Appendix A

Solvent Extraction Separations

Contents

Solvent extraction is a technique which has been highly developed within many national nuclear energy programs because of its suitability as a selective separation process for fission products, actinides, and other radioactive substances. The technique is briefly described in several sections of this book (§§ 5.5.3, 9.2.6, 9.4.3, 15.7.4, 16.3.3, 21.7, and especially in 21.6 on the Purex process). It is based on the formation of uncharged organic metal complexes which are preferentially soluble in organic solvents. The three main types of such compounds are:

(i) organic chelate (i.e. binding through two positions in the organic molecule, like a claw) complexes such as plutonium tetraacetylacetonate, $PuAa_4$ (general formula MA_n), §9.4.3, cf. Figs. 9.3, 9.9. and 9.11;

(ii) inorganic metal complexes forming adducts with solvating organic compounds like TBP and hexone, e.g. $UO_2(NO_3)_2)(TBP)_2$ (or generally ML_nS_s, where L is an inorganic anion and S the organic adduct former, §21.6, cf. Fig. 16.8);

(iii) ion pair complexes between large organic cations (like alkylammonium ions, R_3NH^+) and negatively charge inorganic complexes like $UO_2(SO_4)_3^{4-}$ (generally RB^+ML^-, §5.5.2).

The physical and chemical principles governing the formation of extractable metal complexes, the conclusions which can be drawn about the chemical system from solvent extraction studies, and analytical and industrial applications are described in several monographs, e.g. "Principles and Practices of Solvent Extraction" (1992).

A.1. Single stage batch extractions

Let us consider a solute (e.g. uranium) which is distributed between an organic and an aqueous phase, independent of the kind of compounds the solute forms in the two phases. After equilibrium the weight of solute in the organic phase (*extract*) is w_{org} and in the aqueous phase (*raffinate*) w_{aq}. Thus
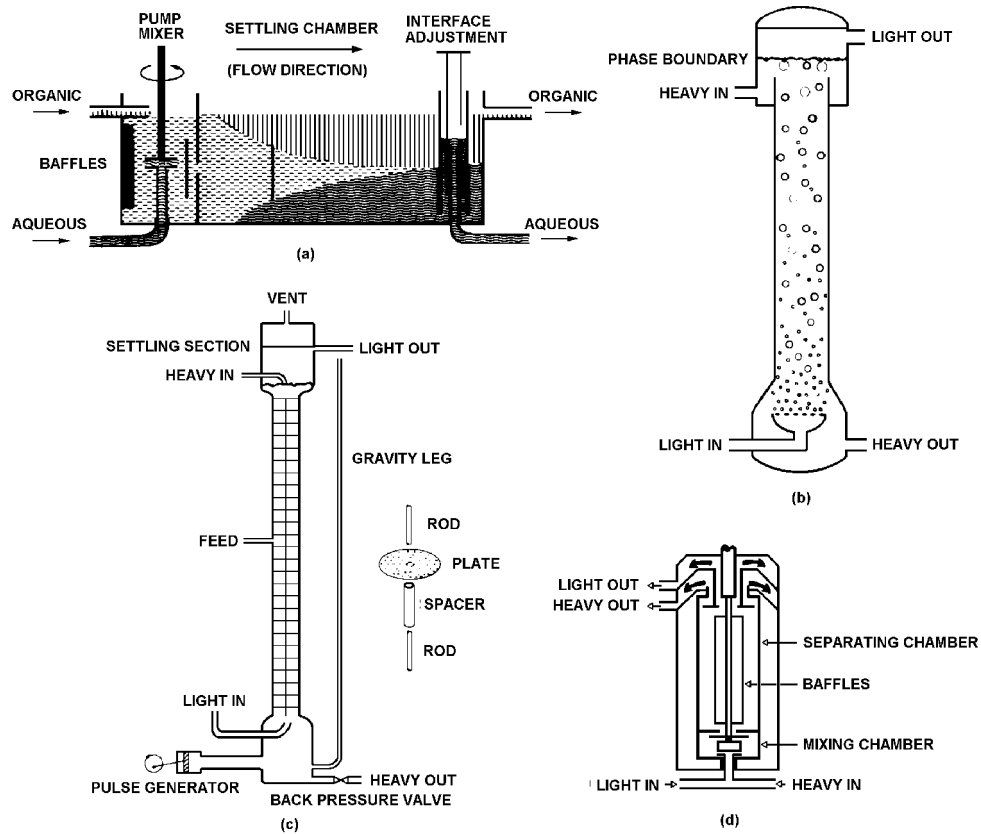
FIG. A.1. Different types of continuous extraction equipment. (a) Mixer-settler. (b) Spray column. (c) Pulsed column. (d) Tubular centrifugal contactor.

