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COLLOID-CHEMICAL MECHANISM OF THE SEPARATION OF SOME ELEMENTS BY EXTRACTION

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Extraction processes are of very great value in radiochemistry, inorganic and analytical chemistry, and also for the fissile materials industry and in chemical technology. Establishment of the mechanism of the extraction of various elements is therefore of great theoretical and practical interest, since it will make possible a systematic choice of extractants and determination of the optimum conditions for the process. In some cases a colloid-chemical mechanism is possible for the extraction of a series of elements. Some elements on passing into the organic phase may be extracted in the form of highly disperse colloidal particles (submicroscopic sols).

The extraction of elements by a colloid-chemical mechanism is due to the diminution in free surface energy of the system when hydrophobic colloidal particles pass from the aqueous phase into the organic phase, and is governed to a first approximation by the difference in surface tension at the aqueous medium–disperse phase boundary of the sol and at the disperse phase–organic solvent boundary.

Thus good extractants should generally have a comparatively low surface tension (γ = 15–25 erg cm^{-2}). In fact, however, this relation is more complex in character.

The process of extraction consists in the vigorous stirring of aqueous solutions with the organic solvent in the presence of air. The aqueous solution and the organic solvent are divided up into fine droplets, and unstable emulsions are formed, which break down rapidly. At the same time the air which is present also forms fine bubbles, and to some extent affects the process of extraction. Highly disperse colloidal particles, on passing into the extractant layer, may be stabilised by the adsorption on them of an oriented monolayer of organic solvent molecules. Sometimes stabilisation requires the use of some ionogenic surface-active agents.

An important role in extraction processes is played by thin layers and films formed at the surface of separation of the two liquid phases. Various physicochemical processes take place in these films, and these play a considerable part in extraction processes (formation and stabilisation of emulsions, etc.).

The interfacial tension in the interphase film at the surface of separation of two liquids is diminished as a result of the increased adhesion between the two liquid phases[1]. Theoretical calculations show that a 1000–3000-fold concentration of a substance is sometimes possible in the surface film[2]

Adsorbed layers, resembling surface gels in structure, form interphase films having considerable elasticity and mechanical strength. Molecules in these layers possess some mobility[3,4].

Some soluble inorganic colloids can form films at the surface of separation of two liquid phases, and act as stabilisers for emulsions[5]. In most cases the formation of colloidal solutions involves the initial formation of globular or shapeless amorphous particles, which then disintegrate, in the process of crystallisation, into finer crystalline particles[6], so that sols have their maximum reactivity at the instant of formation of colloidal solutions. Colloidal solutions may result from hydrolysis, and also from the formation of sparingly soluble compounds in the presence of certain electrolytes. It is also possible that some elements may be adsorbed on sols of substances present in the solution as impurities. Some solutions also show an increased quantity of sols with increasing time of storage.

Elements (W, Mo, Nb, Ta, Ru, Zr, Po, Ce, La, Pb, Th, Sn, Ti, Y, etc.) present in solution in low concentrations tend to form colloidal solutions, and can therefore be extracted by a colloid-chemical mechanism. "Carrierless" radioisotopes may be extracted as a result of the formation of true colloidal solutions of the radioisotopes or may even be adsorbed on foreign colloidal carriers, after which they are extracted.

It has previously been ascertained[7] that thin films are formed on the surface of colloidal solutions of hydrosols of the hydroxides of iron, chromium, and aluminium. It has been suggested[8] that these films are formed as a result of surface coagulation of the sols, and it has been established that the surface of aqueous solutions is negatively charged as a result of orientation of the water dipoles and preferential adsorption of anions in the surface layer[9].

As a result of Brownian motion, positively charged colloidal particles of the sol escape to the surface, where they are partly discharged and are coagulated with the formation of a surface film. The hydration sheath of the colloidal particle is lost together with its charge[10,11].

At the hydrosol–organic solvent interface the colloidal particles are more firmly attached, this being associated with interfacial tension at the colloidal particle–liquid surface[12,13]. It has also been established that the use of an organic solvent is accompanied by a change in stability of the sol, resulting in its rapid coagulation[14].

It had already been ascertained long ago that sols are coagulated under the influence of those non-electrolytes which diminish the dielectric constant of the medium[15]. The coagulating action of a non-electrolyte is stronger the greater the diminution in dielectric constant produced by the non-electrolyte at the interface.

Colloidal particles will concentrate at the interface between liquids if the polarities of the liquids are different[16]. Thus the greater the difference in dielectric constant between the aqueous solution and the non-aqueous phase, the more are colloidal particles concentrated at the boundary with the organic solvent.

