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Studies of the Synergistic Effect

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ABSTRACT

Two aspects of synergism in solvent extraction are reviewed dependence on temperature and on the organic solvent.

Temperature dependence studies allow calculation of the enthalpy and entropy changes associated with the synergistic reaction which is defined as:

$$MX_{n(o)} + mS_{(o)} + MX_nS_{m(o)} \qquad (1)$$

where M = metal cation, X = primary extractant, S = secondary extractant. From the magnitude and signs of the ΔS values, it is often possible to decide whether synergism is associated with replacement of solvate water by adduct molecules with no change in coordination number. Examples of extraction of a number of metals of different oxidation states are discussed to indicate the respective roles of dehydration and coordination number change in synergism.

Complexing organic ligands often show a synergistic effect. A study of the system Eu(III) - benzoic acid - TTA in different solvents is discussed to indicate the roles of water and ligand solubility in the organic solvent.

INTRODUCTION

The term synergism when applied to solvent extraction describes the effect whereby extraction from an aqueous to an organic phase of certain metal species is greater when two extracting agents are present than the sum of the extraction by either of the extractants alone [1,2]. The simplest and most studied of the synergistic extraction systems involves an acidic chelating ligand and a neutral adduct. The latter most often has been an organophorous compound (such as tributylphosphate, TBP) or a pyridine derivative while thenoyltriflouroacetone, HTTA, and similar β-diketones are frequently used as the chelating ligand.

A second class of synergistic extraction systems involves alkylphosphoric, carboxylic or sulfonic acids rather than chelants as the acidic component of the system. This class of synergistic extraction systems shows much smaller synergistic effects and exhibits synergism with fewer metal species.

The primary cause for synergism is accepted generally as an increase in hydrophobic character of the extracted metal complex upon addition of the adduct. Three mechanisms have been proposed to explain the synergism for chelant - adduct. The first of these involves an opening of one or more of the chelate rings and occupation by the adduct molecule(s) of the vacated metal coordination sites(s). In the second mechanism, the chelate rings do not coordinately saturate the metal ion and the residual water(s) occupying the remaining coordination sites are replaced by adduct molecules. The third mechanism involves an expansion of the coordination sphere upon addition of adduct molecules but no replacement of waters. From the extraction constants, it is rarely possible to choose between these alternative mechanisms but enthalpy and entropy data of the synergistic reactions have been used to provide more definitive arguments. Unfortunately, these more complete thermodynamic studies are not numerous. Moreover, the enthalpy and entropy values are calculated in all but a few cases by measurements of the temperature variation of the extraction constant rather than directly by calorimetry. Such temperature coefficient measurements are more open to question.

DISCUSSION

I. HTTA + TBP Systems

To study the applicability of the various mechanisms, let us review measurements of the thermodynamics of extraction of Ca(II), Zn(II), UO_2^{+2}, Ln(III), An(III), and An(IV) cations (Ln=lanthanide and An=actinide) by HTTA + TBP. The overall extraction reaction is written as:

$$M^{n+}_{(aq)} + nHTTA_{(o)} + mTBP_{(o)} = M(TTA)_n(TBP)_{m(o)} + nH^+_{(aq)} \qquad (1)$$

Using the extraction equation for TTA alone - i.e.,

$$M^{n+}_{(aq)} + nHTTA_{(o)} = M(TTA)_{n(o)} + nH^+_{(aq)} \qquad (2)$$

we obtain the "synergistic reaction":

$$M(TTA)_{n(o)} + mTBP_{(o)} = M(TTA)_n(TBP)_{m(o)} \qquad (3)$$

Thermodynamic data for the extraction reactions (1) and (2) allow calculation of the corresponding values for (3).

