

Solvent Extraction of Metal Chelates

I. Application of a Titration Procedure to the Study of the Extraction of Metal Chelates

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A two-phase titration procedure for the study of metalchelate equilibria is presented. Equations expressing the relationship between the apparent mean complexity constant in the two-phase system, the mean complexity constant in a water phase and the distribution coefficients of the uncharged species are derived. The pH-value of 50 % extraction of a metal ion is determined with good approximation by this method. The error introduced by the simplified theoretical treatment is discussed and the predictions are confirmed by independent distribution experiments done, employing lanthanum-140 as tracer.

Extraction is among the few separation procedures where in principle the same laws are valid both for macro and tracer concentrations. Its application thus ranges from large scale technical separations to radiochemical work with practically weightless amounts. In recent years extraction procedures have especially been applied for the separation of metals, thus in the reprocessing of spent reactor fuel and in numerous analytical and radiochemical separations.¹⁻⁴

In the reprocessing of spent reactor fuel by extraction, methods based on the extractability of certain mixed complexes of UO_2^{+2} or Pu^{+4} with nitrate ion and organic solvents containing oxygen are presently the most favoured. The advantage of this method is an extraordinary selectivity of the metals which can be extracted.

The extraction and separation, on a technical scale, of actinides from fission products by chelating agents have been performed with thenoyltrifluoroacetone, an extractive agent evaluated by Reid and Calvin^{5,6}. An advantage of this process is that there is no need for a salting-out agent, thus reducing waste disposal problems. A significant disadvantage, however, is that the rate of chelation is slow, which has serious consequences for a large scale countercurrent extraction.

Other chelating agents of possible use for reprocessing have been investigated mostly by Swedish chemists ⁷⁻⁹.

Apart from its possible use in the reprocessing of spent reactor fuels, an extractive chelating agent might possess other valuable properties, *e.g.* as an analytical reagent. It seems well worth to continue the investigations in a systematic manner to gain more insight into the influence of the properties of the molecule on its usefulness as an extractive agent.

The chelating agents, previously investigated, constitute a rather inhomogeneous assembly of chemically very different compounds, and only uncertain predictions can be made as to the improvement of an existing chelating agent in one or other respects by modifying its molecular structure. Therefore it seems interesting to perform an analysis on series of closely related compounds in the expectation that secondary effects of any nature will remain constant or nearly so throughout the series. The comparison of chelates is then expected to give a more clear picture of the trends in extractive behaviour as a function of the constants of the chelating agent, and as far as their magnitudes are influenced by substituents or steric arrangements of the molecules, as a function of those.

In a systematic investigation of a large assembly there is always the need for a rapid and reliable method to estimate the values to be compared. In the study of metal ion extraction by chelating agents rather laborious methods have been used to determine the distribution coefficients. The most favoured ones seem to be photometric and radiometric methods. This paper presents an easy titration procedure for the study of the extraction of metal chelates, and the signification of the measured constants is discussed and related to the extractive behaviour of the chelating agent. The method has been used on some 1-phenyl-3-methyl-4-acyl pyrazolones ^{10,11} and on some O-oxy-azocompounds.

THEORY

The formation of a complex of type MA_q from a metal ion M^{N+} and the anion of a monobasic chelating agent HA is now generally believed to occur stepwise through intermediates of composition



where q is the maximum coordination number of the metalion for the anion A^- . The notation of charge and of coordinated water has been omitted for simplicity.

