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Association of β-Diketones with Trioctylphosphine Oxide in Solvent Extraction Systems

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Distribution of six β-diketones between hexane, benzene, carbon tetrachloride, or chloroform and 0.1 mol dm^{-3} aqueous perchlorate solutions has been measured in the presence of trioctylphosphine oxide (TOPO). The distribution ratio was, in many cases, enhanced by TOPO; this was explained in terms of association of the β-diketones and TOPO. The association constants were greater when the β-diketone was stronger as an acid and also in the following order of the diluent: $CHCl_3 < CCl_4 < C_6H_6 < C_6H_{14}$. It was concluded that, even though the effect was not very large, still correction for the decrease in the concentrations of both the β-diketone and TOPO is necessary for an accurate estimation of the equilibrium involved in solvent extraction of metal ions containing these two reagents, as in the synergistic solvent extraction of metal ions.

Synergistic solvent extraction of metal ions with mixtures of one chelating extractant and one solvating-type ligand has been found in several systems. The reason for the enhancement of the chelate extraction by additions of such a neutral ligand has been explained in terms of adduct formation of the metal chelate in the organic phase. The formation constants of such adducts can be calculated statistically from the enhancement of the extraction as a function of the ligand concentration. However, an association of the extractants in the organic phase is also possible and, in such a case, they should be taken into the account in order to analyse the extraction data.

In the present paper, the distribution of six β-diketones has been measured in several solvent extration systems as a function of trioctylphosphine oxide (TOPO) concentration in the organic phase. Four inert organic solvents were used as diluents of the reagents. The association equilibria of β-diketones and TOPO in the systems were determined from the distribution data. The effects of the chemical properties of the β-diketones and the diluents on the equilibria are discussed.

Experimental

The β-diketones studied are listed in Table 1 with their abbreviated nomenclatures. The β-diketones and TOPO were supplied by Dojindo & Co., Kumamoto. The organic diluents, sodium perchlorate, and perchloric acid were of analytical grade. Chloroform was washed three times with water before use.

Experiments were carried out in a thermostated room at 298 K. Stock β-diketone solutions were prepared by dissolving weighed amounts of each reagent into each diluent. The concentration of the β-diketone in the stock solutions of TFA and HFA was further checked by titration with a standard sodium hydroxide solution. A TOPO stock solution was also prepared in the same manner, and it was washed several times with water. Mixed solutions containing a β-diketone and TOPO at various concentrations were prepared from these stock solutions.

A portion of an organic solvent containing a β-diketone and TOPO and the same volume of an aqueous solution containing 0.010 mol dm^{-3} perchloric acid and 0.090 mol dm^{-3} sodium perchlorate were placed in a stoppered glass tube, agitated by a mechanical shaker, and centrifuged off. The aqueous phase of the experiments with BZA, BFA, or TTA was transferred into another tube and agitated with a portion of the same diluent containing no TOPO. The amount of the β-diketone thus extracted into the organic phase was determined from the optical absorption at 323(BFA in C_6H_{14}), 330(BFA in C_6H_6), 325(BFA in CCl_4), 305(BZA in C_6H_{14}), 310(BZA in C_6H_6), 307(BZA in CCl_4), 315(TTA in C_6H_{14}), 324(TTA in C_6H_6), and 319(TTA in CCl_4) nm, respectively. In the experiments with AA, TFA, and HFA, the amount in the aqueous phase was obtained by direct measurements of its UV absorption at 273, 280, and 305 nm, respectively, because their recovery in the organic phase was not quantitative by only a single extraction. The distribution ratio was calculated from the β-diketone concentration in the aqueous phase at equilibrium and from that in the initial organic phase.

Statistical

The β-diketones hereafter are represented by HA, and TOPO by L. The chemical species in the organic phase are denoted by a subscript "org", and those in the aqueous phase are given without any subscript.