$$W_{\text{tot}} = W_{\text{org}} + W_{\text{aq}} \tag{A.1}$$

The weight fraction in the organic phase is

$$\psi_1 = P/(P + 1) \tag{A.2}$$

where the index 1 refers to the conditions after one extraction. P is called the *extraction* (or *partition*) *factor* and defined by

$$P = D\theta \tag{A.3}$$

where D is the distribution factor, defined by

$$D = \frac{\text{Concentration of all M-species in the organic phase}}{\text{Concentration of all M-species in the aqueous phase}} \tag{A.4}$$

and θ is the phase volume ratio v_{org}/v_{aq}. The percentage solute extracted, denoted $E(\%)$, is equal to $100\,\psi_1$. The fraction of nonextracted solute left in the organic phase is φ_1, and $\psi_1 + \varphi_1 = 1$,

$$\varphi_1 = 1/(P + 1) \qquad\qquad (A.5)$$

Assume that one wants to separate uranium from the fission product lanthanum using the two-phase system: aqueous 1 M HNO_3, the organic adduct former tributyl phosphate, TBP (100%, i.e. undiluted). In this system $D_U = 20$ for U(VI), while for lanthanum $D_{La} = 0.07$. If one extracts with a phase ratio of 0.5, then $\psi_U = 0.909$ ($E_U = 100\,\psi_U = 90.9\%$) and $\psi_{La} = 0.034$ (E_{La} 3.4%). This may be unsatisfactory with respect to both uranium yield and purity.

The yield can be increased by repeated extractions of the same aqueous phase (multiple extraction with one stationary phase, or "crosscurrent extraction"). For n such extractions one finds that

$$\varphi_n = (P + 1)^{-n} \qquad\qquad (A.6)$$

Suppose $n = 3$ for our example, then $\varphi_{3,U} = 0.00075$, i.e. for the three organic phase volumes taken together $E_U = 100(1 - \varphi_{3,U}) = 99.92\%$. However, for lanthanum $\varphi_{3,La} = 0.902$, i.e. $E_{La} = 9.8\%$. Although the uranium yield is high, the lanthanum impurity may be intolerable.

A more elaborate technique must be employed in order to obtain both high yield and high purity under such conditions. Many such batch laboratory techniques have been described using alternatively fresh organic (*extraction*) and aqueous (*washing*) solutions. The extractions are carried out in special multistage equipment (§A.4).

A.2. Multiple stage continuous processes

A single partitioning of a compound between an organic solvent and water may not be sufficient for isolating it in acceptably pure form and good yield. Various multiple extraction techniques may therefore be required. Such techniques have been described in §21.6.4 and their technical application for uranium production (§5.5.3) and spent fuel reprocessing (§21.6.3).

Continuous processes are preferred in industry, where the most common and simple solvent extraction equipment is the mixer-settler (Fig. A.1(a); cf also Fig. 5.2). This type of equipment is also becoming standard in laboratories engaged in process development. In the uranium industry a single mixer-settler may hold as much as 1000 m^3. The mixer-settlers, each closely corresponding to a single ideal extraction stage, are arranged in batteries containing any number of stages. In these batteries the aqueous and organic phases flow countercurrent to each other (see Fig. A.2).

