

# Prediction of Ideal-stage Requirements in Complex Liquid-liquid Extraction Systems

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A procedure for obtaining equilibrium data and predicting ideal-stage requirements in a complex liquid-liquid extraction system is presented. Preliminary equilibrium data are obtained from a simulated column run involving a series of batch contacts operated in such a manner as to approach steady state countercurrent conditions. The flow ratios and stage requirements for continuous operation are then estimated by trial-and-error by use of a modified McCabe-Thiele method.

The procedure lends itself particularly well to those systems with interdependent distribution of the two components. Data for the separation of hafnium from zirconium are presented to show the utility of the method.

The separation of two components by liquid-liquid extraction has not been successfully reduced to a mathematical relationship for complex systems. Bartels and Kleiman (1) and Klinkenberg (3) have developed mathematical treatments based upon the assumptions of (a) constant distribution coefficient, i.e., a straight equilibrium line, and (b) addition of zero volume in the feed stream. Scheibel (5) has presented a graphical treatment which requires equilibrium data over the entire range of operation. The assumptions of Bartels et al. often do not apply, and complete equilibrium data are often not available.

To facilitate the understanding of extraction calculations in complex systems, an analogy may be drawn from the McCabe-Thiele method used in distillation calculations. The following assumptions are made in this treatment of countercurrent liquid-liquid extraction: (a) there is no volume change in either phase flowing through the equipment and (b) the only solute entering the equipment enters in the feed solution.

A schematic diagram of an extraction unit is presented in Figure 1. An aqueous scrub solution passes countercurrent to organic extract in the scrub section. Aqueous feed solution is introduced into the aqueous line between the scrub and

extraction sections. In the extraction section the combined aqueous phases pass countercurrent to organic solvent. Volumetric flow rates are designated by  $Q$ ; solute concentrations in the aqueous phase by  $X$ , and solute concentrations in the organic phase by  $Y$ , as weight of solute per unit volume of solution. Subscripts  $S$ ,  $F$ ,  $R$ ,  $E$ , and  $T$  identify scrub, feed, raffinate, extract, and solvent streams, respectively.

A material balance on the solute entering and leaving the scrub section yields the equation of the operating line in the scrub section.

$$Y = (Q_S/Q_T)X + Y_E \quad (1)$$

This equation is plotted in Figure 2 as a straight line of slope  $(Q_S/Q_T)$  and intercept  $Y_E$ .

Similarly, the equation of the operating line in the extraction section of the column is

$$Y = (Q_R/Q_T)(X - X_R) \quad (2)$$

This equation is also plotted in Figure 2. It can be shown that the operating lines intersect at a point where  $X = X_F$ , although this point does not necessarily exist in the column.

The transition from one operating line to the other operating line at the feed point is illustrated in Figure 3. At the feed point the composition of the aqueous phase changes; the organic composition, however, remains constant (see Figure 1). Therefore, the composition of the aqueous and organic phases immediately above the feed point lie on the scrub-section operating line; the compositions of the aqueous and organic phases immediately below the feed point lie on the extraction-section operating line. Since the composition of the organic phase does not change, both operating lines have a common

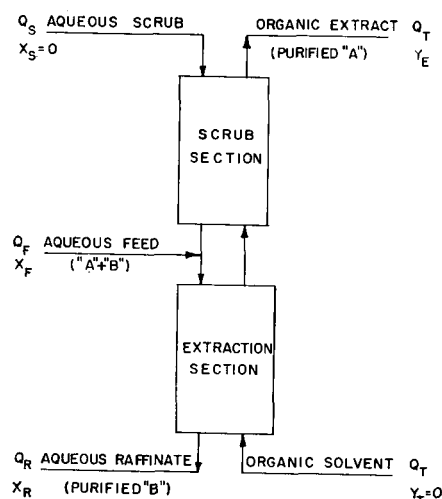


Fig. 1. Schematic diagram of extraction column.

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ordinate at the feed point. Stages can then be stepped off as in the McCabe-Thiele method. Compere and Ryland (2) used a similar treatment in their work.

In multicomponent extraction each component has a separate equilibrium diagram, and if the distribution of each component is independent of the other components, a trial-and-error solution can be used to determine the relationship between stage requirements, flow ratios, and separation of the components. If the equilibrium line is straight, there is a simple mathematical relationship between the stage requirements, flow ratios, and separation. For the separation of some components, however, the equilibrium line is not straight, and the distribution of one component is dependent on the concentration of the other.

