SOLVENT SUBLATION IN WATER-SALT SOLUTIONS BY SODIUM DODECYLSULFATE

O. L. Lobacheva

National Mineral Resources University "Mining", 199106 Saint-Petersburg, olga-59@yandex.ru

ABSTRACT. Theoretical and experimental data of the solvent sublation of Ce (3+), Sm (3+), Y (3+) from nitrate solutions with sodium dodecyl sulphate as a collector were obtained. The ratio of distribution coefficients from pH aqueous phase has been analyzed. Separation coefficients for all pairs of rare earth metals have been estimated.

Key words: solvent sublation, rare earth elements, distribution coefficients, sodium dodecylsulfate

ОТДЕЛЯНЕ НА РАЗТВОРИТЕЛИ ВЪВ ВОДНИ СОЛЕНИ РАЗТВОРИ ЧРЕЗ НАТРИЕВ ДОДЕЦИЛ СУЛФАТ

О. Л. Лобачева
Национален минен университет, 199106 Санкт Петербург, olga-59@yandex.ru

РЕЗЮМЕ. Получени са теоретични и експериментални данни за отделяне на разтворители на Ce (3+), Sm (3+), Y (3+) от нитратни разтвори с натриев додецил сулфат като уловител. Анализирано е съотношението на коефициентите на разпространение от pH водната фаза. Изчислени са приблизително коефициентите за отделяне на всички редки земни метали.

Ключови думи: отделяне на разтворители, редки земни елементи, коефициенти на разпространение, натриев додецил сулфат

Introduction

Solvent sublation, an adsorption-bubble method for surface separation in which floating-up gas bubbles carry a substance they adsorbed (sublate) from one fluid into another. The method was first suggested by Sebba in 1962. The solvent sublation is a combination of flotation of ions or molecules with fluid extraction. In the given case, the term sublate means a chemically individual substance, in which the ion being recovered (colligend) is concentrated on the surface of bubbles. In contrast to the ordinary fluid extraction, the mass transfer in solvent sublation from the aqueous to organic phase involves bubbles. This eliminates a number of problems associated with emulsification. In addition, the volume of the organic phase is comparatively small because of being only determined by the capacity for the sublate and by the cross-sectional area of the apparatus. The process is performed at low gas flow rates not disintegrating the upper layer of the organic fluid. The method is used in recovery of valuable components from lean technological raw materials and wastes formed in ore processing, quantitative determinations of trace amounts of metals and surfactants, and wastewater purification. At the same time, studies devoted to use of solvent sublation to recover valuable components and, in particular, ions of nonferrous and rare-earth metals are few in number and nonsystematic. However, such a specific feature of solvent sublation as the possibility of multiple concentration of metal ions in small amounts of an organic solvent shows that this method is promising for recovery of valuable components with the aim of their subsequent regeneration.

In this study, we examined the possibility of recovering cerium(III), samarium(III), europium(III) ions by solvent sublation, with an anionic surfactant (sodium dodecyl sulfate, NaDS) serving as a collecting agent, and isooctanol, as a flotation extractive agent. The concentration of metal ions in model solutions was 0.001 mol kg^{-1}.

The goal of our study was to determine the optimal solvent sublation conditions of yttrium ions from nitrate solutions.

Experiment

In solvent sublation, we used a classical glass column made in the form of a cylinder with a Schott filter serving as its bottom. A gas (nitrogen) was delivered from a cylinder through a porous partition. In each run, a 200-mL portion of a solution of $Me(NO_3)_3$ under study, containing sodium dodecyl sulfate whose concentration corresponded to the reaction stoichiometry, and 5 ml of the organic phase (isooctanol) were placed in a column 0.035 m in diameter and 0.45 m high.The gas delivery rate was chosen (3.3×10^{-4} m^3 h^{-1}) so that the layer of the organic solvent was not strongly disrupted. A run was performed during 2 h. It should be noted that the presently available data on the nature of the organic phase are scarce. Sebba and others report that the organic phase ("trap") must possess a certain polarity and conform to the main requirements to the organic phase in solvent sublation: density lower than that of water, minimum solubility in water, maximum capacity to accumulate the sublate. Isooctanol used as the organic phase satisfies these requirements.