These equations do not provide complete definition of the reactions which may be of significance in any system. For example, HTTA can exist as a keto, an enol and a keto-hydrate species. The metal combines with the enol form which usually is the dominant one in "organic" solvents (e.g. $K=[HTTA]_e/[HTTA]_k \sim 6$ in wet benzene). The kinetics of the keto $\rightleftarrows$ enol reaction are not fast although they seem to be catalyzed by the presence of an adduct such as TBP or TOPO (3). Such adducts react with the enol form in drier solvents but cannot compete with water in wetter ones. Thus HTTA·TBP and $TBP \cdot H_2O$ species are also present in synergistic systems. Healy (4) measured the extent of such hydration and reported the following water concentrations in hexane:

pure hexane: 0.004 M
0.05 M TBP: 0.006 M
0.20 M HTTA: 0.016 M
0.20 M HTTA + 0.05 M TBP: 0.021 M
0.05 M Th + 0.20 M HTTA + 0.05 M TBP: 0.003 M

Irving (1) has discussed in terms of these complications the pitfalls of using equation (3) as a full description of the synergistic reaction. In the following discussion of thermodynamic values, we reduce this problem somewhat by only using data for either benzene or toluene systems as the two solvents have similar properties (e.g. water solubility, dielectric constant, etc.). In the second part of this paper, solvent and hydration effects are discussed.

A) Calcium(II)

Calcium(II) is found to exhibit a coordination number of 6 in essentially all of its systems. Therefore, it would be expected to be a cation which would not change its coordination number in reaction (3). The thermodynamic values for reactions (1) and (3) are given in Table 1. From the variation of extraction with HTTA and TBP concentrations, the species extracted were identified as $Ca(TTA)_2(HTTA)$ in (1), and $Ca(TTA)_2(TBP)_2$ in (2). Accordingly, reaction (3) is written as:

$$HCa(TTA)_{3(o)} + 2TBP_{(o)} = Ca(TTA)_2(TBP)_{2(o)} + HTTA_{(o)} \qquad (4)$$

The entropy values for the Ca(II) systems (Table I) seem unexpectedly large for reactions (1) and (3). If (1) were merely replacement of 6 H_2O's by 3 TTA chelate rings, the ΔS would be expected to be positive. Similarly replacement of a chelate ring of TTA in (3) by 2 TBP's should result in a negative ΔS. The anamolous entropy cannot be related to chelate ring formation and disruption. We find a reasonable explanation if we assume that the extracted species in reaction (1) is the ion pair $[H(H_2O)_n{}^+][Ca(TTA)_3{}^-]$. The extraction of 4 or 5 waters of hydration would cause the cratic term of the entropy of reaction (1) to be decreased. Then, in reaction (4), the hydration waters would be released to produce the extra positive entropy.

Support for this interpretation of the Ca(II)-TTA extraction system is obtained by comparison with the data for Ca(II) extraction by diethylehexylphosphoric acid (5). The data corresponded

TABLE I

Thermodynamic Data[‡] for Extraction
with HTTA + TBP

$$M(TTA)_n + mS = M(TTA)_nS_m$$

Species	ΔG^x	ΔH^x	ΔS^+	Ref.
$Ca(TTA)_2(HTTA)$	+69.18	-18.4	-298	5
$Ca(TTA)_2(TBP)_2$	-39.13	-9.58	+162	5
$Zn(TTA)_2$	+44.65	-45.6	+ 3	8
$Zn(TTA)_2(TBP)$	-20.46	-28.2	- 26	8
$Eu(TTA)_3$	+41.47	+40.3	- 4	12
$Eu(TTA)_3(TBP)$	-24.73	-24.0	+ 3	11
$Eu(TTA)_3(TBP)_2$	-41.22	-60.0	- 62	11
$UO_2(TTA)_2$	+ 1.26	0	-0.4	13
$UO_2(TTA)_2(TBP)$	-11.59	-21.8	- 34	13
$Th(TTA)_4$	-12.85	+10.7	+ 79	14
$Th(TTA)_4(TBP)$	-26.45	-43.7	- 58	14

[‡] These data are related to equation (1) for $M(TTA)_n$ species and to equation (3) for $M(TTA)_n(TBP)_m$ species.

x $kJ \cdot m^{-1}$

+ $J \cdot m^{-1} \cdot K^{-1}$

to extraction of $HCa(HD_2)_3$; however, the entropy change was 133 $J \cdot m^{-1} \cdot K^{-1}$, or only half of the value for extraction of $HCa(TTA)_3$. This would indicate that the proton is associated with the diethylhexylphosphate dimers, whereas the much more negative ΔS value for the TTA system is understandable if the proton is hydrated rather than attached directly to a bonded TTA molecule.