The β-diketones (which are weak acids) in the aqueous phase may be both in the HA and A^- form, while those in the organic phase may be in the undissociated form HA as well as in the associated form with TOPO, HAL_n. Since n was found to be one or two in the present study and no species containing more than one HA was found, the distribution ratio of HA can generally be written as:

$$D = ([HA]_{org} + [HAL]_{org} + [HAL_2]_{org})/([HA] + [A^-]). \tag{1}$$

The dissociation constant and the two-phase distribution constant of the acid can be written as:

$$K_a = [H^+][A^-][HA]^{-1} \tag{2}$$

$$K_d = [HA]_{org}[HA]^{-1}, \tag{3}$$

and the distribution constant of the neutral ligand is:

$$K_d(L) = [L]_{org}[L]^{-1}. \tag{3'}$$

The association equilibria of HA and L may be represented by:

$$\left.\begin{array}{l} HA_{(org)} + L_{(org)} \rightleftharpoons HAL_{(org)} \\ \beta_{1(org)} = [HAL]_{org}[HA]_{org}^{-1}[L]_{org}^{-1} \end{array}\right\} \tag{4}$$

$$\left.\begin{array}{l}\mathrm{HA}_{(\mathrm{org})} + 2\mathrm{L}_{(\mathrm{org})} \rightleftharpoons \mathrm{HAL}_{2(\mathrm{org})} \\ \beta_{2(\mathrm{org})} = [\mathrm{HAL}_2]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}^{-1}[\mathrm{L}]_{\mathrm{org}}^{-2}\end{array}\right\}. \tag{5}$$

In the absence and presence of L, the distribution ratio may be written as:

$$D_0 = [\mathrm{HA}]_{\mathrm{org}}/([\mathrm{HA}]+[\mathrm{A}^-]) = K_\mathrm{d}/(1+K_\mathrm{a}[\mathrm{H}^+]^{-1}) \tag{6}$$

$$D = K_\mathrm{d}(1+\beta_{1(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}+\beta_{2(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}^2)/(1+K_\mathrm{a}[\mathrm{H}^+]^{-1}). \tag{7}$$

When D in Eq. 7 is obtained at a certain $[\mathrm{H}^+]$, D_0 at the same $[\mathrm{H}^+]$ can be calculated by using the values of K_a and K_d; then the following equation can be written:

$$D/D_0 = 1 + \beta_{1(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}} + \beta_{2(\mathrm{org})}[\mathrm{L}]_{\mathrm{org}}^2. \tag{8}$$

Both perchloric acid and sodium perchlorate are extractable with TOPO, but the extraction of the latter is negligible under the conditions of the present study, as can be calculated from the equilibrium constant:

$$K_\mathrm{ex}(\mathrm{NaClO_4}) = [\mathrm{NaL_3}^+\mathrm{ClO_4}^-]_{\mathrm{org}}[\mathrm{Na}^+]^{-1}[\mathrm{ClO_4}]^{-1}[\mathrm{L}]_{\mathrm{org}}^{-3}. \tag{9}$$

When the solvent is hexane and when the total concentration of the salt is 1 mol dm^{-3}, this value of K_ex $(\mathrm{NaClO_4})$ is $10^{1.01}$ and thus $[\mathrm{NaL_3}^+\mathrm{ClO_4}^-]_{\mathrm{org}}$ should be less than 1×10^{-4} mol dm^{-3} when both $[\mathrm{Na}^+]$ and $[\mathrm{ClO_4}^-]$ are 0.1 mol dm^{-3} and $[\mathrm{L}]_{\mathrm{org}}$ is lower than 0.1 mol dm^{-3}.1) When the salt concentration is 0.1 mol dm^{-3}, as in the present study, this value of the organic concentration of sodium perchlorate solvated with TOPO should be even lower.

The extraction equilibrium of perchloric acid is:2)

$$\left.\begin{array}{l}\mathrm{H}^+ + \mathrm{ClO_4}^- + 2\mathrm{L}_{(\mathrm{org})} \rightleftharpoons \mathrm{HClO_4L}_{2(\mathrm{org})} \\ K_\mathrm{ex}(\mathrm{HClO_4}) = [\mathrm{HClO_4L_2}]_{\mathrm{org}}[\mathrm{H}^+]^{-1}[\mathrm{ClO_4}^-]^{-1}[\mathrm{L}]_{\mathrm{org}}^{-2}\end{array}\right\}. \tag{10}$$