Depending on the coagulating power of organic solvents, a film of varying thickness is formed at the surface of separation of the liquids, non-polar liquids giving the thickest films. When colloidal particles pass into the organic phase, the electrical repulsion decreases, the density of packing of the micelles increases, and also the structure of the micelles becomes more compact owing to the expulsion of water from them. Finely ground powders (quartz, glass, Al_2O_3, etc.) form both stable and unstable suspensions in some ketones[17]. Stable suspensions of some compounds (TiO_2, ZnO) can be formed also in organic solvents (toluene, butyl acetate, etc.)[18]. Stable colloidal solutions of Rhodamine B can be obtained in benzene.

It is to be assumed that an increase in the degree of dispersion of a sol will result in a more complete transfer of the extractable substance to the organic phase. Addition of some substances (starch, etc.) sometimes promotes extraction by stabilising the sols in the aqueous and organic phases.

Several inorganic compounds present in colloidal solution can be extracted by various organic solvents. Study by electrophoresis, electrolysis, and diffusion methods of the properties of the coloured thiocyanato-complexes of iron (obtained by the interaction of $FeCl_3$ and NH_4SCN) has shown that the complex is present in solution in the colloidal state and carries a positive charge; the degree of dispersion of the particles increases in acid medium[19]. It may be supposed on the basis of these investigations that the good extraction by organic solvents of several thiocyanato-complexes (of W, Nb, Ta, Co, etc.) is due to their being present in the aqueous solution in the colloidal state. It is possible that iodine is extracted by various organic solvents (chloroform, etc.) also in the colloidal state.

Some metal halides can form stable sols[20] in concentrated solutions (sulphuric and phosphoric acids, concentrated $CaCl_2$ solution, etc.); perhaps it is this which explains the good extraction of these salts ($FeCl_3$, etc.).

Increase in the HCl concentration up to a certain limit (6–7 *N*) produces an improvement in the extraction of the chlorides of several elements (Ga^{III}, Fe^{III}, Mo^{VI}, As^{III}, Sb^{V}, Te^{IV}). A similar situation occurs in the extraction of bromides (of Fe^{III}, Ga^{III}, and In^{III}). This observation can be explained by the increasing quantities of salts passing into the colloidal state as the acid concentration increases. When the concentrated solutions are diluted with water, the colloidal particles break down, and extraction of the elements ceases.

It has also been found that elements are poorly extracted from dilute solutions of nitric acid (0.5–1 *N*); increase in the nitric acid concentration to 8 *N* produces a marked improvement in the extraction (of Au^{III}, Th^{IV}, U^{VI}, Ce^{IV}), which can also be explained by the formation of sols of the nitrates of these metals in the comparatively concentrated nitric acid. The use of salting-out agents in extraction processes favours the formation of colloidal solutions, since an increasing salt content in the solution is accompanied by the formation of the corresponding sols[21].

It must be assumed that some heteropoly-acids, which are readily extracted, also can form colloidal solutions[22,23]. Readily extractable compounds are formed by the interaction of microquantities of various elements with some organic reagents (cupferron, 8-hydroxyquinoline, 1-nitroso-2-naphthol, dimethylglyoxime, etc.) These reactions result in the formation of sparingly soluble compounds of the elements in the colloidal state, which usually pass readily into the organic phase. A colloid-chemical mechanism can explain the absence of appreciable specificity in the isolation of these compounds by extraction.

Nitrates of lanthanides, actinides, and zirconium form compounds with tri-n-butyl phosphate (TBP), their formulae being $M(NO_3)_3.3TBP$, $M(NO_3)_4.2TBP$, and $MO_2(NO_3)_2.2TBP$. In the tributyl phosphate the nitrates of these metals are solvated and occur in an unionised form[24].

TBP extracts molecular compounds of other elements as well[25]. Numerous investigations have been made of the extraction of uranium and other elements in the form of various compounds, in which a tendency has been observed in some cases for polymeric forms to be produced[26,27]. It must be assumed that these compounds, too, form on extraction colloidal or semi-colloidal solutions, and pass into the organic solvent in the form of sols.

Several dyes (Methylene Blue, Methylene Violet, Congo Red, Benzopurpurin, etc.) form colloidal solutions in aqueous solution[28,29]; therefore the extraction by organic solvents of these dyes and their reaction products with certain elements also can be explained by a colloid-chemical mechanism. Use of surface-active agents makes it possible to extract with various solvents several non-extractable colloidal dyes and the sparingly soluble reaction products which they form with elements.