For countercurrent solvent extraction, either batch or continuously, one finds that for the stationary state and for n stages

$$\varphi_n = (P - 1)/(P^{n+1} - 1) \qquad\qquad (A.7)$$

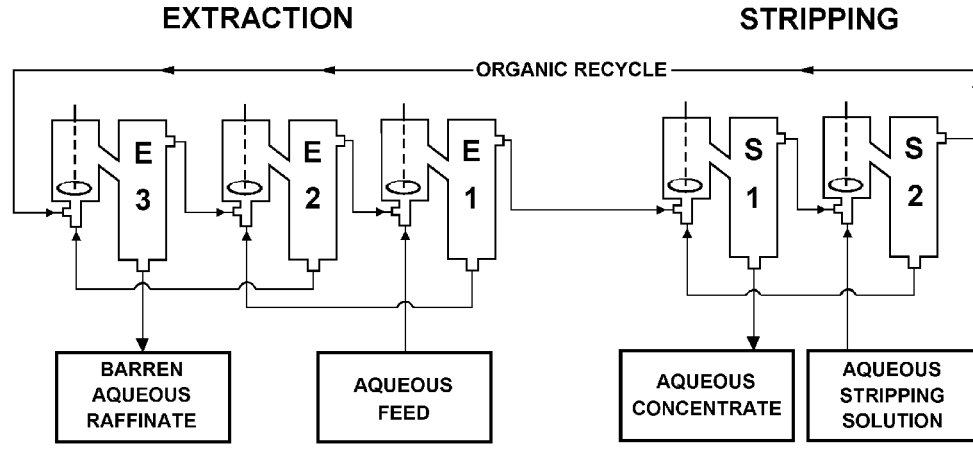**EXTRACTION**   **STRIPPING**

FIG. A.2. Mixer-settler countercurrent solvent extraction battery.

provided P is constant through all stages. In our example one obtains for $\theta = 0.5$ (flow rate ratio organic : aqueous) and $n = 3$ that $E_U = 99.91\%$ and $E_{La} = 3.5\%$. Thus about the same yield of uranium, but with a somewhat lower lanthanum impurity as compared to the crosscurrent extraction procedure. This impurity figure can be lowered substantially by modification of the extraction process according to Figure A.3 so that the extraction battery contains n extraction stages with extraction factor P_1, and $m - 1$ *washing* stages with the extraction factor P_2. Then

$$\varphi_{m,n} = \frac{(P_1 - 1)(P_2^m - 1)}{(P_1^{n+1} - 1)(P_2 - 1)P_2^{m-1} + (P_2^{m-1} - 1)(P_1 - 1)} \tag{A.8}$$

which in the case that $P_1 = P_2$ reduces to

$$\varphi_{m,n} = (P^m - 1)/(P^{m+n} - 1) \tag{A.9}$$

In the latter case, using three extraction stages and one washing stage, we find for our example that E_U is 99.9% and E_{La} is 0.12%. Thus both high yield and high purity are
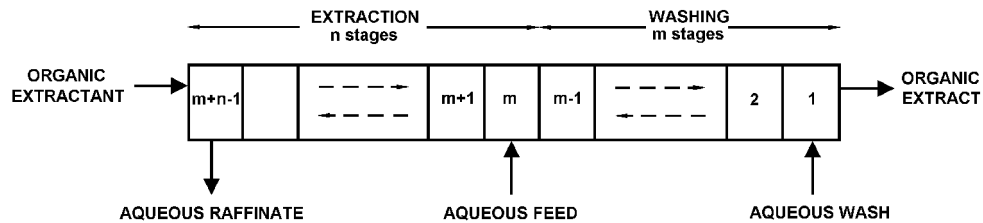