Since the volumes of both phases were always the same and the concentration of TOPO in the aqueous phase was very small, as is seen from the values of $K_\mathrm{d}(\mathrm{L})$ in Table 1, the following equations can be written:

$$\begin{aligned}&[\mathrm{L}]_{\mathrm{org,init}} \\ &\quad= [\mathrm{L}]_{\mathrm{org}} + [\mathrm{HAL}]_{\mathrm{org}} + 2[\mathrm{HAL_2}]_{\mathrm{org}} + 2[\mathrm{HClO_4L_2}]_{\mathrm{org}} \\ &\quad= [\mathrm{L}]_{\mathrm{org}}(1+\beta_{1(\mathrm{org})}[\mathrm{HA}]_{\mathrm{org}}) + 2[\mathrm{L}]_{\mathrm{org}}^2(\beta_{2(\mathrm{org})}[\mathrm{HA}]_{\mathrm{org}} \\ &\qquad+ K_\mathrm{ex}(\mathrm{HClO_4})[\mathrm{H}^+][\mathrm{ClO_4}^-])\end{aligned} \tag{11}$$

$$\begin{aligned}&[\mathrm{HA}]_{\mathrm{org,init}} \\ &\quad= [\mathrm{HA}]_{\mathrm{org}} + [\mathrm{HAL}]_{\mathrm{org}} + [\mathrm{HAL_2}]_{\mathrm{org}} + [\mathrm{HA}] + [\mathrm{A}^-].\end{aligned} \tag{12}$$

From the total concentration of the β-diketone in the equilibrated aqueous phase, the following equation can be obtained:

$$[\mathrm{HA}]_{\mathrm{org}} = K_\mathrm{d}([\mathrm{HA}]+[\mathrm{A}^-])(1+K_\mathrm{a}[\mathrm{H}^+]^{-1})^{-1}. \tag{13}$$

Among the terms in Eqs. 10 to 12, the value of [HA] can be determined experimentally, $[\mathrm{HA}]_{\mathrm{org}}$ can be calculated as above, the constant $K_\mathrm{ex}(\mathrm{HClO_4})$ can be determined by separate experiments in the absence of HA, while $[\mathrm{H}^+]$ and $[\mathrm{ClO_4}^-]$ may be determined experimentally. Then $\beta_{1(\mathrm{org})}$ and $\beta_{2(\mathrm{org})}$ can be determined with a succesive approximation approach by using a least squares computer program. The calculated value of $[\mathrm{L}]_{\mathrm{org}}$ at equilibrium can also be obtained when the best-fit values of these constants are computed in this way. The change in the distribution ratio of HA may be given by D/D_0 (*cf.* Eqs. 6 to 8) and the experimental data may be presented in a figure on the basis of Eq. 8.

When the diluent was hexane or carbon tetrachloride and the TOPO concentration was high, the extraction of perchloric acid was somewhat different from that expected from Eq. 10. This deviation could be explained by assuming extractions of trisolvate of the acid, more precise calculation should be possible by introducing these results into Eq. 11. However, since values of the constants in Eqs. 4 and 5 obtained after this correction were not very much different from those obtained by making no correction, all the calculations were made as follows. The data in these diluents were treated on the basis of the following equation:

$$\begin{aligned}&[\mathrm{L}]_{\mathrm{org,init}} - 2[\mathrm{HClO_4}]_{\mathrm{org,obsd}} \\ &\qquad= [\mathrm{L}]_{\mathrm{org}} + [\mathrm{HAL}]_{\mathrm{org}} + 2[\mathrm{HAL_2}]_{\mathrm{org}},\end{aligned} \tag{14}$$

where $[\mathrm{HClO_4}]_{\mathrm{org,obsd}}$ is the concentration of the extracted acid experimentally obtained by titration of the two phases in the absence of HA. Thus the error of the association constants in hexane and cabon tetrachloride could be a little larger than those in the other diluents.

The enhancement of the extraction of a β-diketone by an addition of TOPO can also be considered as an extraction of the β-diketone with TOPO. These extraction equilibria can be written as:

$$\left.\begin{array}{l}\mathrm{HA} + \mathrm{L}_{(\mathrm{org})} \rightleftharpoons \mathrm{HAL}_{(\mathrm{org})} \\ K_\mathrm{ex1} = [\mathrm{HAL}]_{\mathrm{org}}[\mathrm{HA}]^{-1}[\mathrm{L}]_{\mathrm{org}}^{-1}\end{array}\right\} \tag{15}$$

$$\left.\begin{array}{l}\mathrm{HA} + 2\mathrm{L}_{(\mathrm{org})} \rightleftharpoons \mathrm{HAL}_{2(\mathrm{org})} \\ K_\mathrm{ex2} = [\mathrm{HAL_2}]_{\mathrm{org}}[\mathrm{HA}]^{-1}[\mathrm{L}]_{\mathrm{org}}^{-2}\end{array}\right\}. \tag{16}$$

By introducing Eq. 3, Eqs. 15 and 16 can be rewritten as:

$$K_\mathrm{ex1} = \beta_{1(\mathrm{org})} \times K_\mathrm{d} \tag{17}$$

$$K_\mathrm{ex2} = \beta_{2(\mathrm{org})} \times K_\mathrm{d}. \tag{18}$$

Results and Discussion

The extractions of perchloric acid in 0.1 mol dm^{-3} $(\mathrm{Na,H})\mathrm{ClO_4}$ ionic media with TOPO in the diluents were determined in the manner previously reported.2) The extraction constants of the acid calculated from the present data are listed in Table 1.

