

# Simplifications in the description of solvent extraction equilibria of complex compounds

F. MACÁŠEK

*Department of Nuclear Chemistry, Faculty of Natural Sciences, Komenský University,  
801 00 Bratislava*

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This study deals with the application of the concepts of total complexity and total ligand numbers to the description of the equilibria of complexes in two-phase systems especially in the liquid—liquid extraction of chelates and associates. Some admissible simplifications of substance balances of complexes, possible corrections and applications to the descriptions of the concentration-dependent distribution and extraction titration are presented. The possibility of characterizing the systems containing stoichiometrically comparable amounts of metal and extracting agent on the basis of the corresponding extraction systems (systems with equal concentration of free ligands and distribution ratio of metal) is discussed. An expression for the maximum yield of metal extraction with respect to the amount of extracting agent is derived: it represents the extraction capacity of a chelate system. Some relationships are illustrated by experimental distribution of  $^{59}\text{Fe}^{3+}$  in the extraction with the solutions of acetylacetone in carbon tetrachloride.

The equilibria, in which stoichiometrically comparable amounts of metal and complex-forming agent are involved, occur in the applications of the extraction of chelates and ion associates to substoichiometric analysis, concentration-dependent distribution, exchange extraction reactions, and extraction titrations [1–3]. Besides a simple extraction reaction characterized by the extraction equilibrium constant [4], the description of the extraction equilibria of chelates at a great excess of extracting agent covers also a stepwise formation of various complexes in the rational form put forward by *Rydberg* [5, 6] and *Dyrssen* and *Sillén* [7]. The ligand numbers, *Bjerrum* functions [8], were used for the characterization of the mean composition of individual phases and the variations in the distribution ratio also by *Irving*, *Rossotti*, and *Williams* [9]. The equilibria in two-phase systems of isomolar series as well as the substance balances were analyzed in more detail for the first time by *Komar* [10]. *Irving* and *Pierce* [11] as well as *Jensen* [12] suggested to use a simplified function of the total ligand number in a two-phase system for substance balances and to consider a stepwise formation of chelates and a distribution of one chelate. *Sillén* [13] elaborated the substance balances in systems containing several polynuclear complexes. The complications arising when more detailed balances, which require the application of computer technique [14–16] are considered, result obviously in the fact that the substance balances of metal and agent are reduced to simpler relationships which are easier applicable. The practically convenient conditions established by *Růžička* and *Starý* [17, 18] for the extraction with substoichiometric amounts of agent are known (they were partially corrected by *Perezhogin* and *Alimarin* [19–21]). On the basis of assumptions of constant complexity in the aqueous phase *Kyrš* [22] formulated the

theory of concentration-dependent distribution. *Spivakov* and *Zolotov* [23] proposed a simplified calculation of the concentration of ligand for the extraction with chelates. We have noticed [24] that certain neglects in the initial balances may result in the inapplicability of the derived relationships. In this paper we are going to present generalizations and a more detailed analysis of the simplifications and corrections for practical use.

## Theoretical

### Substance balances

In order to describe the extraction of complex compounds we shall adopt an initial scheme in a possibly broadest form. We shall consider the equilibrium constants at a constant ionic strength and constant concentration of competing ligands [5].

Let a chelating agent be an amphoteric or dibasic acid. Its ionic forms (*e.g.*  $A^-$  and  $H_2A^+$ ) are able to form the associates with minor ions which serve *e.g.* for the preservation of ionic strength and pH. The distribution of these ion pairs may be described by apparent partition coefficients [2]. The substance balance of agent including the forms  $A$ ,  $HA$ , and  $H_2A$  in both phases assumes the form

$$[A]V + [A]_{org}V_{org} + [HA]V + [HA]_{org}V_{org} + [H_2A]V + [H_2A]_{org}V_{org} = \pi[A]V. \quad (1)$$

Thus the function

$$\pi = 1 + P'_A \epsilon + (1 + P_{HA} \epsilon) K_{HA}^{-1} [H] + (1 + P_{H_2A} \epsilon) K_{HA}^{-1} K_{H_2A}^{-1} [H]^2 \quad (2)$$

gives the ratio of analytical concentration of all forms of the free agent (unbound to central atom) to the concentration of the anionic form  $A$  in the aqueous phase. Furthermore, the agent and another possible ligand  $B$  (hydroxyl, water, masking agent, *etc.*) form with extracted metal the complexes



(further relationships can be generalized for arbitrary number of other ligands) which may be distributed between the aqueous and the organic phase. Hence, the balance of agent will assume the form

$$c_A V'_{org} = \pi[A]V + \sum_{mij} i ([M_m A_i B_j]V + [M_m A_i B_j]_{org} V_{org}), \quad (3)$$

the balance of metal will be

$$c_M V' = \sum_{mij} m ([M_m A_i B_j]V + [M_m A_i B_j]_{org} V_{org}). \quad (4)$$

If we use the stability constants and partition coefficients, we obtain

$$c_A \epsilon_0 = \sigma \pi [A] + \sigma [M] \sum_{mij} i \beta_{mij} (1 + P_{mij} \epsilon) [M]^{m-1} [A]^i [B]^j, \quad (5)$$

$$c_M = \sigma [M] \sum_{mij} m \beta_{mij} (1 + P_{mij} \epsilon) [M]^{m-1} [A]^i [B]^j. \quad (6)$$