FIG. A.3. Countercurrent solvent extraction with n extraction and m washing stages.
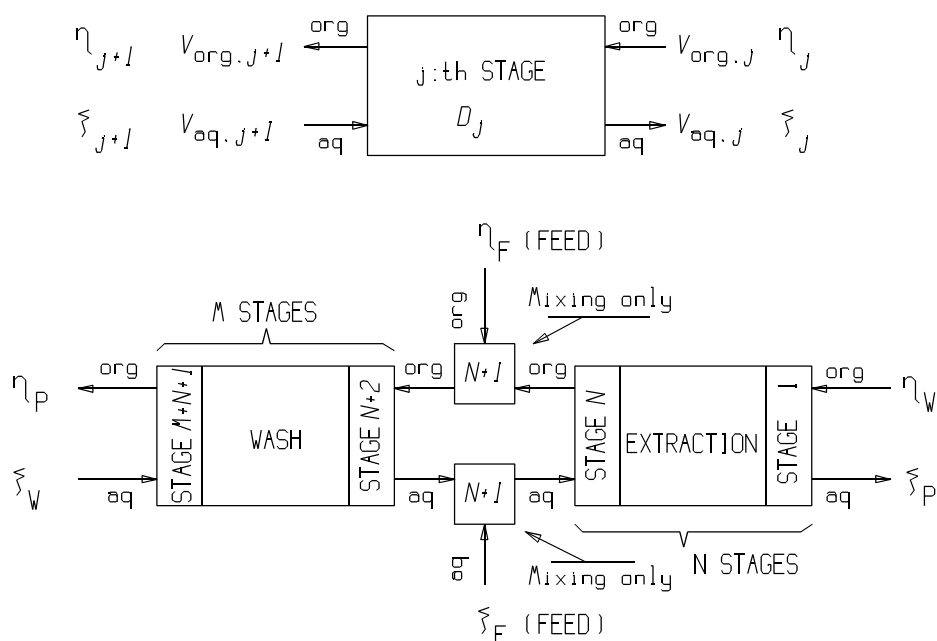
FIG. A.4. Notations for counter current extraction with wash stages

achieved with the countercurrent, central or intermediate feed solvent extraction technique. This is extensively used in uranium production, nuclear fuel reprocessing, and transuranium element separations. When the conditions are selected so that a high ($P \gg 1$) extraction factor is obtained for the desired product and low ones ($P \ll 1$) for the impurities, high purity and good yield can be obtained with relatively few stages. However, θ is always lower in the extraction stages than in the washing stages because the central feed flow rate adds to the wash flow rate in the extraction stages and the organic flow rate is unchanged. Hence, cases with the same P-value in extraction and washing stages seldom occur.

The purpose of the *washing* (or *scrubbing)* stages is to clean the desired product from impurities, and should not be confused with the *stripping* stages, the purpose of which is to transfer the product from the organic phase to a new aqueous phase. However, stripping can also be so arranged that further purification is achieved, sometimes even using a central organic feed, cf. Fig. A.4. If no additional purification is desired after extraction and the extractant is volatile, the organic phase may be distilled, leaving a pure solid product.

A.3. High loadings

A further industrial requirement on solvent extraction processes is high capacity, which means high concentrations of several solutes in the aqueous and organic solvents ("high loading"). The extraction factor P (or distribution factor D_M) may then vary from stage to stage because D-value and phase volumes change. The calculation of the number of stages,

flow rate ratios, etc., needed in order to obtain the desired product has to take this into account.

In order to treat industrial conditions with coupled extraction and washing batteries with central feed where both phase volumes and distribution ratios may change as an effect of the extraction we introduce the mass flow rates: $\xi = X V_{aq}$ and $\eta = Y V_{org}$, where X and Y are the concentrations in the aqueous and organic phases respectively, and V_{aq} and V_{org} are the flow rates of the aqueous and organic phases. We also redefine the extraction factor for the j:th stage, P_j, in terms of actual flow rates out of that stage as

$$P_j = D_j V_{org,j+1}/V_{aq,j} \tag{A.10}$$

where the index $j+1$ means that it flows to the next higher stage and j that it flows to the previous stage, see Figure A.4. Now five useful extraction functions can be defined as follows.

