretical

The first derivative of equation (3), that is equation (6), contains the expression $d\ln a_S/da_{MS}$ which can be evaluated separately *via* the Gibbs–Duhem equation (7). The application of the Gibbs–Duhem equation to a two-phase extraction system is based on the form of the Gibbs function for a multiphase system.[7,†] Corresponding formulae for a system Σ consisting of several phases are obtained by summation over all the phases, that is $dG^{\Sigma} = \sum_{\alpha}\sum_{i} \mu^{\alpha}{}_i dn^{\alpha}{}_i$, when temperature and pressure are constant. Here, $\sum_i$ denotes summation over the components and $\sum_{\alpha}$ denotes summation over the phases.

$$\frac{dy}{da_{MS}} = n\frac{d\ln a_S}{da_{MS}} - \frac{1}{a_{MS}} \qquad (6)$$

$$c_M d\ln a_M + c_S d\ln a_S + c_{MS} d\ln a_{MS} = 0 \qquad (7)$$

Since $a_M = f(a_{MS})$, $a_S = F(a_{MS})$, and $dy/da_{MS} = -\,d\ln a_M/da_{MS}$, equation (7) gives an expression in the desired form, equation (8). Introducing equation (8) into equation (6) we obtain equation (9) which, with the mass balance equations (4) and (10), leads to equation (11). Here, $c_{S(tot.)}$ is kept

$$\frac{d\ln a_S}{da_{MS}} = \frac{c_M}{c_S}\cdot\frac{dy}{da_{MS}} - \frac{c_{MS}}{c_S}\cdot\frac{1}{a_{MS}} \qquad (8)$$

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* Part 5 is ref. 3.

† According to Lewis and Randal (' Thermodynamics,' revised by K. S. Pitzer and L. Brewer, int. student edn., McGraw-Hill, New York, 1961, p. 218), when two phases in equilibrium are present, for example the two liquid phases obtained by mixing diethyl ether and water, the system resembles a single phase of pure substance.

$$\frac{\mathrm{d}y}{\mathrm{d}a_{\mathrm{MS}}}(nc_{\mathrm{M}} - c_{\mathrm{S}}) = \frac{nc_{\mathrm{MS}} + c_{\mathrm{S}}}{a_{\mathrm{MS}}} \qquad (9)$$

$$c_{\mathrm{M}} + c_{\mathrm{MS}} = c_{\mathrm{M(tot.)}} \qquad (10)$$

$$\frac{\mathrm{d}y}{\mathrm{d}a_{\mathrm{MS}}} = \frac{1}{a_{\mathrm{MS}}} \cdot \frac{c_{\mathrm{S(tot.)}}}{nc_{\mathrm{M(tot.)}} - c_{\mathrm{S(tot.)}}} \qquad (11)$$

constant but the total concentration of the species subjected to the extraction, $c_{\mathrm{M(tot.)}}$, is a variable. Further differentiation leads to the second derivative, equation (12). When it is equalized to zero to fulfil the condition for the inflexion point and rearranged, equation (13) is obtained. Here, the asterisk indicates that these values are obtained from the second derivative expression equalized to zero.

$$\frac{\mathrm{d}^2y}{\mathrm{d}a_{\mathrm{MS}}{}^2} = -\frac{c_{\mathrm{S(tot.)}}}{a_{\mathrm{MS}}{}^2[nc_{\mathrm{M(tot.)}} - c_{\mathrm{S(tot.)}}]} - \frac{nc_{\mathrm{S(tot.)}}}{a_{\mathrm{MS}}[nc_{\mathrm{M(tot.)}} - c_{\mathrm{S(tot.)}}]^2} \cdot \frac{\mathrm{d}c_{\mathrm{M(tot.)}}}{\mathrm{d}a_{\mathrm{MS}}} \qquad (12)$$

$$\mathrm{dln}\, a^{*}_{\mathrm{MS}} = -\frac{n\mathrm{d}c^{*}_{\mathrm{M(tot.)}}}{nc^{*}_{\mathrm{M(tot.)}} - c_{\mathrm{S(tot.)}}} \qquad (13)$$

Following the same pattern as in equations (3)—(13), but differentiating equation (3) with respect to a_{S} and when $a_{\mathrm{MS}} = \mathrm{f}(a_{\mathrm{S}})$, equation (14) is obtained which determines the value of a_{S} at the inflexion point.

$$\mathrm{dln}\, a^{*}_{\mathrm{S}} = -\,\mathrm{dln}\, c^{*}_{\mathrm{M(tot.)}} \qquad (14)$$