The complexity of the element  $M$  in individual phases may be expressed as the ratio of the total analytical concentration of the element in a given phase to the concentration of the simple ionic form  $M^{z+}$  in the aqueous phase, *i.e.*

$$X = \sum_{m=1} \sum_{i=0} \sum_{j=0} \beta_{mij} [M]^{m-1} [A]^i [B]^j, \quad (7)$$

$$X_{\text{org}} = \sum_{m=1} \sum_{i=0} \sum_{j=0} \beta_{mij} P_{mij} [M]^{m-1} [A]^i [B]^j. \quad (8)$$

Analogously, the total complexity in a two-phase system may be defined as the ratio of the total analytical concentration of the metal in the system to the concentration of the simple ionic form in the aqueous phase, *i.e.*

$$X_t = \sum_{m=1} \sum_{i=0} \sum_{j=0} \beta_{mij} (1 + P_{mij} \varepsilon) [M]^{m-1} [A]^i [B]^j. \quad (9)$$

As the ligand numbers in individual phases with respect to the ligand A are in general

$$\bar{n} = \frac{\sum_{m=1} \sum_{i=1} \sum_{j=0} i \beta_{mij} [M]^{m-1} [A]^i [B]^j}{X} = \frac{\partial \log X}{\partial \log [A]}, \quad (10)$$

$$\bar{n}_{\text{org}} = \frac{\sum_{m=1} \sum_{i=1} \sum_{j=0} i \beta_{mij} P_{mij} [M]^{m-1} [A]^i [B]^j}{X_{\text{org}}} = \frac{\partial \log X_{\text{org}}}{\partial \log [A]}, \quad (11)$$

the total ligand number in whole system will be

$$\bar{n}_t = \frac{\sum_{m=1} \sum_{i=1} \sum_{j=0} i \beta_{mij} (1 + P_{mij} \varepsilon) [M]^{m-1} [A]^i [B]^j}{X_t} = \frac{\partial \log X_t}{\partial \log [A]}, \quad (12)$$

and analogously *e.g.*  $\bar{p}$ ,  $\bar{p}_{\text{org}}$ , and  $\bar{p}_t$  for the ligand B.

Analogous functions expressed for the central atom will signify the mean degree of polymerization, *e.g.*

$$\bar{m} = \frac{\sum_{m=1} \sum_{i=0} \sum_{j=0} (m-1) \beta_{mij} [M]^{m-1} [A]^i [B]^j}{X} = \frac{\partial \log X}{\partial \log [M]} \quad (13)$$

and

$$\bar{m}_{\text{org}} = \frac{\partial \log X_{\text{org}}}{\partial \log [M]}, \quad \bar{m}_t = \frac{\partial \log X_t}{\partial \log [M]}$$

similarly as in (11) and (12).

Using these expressions we may write the balances (5) and (6) in the following form

$$c_A \varepsilon_0 = \pi [A] \sigma + \frac{\bar{n}_t}{1 + \bar{m}_t} c_M. \quad (14)$$

Further relationships may be obtained from the balance of protons [15] but now it is not necessary to analyze them.

The distribution ratio of metal

$$D = \frac{\sum_{mij} m [M_m A_i B_j]_{\text{org}}}{\sum_{mij} m [M_m A_i B_j]} \quad (15)$$

may be expressed in conformity with the preceding in the form

$$D = \frac{X_{\text{org}}}{X} \frac{1 + \bar{m}_{\text{org}}}{1 + \bar{m}} \quad (16)$$

The universal relationship

$$X_t = X + \varepsilon X_{\text{org}} = X \left( 1 + \varepsilon D \frac{1 + \bar{m}}{1 + \bar{m}_{\text{org}}} \right) \quad (17)$$

may be derived from equations (7–9) and (16). The expression allows to analyze two-phase systems formally in the same way as one-phase systems.

As the possibility of using the simplified forms of the above balances may hardly be assumed for the formation of polynuclear complexes (as known from one-phase systems), we are going to deal exclusively with their application to the systems of mononuclear complexes ( $m = 1$ ,  $\bar{m}$  and  $\bar{m}_{\text{org}} \equiv 0$ ).

### *Expressing of total ligand numbers*

By taking the logarithm of (17) and differentiating it we obtain by means of (10) and (12) for the systems of mononuclear complexes

$$\bar{n}_t = \bar{n} + \frac{\varepsilon D}{1 + \varepsilon D} \frac{\partial \log D}{\partial \log [A]} \quad (18)$$

As known [5, 9], it follows from (10), (11), and (15) that  $\partial \log D / \partial \log [A] = \bar{n}_{\text{org}} - \bar{n}$ . This relation allows to write the subsequent simple expression

$$\bar{n}_t = \bar{n}_{\text{org}} R + \bar{n}(1 - R) \quad (19)$$

instead of (18). The expression is exactly valid for the systems of mononuclear complexes. Provided a single complex  $\text{MA}_n\text{B}_p$  is considered and extracted in maximum yield  $R_{\text{max}} = \varepsilon P_{np} / (1 + \varepsilon P_{np})$  it will be

$$\bar{n}_t = \frac{nR}{R_{\text{max}}} \quad (20)$$

The papers of *Perezhogin* [19–21] are based on the simplification of this type which gives at  $R_{\text{max}} \doteq 1$  as a maximum simplification for  $\bar{n}_t$  (in conformity with *Jensen* [12])

$$\bar{n}_t \doteq nR \quad (21)$$

In this case it is, however, more convenient to calculate  $\bar{n}_t$  from the relationship  $\bar{n}_t \doteq n(1 - 1/D)$ .