$$e_1 = (1 + \sum_{i=1}^{N} \prod_{k=i}^{N} P_k) \tag{A.11a}$$

$$e_2 = (1 + \sum_{i=2}^{N} \prod_{k=i}^{N} P_k) \tag{A.11b}$$

$$s_1 = (1 + \sum_{i=N+2}^{M+N+1} \prod_{k=i}^{M+N+1} P_k) \tag{A.11c}$$

$$s_2 = (1 + \sum_{i=N+3}^{M+N+1} \prod_{k=i}^{M+N+1} P_k) \tag{A.11d}$$

$$\zeta = \prod_{k=N+2}^{M+N+1} P_k \tag{A.11e}$$

Through a series of mass balances we can obtain the following equation for mass flow rate with the outgoing aqueous phase, ξ_P

$$\xi_P = [\xi_W + \eta_W (e_2 \zeta + s_2) + \xi_F s_1 + \eta_F s_2]/(e_1 \zeta + s_2) \tag{A.12a}$$

and the outgoing organic phase, η_P

$$\eta_P = \xi_F + \xi_W - \xi_P + \eta_F + \eta_W \tag{A.12b}$$

The symbols refer to those given above and in Figure A.4. Mass flow rates and conditions inside each battery can in principle be obtained recursively from the relations

$$\xi_{n+1} = \xi_n (1+P_n) - \eta_n \quad \text{and} \quad \eta_{n+1} = \xi_n P_n \tag{A.12c}$$

However, numerical problems tend to make the use of these equations difficult for batteries with many stages. Special cases occur when P either is constant or constantly equal 1.

The flow rates out from any stage can usually be calculated with sufficient accuracy from the apparent molar volumes, Φ_i, of the i compounds according to

$$V_{aq} = V_{0,aq} \sum(1 + \Phi_{i,aq} X_i) \ \text{ and } \ V_{org} = V_{0,org} \sum(1 + \Phi_{i,org} Y_i) \qquad (A.13)$$

where $V_{0,aq}$ and $V_{0,org}$ are the flow rates of the pure unloaded phases in each stage. In many cases one of the central feeds is missing (usually the organic feed) and the corresponding mass and volume flow is zero. The wash stream (index W) is then the real feed for that phase.

When the flow rates vary considerably in the batteries due to loading effects, the whole calculational procedure becomes recursive and a computer code based on these equations may be needed. However, in most cases it is only necessary to treat one, or perhaps two, of the extracted components recursively as it dominates volume changes and defines the P-values for all minor components, e.g. in the high active first stage in the Purex process nitric acid and uranium define the flow rates and extraction factors for all other elements.

In industrial processes it is not only important to extract the desired compound with high yield and purity, but also to be able to strip it again with good efficiency using a minimum amount of chemicals. Contrary to single stage batch extraction, the possibility to vary the P-value by changes in the flow rate ratio (remember that $P = D \times V_{org}/V_{aq}$) makes the use of conditions with D-values for the product not too far from 1 desirable. In such a case the product can be stripped by a decrease in the flow rate ratio (in more dilute form than in the feed) and a moderate decrease in the D-value without the need to introduce new chemicals for stripping. A typical example is the uranium purification part of the Purex process. Here uranium (and nitric acid) is extracted at high concentration in the presence of $1-6$ M HNO_3 and stripped at a low flow rate ratio by more dilute nitric acid. If needed, the separation can be repeated after reconcentration by evaporation.

A.4. Solvent extraction equipment

The less conventional part – from a chemical engineering viewpoint – of a reprocessing plant is the solvent extraction equipment, even though the technique is becoming increasingly common in the chemical industry. The principle of all such equipment is illustrated by Figure A.1(a); it contains a mixing section for efficient transfer of materials between the phases and a settling section for efficient phase separation. The input and outputs provide for connecting stages in the countercurrent extraction scheme (Fig. A.2). *Mixer-settlers* (Fig. A.1(a)) provide good mixing and reasonably good phase separation performance but rather large hold-ups.

For reprocessing the equipment must be highly reliable, have high stage efficiency, short contact times, small liquid inventory (hold-up), be easy to decontaminate and to service, and not least be safe against criticality. High reliability usually means simple design and few (if any) moving parts. The *packed columns* meet this requirement. They are simply long columns (often $10-20$ m with a diameter of $0.3-3$ m) filled with small pieces of material obstructing a straight flow through the column, which is by gravity (Fig. A.1(b)).

However, high stage efficiency requires mechanical agitation of the two phases and clean phase separation, which cannot be met by packed columns.