As an example, consider the separation of *A* and *B* shown in Figure 1. The feed to the extraction column contains both *A* and *B*. It is assumed that the organic solvent preferentially extracts component *A*, and so the organic extract will contain purified *A* and the aqueous raffinate will contain purified *B*. Since some *B* is transferred to the organic stream leaving the extraction section, aqueous scrub solution is introduced at the extract exit to scrub the last traces of *B* from the organic phase. At the raffinate exit organic solvent serves to extract the last traces of *A* from the raffinate phase.

A clearer concept of the problems involved in economically separating *A* from *B* can be obtained by discussing hypothetical equilibrium diagrams for each component, as shown in Figure 4. To minimize the cost of recovering *A* from the organic extract, it is desirable that the concentration of *A* in the extract be kept high and that the amount of *A* returned to the aqueous phase in the scrub section be small. Therefore, the operating line in the scrub section should intersect the equilibrium line for *A* and "pinch-in" stages. A stage is pinched in with respect to component *A* when the phases entering are already so close to equilibrium that very little net mass

transfer of *A* takes place. In the extraction section of the column the operating line should assure high recovery of *A* by reducing its concentration in the raffinate to a low value. To ensure effective use of the available stages, the stages in the extraction section should not be pinched in for *A*.

The extraction of *B* can also be followed in Figure 4 by considering the hypothetical equilibrium diagram for component *B*. For *B*, the operating line in the extraction section should pinch in stages to ensure a high concentration of *B* in the raffinate. However, in the scrub section pinching in, with respect to component *B*, should be avoided, for it is desirable to reduce the concentration of *B* in the extract to a low value. Figure 4 involves a like number of equilibrium stages in each section of the column for each component, although the number of pinched-in stages cannot be clearly shown graphically. It should be noted that a stage pinched in with respect to *A* may accomplish considerable mass transfer of *B*, and vice versa.

The case will now be considered in which the distributions of *A* and *B* are assumed interdependent; i.e., the equilibrium conditions occurring in each stage depend on both the quantity and the quality of solute present. Figure 5 presents such a set of hypothetical equilibrium lines, showing the effect of composition on the distribution between phases. It should be noted that the sums of the concentrations of *A* and *B* are plotted. Following across a horizontal line, composition is seen to have a marked effect on equilibrium conditions, even though the total concentration in the organic phase remains unchanged. Similarly, a vertical line shows composition to have a marked effect even though the total concentration in the aqueous phase remains unchanged. The percentages of *A* and *B* noted in Figure 5 are the percentages of *A* and *B* in aqueous solution prior to an equilibrium contact with an equal volume of organic solvent.

Since the quality, as well as the quan-

tity, of solute varies throughout the extractor, the equilibrium lines necessary for ideal-stage calculations are composites of the lines shown in Figure 5. Two equilibrium lines are involved: one for the extraction section, where compositions are high in *B*, another for the scrub section, where compositions are high in *A*. These composite equilibrium lines, shown dotted in Figure 5, can conveniently be obtained from a simulated column run.

A simulated column run uses a number of separatory funnels to simulate countercurrent extraction conditions. Portions of aqueous scrub, aqueous feed, and organic solvent are brought together in the flow pattern outlined by Scheibel (6). When the pattern has been repeated a sufficient number of times, the compositions of the aqueous and organic phases closely approach the compositions that would be obtained in a countercurrent extractor operating with the same flow ratios and the same number of ideal stages. In this way equilibrium data can be obtained for the two composite equilibrium lines.

Although the choice of flow ratios and number of stages used for a simulated column run is arbitrary, the equilibrium data obtained are generally useful in establishing the form of the composite equilibrium lines. An eight-stage simulated column run, with feed to stage four, for instance, may be assumed to yield equilibrium compositions represented by the small circles on Figure 6. These circles represent points on the composite equilibrium lines, taking into account the interaction of *A* and *B*. The upper line applies to the scrub section where solute compositions are high in *A*;

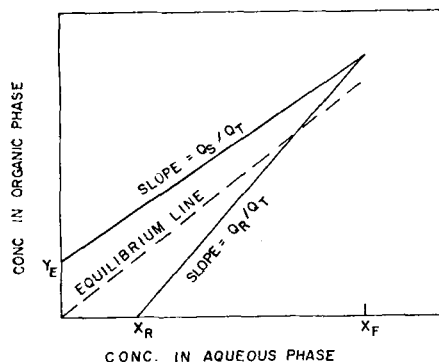


Fig. 2. Locating of operating lines.