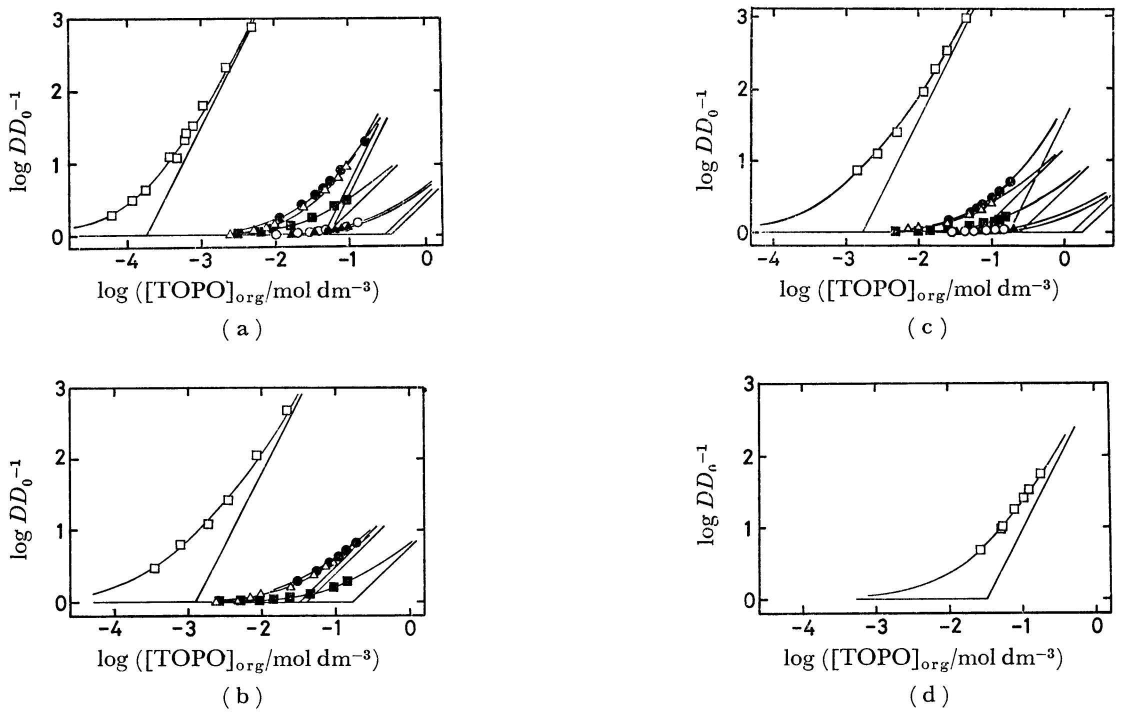
The distribution data of each β-diketone in the four liquid-liquid systems were obtained as a function of $[\mathrm{HA}]_{\mathrm{org,init}}$, $[\mathrm{L}]_{\mathrm{org,init}}$, and $[\mathrm{H}^+]$.

Figure 1 gives the increase in the distribution ratio as a function of the free TOPO concentration, computed in the way described in the preceding section. The solid curves are the calculated values obtained by introducing the association constants into Eq. 8. Each of the curves has two asymptotes. One of them has a slop zero and the other has a slop +1 or +2. This corresponds to the highest complex in the system, HAL or $\mathrm{HAL_2}$. Since the calculated curves fit well with the experimental data, the constants in

TABLE 1. REAGENTS STUDIED

Abbreviated notation	Name	pK_a a)	log K_d b)				Remarks
			C_6H_{14}	C_6H_6	CCl_4	$CHCl_3$	
AA	Acetylacetone	8.67	−0.05	0.70	0.51	1.36	(1)
BZA	Benzoylacetone	8.39	2.30	3.02	2.81	3.64	(2)
TFA	Trifluoroacetylacetone	6.13	−0.54	0.04	−0.22	0.27	(3)
BFA	Benzoyltrifluoroacetone	6.03	1.75	2.61	2.39	2.84	(4)
TTA	2-Thenoyltrifluoroacetone	6.33	0.75	1.61	1.32	1.85	(5)
HFA	Hexafluoroacetylacetone	4.46	−2.04	−1.91	−1.92	−1.75	(6)
TOPO	Trioctylphosphine oxide	—	3.83	4.78	5.24	5.51	(7)