In *pulsed columns* (Fig. A.1(c)) the mechanical agitation provides good mixing but poor phase separation. Each plate is perforated (a sieve). The organic and aqueous phases separate between the plates ("settling chambers"). In the down movement (< ¼ of the interplate distance) the aqueous phase is forced through the sieves, forming droplets, which by gravity fall through the lighter organic phase and coalesce when reaching the interface boundary. In the upward stroke, organic droplets form and rise through the aqueous phase until they meet the organic phase boundary.

The phase separation in a mixer-settler battery or in a column is usually not better than ~ 99%, i.e. each outgoing phase contains some percent entrained droplets of the other phase. This separation efficiency can be improved to almost 100% by using *centrifugal extractors* (Fig. A.1(d)). Centrifugal extractors effect good mixing, good phase separation, and have very small hold-ups. The organic-aqueous phase contact time in centrifugal extractors can be made much shorter than in mixer-settlers or columns. The small hold-up volume and short residence time cooperate to reduce radiation decomposition.

Packed columns were used in the first Windscale plant (Sellafield, UK). Pulsed columns were used at Hanford (USA), in the old Eurochemic plant at Mol (Belgium), and are currently in use in the newer La Hague and THORP plants. Mixer-settlers have been used at Savannah River (USA), in the Magnox plant at Sellafield (UK), and at La Hague (France). Centrifugal extractors have been installed at Savannah River and at La Hague.

A.5. Exercises

A.1. In a solvent system the distribution ratio, D_U, is 2 for uranium and D_{Cs} is 0.003 for cesium. If 99.5% U is to be extracted in a repeated batch fashion (eqn. (A.5)), (a) how much Cs is coextracted? If instead a countercurrent process is used with 10 extraction and 2 wash stages, what percentage of (b) uranium and (c) cesium is extracted? In an extraction equipment D_{Cs} 0.003 cannot be maintained, because droplets are carried over between stages; the practical value will be D'_{Cs} 0.02. (d) How much cesium is extracted in this latter case with the countercurrent equipment? Assume equal phase volumes.

A.2. After scrubbing the solvent (1M TBP in kerosene) with a carbonate solution it should be reacidified to equilibrium with 6 M nitric acid before reuse in reprocessing operations. Assume that the partial molar volume of nitric acid can be neglected for both the organic phase and the aqueous phase. Thus, in this example extraction of nitric acid will not increase the volume of the organic phase nor reduce the volume of the aqueous phase. Extraction of nitric acid is assumed to only occur as the complex TBP.HNO3. For simplicity we will assume that the equation $D_{HNO3} = k_{ex} \times [HNO_3]_{aq} \times [TBP]_{free,org}$, with $k_{ex} = 0.1$ can be used to calculate the D-value for nitric acid. The reacidification will be performed in a simple counter current mixer-settler battery. (a) How many stages and (b) what flow rate ratio (org/aq) would be needed in order to produce the required nitric acid concentration in the organic phase using the smallest possible feed of 6.4 M nitric acid? (c) What would be the concentration of the spent nitric acid?

A.6. Literature

G. H. MORRISON and H. FREISER, *Solvent Extraction in Analytical Chemistry*, Wiley, 1957.

Y. MARCUS and A. S. KERTES, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley, 1969.

A. K. DE, S. M. KHOPKAR and R. A. CHALMERS, *Solvent Extraction of Metals*, Van Nostrand Reinhold, 1970.

YU. A. ZOLOTOV, *Extraction of Chelate Complexes*, Humprey Sci. Publ., Ann Arbor, 1970.

T. SEKINE and Y. HASEGAWA, *Solvent Extraction Chemistry*, Marcel Dekker, 1977.

T. C. LO, M. H. I. BAIRD and C. HANSON, *Handbook of Solvent Extraction*, Wiley, 1983.

G. RITCEY and A. W. ASHBROOK, *Solvet Extraction. Part I and II*, Elsevier, 1984.
J. RYDBERG, C. MUSIKAS and G. CHOPPIN, *Principles and Practices of Solvent Extraction*, Marcel Dekker, 1992.
(Journal of) *Solvent Extraction and Ion Exchange*, Marcel Dekker (Vol. **11**, 1993).