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M. Milanova[a]; T. Horozov[a]; A. Nikolov[a]; D. Todorovsky[a]
[a] FACULTY OF CHEMISTRY, UNIVERSITY OF SOFIA, SOFIA, BULGARIA

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NOTE

On the Liquid Membrane Extraction of Lanthanum and Neodymium

M. MILANOVA, T. HOROZOV, A. NIKOLOV, and
D. TODOROVSKY
FACULTY OF CHEMISTRY
UNIVERSITY OF SOFIA
1, J. BOURCHIER AVENUE, SOFIA 1126, BULGARIA

ABSTRACT

Comparison of liquid–liquid extraction and liquid–membrane extraction is made on the basis of some experimentally established parameters of the La and Nd separation process. The observed effects confirm the important role of surfactants in the LME process.

INTRODUCTION

Data on the application of liquid–membrane extraction (LME) for lanthanide separation are quite limited. Results on the LME of Eu and La from hydrochloric acid (1, 2) as well as on the LME of Sm, Er, and Gd from HNO_3 by bis-(2-ethylhexyl)-phosphoric acid (DEHPA) (3) have been published. The influence of the experimental conditions on the extraction rate of La, Nd, Eu, Gd, Dy, and Yb has been studied (4). The assumption for the significant role of the surfactants on the extraction rate and on the membrane selectivity is becoming increasingly dominant (5, 6). A comparative theoretical treatment of liquid–liquid extraction (LLE) and LME is presented in Ref. 7.

The present work is an attempt at a comparative experimental study of the LLE and LME of La and Nd in which the extraction and stripping stages of the process are considered separately.

EXPERIMENTAL

LME

The organic membrane phase consisted of a 0.15-M DEHPA (Fluka) and 0.076 M polyoxyethylene-2-oleyl-ether (Brij 92, Sigma) solution in kerosene (boiling point 175°C). This solution (10 cm^3) and an equal amount of the stripping one (1 M HCl) were sonicated for 30 seconds in an ultrasonic disintegrator (sonic power 180 W). The emulsion thus prepared was agitated for 4–20 minutes at 298 K (stirring speed 2 s^{-1}) with 700 cm^3 of the feed lanthanide solution [1.0×10^{-4} mol/dm^3 $Ln(NO_3)_3$]. The emulsion obtained breaks down 210 seconds after agitation is stopped.

The pH of the feed solution was adjusted to 1.85. Preliminary experiments carried out at pH 1.5–5 showed that pH values lower than 1.9 ensure sufficiently clear solutions after the emulsion break-down. This could be connected with the sharp decrease of the DEHPA distribution ratios at $pH < 1.8$ (12).

In some experiments the feed solution was preliminarily saturated with DEHPA by shaking for 20 minutes with 0.3 M DEHPA in kerosene.

LLE

As the main interest in the present work was toward the LME elementary processes, the LLE was carried out under the same conditions as the LME. Naturally, the extracting phase did not contain a surfactant.

In both processes the concentration changes of Ln^{3+} ions in the aqueous phases were measured after the processes. The main process characteristics were calculated on this basis.

RESULTS AND DISCUSSION

The results obtained for the distribution coefficients, separation factors, degree of leaching, and coefficients of concentrating are shown in Table 1 (for an explanation of the symbols, see the Appendix). The reproducibility of the results for D and F at 18.5 min extraction time without preliminary saturation of the feed phase is rather poor due to the partial destruction of the emulsion. The relative volume changes of the organic and stripping phases after the process are 5–20% (up to 50% in some cases). The preliminary feed phase saturation with a carrier decreases the DEHPA leakage into the feed solution. At the same time, it leads to the swelling of the stripping phase, more strongly expressed for the Nd solution.