(1): 2,4-Pentanedione, (2): 1-phenyl-1,3-butanedione, (3): 1,1,1-trifluoro-2,4-pentanedione, (4): 4,4,4-trifluoro-1-phenyl-1,3-butanedione, (5): 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, (6): 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, (7): log K_d of TOPO taken from Ref. 15. a) Taken from Ref. 14 when aqueous phase is 0.1 mol dm^{-3} $NaClO_4$. (b) log K_d of β-diketones taken from Ref. 14. log K_d of TOPO taken from Ref. 15 when aqueous phase is 0.1 mol dm^{-3} $NaClO_4$.



(a) (c) (b) (d)

Fig. 1. Enhancement of distribution ratio as a function of calculated TOPO concentrations at equilibrium. The diluents are (a) C_6H_{14}, (b) C_6H_6, (c) CCl_4, and (d) $CHCl_3$. The β-diketones are AA(▲), BZA(○), TFA(●), BFA(■), TTA(△), and HFA(□). The curves are calculated by introducing the constants in Table 2 into Eq. 8. The straight lines are the asymptotes for the curves. Initial concentrations of the β-diketones (mol dm^{-3}) are as follows (The nomenclatures see Table 1).
(a): 1.0×10^{-4}(AA), 2.0×10^{-3}(BZA), 2.0×10^{-3} (TFA), 1.7×10^{-2} (BFA), 2.5×10^{-4}(TTA), and 2.0×10^{-2} (HFA), (b): 2.0×10^{-3}(TFA), 5.0×10^{-3}(TFA), 1.5×10^{-3}(TTA), and 2.0×10^{-2}(HFA), (c): 5.0×10^{-3}(AA), 2.0×10^{-2}(BZA), 2.0×10^{-3}(TFA), 5.0×10^{-3}(BFA), 7.5×10^{-4}(TTA), and 2.0×10^{-2}(HFA), (d): 2.0×10^{-2} (HFA).

Table 1 are reasonable.

The values of the equilibrium constants in Tables 1 and 2 may be summarized as follows.

(i) The distribution constants of TOPO are greater in the following order of the diluent: hexane<benzene<carbon tetrachloride<chloroform, while those of the β-diketones are greater in the order of hexane<carbon tetrachloride<benzene<chloroform.

(ii) The association constants between a certain β-diketone and TOPO are affected by diluent; it is greater in the order of chloroform<carbon tetrachloride<benzene<hexane, although the association constants of acetylacetone and benzoylacetone in benzene could not be determined in the range of the experimental error. This means that the tendency of the association is, in general, greater when the solvent-solute interactions are weaker. The order of $\beta_{n(org)}$ in the diluent, carbon tetrachloride<benzene, should indicate that the difference in the solvent-solute interactions of the β-diketones has a greater effect on

Table 2. Summary of equilibrium constants

		Diluents			
		C_6H_{14}	C_6H_6	CCl_4	$CHCl_3$
AA	$\log \beta_{1(org)}$	0.65	—b)	−0.4	nil
	$\log K_{ex1}$	0.64	—b)	0.12	nil
BZA	$\log \beta_{1(org)}$	0.62	—b)	−0.3	nil
	$\log K_{ex1}$	2.65	—b)	2.55	nil
TFA	$\log \beta_{1(org)}$	1.84	1.43	1.20	nil
	$\log \beta_{2(org)}$	2.40	nil	1.63	nil
	$\log K_{ex1}$	1.30	1.47	0.98	nil
	$\log K_{ex2}$	1.86	nil	1.41	nil
BFA	$\log \beta_{1(org)}$	1.37	0.83	0.59	nil
	$\log K_{ex1}$	3.12	3.44	2.98	nil
TTA	$\log \beta_{1(org)}$	1.62	1.46	1.18	nil
	$\log \beta_{2(org)}$	2.72	nil	nil	nil
	$\log K_{ex1}$	2.37	3.07	2.50	nil
	$\log K_{ex2}$	3.43	nil	nil	nil
HFA	$\log \beta_{1(org)}$	4.22	3.73	3.55	2.09
	$\log \beta_{2(org)}$	7.51	5.78	5.57	2.80
	$\log K_{ex1}$	2.18	1.82	1.63	0.34
	$\log K_{ex2}$	5.47	3.87	3.65	1.05
TOPO	$\log K_{ex}(HClO_4)$a)	2.97	2.74	1.51	0.54c)