Equations (13) and (14) determine, for a given $c_{\mathrm{S(tot.)}}$, a_{MS} and a_{S} values at the inflexion point of a sigmoid curve lying in the space (y, a_{S}, a_{MS}). For different $c_{\mathrm{S(tot.)}}$ values, but for the same extraction system, a family of sigmoid curves is obtained. The inflexion points of the sigmoid curves also form a curve in the same system that allows the integration of equations (13) and (14). By a further rearrangement equation (15) is obtained, where P represents an integration constant.

$$\ln\frac{(a^{*}_{\mathrm{S}})^n}{a^{*}_{\mathrm{MS}}} = \ln\frac{nc^{*}_{\mathrm{M(tot.)}} - c_{\mathrm{S(tot.)}}}{[c^{*}_{\mathrm{M(tot.)}}]^n} + P \qquad (15)$$

Evaluation of the integration constant is based on the assumption that the chemical activities of the species in the organic phase are equal to their stoicheiometric concentrations. Then, the second derivative of equation (5) equalized to zero gives equation (16), derived previously.[3] Together with equation (15), it leads to equation (17). Here, the superscript (id.) denotes the ideal case. Finally, equation (18) is obtained

$$\frac{[a_{\mathrm{S}}^{*(\mathrm{id.})}]^n}{a_{\mathrm{MS}}^{*(\mathrm{id.})}} = \frac{[c_{\mathrm{S}}^{*(\mathrm{id.})}]^n}{c_{\mathrm{MS}}^{*(\mathrm{id.})}} = \frac{[c_{\mathrm{S(tot.)}}]^{n-1}n^{3n/2}}{(n + n^{3/2})^{n-1}} \qquad (16)$$

$$P = \ln\frac{[c_{\mathrm{M(tot.)}}^{*(\mathrm{id.})}]^n[c_{\mathrm{S(tot.)}}]^{n-1}n^{3n/2}}{[nc_{\mathrm{M(tot.)}}^{*(\mathrm{id.})} - c_{\mathrm{S(tot.)}}](n + n^{3/2})^{n-1}} \qquad (17)$$

which expresses the $(a^{*}_{\mathrm{S}})^n/a^{*}_{\mathrm{MS}}$ in terms of the total analytical concentrations of the extractant and species undergoing the extraction process. In practice, the logarithm (base 10) of equation (2) can be taken and the expression for the quotient $(a^{*}_{\mathrm{S}})^n/a^{*}_{\mathrm{MS}}$ introduced from equation (18) to calculate K as $\log K = \log(1/a^{*}_{\mathrm{M}}) - \log[(a^{*}_{\mathrm{S}})^n/a^{*}_{\mathrm{MS}}]$.

$$\frac{(a^{*}_{\mathrm{S}})^n}{a^{*}_{\mathrm{MS}}} = \frac{[nc^{*}_{\mathrm{M(tot.)}} - c_{\mathrm{S(tot.)}}][c_{\mathrm{M(tot.)}}^{*(\mathrm{id.})}]^n}{[nc_{\mathrm{M(tot.)}}^{*(\mathrm{id.})} - c_{\mathrm{S(tot.)}}][c^{*}_{\mathrm{M(tot.)}}]^n} \cdot \frac{[c_{\mathrm{S(tot.)}}]^{n-1}(n^{3n/2})}{(n + n^{3/2})^{n-1}} \qquad (18)$$

$$\frac{(a^{*}_{\mathrm{S}})^n}{a^{*}_{\mathrm{MS}}} = B\,\frac{[c_{\mathrm{S(tot.)}}]^{n-1}(n^{3n/2})}{(n + n^{3/2})^{n-1}} \qquad (19)$$

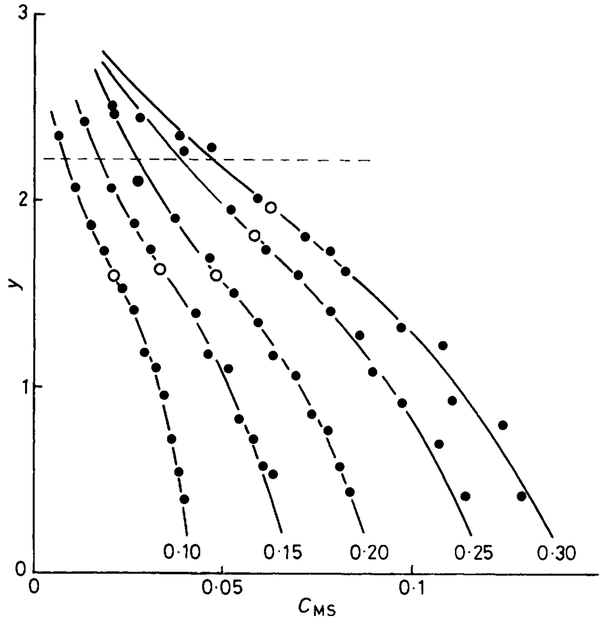

Figure. Distribution data[5] on the extraction of uranyl nitrate with tri-n-butyl phosphate in n-hexane using equation (3). The numbers denote extractant concentrations (mol dm^{-3}), the dashed line the mean value of log K obtained, and open circles represent the positions of inflexion points