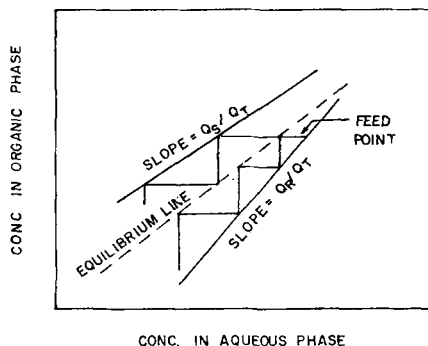


Fig. 3. Transition between operating lines at feed point.

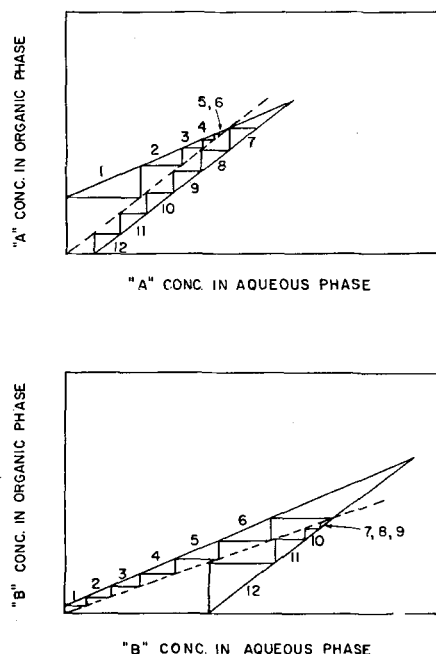


Fig. 4. Hypothetical equilibrium diagrams.

the lower line applies to the extraction section where solute compositions are high in *B*. Drawing horizontal and vertical lines from each point permits reconstruction of the stages and the operating lines. The quantity of solute in each phase can be conveniently shown in Figure 6; the quality of the solute—as determined by spectrographic analysis, for example—cannot be conveniently shown.

Analysis of the extract from the simulated column run indicates whether three ideal stages, operating at the flow rates

chosen, are adequate to produce extract of the desired purity. It is extremely unlikely that the arbitrary choice of flow ratios and number of stages will prove entirely satisfactory. However, the knowledge gained from such a run permits trial-and-error calculations to be made by use of other flow rates and different numbers of stages. Such a trial-and-error calculation is illustrated in Figure 7. Although the composite equilibrium lines involved at other flow ratios will not be identical, the line from the simulated column run serves as a good approximation and is useful in defining the regions of operability in complex systems.

Figure 7 shows how data from a simulated column run can be used to estimate extractor performance under other operating conditions. Suppose the analysis of the extract from the eight-stage simulated column run indicated the need for an additional stage in the scrub section, to obtain *A* of the desired purity. What flow rates should be used if twelve ideal stages are available?

The equilibrium lines obtained from the twelve-stage run because the concentrations encountered are quite similar. The trial-and-error solution involves drawing various sets of operating lines, each set intersecting at the feed concentration. The correct set of operating lines shows four ideal stages in the scrub section and eight ideal stages in the extraction section, with a common ordinate for the feed stage and the last scrub-section stage. When these conditions have been satisfied, the relative flow rates can be determined from the slopes of the operating lines. Thus in Figure 7,  $Q_S/Q_T = 0.32$  and  $Q_R/Q_T = 0.59$ . Relative to a solvent rate of unity,  $Q_S = 0.32$  and  $Q_R = 0.59$ . Since  $Q_R = Q_S + Q_F$ ,  $Q_F = 0.27$ . Hence the flow rates of all streams can be determined relative to the solvent rate.

As an example of the utility of this method of handling complex extraction systems, data will be presented for the

separation of hafnium from zirconium (4). Zirconium is found in nature with approximately 2½% hafnium as an impurity. For many specialized uses, it is desirable to separate the hafnium from zirconium. Nitrates of the two elements are readily soluble in water. Concentrations of hafnium and zirconium compounds are reported as weight of oxide per unit volume or as molarity based on oxide concentration. Use of such nomenclature eliminates assumptions regarding the exact ionic species in solution. For analysis, the hafnium and zirconium were precipitated as hydroxides, ignited to oxides, and the weight ratio of hafnium to zirconium determined spectrographically.

In the example to be cited, the feed solution was an aqueous solution of approximately 1M Zr (123 g. oxide/liter), analyzing  $(\text{Hf/Zr} \times 100) = 2.4$ . Tributyl phosphate was used as the selective solvent for zirconium after dilution with *n*-heptane to improve the mechanical separation of the two phases. Nitric acid was found to be necessary for efficient separation of the two elements.

Figure 8 shows that the system under consideration falls into the category suggested by Figure 5. Figure 8 was experimentally determined by single-batch equilibrium contacts between solvent (acidified so that no net mass transfer of nitric acid occurred) and a 5N nitric acid solution containing the indicated ratios of hafnium and zirconium nitrates as solute. It can be seen that the distribution of the oxides is affected by their quality.