Assuming the formation of polynuclear complexes, hydrolysis products and competing complexes negligible — an assumption which can be regarded valid in dilute acid solutions of a metalnitrate or metal-perchlorate and a chelating agent — the total concentration C_M of metal in a homogeneous solution can be expressed as

$$C_M = \sum_{i=0}^{i=q} [MA_i] = [M] \sum_{i=0}^{i=q} \beta_i [A]^i \quad (2)$$

where we have introduced the formation constants, K_i , and the complexity products, β_i ^{12,13}, defined as

$$K_i = \frac{[MA_i]}{[A][MA_{i-1}]} \quad (3) \quad \beta_i = K_1 K_2 \cdots K_i \quad (4)$$

$$\beta_0 = 1 \quad (5)$$

Similarly we may express the concentration $[A_b]$ of ligands A bound to metal ions as

$$[A_b] = \sum_{i=0}^{i=q} i [MA_i] = [M] \sum_{i=0}^{i=q} i \beta_i [A]^i \quad (6)$$

The formation function \bar{n} for a system of metal ions and ligands defined as the average number of ligands bound per metal ion present^{12,13} can be expressed as

$$\bar{n} = \frac{[A_b]}{C_M} = \frac{\sum_{i=0}^{i=q} i [MA_i]}{\sum_{i=0}^{i=q} [MA_i]} = \frac{\sum_{i=0}^{i=q} i \beta_i [A]^i}{\sum_{i=0}^{i=q} \beta_i [A]^i}$$

$$= \frac{K_1[A] + 2K_1K_2[A]^2 + \dots + NK_1 \cdots K_N[A]^N + \dots + qK_1 \cdots K_q [A]^q}{1 + K_1[A] + K_1K_2[A]^2 + \dots + K_1 \cdots K_N[A]^N + \dots + K_1 \cdots K_q [A]^q} \quad (7)$$

In a two phase system of equal volumes of the phases, where only the uncharged species MA_N is assumed to be distributed between the organic phase and water with a distribution coefficient λ defined as

$$\lambda = \frac{[MA_N]_{\text{org}}}{[MA_N]} \quad (8)$$

a new formation function \bar{n}_E may be defined

$$\bar{n}_E = \frac{[A_{b,E}]}{C_M} = \frac{K_1[A] + 2K_1K_2[A]^2 + (1+\lambda)NK_1K_2 \cdots K_N[A]^N + \dots}{1 + K_1[A] + K_1K_2[A]^2 + \dots + (1+\lambda)K_1K_2 \cdots K_N[A]^N + \dots} \quad (9)$$

valid for the heterogeneous system, but expressed in variables occurring only in the water phase. The system will now behave as if the formation constant K_N has been multiplied by the factor $(1 + \lambda)$. If, as is often the case for chelates,

$$N = q \quad (10)$$

then the mean complexity constant K_{av} for the two phase system determined by standard procedures¹²⁻¹⁶ will be

$$K_{av} = \sqrt[N]{\beta_N(1 + \lambda)} \quad (11)$$

The spreading factor ^{12,13}, x , which is a measure of chemical effects on the successive formation constants, is defined as

$$\frac{(i+1)(N-i+1)}{i(N-i)} x^2 = \frac{K_i}{K_{i+1}} \quad (12)$$

In a two phase system for $1+i=N$ we get

$$\frac{2N}{N-1} x^2 = \frac{K_{N-1}}{K_N(1+\lambda)} \quad (13)$$

As $(1+\lambda) \gg 1$ for systems of practical interest the spreading factor will be small. This means, according to Bjerrum ^{12,13}, that a plot of \bar{n}_E against $\log [A]$ will be steep at the inflection point, corresponding to almost simultaneous dissociation of the N ligands from the complex; especially so because the formation constants K_1, K_2, \dots, K_N usually do not differ very much ¹⁸.

To determine $K_{av} = \sqrt[N]{\beta_N(1+\lambda)}$, \bar{n}_E must be known as a function of $[A]$.

In a two phase system containing HA and metal salt MX_N it is possible to write the material balance regarding HA in a way that relates the concentration of some species in the organic phase to the actual concentrations of the water phase, simply by dividing by the volume ratio of the phases, thus

$$C_A = [A] + [HA]^{org} + [A_{b,E}] + [HA] \quad (14)$$

In this expression $[A]$ and $[HA]$ are solely contained in the water phase, $[HA]^{org}$ represents the amount HA extracted into the organic phase and $[A_{b,E}]$ represents the sum of intermediary complexes in both phases.

