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Abstract

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ON THE MECHANISM OF THE ELEMENTARY ACT OF EXTRACTION OF INNER-COMPLEX COMPOUNDS

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One of the interesting questions in the theory of extraction of inner-complex compounds (i.c.c.), the question of where the extractable compound is formed—in the aqueous phase or at the interface*—has so far not had a definite solution. Here what is meant is the case when the reagent is introduced as a solution in an organic solvent, while the element to be extracted is in the aqueous phase.

The equilibrium result of extraction, generally speaking, does not depend on the mechanism of the elementary act, i.e., on where the extractable compound was formed. In other words, the distribution coefficient of the given element under the given conditions will be the same no matter how the process proceeds. However, the mechanism of the elementary act is closely connected with the kinetics of extraction processes (if the rate of extraction is determined by the rate of the chemical processes in the system; as is known, the rate of extraction also depends on the rate of mass transfer). Clarifying the question of the mechanism of the elementary act and of the specific way in which the rate of attainment of extraction equilibrium is connected with this mechanism would make it possible in a number of cases to control this rate and thereby to increase the selectivity of extraction separations.

Consideration of the experimental material relating to the extraction of i.c.c. makes it possible to conclude that most of the available data indicate the formation of the extractable compounds in the aqueous phase (at least predominantly) (1). However, it is sometimes believed that formation occurs at the phase interface. Thus, Geiter (2) came to this conclusion while studying the extraction of copper dithizonate (see also (3)).

One possible way of resolving this question is apparently the study of the kinetics of extraction of i.c.c. by different solvents. The solvents should be chosen in such a way that the distribution constants of the reagent between them and water differ substantially, while the extraction conditions should be such that the rate-determining factor in the kinetic sense is the rate of chemical interactions and not the rate of mass transfer. The essence of the method is as follows.

Let the requirement concerning the ratio of the rates of chemical reactions and mass transfer be satisfied (the reagent and the i.c.c. are transferred at a high rate). In that case, if the compound is formed in the aqueous phase, the rate of extraction will be the greater, the higher the concentration of the reagent in the aqueous phase (at constant pH). This concentration, at an equal initial concentration of the reagent in the organic phase, depends on the distribution constant P_{HA} of the reagent (o/w) between the selected solvents and water; it is the lower, the higher P_{HA}. In other words, equilibrium should be established more rapidly when using solvents with a lower P_{HA} (i.e., such—although this is not entirely rigorous—in which the reagent is less solvent). If, however, formation of the compound occurs at the phase boundary, then the extraction rate is determined by the concentration of the reagent in the organic phase and will, conversely, be higher for the solvent with a high P_{HA} (in which the reagent is more soluble).

As for the requirement that the rate of mass transfer be higher than the rate of the chemical reactions, generally speaking, this condition is not difficult to satisfy for inner-complex compounds. The feasibility of this condition is confirmed by the dependence of the extraction rate on pH; such a dependence should not exist if mass transfer is the determining factor. Of substantial importance here is the rate (intensity) of mixing. At low mixing rates mass transfer may be the slowest stage, since the hydrodynamic conditions are unfavorable. As the mixing rate is increased, the importance of the transfer stage decreases, and the chemical reactions have a greater probability of becoming rate-determining.

Irving and others ([4,5]) drew attention to the different rates of extraction of zinc dithizonate by chloroform and carbon tetrachloride (faster in the case of CCl_4) and associated this with the different distribution of dithizone between the solvent and water (P_{HA} for $CHCl_3$ is substantially higher than for CCl_4). In their opinion, these data could indicate that the dithizonate is formed in the aqueous phase. There appear to be no other experimental data in the literature on the kinetics of extraction of inner-complex compounds by different solvents that could be used to clarify the question of the mechanism of the elementary act. Some authors have studied the rate of extraction of inner-complex compounds by different solvents without having the problem under discussion in mind, but these data are not easy to use, since the identity of the conditions for obtaining kinetic curves for different solvents is not always guaranteed (for example, equality of pH).

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* Formation of the compound in the organic phase is apparently excluded, since for this the extracted element would have first to pass in one way or another into the organic phase, which in most cases is difficult.

We studied the rate of extraction of inner-complex compounds formed by metals (Co, Fe, In, Sc, U, Zn) with six organic reagents—acetylacetone, benzoylacetone, dibenzoylmethane (DBM), thenoyltrifluoroacetone (TTA), benzoylphenylhydroxylamine (BPHA), and 1-(2-pyridylazo)-2-naphthol (PAN). The dependence of extraction on the phase-contact time was studied at various pH values and reagent concentrations and with the use of different solvents.