The simplifications (20) and (21) may be used if the ratio

$$k = \frac{\bar{n}}{n\varepsilon D} \quad (22)$$

is close to zero (the distribution ratio  $D$  has to be of  $10^2$  order of magnitude). This fact necessitates the verification of the last condition of the neglect of chelates in the aqueous phase when dealing with systems with *a priori* low distribution ratios (low  $P_{np}$

or substoichiometric region). In particular, the condition (22) need not be fulfilled mainly in the systems of complexes with a large spread factor of consecutive stability constants ( $K_i \gg K_{i+1}$ ) and low complexity with respect to competing ligands and a considerable part of agent may be bonded to lower and non-extractable complexes. Provided the values of consecutive constants are not known except the parameter of the mean stability constant  $a$ , the condition  $k \ll 1$  may be examined in the form

$$(n-i)pA \leq \log \left( \frac{n\epsilon P_{i0}}{i} \right) + (n-i)a + i(n-i)b + \log k, \quad (23)$$

where the value  $pA$  corresponds to a given distribution ratio,  $i$  may be selected according to the assumed composition of the aqueous phase and the spread factor  $b$  is of minimum statistical probability [8].

### Concentration-dependent distribution

Let us consider how the distribution ratio varies in a system with constant amount of agent at a constant pH and a concentration of competing ligands if the system with negligible amount of extracted metal turns to a system with macroamount  $G_M$ . This case is of practical importance in the method of the concentration-dependent distribution [22] as well as of extraction titrations [3]. The quantities  $D$  and  $X$  in the system with  $G_M \rightarrow 0$  will be denoted with index 0.

Provided no polynuclear complexes ( $m = 1$ ) arise, we shall obtain on the basis of (7), (8), and (15)

$$\frac{D}{D_0} = \frac{X_{\text{org}}}{(X_{\text{org}})_0} \frac{X_0}{X}. \quad (24)$$

If we express the changes in complexity by means of the first terms of Taylor series or Lagrange formula as

$$\log X_0 = \log X + \frac{\partial \log X}{\partial \log [A]} (\log [A]_0 - \log [A]) \quad (25)$$

we obtain with respect to (10)

$$\log X_0 - \log X = \bar{n} (\log [A]_0 - \log [A]). \quad (26)$$

From (14) it is obvious that

$$[A]_0 = \frac{c_A \epsilon_0}{\pi \sigma}. \quad (27)$$

Analogously, from the change in  $X_{\text{org}}$  according to (8) and (11) we obtain from (24)

$$\log D = \log D_0 + (\bar{n}_{\text{org}} - \bar{n}) \log \left( 1 - \frac{\eta \bar{n}_t}{n} \right). \quad (28)$$

If this relationship is transformed to the form

$$\left[ 1 - \left( \frac{D}{D_0} \right)^{\frac{1}{\bar{n}_{\text{org}} - \bar{n}}} \right] \frac{1 + \epsilon D}{\bar{n} + \bar{n}_{\text{org}} \epsilon D} = \frac{G_M}{G_A} \quad (29)$$

the equation derived by *Kyrš* [22] ensues from it as a special case for  $\bar{n} = 0$  and  $\bar{n}_{\text{org}} = n$ . It is, however, obvious that no simplifications except  $\bar{n} = \text{const}$  and  $\bar{n}_{\text{org}} = 0$  (choice of pH of the extraction or other conditions) have been applied. From the point of view of the sensitivity of the method of the concentration-dependent distribution the value

$$\frac{\partial \log D}{\partial \log \eta} = \frac{R(\bar{n}_{\text{org}} - \bar{n}) + \bar{n}}{R[1 - (n - \bar{n})(1 - R)] + \left(\bar{n} - \frac{n}{\eta}\right) / (\bar{n}_{\text{org}} - \bar{n})} \quad (30)$$

is of importance ( $n$  is an arbitrary stoichiometric coefficient in the ratio  $\eta$ ). This value shows for  $\bar{n}_{\text{org}} = n$  that the region of applicability of that method, practically defined as  $d \log D / d \log \eta \leq -0.5$  for  $R \rightarrow 1$  [22], begins with the value of the ratio

$$\eta \geq [2(n - \bar{n}) + 1]^{-1} \quad (31)$$

what indicates that the sensitivity of method decreases with increasing  $\bar{n}$  up to the stoichiometric ratio  $\eta = 1$ . It means practically that the method is suited for the use at such composition of the aqueous phase where no chelation with agent is observed (sufficient masking).