An expression describing the behaviour of the chelating agent in the above system can be obtained from the following equations combined with (14) and (9)

$$K_d = \frac{[HA]^{org}}{[HA]} \quad (15) \qquad K_a = \frac{[H][A]}{[HA]} \quad (16)$$

defining the acid dissociation constant K_a and the distribution coefficient K_d of the chelating agent.

We get

$$K_b = \frac{K_a}{1+K_d} = \frac{[H][A]}{C_A - \bar{n}_E \cdot C_M - [A]} = \frac{[H](C_A - [HA] - [HA]^{org} - [A_{b,E}])}{[HA] + [HA]^{org}} \quad (17)$$

This is an equation from which to determine $[A]$, when $[A_{b,E}]$ or \bar{n}_E is known.

For $[A_{b,E}] = 0$ this equation shows that an acid in a two phase system will behave as if it has an acid dissociation constant K_b , where

$$pK_b = pK_a + \log (1 + K_d) \quad (18)$$

This equation is derived under the assumption that no association or dissociation of HA occur in the organic phase (eqn. 15).

To determine $[A_{b,E}]$ a method proposed by Calvin and Melchior¹⁴ has been further evaluated.

Assuming only uncharged species to be extracted it is possible to express the electroneutrality equation for the water phase during a titration with NaOH by

$$[H] + [Na] + \sum_{i=0}^{i=N} (N-i) [MA_i] = [X] + [A] + [OH] \quad (19)$$

Inserting

$$[X] = N \cdot C_M \quad (20)$$

and eqns (2) and (6) this reduces to

$$[H] + [Na] - [A_{b,E}] - [OH] = [A] \quad (21)$$

From (14) and (21) we obtain

$$C_A = [H] + [Na] + [HA] + [HA]^{org} - [OH] \quad (22)$$

Now assuming C_A constant, $[H]$ constant and therefore $[OH]$ constant we get, by differentiation

$$dC_A = 0 = d[Na] + d([HA] + [HA]^{org}) \quad (23)$$

This represents a relation between the change in $([HA] + [HA]^{org})$ as a function of a change in $[Na]$ during a simultaneous addition of NaOH and MX_N to the system in such a way that pH is kept constant. Integrating between the case where no metal salt has been added and the case where C_M has been added we obtain

$$\begin{aligned} \int_a^b d[Na] &= [Na_2] - [Na_1] = - \int_a^b d([HA] + [HA]^{org}) \\ &= - \int_0^{A_b^M} \frac{d([HA] + [HA]^{org})}{d[A_{b,E}]} d[A_{b,E}] \end{aligned} \quad (24)$$

where the integration limit a corresponds to a point on the titration curve of the chelating agent without metal salt added and b to a point at the same pH on the titration curve obtained with MX_N added in total concentration C_M . It is assumed that no Na-complexes have been formed.

From eqn (17) upon differentiation with respect to $[A_{b,E}]$ we obtain

$$\frac{d([HA] + [HA]^{org})}{d[A_{b,E}]} = - \frac{[H]}{[H] + K_b} \quad (25)$$

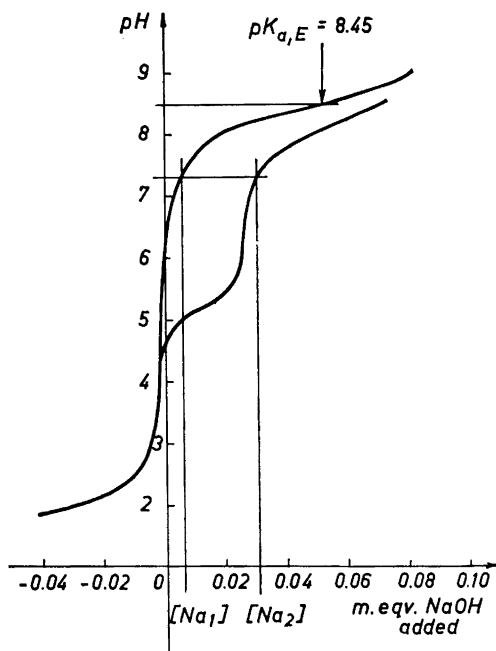


Fig. 1. Titration curve and complex-extraction titration curve for the system TTA, lanthanum ion, chloroform-water.