We conclude that in Ca(II) extraction, synergism is not associated with an increase in coordination number but is due to a favorable entropy change, probably related to a difference in the hydration of the simple tris-TTA complex and the TTA-TBP species.

B) Zinc(II)

Zinc(II) can have coordination numbers of 4, 5 and 6. Swift and Sayre (6) report $Zn(H_2O)_4^{+2}$ as the normal hydrated species while Graddon, et al, (7) report the formation in benzene of ZnL_2X (where L=β-diketonate chelator and X=monodentate adduct) resulting in C.N. = 5. Study of Zn(II) extraction (8) by HTTA + TBP provided insight into the change in ΔS associated with expansion of the coordination number of zinc from 4 to 5.

The values obtained for Zn(II) for reactions (1) and (3) are listed in Table I. As expected, the increase of the coordination number from 4 to 5 by addition of TBP to $Zn(TTA)_2$ is accompanied by a negative value of ΔS. Replacement of 4 H_2O's although it is smaller than might be expected. Kassierer and Kertes (9a) also report negative ΔS values for reaction (3) when a nitrogen containing Lewis base is added to $Zn(TTA)_2$ in $CHCL_3$. However, in another study (9b) they concluded that the synergistic reaction involves displacement of two waters of hydration from $Zn(TTA)_2(H_2O)_2$ but did not discuss how this explains the negative ΔS. Our assumption of the change of C.N. from 4 to 5 associated with the negative entropy change seems more reasonable as their reaction model would result in a positive ΔS.

C) Lanthanides

Trivalent lanthanide systems have been shown to exhibit variable coordination ranging from C.N. = 6 to C.N. = 12 with 8 and 9 rather common. Kassierer and Kertes (10) reported a ΔS value for the synergistic reaction between $Nd(TTA)_3$ and 2,2, dipyridylbenzene in benzene solvent of $-34\ J{\cdot}m^{-1}{\cdot}K^{-1}$ for the formation of $Nd(TTA)_3S$ and of $-100\ J{\cdot}m^{-1}{\cdot}K^{-1}$ for that of $Nd(TTA)_3S_2$. They interpret these values as supporting a model of replacement of water from the hydrated β-diketonate complex by the first adduct but not by the second. Data from Mathur, et al, (11) in Table 1 give a very small entropy change for the formation of $Eu(TTA)_3(TBP)$, which is consistent with a replacement of 1 or 2 water molecules. However, the formation of $Eu(TTA)_3(TBP)_2$ is accompanied by a large negative entropy change. This agrees with the data of ref. 10 and supports a model in which $Eu(TTA)_3(TBP)_2$ is fully dehydrated and the addition of the second TBP proceeds via expansion of the coordination sphere from 7 to 8. The large negative increase in enthalpy for addition of the second TBP is consistent with this model.

Kandil and Farah (12) have obtained data on the Eu-TTA-TOPO (trioctylphosphine oxide) system in benzene. The formation of $Eu(TTA)_3(TOPO)$ has $\Delta H = -28.8\ kJ \cdot m^{-1}$ and $\Delta S = +29\ J \cdot m^{-1} \cdot K^{-1}$ while the values for $Eu(TTA)_3(TOPO)_2$ are $-40\ kJ \cdot m^{-1}$ and $+95\ J \cdot m^{-1} \cdot K^{-1}$, respectively. Mathur, et al, reported similar values except for the ΔS of the $Eu(TTA)_3(TOPO)$ for which they find $+22\ J \cdot m^{-1} \cdot K^{-1}$.

