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Mass Transfer Studies of Nd, U, Np and Pu across Liquid–Liquid Interfaces*

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The rate-controlling step in the extraction of lanthanides and actinides from aqueous systems by organophosphorus reagents may involve diffusion in either phase, complex formation or the elimination of water from ionic solvation layers. The determination of the importance of these factors is paramount for a variety of industrial operations, e.g., for an effective modelling of the PUREX process. Experimental data have been obtained in unstirred solutions by use of an Analytical Ultracentrifuge for regions much closer to the interface of immiscible liquid–liquid systems than have hitherto been reported [1, 2]. From a comparison of the experimentally observed concentration profiles with calculated profiles, conclusions about the transfer mechanism may be drawn, since the diffusion coefficients in the aqueous and the organic solutions have been measured by the same technique.

Experimental

A Beckman Model E Analytical Ultracentrifuge was used to record the transport behaviour of the solute molecules by means of both the Schlieren and UV optical systems. All measurements were carried out in a cell containing a capillary-type centrepiece, the two compartments of which could be filled separately. For the extraction measurements one sector was filled with 0.12 ml of the aqueous test solution and the other sector was filled with 0.36 ml of the organic extractant. The diffusion measurements were performed by a similar procedure, e.g., the compartments were filled with an organic solution and the organic solvent respectively. The cell was filled carefully into a titanium rotor and accelerated to a final measurement velocity of 5.200 rpm. The temperature of the rotor was controlled at 25.00 ± 0.01 °C by a thermistor unit. At a velocity of 1000 rpm the solvent was pressed through the capillary into the solute sector by the centrifugal force, creating a sharp boundary by overlaying the test solution.

The light rays passing through the cell were deviated by the refraction at the boundary. Since it has been shown that the refractive index is a linear function of the solute concentration, the Schlieren optical system provided a plot of the actual change in concentration at the boundary. Photographic images were obtained at preselected intervals. Using the UV optical system the concentration profiles were obtained by plotting the absorption values *versus* the distance from the axis of rotation. The diffusion coefficients were calculated in the usual way from the height and the area of the Schlieren peaks and the patterns recorded by the UV system at different times during the run [3]. Since both optical systems were used simultaneously, the absorption optics showed the transport of the coloured particles, while the Schlieren optical system presented the sum of all moving species contributing to the refraction. The error of the results was ±3% or even less for high concentrations.

Results and Discussion

Under the influence of a centrifugal field, the boundary between two solutions was stabilized. Information concerning the mass transport caused by a concentration gradient was obtained by the optical systems without disturbing the liquid–liquid interface. After calibrating the optical systems, a variety of physicochemical data were determined for each element, including diffusion coefficients, distribution coefficients and extraction profiles. Measurements were also carried out in the presence of high concentrations of $UO_2(NO_3)_2$ and at various concentrations of nitric acid.

The results of our diffusion measurements of U and Pu in aqueous and non-aqueous systems have

TABLE I. Transport Coefficients in the System 0.3 M $Nd(NO_3)_3$–3.0 M HNO_3–TBP/n-Dodecane

Time (s)	Transport coefficient	
	$10^9 \times \beta_m$ (mol cm^{-2} s^{-1})	$10^9 \times \beta_c$ (mol cm^{-2} s^{-1})
57	2.25	2.2793
209	0.67	0.6665
393	0.52	0.5279
569	0.42	0.4468
746	0.40	0.3950
930	0.35	0.3516
1190	0.30	0.3113

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TABLE II. Transport Coefficients in the System $Nd(NO_3)_3$–3.0 M HNO_3–TBP/n-Dodecane

$Nd(NO_3)_3$ (mol^{-1})	Time (s)	Transport coefficient		Diffusion $10^6 \times D$ ($cm^2\ s^{-1}$)
		$10^{10} \times \beta_m$ ($mol\ cm^{-2}\ s^{-1}$)	$10^{10} \times \beta_c$ ($mol\ cm^{-2}\ s^{-1}$)	
0.10	1072	1.1	1.0843	1.60
0.20	1068	2.2	2.0860	1.47
0.30	1190	3.2	3.1133	1.60
0.40	1138	4.1	4.1729	1.55

TABLE III. Transport Coefficients in the System 0.3 M $Nd(NO_3)_3$–HNO_3–TBP/n-Dodecane

HNO_3 (mol^{-1})	Time (s)	Transport coefficient		Diffusion $10^6 \times D$ ($cm^2\ s^{-1}$)
		$10^{10} \times \beta_m$ ($mol\ cm^{-2}\ s^{-1}$)	$10^{10} \times \beta_c$ ($mol\ cm^{-2}\ s^{-1}$)	
0.50	1099	3.8	3.7510	2.46
1.50	1060	4.0	3.8790	1.91
3.00	1190	3.0	3.1133	1.60
4.50	1047	2.5	2.6104	1.61

been published and may be taken into consideration to elucidate the interacting forces between the solvent [3, 4]. From the values of the organic complexes the Stokes' radii can be derived in order to decide whether monomers or aggregates are the predominant species. Furthermore, the diffusion and distribution coefficients were needed to calculate the theoretical concentration profiles of the extraction experiments. For that calculation the procedure of Scott *et al.* was applied [5].

The distribution behaviour of Nd, representing the lanthanides, between aqueous nitric acid and a 30/70 v/v mixture of tributyl phosphate in dodecane was chosen to show the results. Since the partition coefficient is 0.02, the change in the concentration in the aqueous phase is less than 2%. Therefore only the organic phase has to be taken into account for the calculations. The diffusion coefficient $D = 1.6 \times 10^{-6}\ cm^2\ s^{-1}$ was independent of the concentration in TBP/dodecane, the value being four times smaller than in aqueous solutions. There was very good agreement between the calculated concentration profiles and the experimental data, indicating that there was no hindrance of the transport at the boundary. The transport coefficients given in Tables I–III were determined at the beginning of the extraction these values decrease by a factor of 10 during the first 15 min. No influence of the aqueous nitric acid concentration was to be seen. By an additional gradient of uranyl nitrate, however, the transport of neodymium nitrate was accelerated. Thus, by considering the various laws of diffusion and the results of experiments involving the relevant elements in single-phase systems using the same technique, it has been proved that it is possible to describe the kinetics of extraction and to isolate the principal rate-determining step, which is the diffusion in the organic layer.

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