It is thus possible to integrate eqn (24) for $[H] = \text{constant}$ leading to

$$([Na_2] - [Na_1]) \frac{[H] + K_b}{[H]} = [A_{b,E}] \quad (26)$$

As corresponding values are $[A_{b,E}] = 0$, and $[Na] = [Na_1]$, and $[H]$ and $[OH]$ may be neglected at not extreme pH values, we get

$$[A_{b,E}] = ([Na_2] - [Na_1]) \frac{C_A}{C_A - [Na_1]} \quad (27)$$

$([Na_2] - [Na_1])$ is the difference between the titration curves with and without added metal salt on a line of constant pH. An actual example of a two phase titration is shown in Fig. 1. The values necessary to calculate $[A_{b,E}]$ are indicated.

As a $\log [A]$ versus pH diagram for an acid is linear except at pH values near the pK_a value of the acid, a plot of \bar{n}_E or $[A_{b,E}]$ against pH will have the same form as the formation function except at $pH = pK_a + \log(1 + K_d)$.

At the inflection point $\bar{n}_E = N/2$. Inserting this value into eqn (17) it is possible to calculate the $\log [A]$ value corresponding to the inflection point. This determines $\log K_{av}$ by the relation

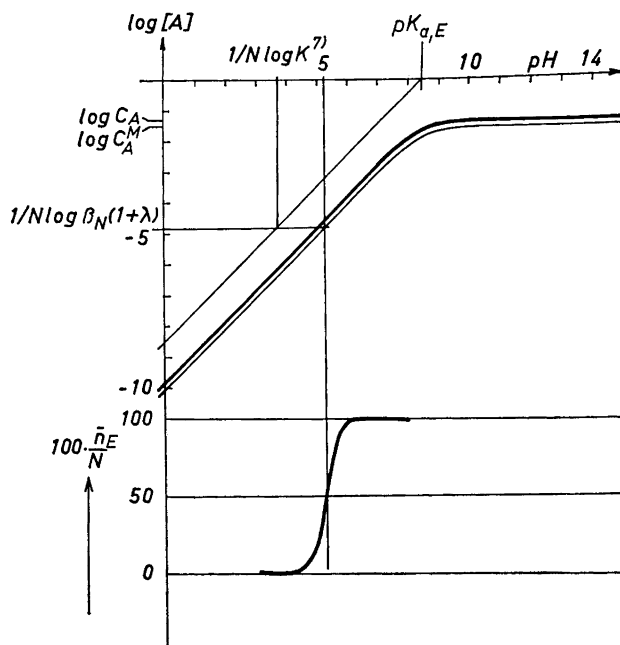


Fig. 2. The percent extraction curve for lanthanum ion in the TTA, chloroform-water system.

$$\log [A'] = -\log K_{av} = -\frac{1}{N} \log \beta_N (1+\lambda) \quad (28)$$

A graphical solution is most convenient and is shown in Fig. 2.

Assuming $\lambda \gg 1$ and $[A]$ not too small, eqn (9) may be approximated to

$$\bar{n}_E = \frac{[MA] + 2[MA_2] + \dots + N[MA_N] + \lambda N[MA_N]}{C_M} \cong \frac{\lambda N[MA_N]}{C_M} \quad (29)$$

Introducing an expression for the per cent metal extracted, % E, as

$$\% E = \frac{[MA_N]^{org}}{C_M} 100 \% \quad (30)$$

and combining it with eqns (8) and (29) we obtain

$$\% E = \frac{\bar{n}_E}{N} 100 \% \quad (31)$$

Eqn (31) shows that a plot of $100 \bar{n}_E/N$ against pH will conform with the per cent extraction curve for $\lambda \gg 1$.