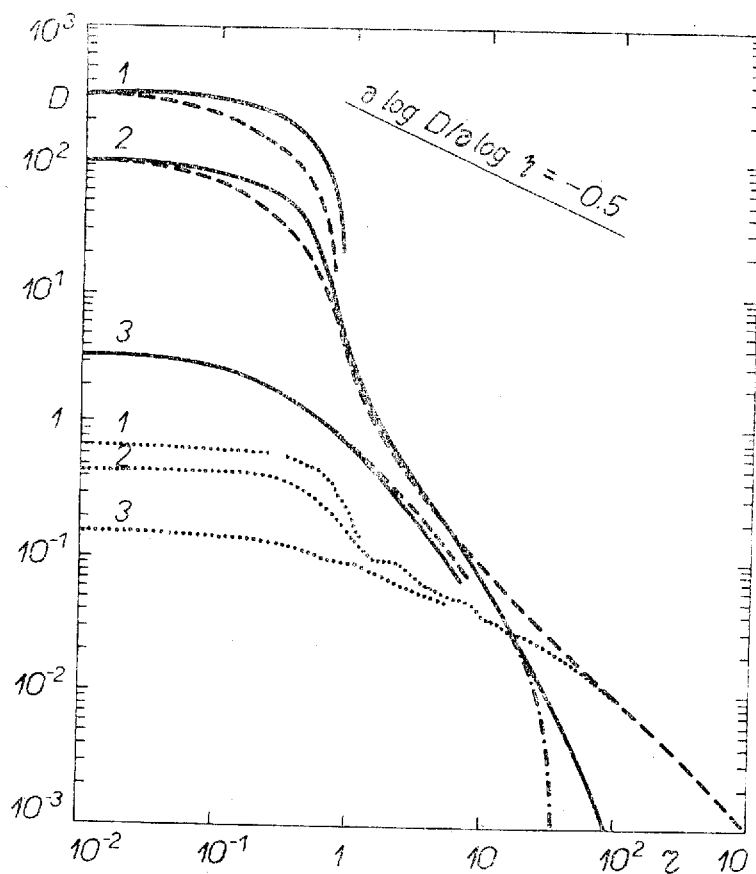
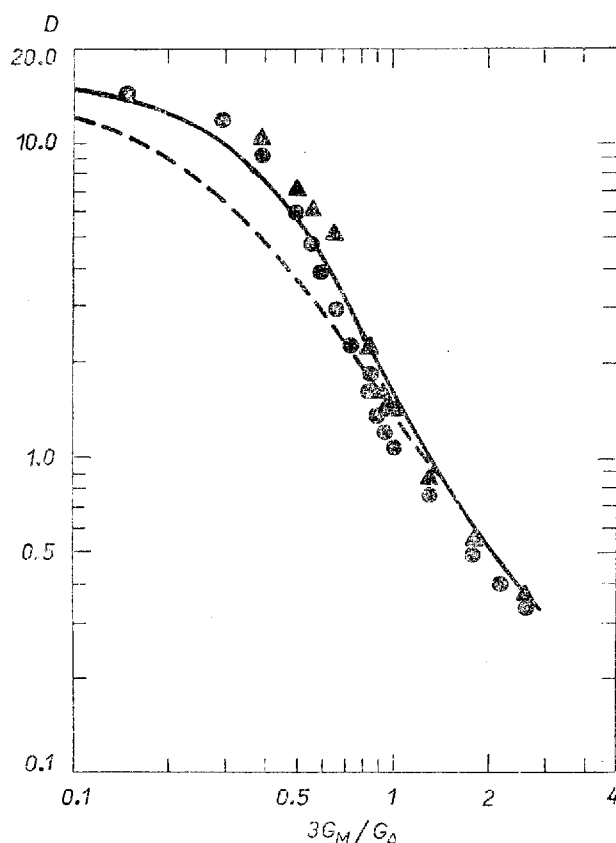


Fig. 1. Theoretical curves of concentration-dependent distribution of the chelate  $\text{MA}_3$  ( $P_{30} = 10^3$ ;  $\beta_{30} = 10^{12}$ ;  $a = 4$ ). — substance balance with stepwise chelation ( $b = 0.25$ ); - - - neglect of lower chelates ( $b = -3$ ); - . - . - correction  $\bar{n} = 0.03$ ; ..... ratio  $\bar{n}/n$  for "total" balance ( $b = 0.25$ ).  
 $\pi/G_A$ : 1.  $4.63 \times 10^3$ ; 2.  $1.17 \times 10^4$ ; 3.  $5.60 \times 10^5$ .

Fig. 2. Concentration-dependent distribution of  $\text{Fe}^{3+}$  in a system acetate buffer solution (pH 4.0)—0.01 M acetylacetone in  $\text{CCl}_4$ . ● Distribution found radiometrically; ▲ distribution found spectrophotometrically; ——— curve calculated on the basis of constants from literature [1, 25] (for acetylacetone  $\beta_{10} = 1.86 \times 10^9$ ,  $\beta_{20} = 9.54 \times 10^{17}$ ,  $\beta_{30} = 7.36 \times 10^{23}$ ;  $P_{30} = 10^3$ ; for  $\text{OH}^-$   $\beta_{01} = 1.82 \times 10^{11}$ ,  $\beta_{02} = 9.22 \times 10^{21}$ ; — — — the same according to (29) for  $\bar{n} = 0$ .



These considerations may be illustrated by a theoretical distribution of the chelate  $\text{MA}_3$  with total substance balance of all complex forms and under neglect of  $\bar{n}$  for different values of  $D_0$  determined by the concentration  $c_A$  and pH, i.e. by the ratio  $\pi/G_A$  (Fig. 1). The distribution of the tris(acetylacetonato)iron(III) chelate found experimentally (Fig. 2) also confirms and illustrates the established relations.