TOPO has a higher equilibrium constant for formation of $TOPO \cdot H_2O$. Therefore, the adduct releases a water molecule in reaction 3, adding a positive contribution to ΔS. Based on comparison with the data of TBP system, release of the extra H_2O in the TOPO reaction would seem to be related to an extra positive ΔS contribution of 25-30 $J \cdot m^{-1} \cdot K^{-1}$. It is more difficult to evaluate the significance of the ΔS value for formation of $Eu(TTA)_3(TOPO)_2$. TOPO reacts with HTTA more than does TBP and also catalyzes the HTTA keto-enol equilibrium.

In conclusion, it would seem that the extracted β-diketonate species is $Ln(TTA)_3(H_2O)_n$ where n = 1 or 2. The first TBP replaces the n H_2O molecules and the second expands the coordination sphere. In both adduct formation steps, it is the negative enthalpy which causes synergism since the entropy is neutral or opposes the synergistic reaction. This enthalpy must reflect the strength of the Ln-TBP attraction.

D) Uranyl, UO_2^{+2}

The values for formation of $UO_2(TTA)_2(TBP)$ are listed in Table 1. The negative entropy and enthalpy values would imply no replacement of H_2O molecules and suggest a model whereby the mechanism of the synergistic reaction would involve expansion of the coordination sphere of uranium. The $UO_2(TTA)_2(TOPO)$ values are not as negative, which again reflect the effect of dehydration of TOPO upon adduct formation.

E) Thorium(IV)

The tetravalent actinides, Th(IV), U(IV) and Pu(IV) have been shown to form $An(TTA)_4(TBP)$. Patil, et al, (14) measured the temperature dependence of the extraction of Th(IV) with the results shown in Table 1. The large positive values of ΔS and the positive ΔH for the formation of $Th(TTA)_4$ are consistent with extensive cation dehydration. The negative values associated with $Th(TTA)_4(TBP)$ formation indicate simple addition of adduct whereby the coordination number of Th(IV) increases from 8 to 9. Extraction and spectrophotometric studies of Pu(IV) (15) and U(IV) (16) in TTA + TBP systems have been interpreted also as support for a model of expansion of the C.N. from 8 in $M(TTA)_4$ to 9 in $M(TTA)_4(TBP)$.

II. THERMODYNAMIC SUMMARY

The uncertainties of HTTA-TBP, $TBP-H_2O$ and HTTA(keto)= HTTA(enol) interactions make the preceeding interpretation of measured enthalpy and entropy changes somewhat uncertain. However, much of this uncertainty can be eliminated by considering the change for reactions such as:

$$M(TTA)_n(S) + N(TTA)_m = M(TTA)_n + N(TTA)_m(S) \qquad (4)$$

We choose $UO_2(TTA)_2 \cdot TBP$ as the reference and let $N(TTA)_m$ be $Zn(TTA)_2$, $Eu(TTA)_3$ and $Th(TTA)_4$ successively. The results are listed in Table 2 as well as data for the reaction.

$$UO_2(TTA)_2(TBP) + Eu(TTA)_3(TBP) = UO_2(TTA)_2 + Eu(TTA)_3(TBP)_2 \qquad (5)$$

If the previous interpretations are valid, both $Zn(TTA)_2$ and $UO_2(TTA)_2$ are anhydrous and addition of TBP represents an

TABLE 2

Thermodynamic Values of the Reaction:

$UO_2(TTA)_2(TBP) + N(TTA)_m = UO_2(TTA)_2 + N(TTA)_m(TBP)$

$N(TTA)_m$	ΔG^x	ΔH^x	ΔS^+
$Zn(TTA)_2$	-8.9	-6.4	+ 8
$Eu(TTA)_3$	-13.1	-2.2	+37
$Th(TTA)_4$	-14.9	-21.9	-24
$Eu(TTA)_3(TBP)$	-4.9	-14.2	-31

x $kJ \cdot m^{-1}$

+ $J \cdot m^{-1} \cdot K^{-1}$

increase in C.N. of 4 to 5 for both Zn^{+2} and UO_2^{+2}. The entropy and enthalpy changes are small, consistent with no dehydration and the increase in the coordination sphere of Zn(II) is negated by the decrease of that of UO_2^{+2}. Conversely, the reaction with $Eu(TTA)_3$ has a large, positive entropy, which is expected if H_2O molecules are released. In the reaction with $Eu(TTA)_3(TBP)$, ΔS is negative; no H_2O's are released and the C.N. of Eu(III) increases from 7 to 8 while that of UO_2^{+2} decreases from 5 to 4. $Th(TTA)_4$ reacts with a negative entropy; it's C.N. increases from 8 to 9 while, again, that of UO_2 decreases from 5 to 4.