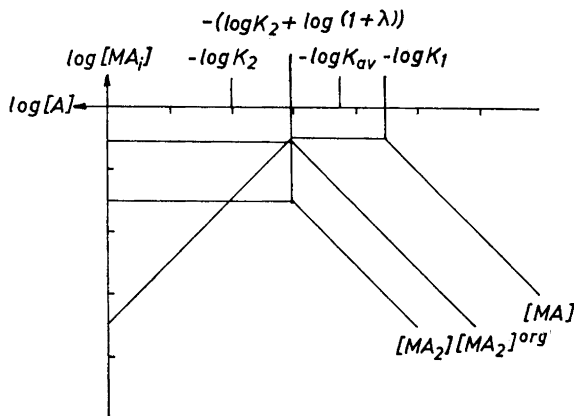


Fig. 3. A logarithmic diagram of metal chelate formation in a two phase system.

The $\log [A]$ versus pH diagram¹⁷ in Fig. 2 is drawn using the experimental pK_b value determined graphically as shown in Fig. 1. $[A_b]$ is calculated by use eqn (27), and % E determined from eqn (31) is then plotted against pH as shown in Fig. 2.

A new $\log [A]$ versus pH diagram is then constructed according to a total concentration $C_A - \bar{n}_E \cdot C_M$, where $\bar{n}_E = N/2$, and the $\log [A']$ value corresponding to % E = 50 % is found graphically. This represents a determination of the mean complexity constant K_{av} by relation (28). This constant is independent of the total concentration of the chelating agent. Assuming $C_A = 1$ and $[A_b]$ negligible, the pH of 50 % extraction of tracer concentrations of metal by a 1 M solution of extractive agent can be found graphically. This constant is equal to $\frac{1}{N} \log K$ defined by Dyrssen⁷ and used by him to compare the chelating agents.

The general case where λ can have any value is better surveyed on a $\log[A] - \log[MA_i]$ ($i = 0, 1, 2, \dots, N$) diagram. For simplicity only the case $N = 2$ will be treated.

Noting the formal analogy between acid dissociation and complex dissociation, Fig. 3 can be constructed. The diagram resembles that of a dibasic acid¹⁷. The species MA_2 , which alone is assumed to be extractable, have to be shared between the two phases with the distribution coefficient λ defined by eqn (8).

If λ is small the inflection point on the actual % E curve will correspond more to the second formation constant K_2 than to the mean complexity constant K_{av} , and accordingly, the inflection point on the actual extraction curve is expected to occur^{12,13} for $\bar{n}_E = 3/2$.

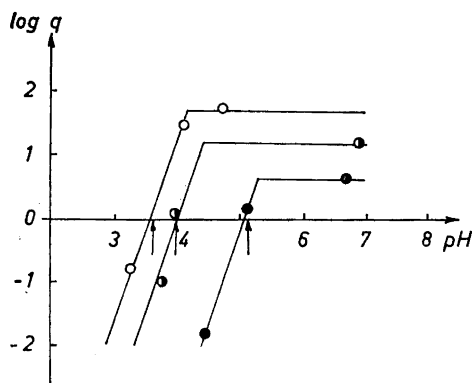


Fig. 4. Distribution data for the lanthanum ion with different chelating agents in chloroform. ○ 1-Phenyl-3-methyl-4-chloroacetyl-pyrazolone-5. ◐ Ethyl ester of 1-phenyl-3-methyl-4-carboxy-pyrazolone-5. ● Thenoyltrifluoroacetone.