The complicated equation (18) can be simplified to the form (19) where the term B is easily recognised from equation (18). It is interesting to note that equation (19) is reduced to $a^{*}_{\mathrm{S}}/a^{*}_{\mathrm{MS}} = B$ for $n = 1$. However, the quotient B can be approximately equated to unity if $c^{*}_{\mathrm{M(tot.)}}$ does not differ much from $c_{\mathrm{M(tot.)}}^{*(\mathrm{id.})}$ and if $c^{*}_{\mathrm{M(tot.)}} \gg c_{\mathrm{S(tot.)}}$.

In practice, the value of the quotient B can be determined without difficulty. $c^{*}_{\mathrm{M(tot.)}}$ is calculated by equation (10), where c^{*}_{M} is taken from the extraction isotherm (c_{MS}, c_{M}) for c^{*}_{MS}, the abscissa value of the inflexion point. $c_{\mathrm{M(tot.)}}^{*(\mathrm{id.})}$ is calculated by equation (10) in the same way but $c_{\mathrm{MS}}^{*(\mathrm{id.})}$ is evaluated by equation (20), obtained from the second derivative of equation (5) equated to zero. The a_{MS} value, needed to plot equation (3) as $y = \mathrm{f}(a_{\mathrm{MS}})$, can be calculated from the experimental data on c_{MS} and c_{M} by means of graphical integration.[8,9] However, it may be avoided by presenting equation (3) as $y = \mathrm{f}(c_{\mathrm{MS}})$ provided that the total concentration of the extractant is maintained constant throughout. Then, c_{S} is a function of c_{MS} and a_{S} is also a function of a_{MS}. Therefore, we may replace a_{MS} by c_{MS}. For the systems previously investigated [4,5] the differences between the ordinate values of the inflexion points obtained by plotting the data as $y = \mathrm{f}(a_{\mathrm{MS}})$ or $y = \mathrm{f}(c_{\mathrm{MS}})$ are within the error in the location of the inflexion point. The a_{M} values, necessary to obtain y, as it is defined in equation (3), are given in the literature.

$$c_{\mathrm{MS}}^{*(\mathrm{id.})} = \frac{c_{\mathrm{S(tot.)}}}{n + n^{3/2}} \qquad (20)$$

Results and Discussion

Starting from experimental data[5] on the extraction of uranyl nitrate with tri-n-butyl phosphate the value of B for five total concentrations of the extractant in the range 0.1—0.3 mol dm^{-3} was calculated. It was found that $B = 1.00 \pm 0.05$ for all extractant concentrations, justifying the substitution of quotient B with unity in equation (19). Naturally, the value of B has to be calculated for every extraction system. The extraction constant was determined, using the same experimental data, according to equations (3) and (19) as $\log K = 2.23 \pm 0.11$. It is in very good agreement with the value 2.25 critically evaluated by Marcus.[10] The lower value, $\log K = 1.65 \pm 0.21$, obtained previously[5] is the consequence of the mathematical treatment of equation (5), where activities of the species in the organic phase are equalized with their concentrations, and the assumption that it can be extended to real extraction systems.

The Figure illustrates a graphical presentation of previous experimental data[5] as $\log (1/a_M) = f(c_{MS})$. The lines are the best fit of the data obtained by the least-squares procedure on the third degree polynomial. The extraction constant values have been calculated using equation (3) where y has been equalized with the ordinate value of the inflexion points and the value of a_S^2/a_{MS} has been evaluated by equation (18) for the corresponding total concentrations of tri-n-butyl phosphate.

I have presented a new approach for evaluation of the thermodynamic extraction constants based on the use of distribution data belonging to the middle parts of the extraction isotherms. In this range, determination of concentrations of different species in the aqueous and organic phase is more certain than in very dilute solutions. The method does not demand any extrapolation of the apparent equilibrium constants to infinite dilution, but the values of thermodynamic extraction constants obtained are only trustworthy if activities, that are available, represent the quantities needed to evaluate y in equation (3). However, it has no influence on the general validity of the method presented in equations (3)—(18).

Acknowledgements

I am indebted to Dr. M. M. Kopecni and Dr. S. K. Milonjic, from the same Laboratory, for careful reading of the manuscript and valuable discussions.

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Received 30th December 1981; *Paper* 1/1989