The possibilities must be noted of the extraction of microquantities of various elements which form sparingly soluble compounds with organic reagents. In most cases these compounds dissolve well in the appropriate organic solvents, and therefore should be readily extracted by a colloid-chemical mechanism. Research on these lines will probably yield a considerable number of methods for the separation of microquantities of various elements by extraction.

Associated molecules are sometimes formed in solution under the influence of cohesive forces.

At the present time a considerable number of molecular compounds are known, formed both by inorganic and by organic molecules. Several substances form polymeric compounds, among which are silver and gold cyanides, silver thiocyanate, and hydrargillite $[Al(OH)_3]_n$. The hydroxide, carbide, sulphide, and silicide of iron[30] also can form polymers.

In the formation of the thiocyanato-complex of molybdenum, Mo^V undergoes reaction in dimeric forms[31].

It has been suggested that ferric chloride occurs in the form of dimers $[FeCl_3]_2$ in benzene, as also in aqueous solution[32,33]. Polymerisation of iron is possible in an ether layer, with formation of the compound $[HFeCl_4]_n$.[34] It is also possible that similar associated molecules of ferric chloride and other halide salts can exist in some other organic solvents, and under the influence of the organic solvents can then form colloidal solutions.

The extraction of associated molecules can be represented as their interaction with the organic solvent to form a sol, which then passes into the organic phase. The extraction of elements present as ions in the solution can also be represented as interaction with the organic extractants, yielding associated molecules which subsequently aggregate and form sols capable of extraction. It can be assumed that an equilibrium between simple molecules, aggregated molecules, and colloidal particles is sometimes established in extraction processes.

Extraction can take place at very high temperatures. At 1150°–1200° molten metallic magnesium can be used to extract plutonium from molten metallic uranium containing up to 1% of Pu. Plutonium can be extracted also from a U–Cr alloy melting at a lower temperature (860°).

The extraction is carried out with vigorous agitation of the two immiscible phases either mechanically or by an induction method. The partition coefficient is 2. The process takes place very slowly in the absence of stirring[35,36]. Colloidal particles of plutonium must be assumed to pass into the metallic magnesium. Other similar processes are also known[37].

It has previously been established that colloidal solutions can be formed in two-phase metallic alloys[38]. Various radioisotopes can occur in solution in a colloidal state[39–43].

Study of the adsorption of microquantities of some radioisotopes (Zr, Po, etc.) on hydrophobic non-ion-exchange surfaces (paraffin wax, Floroplast 4) shows that these radioisotopes may be present in solution in molecular form[44].

It has been found that ^7Be at concentrations below 10^{-9} M in 0.01 *N* HNO_3 is present in the solution in the form of a radiocolloid. From the Einstein–Stokes equations the mean radius of the aggregates was calculated as 7 Å at pH 2[45] and 22 Å at pH 10. It has also been found that some radioisotopes can be adsorbed on other colloidal particles present in the solution[46].

Methods of centrifuging, ultrafiltration of the solutions, and adsorption on activated charcoal have been used to study the radioisotopes ^{90}Y and ^{125}Sb at concentrations of $\sim 10^{-8}$ M. It was found that the yttrium isotope forms radiocolloids and is poorly adsorbed on colloidal impurities. The antimony isotope is present in solution in the form of radiocolloids, and also as chloro- and chlorohydroxo-complexes.

At a concentration of $\sim 10^{-7}$ M in nitric-acid solution ^{111}Ag forms a truly colloidal solution, and is not adsorbed on impurities[47]. The state of the radioisotopes ^{65}Zn and ^{90}Y in solution has also been studied[48].

At the present time extraction methods are employed with various radioisotopes at extremely low concentrations.

A study has also been made of the extraction with tributyl phosphate of fission rare-earth radioisotopes[49,50]. All these results show that some radioisotopes can be

extracted in the colloidal state by themselves, or else are adsorbed on colloidal impurities and are extracted together with the latter.

Extraction by a colloid-chemical mechanism can be represented as follows: if the element to be separated is present in solution in the form of highly disperse sols (submicroscopic sols and semi-colloids), these sols pass into the organic phase as a result of the decrease in free surface energy of the system. If, however, the element to be separated is present in the form of ions in the solution, extraction involves the formation of an unstable emulsion with the production of a very large surface of interaction between the extractant and the aqueous solution. Associated molecules of the extractable compound then arise in the interfacial film, and these aggregate to particles of a sol, which subsequently pass into the organic phase.