II. HTTA+BENZOIC ACID SYSTEMS

Many authors have discussed the role of the solvent in synergistic extractions. Akiba (17) has correlated the values of β_n of Eu(III) and UO_2^{+2} with TTA+TBP and TTA+TBPO (tributylphosphine oxide) in a number of solvents with the activity coefficients in the organic phase as evaluated by regular solution

TABLE 3

Formation Constants for the Synergistic Reactions with $Eu(TTA)_3$

Solvent	Benzoic Acid (17) log β_1	Benzoic Acid (17) log β_2	TBP (18) log β_1	TBP (18) log β_2
CCl_4	4.42	8.24	5.05	8.40
C_6H_6	2.94	5.28	4.70	8.00
$CHCl_3$	-	5.46	3.40	5.20

theory. No correlation is found for Akiba's data between log β_n and the solvent dielectric constant but there is a linear relation (slope $\sim$-1) between log β_n and the water solubility in each solvent. Activity coefficients unfortunately provide little insight into the physical and chemical effects involved.

The effect of hydration in the organic solvent is shown in the system Eu(III) + Benzoic acid + HTTA. Europium forms benzoate complexes in the aqueous phase but no extraction of $Eu(Ben)_3$ is observable. When HTTA is present, synergic extraction is observed which can be shown to be identified with the species $Eu(TTA)_3(HB)_n$ where n = 1 and 2 (18). The values for the synergistic reaction constants are compared with those for $Eu(TTA)_3(TBP)_n$ (17) in Table 3.

We have analyzed the data for extraction of benzoic acid into several organic aolvents (19). The species which provided a satisfactory analysis of the benzoic acid extraction and the associated increase of water solubility in the organic phase were: HBen; $HBen{\cdot}H_2O$; $HBen{\cdot}(H_2O)_2$; $(HBen)_2$; $(HBen)_2{\cdot}H_2O$. The dependence of the extraction coefficient D of the total benzoic acid in the organic phase to that in the aqueous phase is shown in Figure 1. As the dielectric constant of the solvent increases the solubility of the benzoic acid also increases. Figure 2

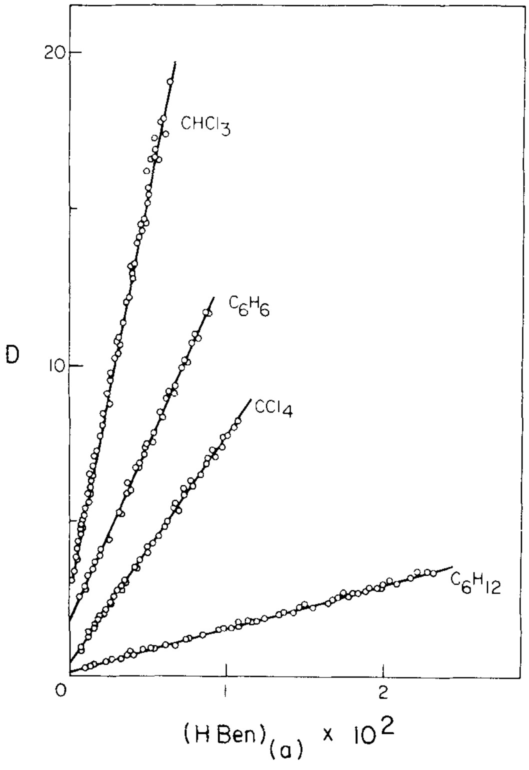

Figure 1. Dependence of the extraction coefficient D for benzoic acid in different solvents on the aqueous phase concentration of the benzoic acid.