*Calculation of the equilibrium concentration of a chelating ligand  
in systems with macroamount of metal*

For the systems with mononuclear complexes equation (14) may be written in the form

$$\sum_{i=0}^{n+1} \sum_{j=0} \{ \sigma \pi \gamma_{i-1,j} + \gamma_{ij} (ic_M - c_A \epsilon_0) \} [A]^i = 0, \quad (32)$$

where

$$\gamma_{ij} = \beta_{ij} [B]^j (1 + P_{ij} \epsilon) \quad (33)$$

and  $\gamma_{kj} = 0$  if  $0 > k > n$ . Anyway, the solution of this equation is tedious and practically purposeless. If  $[A]$  is to be calculated for the extractions with the solutions of chelate  $\text{MA}_n$  [23, 24] in which only non-extractable complexes  $\text{MB}_j$  arise (complexity  $X_B$ ), equation (32) is reduced under the similar conditions to

$$[A] = \{ c_A \epsilon_0 X_B / \sigma \pi \beta_{n0} (1 + P_{n0} \epsilon) \}^{\frac{1}{n+1}} \quad (34)$$

the applicability of which is not limited by the values of pH in contrast to the equation in paper [24]. Obviously, the effect of  $\bar{n}$  according to equation (14) can manifest itself

by an increased value of  $[A]$  calculated by relation (34) and may be eliminated merely by iteration provided  $\bar{n}$  is known as a function of  $pA$ .

### Corresponding extraction systems

The distribution ratio of metal in extraction systems in which no polynuclear complexes are formed is only a function of the equilibrium concentrations of ligands according to (16). The extraction systems with different concentrations of metal and equal concentrations of free ligands which must therefore show an equal distribution ratio of metal may be called the corresponding extraction systems in analogy with one-phase systems [8]. Since we do not know  $D$  as an explicit function of the concentrations  $c_A$ ,  $c_M$ , and  $pH$  or other components, it is possible to use the corresponding systems for finding out some parameters (ligand numbers, concentrations of free ligands). A system containing a negligibly small amount of metal in comparison with agent will be called shortly a microconcentration system. In such a system it is possible to calculate for instance  $[A]$  according to (27). In accordance with (30), we may consider such an amount of metal to be negligibly small which corresponds to a certain tolerable value of the change in distribution ratio if the concentration of metal increases, *e.g.*  $d \log D / d \log \eta < -0.1$ , that means

$$c_M < 0.1 c_{A\epsilon_0} / n^2. \quad (35)$$

This condition is fulfilled *e.g.* by a radioactive tracer with the molar activity exceeding  $10^{12} \text{ s}^{-1} \text{ mol}^{-1}$  (*ca.*  $30 \text{ Ci mol}^{-1}$ ) even at  $10^{-6} \text{ M}$  concentrations of agent provided other complex-forming elements are not present in comparable concentrations.

If the distribution ratio of metal in a microconcentration system has been determined, it is possible under certain assumptions to find the conditions of equal distribution of the macroamount of element (macroconcentration corresponding system).

For the corresponding systems of mononuclear complexes the subsequent expression follows from (14) at a constant  $pH$  of the aqueous phase

$$d(c_{A\epsilon_0}) = \bar{n}_t dc_M, \quad (36)$$

*i.e.* the system with concentrations  $(c_A)_1$  and  $(c_M)_1$  will correspond to the system with concentrations  $(c_A)_2$  and  $(c_M)_2$  provided that

$$(c_{A\epsilon_0})_2 - (c_{A\epsilon_0})_1 = \bar{n}_t [(c_M)_2 - (c_M)_1]. \quad (37)$$

This equation cannot be used *e.g.* for the calculation of the concentration of agent convenient for the extraction of a certain amount of metal without any simplifying estimate of  $\bar{n}_t$  (see above). But it enables us to calculate  $\bar{n}_t$  if the corresponding extraction systems have been found (Fig. 3, Table 1) or to calculate  $[A]$

$$[A] = \frac{1}{\sigma\pi} \frac{(c_{A\epsilon_0})_1 (c_M)_2 - (c_{A\epsilon_0})_2 (c_M)_1}{(c_M)_2 - (c_M)_1} \quad (38)$$

regardless of the formation of hydroxo or mixed complexes.

At a constant concentration of the extracting agent the condition of the corresponding systems

$$[A]d(\sigma\pi) + c_M d\bar{n}_t + \bar{n}_t dc_M = 0 \quad (39)$$

may be applied if  $\bar{n}_t$  is constant at a given concentration of  $[A]$  (negligible formation of hydroxo complexes, competing ligands are strong bases). The required increase of  $pH$