The results of an eight-stage simulated column run are shown in Table 1. Feed containing 2.4 parts by weight of hafnium/100 parts by weight of zirconium  $[(\text{Hf/Zr}) \times 100 = 2.4]$  was separated into organic extract  $[(\text{Hf/Zr}) \times 100 = 0.012]$  and aqueous raffinate  $[(\text{Hf/Zr}) \times 100 = 34]$ . Since acidified solvent was used, there was only a small amount of acid transferred between phases; the

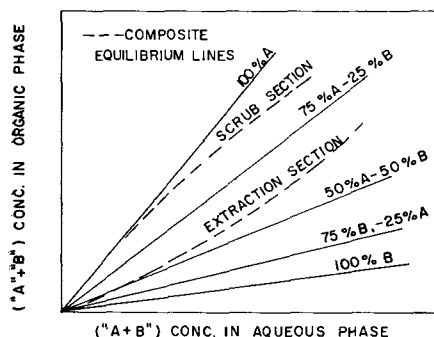


Fig. 5. Composite equilibrium lines.

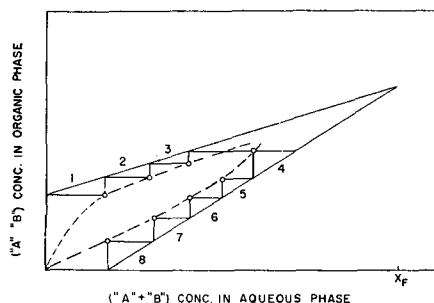


Fig. 6. Eight-stage simulated column run.

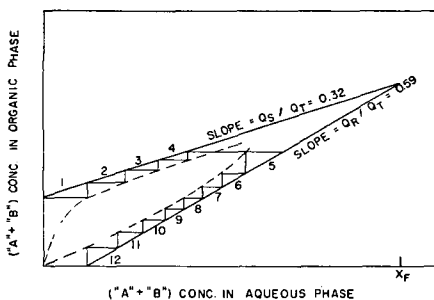


Fig. 7. Twelve-stage trial-and-error calculation.

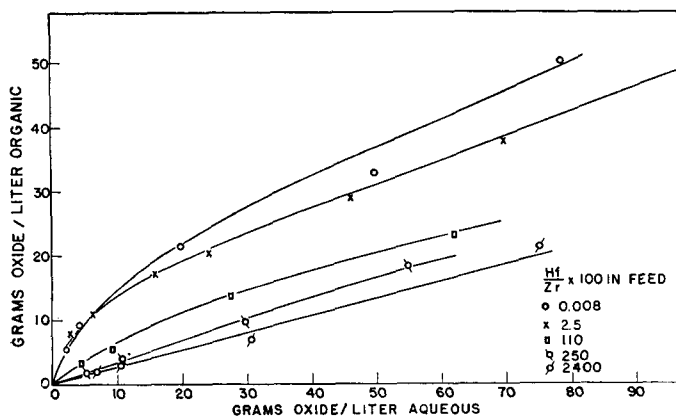


Fig. 8. Effect of hafnium on distribution of hafnium zirconium.

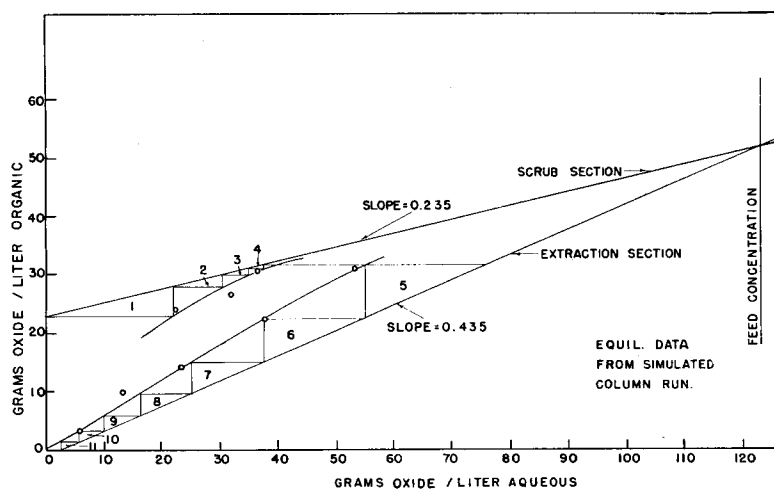


Fig. 9. Modified McCabe-Thiele diagram for stage calculation.