The reagents and solvents were carefully purified. Acetylacetone was purified from acetic acid and then distilled. Benzoylacetone, "pure," was recrystallized from ethanol; m.p. 54–57°. Dibenzoylmethane, "pure," was recrystallized twice from methanol, then dissolved in benzene, the solution was washed with concentrated hydrochloric acid and with water, and the benzene was evaporated; the DBM obtained was recrystallized several more times from methanol; m.p. 68–73°. Imported thenoyltrifluoroacetone was stored in a dark vessel and was not subjected to further purification. BPHA was synthesized according to ([6,7]) and purified by recrystallization from water. PAN, "pure," manufactured by Chemapol, Czechoslovakia, was not further purified. Chloroform in most cases was purified by washing with concentrated H_2SO_4 and several times with water, and was then distilled; in this way $CHCl_3$ contained no alcohol, and therefore it was stored in a dark vessel and only for a short time. Benzene was purified from thiophene and other impurities and distilled. CCl_4 was purified with subsequent distillation. The solvents were identified by their boiling point and, in a number of cases, by their refractive index. Solutions of the reagents in the solvents were prepared by accurate weighing. Working solutions of the elements were solutions of chlorides (Co, Fe, Sc, Zn), nitrates (U), or perchlorates (In). Solutions of readily hydrolyzable elements contained the corresponding acid.

Extraction was carried out in 50-ml conical flasks with ground-glass stoppers. Shaking was performed in an air thermostat at $25 \pm 0.2°$ by means of a shaker with constant and rather high intensity: 140 oscillations per minute with an amplitude of about

25 mm. If the shaking time was short, the initial solutions were first thermostated. To an aliquot portion of the working solution of the element, buffer solution was added to 5 or 10 ml, and then, carefully so as not to cause mixing, respectively 5 or 10 ml of a solution of the reagent in the solvent. Shaking was carried out immediately thereafter. A large number of flasks for two solvents were shaken simultaneously; then, after specified intervals of time, two flasks were removed—one for each solvent. Extraction with different solvents was thus carried out simultaneously and under strictly identical

Table 1

Systems studied

Reagent (HA)	Element	$[Me]_{\text{aq}}$, g-atom/l	Solvents	$[HA]_0$, mole/l	pH	Buffer solutions
Acetylacetone	Fe (III)	$3.5 \cdot 10^{-4}$	$CHCl_3$, CCl_4	0.1	1.3—1.4	Chloride
Acetylacetone	U (VI)	$4.3 \cdot 10^{-4}$	$CHCl_3$, C_6H_6, CCl_4	0.1	6.7	Borate
Acetylacetone	U (VI)	$1.4 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.1	7.1	»
Acetylacetone	U (VI)	$1.4 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.05	7.1	»
Acetylacetone	U (VI)	$1.4 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.01	6.3	»
Benzoylacetone	U (VI)	$5.7 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.1	5.8	Biphthalate
Dibenzoylmethane	Fe (III)	$5.3 \cdot 10^{-6}$	$CHCl_3$, C_6H_6	0.05	3.7; 5.0; 5.6	»
»	Fe (III)	$7.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.01	4.2; 4.5	»
»	Fe (III)	$7.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.05	3.8; 4.0; 4.2	»
»	Fe (III)	$7.0 \cdot 10^{-4}$	$CHCl_3$, CCl_4	0.01	5.5	»
»	Sc	$3.1 \cdot 10^{-6}$	$CHCl_3$, CCl_4	0.05	4.1; 5.1; 5.3; 6.0	»
»	Sc	$3.1 \cdot 10^{-6}$	$CHCl_3$, CCl_4	0.01	6.0	»
»	U (VI)	$5.7 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.1	5.5	»
Thenoyltrifluoroacetone	Zn	$2.8 \cdot 10^{-4}$	C_6H_6, CCl_4	0.05	8.0	Borate
Benzoylphenylhydroxylamine	Cu (II)	$6.5 \cdot 10^{-7}$	$CHCl_3$, C_6H_6	0.01	7.1; 7.7; 8.2; 9.2	»
Benzoylphenylhydroxylamine	Cu (II)	$6.5 \cdot 10^{-7}$	$CHCl_3$, C_6H_6	0.05	8.2	»
Benzoylphenylhydroxylamine	Fe (III)	$7.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.01	1.7; 2.6; 4.2	Acetate
Benzoylphenylhydroxylamine	Fe (III)	$7.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.05	2.6	»
Benzoylphenylhydroxylamine	Fe (III)	$7.0 \cdot 10^{-4}$	$CHCl_3$, CCl_4	0.01	1.7	»
Benzoylphenylhydroxylamine	In	$3.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.002	4.7; 6.0	»