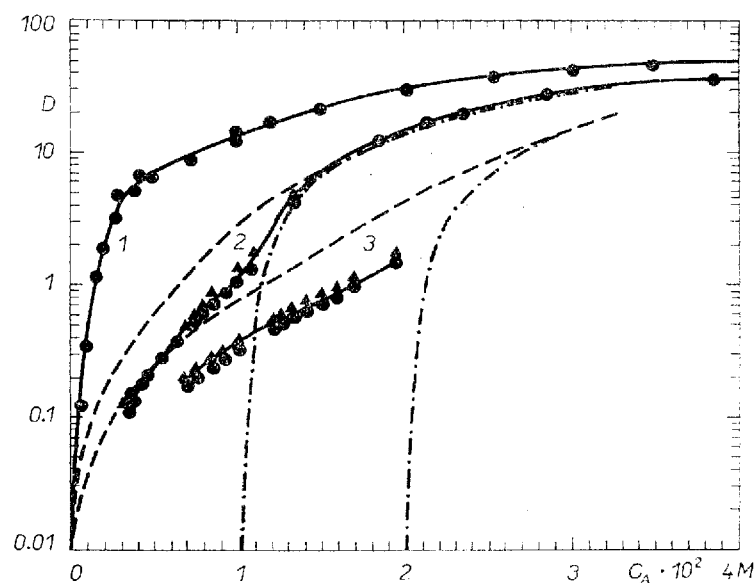


Fig. 3. Extraction of  $\text{Fe}^{3+}$  with the solutions of acetylacetone in carbon tetrachloride at constant pH 4.0 ( $\epsilon_0 = 1$ ). 1.  $c_M = 1.94 \times 10^{-4} \text{ M}$ ; 2.  $c_M = 3.39 \times 10^{-3} \text{ M}$ ; 3.  $c_M = 6.79 \times 10^{-3} \text{ M}$ . — — — system corresponding to curve 1 for  $\bar{n}_t = 3R$  ( $\bar{n} = 0$ ); — . — . — the same for the maximum possible  $\bar{n}_t = 3$ .

in a macroconcentration system (the pH of which is expressed by the value of  $\pi$ ) with respect to the corresponding macroconcentration system (the pH of which corresponds to  $\pi_0$ ) follows from (39) and is given by subsequent relation

$$\pi = \pi_0 \left( 1 - \frac{\eta \bar{n}_t}{n} \right) \quad (40)$$

or

$$\log \pi = \log \pi_0 + \log \left( 1 - \frac{\eta \bar{n}_t}{n} \right). \quad (41)$$

Table 1

Values of  $\bar{n}_t$  and  $\bar{n}$  in corresponding systems at constant pH (curves in Fig. 3) calculated according to equations (37) and (19)

$D$	$\bar{n}_t = 3R$ ( $\bar{n} = 0$ )	For curves 1 and 2		For curves 1 and 3	
		$\bar{n}_t$	$\bar{n}$	$\bar{n}_t$	$\bar{n}$
0.20	0.50	1.07	0.68	0.97	0.57
0.30	0.69	1.36	0.87	1.24	0.71
0.40	0.86	1.63	1.08	1.48	0.87
0.50	1.00	1.81	1.21	1.63	0.94
0.80	1.33	2.20	1.55	2.07	1.32
1.0	1.50	2.37	1.75	2.29	1.58
1.5	1.80	2.67	2.18	2.54	1.85
2.0	2.00	2.82	2.46	2.73	2.20
3.0	2.25	2.91	2.63	—	—

The effect of  $\bar{n}$  on the value of logarithmic expression may be included in the correction factor normalized in the form

$$f = -\log \left[ 1 - \frac{\bar{n}(\eta - \delta)}{n(1 - \delta)} \right], \quad (42)$$

where

$$\delta = \frac{\sum_i \sum_j i[\text{MA}_i\text{B}_j]_{\text{org}} V_{\text{org}}}{G_A} = \frac{\bar{n}_{\text{org}}}{n} \eta R < 1 \quad (43)$$

is the coefficient of utilization of the agent employed in extraction in a macroconcentration system. Then equation (41) can be written in the form

$$\log \pi = \log \pi_0 + \log (1 - \eta R) - f. \quad (44)$$

The shift in the value of  $\log \pi$  caused by the existence of chelates in the aqueous phase may be important especially for the extraction with substoichiometric amounts of agent ( $\eta > 1$ ) as it follows from (42) and since  $1 < \pi < \pi_0$ , the corresponding macroconcentration system is to be achieved only if the subsequent inequality is valid at a given  $D$

$$\frac{\bar{n}_t}{n} < \frac{\pi_0 - 1}{\pi_0 \eta}. \quad (45)$$

If this condition is fulfilled, it is possible to simplify still more the conditions necessary to achieve the corresponding system by raising the pH in a macroconcentration system. If the dissociation of free agent is suppressed ( $\pi \gg 1$ ), equation (2) yields (44) as an explicit change in pH

$$\text{pH} = \text{pH}_0 - \log (1 - \eta R) + f, \quad (46)$$

where  $\text{pH}_0$  is the value at which the metal is extracted in the yield  $R$  in a microconcentration system with a given amount of agent. For a quick estimate of pH of the extraction of stoichiometric chelate (e.g. the equivalence point at extraction titrations,  $\eta R = \delta = 0.99$ ) we obtain approximately at  $\bar{n} = 0$

$$\text{pH} = \text{pH}_0 + 2. \quad (47)$$

The significance of the correction factor  $f$  increases evidently especially in stoichiometric and substoichiometric region ( $\eta \geq 1$ ) if the required portion  $\delta$  is close to one.