shows the variation in the concentrations, C, in benzene of the $HBen_{(o)}$, $HBen \cdot H_2O_{(o)}$, $HBen(H_2O)_{2(o)}$ and $HBen_{2(o)}$ species as the benzoic acid concentration in the aqueous phase increases. At lower concentrations, the predominant organic phase species in benzene is the unhydrated monomer. However, for $(HBen)_{(aq)}$ 10^{-3} M, the dimer is the predominant form. The mole fraction of unhydrated monomer varies in different solvents; 0.14 in C_6H_{12}, 0.26 in CCL_4, 0.46 in C_6H_6 and 0.55 in $CHCl_3$. This is in the opposite direction from the trend in log β_n values in Table 3. A reasonable conclusion is that solvation of the benzoic acid

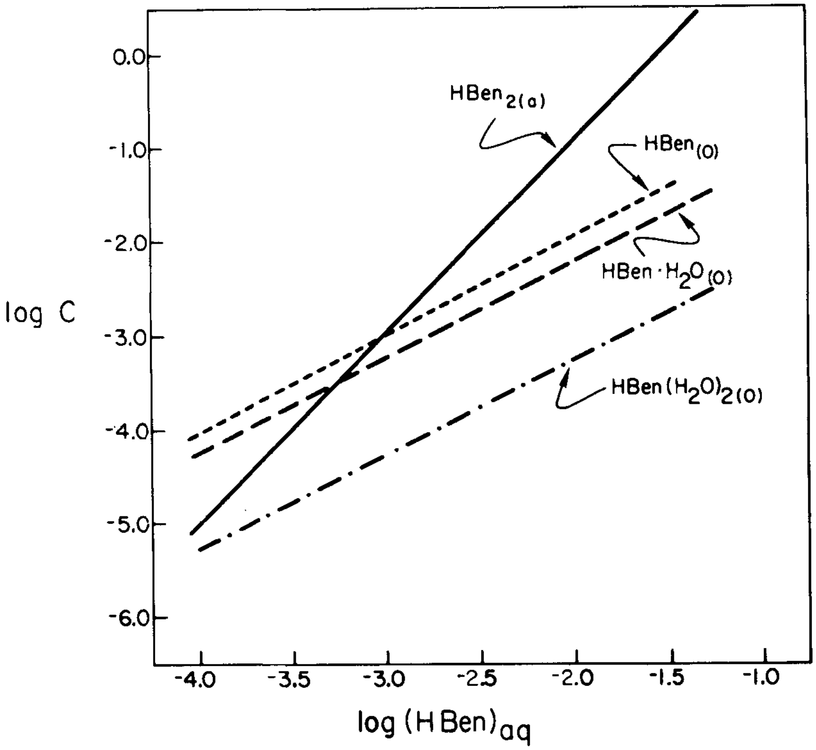

Figure 2. Variation of the concentrations, C, in moles benzoic acid per liter solution, in benzene as a function of the concentration of undissociated benzoic acid in the aqueous phase.

is much stronger in benzene and in chloroform than it is in carbon tetrachloride and this solvation competes more strongly with the synergistic reaction in C_6H_6 and $CHCl_3$ than in CCL_4. By comparison, solvation of TBP is not significant in CCL_4 or in C_6H_6 but seems to play a role in $CHCL_3$.

IV. SOLVENT EFFECT SUMMARY

The role of the adduct in increasing the hydrophobic nature of the extracted complex had been stressed by many authors. This would explain the greater synergistic effect with more hydrophobic solvents. Akiba has attempted a more detailed explanation of the role of the solvent by relating it to activity coefficients. Our studies with benzoic acid indicate that the solvation of the adduct by the solvent can play a significant role in the solvent effect in synergism. Studies of solvent - adduct interaction for TBP, TOPO, etc. would clarify the generality of this observation.

Finally the role of water dissolved in the organic solvent in the synergistic reaction suggests that calorimetric mearsurments of anydrous systems may not provide proper data to assess the mechanisms of reaction in wet extractions.

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