The solvent sublation process was performed to constant residual concentration of C e (3+), Sm (3+), Y (3+) ions, found by the standard method [12]. The solution pH values were monitored using an anion-7010 ion meter with a glass electrode. The solution pH values were determined using solutions of nitric acid or sodium hydroxide. Solutions of the metal salt were prepared by gravimetry from Me-nitrate hexahydrates of chemically pure grade.

To find the content of the dodecyl sulfate ion (DS^-) in solution, we chose the potentiometric titration with an anion-selective membrane. the method developed at the chair of physical chemistry, St. Petersburg state university, can determine the concentration of dodecyl sulfate ions from the variation of the electromotive force of a galvanic cell in the course of titration. the titration was performed with a solution of cetyltrimethylammonium chloride of " chemapol" brand with a concentration of 0.001 mol kg^{-1}. The relative error of titration was 2%.

The distribution coefficient, which is the ratio between the substance concentrations in both phases, is dependent on the distribution conditions and independent of phase volumes.

It has been shown in numerous studies that the distribution of a substance in solvent sublation is determined by its ability to be adsorbed on walls of bubbles passing through the solution and is independent of the phase volume ratio. Thus, the sublate adsorption is the key factor of the process.

The solvent sublation was performed in a pH range of 5.5–8.0. The results are listed in Tables 1, 2 and pictured in Figs. 1, 2.

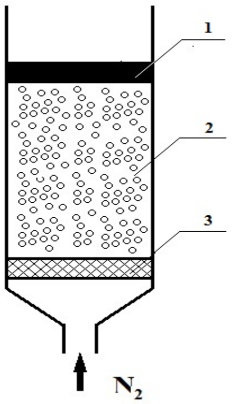

Fig. 1. Solvent sublation column: 1- organic phase (2-octanol), 2-aqueous solutions ($Me(NO_3)_3$ + NaDS), 3- Shott filter

Table 1. *Degree of recovery, α, and distribution coefficient of Y(III) at a process duration of 120 min and c_0 = 0.001 mol kg^{-1}*

pH	c_{or}	c_{aq}	K_d	α
	mol kg^{-1}			
5.5	0.0098	7.0	0.32	24.56
6.0	0.0090	7.5	0.29	22.62
6.8	0.0366	0.8	11.10	91.73
7.4	0.0396	0.02	102.09	99.03
8.0	0.0342	1.0	5.99	85.71

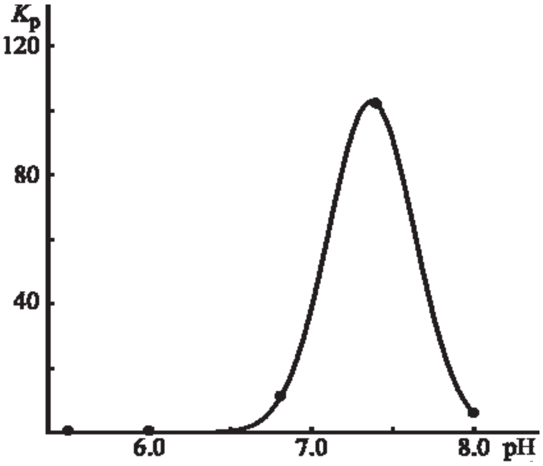

Fig. 2. Distribution coefficient K_d of yttrium(3+) ions vs. the solution pH at an initial Y^{3+} concentration of 0.001 mol kg^{-1}

It can be seen from experimental data that yttrium ions are removed in the initial phase of the process (5–10 min), compared with further flotation. thus, it is possible to find the optimal duration of the flotation process in yttrium nitrate solutions with an initial concentration of 0.001 mol kg^{-1}. The kinetic curves of solvent sublation show that the maximum recovery of yttrium ions occurs at pH 7.4 in the course of 30 min.

In the course of time, the concentration of yttrium ions asymptotically approaches a certain final value, which is characteristic of the attainment of a steady state by the system. The kinetic dependences in fig. 1 can be described by first-order reaction equations, in agreement with Posner and Alexander's theory.