### *Extraction capacity of chelate systems*

The maximum possible coefficient of utilization of agent in the chelate system according to (43) can be called extraction capacity of the system

$$\delta_{\text{max}} = C. \quad (48)$$

Equations (40) and (43) give for the maximum increase in pH ( $\pi \rightarrow 1$ )

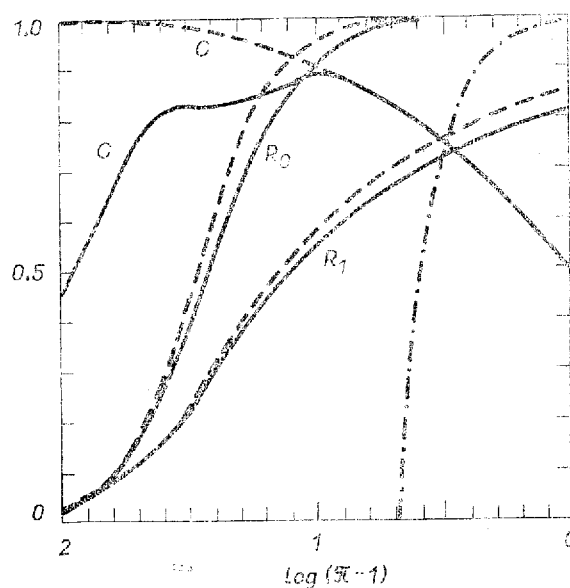
$$C = \frac{\bar{n}_{\text{org}}}{\bar{n}_t} \frac{\pi_0 - 1}{\pi_0} R. \quad (49)$$

For the extraction of one chelate  $MA_nB_p$  ( $\bar{n}_{org} = n$ ) using (19) and (23) we obtain

$$C = \frac{1}{1+k} \frac{\pi_0 - 1}{\pi_0}. \quad (50)$$

The extraction capacity is thus limited by two factors: the presence of chelates in the aqueous phase and the dissociation degree of a free agent. Its course in the region of high dissociation of the agent as a function of pH is shown in Fig. 4. At the same time it is evident that according to (43) the maximum capacity is achieved in the extraction of stoichiometric chelate and not in the extraction with substoichiometric amounts of agents as the neglect of  $\bar{n}$  ( $k = 0$ ) would suggest.

Fig. 4. Theoretical dependence of the extraction capacity of microconcentration system ( $C$ ), the yield of extraction of microamounts ( $R_0$ ), and the stoichiometric chelate ( $R_1$ ) on pH. Composition of the chelate  $MA_3$ ,  $P_{30} = 10^3$ ,  $G_A = 3 \times 10^{-4}$ ,  $a = 4$ .  
 - - - - for the spread factor  $b = -1.5$ ; ——— for  $b = 0.25$ ; - . . . - region in which hydroxide is precipitated.



A real hindrance of the limiting increase in pH in a macroconcentration system up to the values  $pH > pK_{HA} + \log(1 + P_{HAE})$  ( $\pi \rightarrow 1$ ) is the hydrolysis of metal in the alkaline region. The allowable increase in pH (so that the solubility product  $S_h$  of the hydroxide  $M(OH)_z$  would not be exceeded) ensues as a limitation

$$pH \leq 14 + \frac{1}{n} [\log S_h - \log c_M + \log(1 - R) + \log X]. \quad (51)$$

Though the complexity  $X$  (e.g. masking in the extraction) raises the pH value at which hydroxide is precipitated it equally raises the value of pH necessary for the extraction in the corresponding microconcentration system which can be derived from the extraction constant

$$pH_0 \geq \frac{1}{n} (\log D - \log K) + \frac{1}{n} \log X - \log c_A. \quad (52)$$

At a given ratio  $\eta$  the increasing concentration of agent decreases the value of  $pH_0$  more rapidly than the pH at which the precipitation of hydroxide sets in and for this reason a certain minimum concentration will occur in the stoichiometric region of the metal and the agent where the hydrolysis will not hinder the effective extraction of chelate. If the above relations are to be used for the calculation of this necessary concentration of chelate by means of (46), (51), and (52) we come to the conclusion that

$$(n - 1) \log c_A > (f - 12)n - \log n - \log K - \log S_h \quad (53)$$

must hold provided the chelate of the concentration  $S_{MA} = c_A/n$  ought to be extracted in the 99% yield ( $R = 0.99$ ). Because of the low solubility of the majority of extractable chelates this condition is essentially a postulate of minimum solubility of chelate from the point of view of its effective extractability. Provided the conditions involved in the derivation of (46) could not be kept, it is possible to proceed from the corresponding extraction curves. One may construct the relationship between  $R$  and pH in a micro-concentration system at the concentration of agent  $c_A = nS_{MA}$  or less. Then this graphically constructed function (51) can be used to estimate the real increase in pH in the corresponding macroconcentration system and find out whether the conditions for the increase of pH in a macroconcentration system allow according to (44) to achieve the required extraction capacity.