A qualitative explanation of these observations could be found in the formation of reverse micelles (containing DEHPA, M^{n+}, and H_2O) in the organic membrane (9) which is favored by preliminary saturation. The compounds formed (in which the Ln^{3+} ions probably partially retain their hydrate water) dissolve considerably better in the organic phase than in the aqueous one (10). Thus, a water flow from V_1 to V_2 and V_3 takes place. The greater hydration and stronger interaction of the Nd^{3+} ions with

TABLE 1
Some Characteristics of the Extraction Processes

				R (%)						D									
		K		La			Nd			La		Nd		F		Y			
Method	t (min)	La	Nd	R^e	R^r	R	R^e	R^r	R	D^e	D^r	D^e	D^r	F^e	F^r	La	Nd		
LME	4.5	17	20	41	60	24	48.0	52	25	52	0.8	69.0	1.03	1.3	1.3	0.59	0.517		
		±3	±2	±5	±5	±3	±0.1	±2	±1	±10	±0.2	±0.0	±0.1	±0.3	±0.3	±0.04	±0.002		
	5.5	28	18	52	73	37	48.0	54	26	80	0.4	69	1.1	0.86	2.5	0.48	0.52		
		±2	±3	±2	±5	±2	±0.5	±10	±5	±7	±0.1	±1	±0.4	±0.08	±1.1	±0.02	±0.004		
	10.5	92	37	85	73	59	84	61	51.0	325	0.22	401	0.83	1.2	3.8	0.19	0.16		
		±13	±3	±3	±2	±4	±1	±1	±0.0	±74	±0.05	±32	±0.06	±0.3	±0.9	±0.03	±0.01		
	18.5	120	92	88	82	72	89	68	60	870	0.13	974	0.4	1.1	3.3	0.10	0.11		
		±42	±37	±4	±4	±3	±5	±9	±5	±264	±0.02	±491	±0.1	±0.6	±0.9	±0.05	±0.05		
	18.5[a]	53.1	29.5	94.9	86	81.3	94	51	48	1373	0.23	1209	1.5	0.9	6.4	0.05	0.06		
		±0.2	±0.6	±0.4	±1	±0.5	±1	±2	±2	±101	±0.01	±226	±0.1	±0.2	±0.4	±0.004	±0.02		
LLE	60	50	58	91	85	64	97	90	75	680	0.28	2770	0.12	4.1	0.43	0.095	0.026		
		±10	±4	±1	±9	±7	±1	±7	±6	±9	±0.12	±530	±0.06	±0.9	±0.28	±0.01	±0.006		
	60[a]	60	63	94	91	75	98	91	80	1140	0.09	4620	0.09	3.0	1.0	0.06	0.02		
		±1	±2	±2	±1	±3	±1	±3	±6	±360	±0.01	±223	±0.03	±1.0	±0.3	±0.06	±0.01		

[a] The experiments were carried out with preliminary saturation of the aqueous phase.

DEHPA ensures a greater increase of V_3 compared to the one caused by the La^{3+} ions.

The volume changes make some contribution to the observed effects. Moreover, in certain cases they are dominating. For instance:

$$K_{La(+)}/K_{La(-)} = V_{3,La(-)}/V_{3,La(+)}$$

$$D^r_{La(-)}/D^r_{La(+)} = (V_3/V_2)_{La(-)}/(V_3/V_2)_{La(+)}$$

where (−) and (+) represent experiments without and with preliminary saturation, respectively.

However, most of the experimental observations could not be explained by the volume changes, especially for Nd. For example, the above-mentioned relations are not retained for Nd extraction. The value of D^e_{Nd} is considerably lower and the D^r values (especially that of D^r_{Nd}) are considerably higher than those for LLE.

These facts lead us to suppose that the lanthanide flow forward (into) and backward (out of) the organic phase is complicated by surfactant adsorption on the interface. This effect is proportional to the degree of adsorption and is not equally pronounced for the different Ln^{3+} ions, i.e., the membrane shows some selectivity for La and Nd. The relatively weak surfactant adsorption at the feed–membrane solutions interface is reflected only on the Nd permeation, decreasing D^e_{Nd}. In the stripping stage, the effect on D^r_{Nd} is strongly expressed (especially after the saturation) but it is also seen for La.