The results of these calculations are listed in Table 2. The first order of the solvent sublation process indicates that it occurs in the steady diffusion mode, in which the diffusion of particles being recovered in the stern layer near the surface of gas bubbles is the rate- determining stage. The adsorption of the particles being recovered at the solution–air interface is described by the stern adsorption model in which adsorption occurs on a certain area in a monomolecular layer [16]. Attention is attracted by the fact that three kinds of kinetic curves are observed (considered experimental data), depending on the pH value: (1) at pH 5.5–6.0, the process of solvent sublation recovery of yttrium passes to the steady mode with high equilibrium concentrations and maximum degree of recovery of 25%; (2) at pH 6.8–7.4, the equilibrium concentration decreases, with a tendency toward an increase in the process rate; and (3) at pH 8.0, the rate of yttrium recovery sharply falls.

The observed behavior can be explained by analysis of forms of diffusing species at various pH values. It was found in [17] that monohydroxo complexes of yttrium are formed in an aqueous solution at ph values in the range from 5.46 to 6.7; at pH 6.7–7.2, dihydroxo complexes are formed; at ph 7.2–7.4, the hydroxide is formed; and at pH 7.4, the hydrate formation ends.

In [18], the dissociation constant of dodecyl sulfuric acid was found to be 1.7 × 10^{-6} and, accordingly, pK 5.77. At pH = p*K*, the degree of dissociation is 50%. At pH 4.8, it is about 10% and solvent sublation hardly occurs because the dodecyl sulfate interacts with yttrium cat ions in the anionic form. At pH 6.8, the degree of dissociation of dodecyl sulfuric acid exceeds 90% and must hardly affect the recovery of yttrium as the pH value is raised further.

Table 2. *Steady-state yttrium concentrations in the aqueous phase and rate constants of solvent sublation in relation to pH*

pH	c_{aq}, M × 10^4	k, min^{-1}
5.5	7.00	0.046
6.0	7.50	0.007
6.8	0.84	0.027
7.4	0.02	0.169
8.0	1.00	0.019

The concentration gradients of dodecyl sulfate anions and monohydroxo complexes of yttrium in the stern layer increase with ph because of the growing degrees of both dissociation and complexation. as a result, the rate constant becomes more than two times larger. $Y(OH)(C_{12}H_{25}OSO_3)_2$ is the form being recovered (sublate). in the equation of the mass action law, the concentration of dodecyl sulfate anions is squared, the equilibrium is shifted toward the reverse reaction, and, consequently, the degree of recovery of Y^{3+} ions does not exceed 25%. At pH 6.8–7.4, yttrium is in the aqueous phase in the form of dihydroxo complexes, and at pH 7.2–7.4, partly as $Y(OH)(C_{12}H_{25}OSO_3)_2$ because no hydroxide precipitate is formed. $Y(OH)(C_{12}H_{25}OSO_3)_2$ is the sublate. Because the exponent at the concentration of dodecyl sulfate anions decreases to unity and less, the equilibrium shifts toward the forward reaction. The rate constant of the process decreases at pH 6.8 and then increases at pH 7.4 in accordance with the variation of the concentration gradient of dihydroxocomplexes.

Table 3. *Degree of recovery, α, and distribution coefficient of Sm(III) at a process duration of 120 min and* c_0 *= 0.001 mol* kg^{-1}

pH	C org	Caq·10^4	$K_{equilib}$	α %
5,1	0,0135	6,60	0,51	33,9
6,1	0,0141	6,30	0,54	35,4
6,9	0,0314	2,10	3,66	78,5
8,0	0,0392	0,17	55,56	98,2
9,9	0,0374	0,65	14,43	93,5

As stated, in aqueous solutions at pH 5.3-6.1 is formed $Sm(OH)(C_{12}H_{25}OSO_3)_2$. Thus, removal Sm (III) occur in the forms of monohydroxododecylsulfate and $Sm(C_{12}H_{25}OSO_3)_3$.

So far as Ce(III), these cations form $Ce(OH)(C_{12}H_{25}OSO_3)_3$, which are removed from dilute aqueous solutions by solvent sublation process at pH=6.

Conclusions

The forms in which the dodecyl sulfate and Me (3+) are present in the aqueous phase vary with its pH value, which results in that there are three different solvent sublation mechanisms.

Acknowledgments

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