If the formation curve $(\bar{n}_E - \log[A])$ has a rather large slope at the inflection point (larger than 0.5) indicating a small spreading factor x (less than 1)^{12,13}, then from eqn (13)

$$\frac{K_1}{K_2(1+\lambda)} < 4 \quad (32) \quad \log K_1 - \log K_2(1+\lambda) < 0.6 \quad (33)$$

$$\log K_{av} = \frac{1}{2} [\log K_1 + \log K_2(1+\lambda)] < 0.3 + \log K_2(1+\lambda) \quad (34)$$

$$\log K_{av} - \log K_2(1+\lambda) < 0.3 \quad (35)$$

Eqn (35) indicates a systematic error in this case less than 0.3 pH units in the determination of the 50 % extraction value by this simple procedure. A correction may be made by the use of the relation between the average spreading factor and the midpoint slope of the formation curve^{12,13}, but if the slope is well above 0.5 a correction should not be necessary, as in this case other errors are expected to dominate.

In the theoretical considerations given above certain approximations have been introduced. Generally they can be assumed to be justified under the specified conditions, but as actual systems deviate more or less from this simplified system, the ultimate precision of the equations obtained is hard to judge from theoretical considerations alone. Therefore as a check of the reliability of the method, some distribution experiments have been performed with ¹⁴⁰La as a tracer and with some chelating agents, to determine the actual pH's of 50 % extraction of La⁺³ to see how they correspond to the values obtained by the titration procedure.

METHODS

Titration procedures. The two phase titrations were made by equilibrating 2 ml of a 0.05 M solution of the chelate in chloroform with 2 ml of a water phase containing varying amounts of 0.1 N NaOH (or 0.1 N HClO₄) and 0.1 M NaClO₄ solution corresponding to different points on the titration curve. A set of 8–12 points were chosen corresponding to increasing amounts of base added, and the whole titration curve was obtained by simultaneous equilibration of the phases. Containers were 6 ml weighing bottles. After shaking to equilibrium — in most cases 10 min were sufficient — the pH of the water phase was measured when in contact with the organic layer.

The complex-extraction titrations were performed in the same manner except that 250 μ l of the 0.1 M NaClO₄ solution was omitted and instead 250 μ l of a ca. 0.05 M metal nitrate or metal perchlorate solution added. In the case of Th⁴⁺ only 100 μ l was added. To be sure that equilibrium had been obtained some points were remeasured after a certain interval of time.

All measurements were performed at room temperature. ($22 \pm 1^\circ\text{C}$).

A Radiometer PHM-22 with a Radiometer glass-electrode type G 202 B and a Radiometer calomel electrode type K 100 with capillary drawn tip was used for the measurements.

Fig. 4 shows an actual set of curves obtained with thenoyltrifluoroacetone and La(NO₃)₃. Fig. 2 shows the plot of % E for the same combination.

Distribution experiments. 15 ml of a 0.05 M solution of the chelating agent in chloroform were shaken to equilibrium in a separatory funnel with 15 ml of a water phase containing varying amounts of NaClO₄ and NaOH at ionic strength 0.1 and tracer amounts of ¹⁴⁰La. (¹⁴⁰La was obtained by 2 h irradiation of 50 mg of La(NO₃)₃ · 6 H₂O in D.R.1, Risø, at a flux of ca. 10^{10} n/sec.cm².) The sample was dissolved in 5 ml of water and 50 μ l of the solution added to the separatory funnel.

The distribution coefficient q of La³⁺ was determined by measuring the γ -activity of 10 ml samples of the centrifuged water and chloroform phases with a conventional γ -counting unit equipped with a well-crystal. The pH of the water phase was measured for each distribution determination. The pH of 50 % extraction of La³⁺ was determined as the point where a curve representing a plot of $\log q$ against pH intersected the line $\log q = 0$ shown in Fig. 4.

CONCLUSION

In Fig. 4 the pH's of 50 % extraction of La³⁺, determined by the titration method is indicated by an arrow. The agreement between the two procedures is thus very good, as is to be expected, as often as the formation function \bar{n}_E shows a large slope at the inflection point.

The present titration procedure is expected to offer an easy method by use of which the possibility of a given separation of metal ions by extraction with a given chelating agent can be checked, and a method by use of which the search for a useful extractive agent for a given separation of metal ions has become less tedious.

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