Reagent (HA)	Element	$[Me]_{\text{aq}}$, g-atom/l	Solvents	$[HA]_0$, mole/l	pH	Buffer solutions
Benzoylphenylhydroxylamine	In	$3.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.01	3.3; 4.2; 4.4; 4.9	»
Benzoylphenylhydroxylamine	In	$3.0 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.05	4.1	»
Benzoylphenylhydroxylamine	Zn	$2.8 \cdot 10^{-4}$	$CHCl_3$, C_6H_6	0.05	8.0	Borate
1-(2-pyridylazo)-2-naphthol	U (VI)	$4.2 \cdot 10^{-5}$	$CHCl_3$, C_6H_6	$6.4 \cdot 10^{-4}$	7.0	»

conditions. After phase separation for a specified time (in a number of cases centrifugation was carried out), aliquot portions of the organic (and often also the aqueous) phases were taken for analysis for the extracted element. In the aqueous phase the pH was measured potentiometrically (glass electrode).

In most cases radioactive isotopes were used, and the analysis was carried out by radiometric methods. β-activity (Fe^{59}, In^{114}) was measured with an MST-17 end-window counter and an ordinary counting setup. To measure γ-activity (Co^{60}, Sc^{46}, Zn^{65}), a scintillation counter with a NaJ(Tl) crystal was used; aliquot portions of the solutions were measured in standard test tubes. Uranium was determined photometrically in the form of the pyridylazonaphtholate and as a complex with arsenazo III, and spectrophotometrically in the form of the acetylacetonate (365 mμ), benzoylacetonate (380 mμ), and dibenzoylmethanate (400 mμ).

In all, more than 100 kinetic curves were obtained. Table 1 presents the systems studied by us. In Figs. 1 and 2, as an example, some data for two systems are given. The results obtained indicated that the extraction rate of the intracomplex compounds studied depends on pH; other conditions being equal, the extraction rate with

increases with increasing pH. The concentration of the reagent has a considerable effect: as a rule, the rate of extraction is higher the greater the concentration of the reagent. These data, especially the dependence on pH, show that the slowest stage is the formation of the inner-complex compound, and not mass transfer. In practically all the systems studied, benzene and especially CCl_4 extract faster than $CHCl_3$.

Fig. 1

Fig. 2

Fig. 1. Extraction of scandium dibenzoylmethanate ($3.1 \cdot 10^{-6}$ g-atom/l) by

0.05 M solutions of DBM in $CHCl_3$ and CCl_4.
1 –$CHCl_3$, pH 5.1; 2 –$CHCl_3$, pH 5.3; 3 –CCl_4, pH 5.1; 4 –CCl_4, pH 5.3.

Fig. 2. Extraction of iron(III) benzoylphenylhydroxylaminate ($7.0 \cdot 10^{-4}$ g-atom/l) by 0.01 M solutions of BPHA in $CHCl_3$ and CCl_4 at pH 1.7.
1 –$CHCl_3$; 2 –CCl_4.

The distribution constants of the reagents for these solvents are in most cases different. They decrease in the series $CHCl_3 > C_6H_6 > CCl_4$. Consequently, extraction is faster with those solvents in which the reagent is less soluble. For example, $\lg P_{\mathrm{HA}}$ of dibenzoylmethane for the $CHCl_3$–H_2O system is 5.40, and for the CCl_4–H_2O system 4.51 (^{8}), and the dibenzoylmethanates of iron(III) and scandium are extracted faster by carbon tetrachloride. Similarly, in the case of the extraction of iron acetylacetonate ($\lg P_{\mathrm{HA}}$ for $CHCl_3$ is 1.40, for CCl_4 0.52 (^{9})); CCl_4 extracts at a higher rate. Several other examples are given in Figs. 1 and 2.

Thus, the data obtained indicate that the extracted inner-complex compounds are formed in the aqueous phase. The entire extraction process consists of 1) distribution of the reagent between the phases, 2) formation of the inner-complex compound in the aqueous phase, and 3) distribution of this compound. A detailed presentation of the experimental data will be published.

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Note: Figure translations are in progress. See original paper for figures.