a) For the extraction of perchloric acid with TOPO, the following constants were also obtained: $K_{ex}(HClO_4)_1 = [HClO_4(TOPO)]_{org}[H^+]^{-1}[ClO_4^-]^{-1}[TOPO]^{-1}_{org}$, $K_{ex}(HClO_4)_3 = [HClO_4(TOPO)_3]_{org}[H^+]^{-1}[ClO_4^-]^{-1} \times [TOPO]^{-3}_{org}$, $\log K_{ex}(HClO_4)_1 = 0.54(CHCl_3)$, $\log K_{ex}(HClO_4)_3 = 4.32(C_6H_{14})$, $2.60(CCl_4)$. b) Erroneous. c) Aq phase 1.0 mol dm^{-3} $NaClO_4$. Taken from Ref. 2.

the magnitude of the constant than the difference in those of TOPO.

(iii) When the solvent is chloroform, the association is observed only between HFA and TOPO. With the other β-diketones, a slight decrease in the distribution ratio with an increase in the TOPO concentration is observed.

(iv) Among the β-diketones in a certain given diluent, the association constant is larger when the K_a is higher (stronger as an acid).

The synergistic effect in metal extractions with β-diketones by TOPO or TBP is very well known, but such associations between the β-diketone and TBP or TOPO have not often been discussed quantitatively. The antagonistic effect caused by association of an acidic extractant and a neutral ligand was pointed out by Wang *et al.*[3,4] and also by Healy *et al.*[5,6] However, these reports gave only qualitative discussions. This problem has also been considered by several authors.[7–11] Recently, Khopkar and Mathur have discussed this problem on the basis of their experiments about solvent extraction of metal ions with TTA and TOPO[12] or TBP.[13] They described how the extraction curves in such synergistic systems can be well explained by assuming associations of the β-diketone and the neutral ligand. They determined the association constants between TTA and TBP or TOPO in those extraction systems and gave values $10^{0.57}$ and $10^{1.14}$ for the $\beta_{1(org)}$ of TTA with TBP and TOPO in xylene.

The observations in the present study can be explained by assuming that the β-diketone is extracted with the neutral ligand. As is seen from Eqs. 17 and 18, the extraction constant is the multiplication of K_d and $\beta_{n(org)}$. When pK_a values are similar, $\beta_{n(org)}$ may not be much different. Thus among a group of β-diketones of similar pK_a values, the magnitude of K_{ex1} and K_{ex2} should be dependent on the K_d values, which are higher when the molar volume is larger.

The extraction equilibria of metal ion M^{m+} in such synergistic systems can be written as:

$$M^{m+} + mA^- \rightleftarrows MA_{m(org)};$$

$$K_{ex,m} = [MA_m]_{org}[M^{m+}]^{-1}[A^-]^{-m} \tag{19}$$

$$MA_{m(org)} + nL_{(org)} \rightleftarrows MA_mL_{n(org)};$$

$$\beta_{m,n(org)} = [MA_mL_n]_{org}[MA_m]^{-1}_{org}[L]^{-n}_{org}, \tag{20}$$

and the enhancement of the metal extraction can be written as:

$$D/D_0 = 1 + \sum \beta_{m,n(org)}[L]^n_{org}, \tag{21}$$

where $D_0 = K_{ex,m}[A^-]^m$. When both $[A^-]$ and $[L]_{org}$ are lowerd by association, the value D/D_0 should be underestimated if no correction for the decreases in the concentrations would be made, and should cause an underestimation of the $\beta_{m,n(org)}$ values which were calculated by Eq. 21. At the same time, if no correction for the decrease in $[L]_{org}$ by associations with HA would be made, it should also cause an underestimation of $\beta_{m,n(org)}$. Thus although it seems to be necessary to recalculate the previously reported values of the adduct formation of metal chelate from such a standpoint, marked differences between the previous values and recalculated values should be found only in HFA–TOPO systems because the $\beta_{n(org)}$ are large enough to affect the results only in the HFA–TOPO systems. The differences will be slight in other systems.

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