The LME separation factors F^e are near unity and are time-dependent, which shows a kinetic contribution to the extraction sequences. The distribution ratios D^e are considerably higher, but the F^e values are considerably lower than the ones found in Ref. 4. Since Teramoto's carrier itself is less effective than DEHPA [at least under the conditions of LLE (11)] it may be supposed that the better F^e values in Ref. 4 are due to the application of Span 80 as a surfactant, which is probably more effective (i.e., selective) than the Brij 92 used by us.

Some other remarks should also be made. The products $D^e(V_2^0/V_1)$ calculated from our results lay in the upper part of the values range in which (according to Ref. 7) the practical effect of the LME application could be expected. As can be seen from Table 1, LME has about twice as much concentrating power as LLE, even for the shorter times of the LME process. That ratio is just a little higher than the expected one derived from theoretical calculations (7).

Figure 1 allows comparison of our data with those obtained experimentally and theoretically by Teramoto et al. (4) for another carrier. It may be supposed that the influence of pH is related to the chemical nature of the carrier.

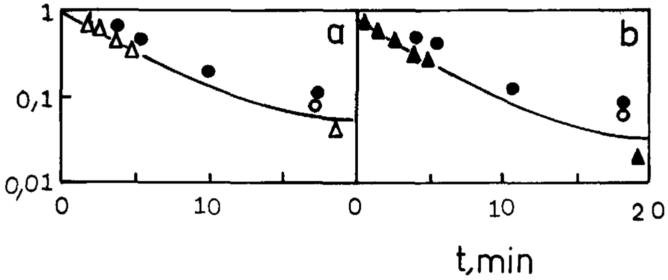

FIG. 1 Extraction stage rate of LME of La (a) and Nd (b): this work without (●) and with (○) preliminary carrier saturation of the aqueous phase; pH = 2.67 (△), pH = 2.50 (▲) (4), and the theoretical values calculated by the model suggested in Ref. 4 (full line).

The extraction equilibrium constants for both variants of the extraction process for La are very close: LME 0.12 and LLE 0.20. Such a similarity should be expected because of the identical nature of the chemical processes determining these equilibria. The difference for Nd is a little greater: LLE 0.78, LME 0.13, which indicates the stronger influence of the surfactant on the Nd extraction process.

CONCLUSION

The observed effects during LME of La and Nd are due to the partial destruction of the emulsion (producing changes in the organic and stripping phase volumes) and, mainly, to surfactant adsorption at the interfaces. The adsorption disturbs Ln permeation in and out of the organic phase. The effect of the surfactant depends on the degree of its adsorption and on the nature of Ln^{3+}. The stopping effect of the membrane is better expressed for Nd. As a result of this effect, the separation of La and Nd is expressed during the stripping stage.

The LME process is kinetically controlled, i.e., LME selectivity is due to the different kinetics of complex transport.

Our results confirm the assumption that the effectiveness of LME depends on the surfactant type. LME seems to be a convenient method for concentrating lanthanide.

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APPENDIX (Symbols and Definitions)

Subscripts: 1 = feed aqueous phase
2 = organic phase
3 = stripping phase
Superscripts: 0 = initial
e = extraction stage
r = reextraction stage
t = time
Coefficient of concentrating: $K_{\text{Ln}} = (C_3/C_1^0)_{\text{Ln}}$
Degree of leaching: $R_{\text{Ln}}^e = (C_2V_2/C_1^0V_1^0)_{\text{Ln}} \times 100$
$R_{\text{Ln}}^r = (C_3V_3/C_2V_2)_{\text{Ln}} \times 100$
$R_{\text{Ln}} = (C_3V_3/C_1^0V_1^0)_{\text{Ln}} \times 100$
Decrease of Ln^{3+} concentration in the feed solution: $Y = C_1^t/C_1^0$

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