When the sol passes into the organic phase it may completely dissolve with the formation of a true solution. There may be cases in which a sol becomes uniformly distributed in the organic solvent, when colloidal solutions are formed; in most cases the degree of dispersion of the sol is then diminished.

Finally, it is possible that, after the sol has passed into the layer of organic solvent, it will probably aggregate and separate in the interfacial film (and also at the organic solvent–glass interface) as a suspension.

It is seen from the above that particles of various sols can be formed and pass from the aqueous medium into the organic solvent. When a hydrosol is shaken up with an organic liquid, it sometimes happens that after some time the particles collect at the interface between the two liquids. At low concentrations of the sol, however, this process is slowed down, and it is therefore possible to isolate the element together with the organic phase.

We have carried out experiments on the extraction from colloidal solutions of various elements and compounds with organic solvents (Table 1).

These experiments show that diverse compounds can be extracted from colloidal solutions formed by sparingly soluble compounds.

The most stable sols are formed in chloroform, those obtained in diethyl ether being less stable. It is advisable to separate the organic solvent rapidly from the aqueous solution after extraction, since in some cases unstable colloidal solutions can be formed in the organic solvent. When the sol is readily soluble in the organic solvent, a comparatively large amount of substance can be extracted.

As a practical result of the ideas which we have developed on the colloid-chemical mechanism of extraction, we have worked out a method for the extraction of microquantities of many elements in the form of sparingly soluble compounds.

Table 2 illustrates the application of this method to several elements. It can be seen that a colloidal solution of gold containing 0.1 μg of Au is extracted comparatively well (20–25%). Microquantities of zinc (20 μg) in the form of carbonates are extracted to the extent of 20–25%. Lead chromate is extracted well (75–90%); if $BaCrO_4$ is used as carrier, unweighable amounts of lead (RaD) are extracted to the extent of 75%.

An interesting phenomenon is observed in the extraction of unweighable amounts of RaD (Pb) in the form of sulphate when different carriers are used. In the absence of carrier, RaD is poorly extracted; use of $PbSO_4$ and $SrSO_4$ as carriers also gives unsatisfactory results. With $BaSO_4$ as carrier, however, extraction is increased to 30%. This difference probably depends on the solubilities of the sulphates of these compounds, and also on their chemical composition.

TABLE 1. Extraction of some elements from colloidal solutions.

Chemical compound	Organic solvent	Chemical compound	Organic solvent
Au	$CHCl_3$ and CCl_4	$BaSO_4$	ether and $CHCl_3$
Ag	ether and $CHCl_3$	Ag_2CrO_4	ether and $CHCl_3$
S	ether and $CHCl_3$	$PbCrO_4$	$CHCl_3$
CoS	$CHCl_3$	SiO_2	ether and $CHCl_3$
Ag_2S	$CHCl_3$	$Co(OH)_2$	$CHCl_3$
AgCl	$CHCl_3$	$Co(AlO_2)_2$	$CHCl_3$
AgI	$CHCl_3$ and CCl_4	$Ag_2C_2O_4$	$CHCl_3$
$SrSO_4$	ether and $CHCl_3$	Ag_2CO_3	$CHCl_3$

TABLE 2. Extraction of microquantities of some elements in the form of sparingly soluble compounds.