TABLE 1. SIMULATED COLUMN RUN

8 stages, feed to stage 4  
 Feed : scrub : solvent = 1.0 : 1.18 : 4.85  
 Feed: 1.0 M Zr—5.09 N HNO<sub>3</sub>—0.16 M SO<sub>4</sub>  
 Hf/Zr × 100 = 2.4  
 Scrub: 5.02 N HNO<sub>3</sub>  
 Solvent: 60% TBP—40% heptane, 1.82 N HNO<sub>3</sub>

Stage	g. oxide/ liter	Organic N HNO <sub>3</sub>	Hf/Zr × 100	g. oxide/ liter	Aqueous N HNO <sub>3</sub>	Hf/Zr × 100
1	24.0	1.90	0.012	22.5	5.09	<0.010
2	26.7	1.97	0.010	32.1	5.14	0.11
3	30.8	1.92	0.028	36.5	5.25	0.68
4	31.0	1.95	0.022	53.3	5.13	2.2
5	22.4	1.94	0.22	37.7	4.99	4.1
6	14.2	1.87	0.26	23.6	5.10	8.8
7	10.0	1.85	1.0	13.1	5.00	22
8	3.32	1.80	4.2	5.80	5.06	34

TABLE 2. STAGewise ANALYSES OF MIXER-SETTLER RUN

Stage	g. oxide/ liter	Organic N HNO <sub>3</sub>	Hf/Zr × 100	g. oxide/ liter	Aqueous N HNO <sub>3</sub>	Hf/Zr × 100
1	22.2	1.95	<0.010	17.5	5.21	<0.010
2	29.3	2.02	<0.010	27.5	5.30	<0.010
3	31.4	2.03	<0.010	33.5	5.46	<0.010
4	31.8	2.03	0.043	34.9	5.46	0.24
5	32.2	2.03	0.11	52.8	5.15	3.6
6	21.1	1.99	0.60	30.8	5.15	6.8
7	13.7	1.93	0.27	19.9	5.05	9.8
8	7.66	1.89	1.9	11.6	4.97	20
9	4.14	1.86	4.8	8.06	4.97	36
10	1.98	1.83	10	5.32	4.75	67
11	1.03	1.77	23	3.71	4.52	110
12	0.66	1.68	32	3.14	4.12	140
13	0.46	1.50	42	2.99	3.49	130
14	0.29	1.18	28	3.54	2.56	72

major components transferred were hafnium and zirconium. The equilibrium data obtained were plotted, as suggested in Figure 6, to locate the composite equilibrium lines for the scrub and extraction sections of the column.

It was desired to use these data in choosing operating conditions for a

continuous run. From the simulated column run it was decided to use four stages in the scrub section, to assure zirconium product containing less than 100 p.p.m. of hafnium [(Hf/Zr) × 100 = 0.01]. The same feed concentration was used. The oxide concentration of the raffinate was arbitrarily chosen as 2.5

g./liter. Figure 9 shows the trial-and-error graphical solution, utilizing the raffinate concentration, feed concentration, and number of scrub stages already chosen. It was estimated that seven extraction stages should be used. From the slopes of the operating lines in Figure 9,  $Q_S/Q_T = 0.235$  and  $Q_R/Q_T = 0.435$ .

The organic extract obtained from the continuous run was to be stripped of solute in another extractor, and the solvent recirculated. In the stripping of the purified zirconium from the extract, some nitric acid would also be removed. Thus the recycled solvent would contain less acid than the acidified solvent used in the simulated column run. To compensate for the use of acid-deficient solvent, three additional stages were added to the extraction section.

A continuous extraction run was then made. Fourteen mixer-settler stages were operated, with feed, scrub, and solvent flows as estimated above. After steady state had been attained, each stage was isolated and mixing continued to obtain the equilibrium data reported in Table 2.

The effect of acid-deficient solvent is evident from the [(Hf/Zr) × 100] aqueous analyses for stages 13 and 14. At the lower acidities prevailing in those stages there was some loss of raffinate quality. Taking into account the analytical difficulty of distinguishing between hafnium contents below 100 p.p.m., the run produced satisfactory product and raffinate. The equilibrium data reported in Table 2 show the equilibrium line in the continuous run to be actually somewhat higher than that obtained in the simulated column run. This shift reflects the higher nitric acid concentration in stages 1 through 7 of the continuous run.

The use of simulated column runs to obtain extraction data is recommended for complex systems where the distributions of the components are interdependent. A modified McCabe-Thiele graphical method can then be applied to determine flow-rate ratios, ideal-stage requirements, and feed-point location.

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