### Experimental

The extraction was carried out with anal. grade chemicals. The extraction mixtures with the volume ratio of the aqueous to the organic phase 1 : 1 were prepared by mixing a stock solution of standardized 0.01 M-FeCl<sub>3</sub> with acetylacetone (molar ratio 1 : 1) with 0.01 M solution of acetylacetone (UCB Belgium, content of acetic acid < 0.2%) in carbon tetrachloride and pure carbon tetrachloride. The pH value of the aqueous phase was adjusted with acetate buffer solution (2 M-CH<sub>3</sub>COONa and 2 M-CH<sub>3</sub>COOH) and measured after equilibrium establishment with a precise OP-205 (Radelkis) pH-meter. The ionic strength was kept at the approximate value of 0.1 by adding 2 M solution of sodium perchlorate. The systems were agitated at 20°C for 4–8 hours until the attainment of equilibrium. Radionuclide <sup>59</sup>Fe (ÚVVVR, Prague) detected by means of a one-channel VA-M-160 (Vakutronik) spectrometer with a well type NaI(Tl) crystal was used for the indication of Fe<sup>3+</sup>. The spectrophotometric determination of tris(acetylacetonato)iron(III) chelate was performed at  $\lambda = 440$  nm on an OF 402 (MOM Budapest) spectrophotometer. The theoretical curves were calculated on an ODRA 1013 computer or on a Hewlett–Packard 9100 B calculator.

### Conclusion

The analysis of the results obtained showed the possibilities of simplifying the substance balances and the relationships derived for the extraction of macroamounts of complexes especially in the case of the stepwise formation of complexes. By means of the corresponding extraction systems it is possible to derive the conditions of extraction for the systems with comparable amounts of metal and agent without understanding a number of theoretical constants. Because of the complications caused by a possible change in complexity at great variations of pH in the corresponding systems, the formation of polynuclear complexes, and eventual variations of ionic strength in macroconcentration systems, the experimental investigation of the relations obtained demands more extensive material. In spite of this the starting relationships employed by us enable to weigh the necessity as well as the admissibility of the used simplifications when preferring the extraction reaction of a certain type or to introduce some proper corrections into calculations. Special attention should, however, be given to the simplifications concerning the formation of polynuclear complexes by the transition to macroconcentration systems.

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## Symbols

M	central atom
z	charge of the central atom
A	anionic ligand (anion of a weak acid HA, H <sub>2</sub> A)
B	competing ligand or associated ion
e	charge of the competing ligand or associated ion (negative, zero, or positive)
M <sub>m</sub> A <sub>i</sub> B <sub>j</sub>	complexes
$\bar{n}$ , $\bar{p}$	mean ligand numbers of complexes in the aqueous phase
$\bar{n}_t$ , $\bar{p}_t$	mean ligand numbers in a two-phase system
n, p	number of ligands A and B in an extracted complex (provided it is single)
[M], [A]	equilibrium concentrations of the particles M <sup>z+</sup> , A <sup>-</sup> etc. in the aqueous phase (charges are omitted)
V', V' <sub>org</sub>	initial volumes of the aqueous and organic phase
V, V <sub>org</sub>	equilibrium volumes of the aqueous and organic phase
$\sigma = V/V'$	volume change during extraction
$\varepsilon_0 = V'_{org}/V'$	initial phase volume ratio
$\varepsilon = V_{org}/V$	equilibrium phase volume ratio
c <sub>A</sub>	molar concentration of chelating agent in the starting aqueous phase
G <sub>A</sub> = c <sub>A</sub> V' <sub>org</sub>	substance amount of the extracting agent
c <sub>M</sub>	molar concentration of extracted element M in the starting aqueous phase
G <sub>M</sub> = c <sub>M</sub> V'	substance amount of the extracted element
$\eta = nG_M/G_A$	stoichiometric ratio of the element to the extracting agent
$\delta = nRG_M/G_A$	coefficient of utilization of extracting agent
$R = \varepsilon D/(1 + \varepsilon D)$	yield of distribution
D	distribution ratio (ratio of the total analytical concentration of extracted element in the organic phase to the concentration in the aqueous phase at equilibrium)
$P_{mij} = [M_m A_i B_j]_{org}/[M_m A_i B_j] \equiv K_D(M_m A_i B_j)$	partition coefficient of the complex M <sub>m</sub> A <sub>i</sub> B <sub>j</sub>
$P_{HA} = [HA]_{org}/[HA]$	partition coefficient of the molecules HA
P' <sub>A</sub> , P' <sub>H<sub>2</sub>A</sub>	apparent partition coefficient of anions A <sup>-</sup> and cations H <sub>2</sub> A <sup>+</sup> of the agent HA (extraction of associates)
$K = [MA_n]_{org}[H]^n/[M][HA]^n$	extraction equilibrium constant (concentration product)
$\beta_{mij} = [M_m A_i B_j]/[M]^m[A]^i[B]^j$	stoichiometric constants of the stability of complexes M <sub>m</sub> A <sub>i</sub> B <sub>j</sub>
$\beta_{ij}$	stability of complexes MA <sub>i</sub> B <sub>j</sub> (conventionally $\beta_{00} = 1$ )
$K_i = [MA_i B_j]/[MA_{i-1} B_j][A]$	consecutive stoichiometric stability constants of complexes MA <sub>i</sub> B <sub>j</sub>
$a = 1/n \log \beta_n$	parameter of the mean stability constant
$b = 1/2 (\log K_i - \log K_{i+1})$	mean spread factor of stability constants
$K_{HA} = [H][A]/[HA]$	dissociation constant of the agent HA
$K_{H_2A} = [H][HA]/[H_2A]$	dissociation constant of the molecules H <sub>2</sub> A
$S_h = [M][OH]^z$	solubility product of hydroxide M(OH) <sub>z</sub>

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