Radio-isotope	Amount of carrier, μg	Precipitant	Extractant	Radio-isotope extracted, %	Remarks
Au^{198}	Au 0.1	ascorbic acid*	$CHCl_3$	18.6	3 ml of aqueous soln. and 3 ml of extractant taken for all expts.
Au^{198}	Au 0.1	quinol*	$CHCl_3$	25.1	
Au^{198}	Au 0.1	»	ether	14.3	
Zn^{65}	Zn 20	Na_2CO_3	$CHCl_3$	16.7	
Zn^{65}	Zn 20	$K_4Fe(CN)_6$	$CHCl_3$	8.6	
Zn^{65}	Zn 20	Na_2CO_3	CCl_4	20.1	
Pb^{210} (RaD)	Pb 200	K_2CrO_4.	$CHCl_3$	88.0	2 extractions
Pb^{210}	Ba 23	K_2CrO_4	$CHCl_3$	76.0	measurements made after equilibrium reached between RaD and RaE
Pb^{210}	Pb 20	K_2CrO_4	$CHCl_3$	58.2	3 ml 0.1 *N* KCl taken
Pb^{210}	Pb 20	Na_2SO_4	$CHCl_3$	0.0	
Pb^{210}	Sr 90	Na_2SO_4	$CHCl_3$	0.6	
Pb^{210}	Ba 22	Na_2SO_4	$CHCl_3$	30.0	
Pb^{210}	none	H_2SO_4	$CHCl_3$	5.5	
Pb^{210}	Pb 20	H_2SO_4	$CHCl_3$	0.5	
Pb^{210}	Sr 90	H_2SO_4	$CHCl_3$	0.6	
Pb^{210}	Ba 22	H_2SO_4	$CHCl_3$	30.6	
Ag^{110}	Ag 19	KCl	$CHCl_3$	48.7	
Ag^{110}	Ag 19	K_2CrO_4	$CHCl_3$	53.0	
Ag^{110}	Ag 19	K_2CO_3	$CHCl_3$	20.6	
Ag^{110}	Ag 19	$H_2C_2O_4$	$CHCl_3$	35.3	
Co^{60}	Co 20	K_2CO_3	$CHCl_3$	21.0	
Co^{60}	Co 20	Na_2S	$CHCl_3$	56.0	3 extractions
Co^{60}	Co 20	NaOH	$CHCl_3$	26.6	
Co^{60}	Co 20+Al 80	NaOH	$CHCl_3$	80.5	3 extractions[81]
Sr^{90}	Sr 85+Ba 44	H_2SO_4	$CHCl_3$	30.8	
Sr^{90}	Sr 85	K_2CO_3	$CHCl_3$	23.1	
Pb^{210} (RaD)	Pb 26	Na_2S	$CHCl_3$	45.6	3 extractions
In^{114}	In 23	NaOH	$CHCl_3$	13.2	
In^{114}	In 23	K_2CrO_4	$CHCl_3$	34.4	3 extractions
In^{114}	In 23	KNO_3	$CHCl_3$	12.4	
Tl^{204}	Tl 63	Na_2S	$CHCl_3$	12.1	
Tl^{204}	Tl 63	Na_2S	CCl_4	25.8	
Tl^{204}	Tl 63	NaOH	$CHCl_3$	3.0	
Tl^{204}	Tl 63	NaOH	CCl_4	15.3	
Tl^{204}	Tl 63	KI	$CHCl_3$	27.3	3 extractions
Tl^{204}	Tl 63	KI	CCl_4	98.6	3 extractions
Tl^{204}	Tl 63	$K_4Fe(CN)_6$+NaOH	$CHCl_3$	12.1	
Tl^{204}	Tl 63	$K_4Fe(CN)_6$+NaOH	CCl_4	69.8	3 extractions

* Colloidal particles of Au separated.

Thus the coprecipitation of microquantities of a substance can be studied by using the colloid-chemical method of extraction. Minute quantities of a substance ("carrierless" radioisotopes) can be isolated by extraction with the use of a microcollector (20–100 μg of M) for coprecipitation.

It is interesting that very small amounts of sparingly soluble compounds of elements are not extracted; this can be explained by the impossibility of a solid phase being formed; employment of an appropriate microcollector (10–100 μg of M) results in the formation of colloidal solutions, which can then be extracted. Microquantities of silver are relatively well extracted in the form of AgCl 50%, Ag_2CrO_4 50%, $Ag_2C_2O_4$ 35%, and Ag_2CO_3 20%. Cobalt is extracted well in the form of cobalt aluminate $Co(AlO_2)_2$ 80%, CoS 56%, and $Co(OH)_2$ 25%.

The efficiency with which sols are extracted depends on the relative volumes of extractant and of aqueous phase.

Additional work which we have carried out has shown that good results are obtained in the extraction of microquantities of several other elements in the form of sulphides and various sparingly soluble compounds. An advantage of this method is the rapid separation from solution (5–10 min) of the element to be determined and the simplicity with which the precipitated compound is converted into a soluble state without the introduction of foreign impurities. The method makes it possible to isolate microquantities of various elements in the form of sparingly soluble compounds.

The mechanism of the transfer of elements to the organic phase can be represented as follows: (*a*) a sol present in the aqueous solution passes into the organic solvent; (*b*) the compounds to be extracted form, under the influence of the organic solvent, associated molecules, which aggregate to sols, the latter then passing into the organic solvent. Elements may be present in the solvent in the following states: particles of hydrosol which pass into the solvent and dissolve in it; particles of the sol which pass into the solvent and exist in it in the form of a colloidal solution, when the particle size may even increase; particles of the sol which pass into the organic solvent, then rapidly aggregate, and separate in the interfacial film in the form of a coarse suspension.

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