LIQUID EXTRACTION

REFERENCES: *Specialized books:* Treybal, "Liquid Extraction," 2d ed., McGraw-Hill, New York, 1963. Alders, "Liquid-Liquid Extraction," 2d ed., Van Nostrand, Princeton, N.J., 1959. Sherwood and Pigford, "Absorption and Extraction," 2d ed., McGraw-Hill, New York, 1952. Molyneux, "Chemical Plant Design," vol. 1, Butterworth, Washington, D.C., 1965. Garner, Ellis, *et al.*, in Cremer and Davies (eds.), "Chemical Engineering Practice," vol. 5, Academic, New York, 1958. Craig, Craig, and Scheibel, in Weissberger (ed.), "Techniques of Organic Chemistry," vol. III, Part 1, 2d ed., Interscience, New York, 1956. "Proceedings, 7th World Petroleum Congress, Mexico City," vol. 4, Elsevier, Amsterdam, 1967. Marcus and Kertes, "Ion Exchange and Solvent Extraction of Metals," Wiley, New York, 1967. Jamrack, "Rare Metal Extraction by Chemical Engineering Techniques," Macmillan, New York, 1963. Flagg *et al.*, "Chemical Processing of Reactor Fuels," Academic, New York, 1961. McKay *et al.* (eds.), "Solvent Extraction Chemistry of Metals," Chemical Rubber Co., Cleveland, 1967. Dryssen *et al.* (eds.), "Solvent Extraction Chemistry," North-Holland, Amsterdam, 1967.

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London, 1968. Foust *et al.*, "Principles of Unit Operations," Wiley, New York, 1960. McCabe and Smith, "Unit Operations of Chemical Engineering," 2d ed., McGraw-Hill, New York, 1967. Pratt, "Countercurrent Separation Processes," Elsevier, Amsterdam, 1967. Oliver, "Diffusional Separation Processes," Wiley, New York, 1966. Sawistowski and Smith, "Mass Transfer Process Calculations," Interscience, New York, 1963. Smith, "Design of Equilibrium Stage Processes," McGraw-Hill, New York, 1963. Treybal, "Mass-transfer Operations," 2d ed., McGraw-Hill, New York, 1968.

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Much of what follows is based on material by J. C. Elgin and R. L. Pigford in the previous editions.

INTRODUCTION

Processes for the separation of the components of a solution which depend upon the unequal distribution of the components between two immiscible liquids are known as liquid-liquid extraction, or more simply as liquid extraction, processes, and sometimes as solvent extraction (although the last is frequently also applied to the process of leaching a soluble substance from a solid with a liquid solvent).

The process may be carried out in a number of ways. In most instances, the liquid solution to be treated is contacted intimately with a suitable incompletely miscible liquid which preferentially extracts one or more components. For example, acetone may be preferentially extracted from solution in water by contacting the water with chloroform. The chloroform then is found to contain a large part of the acetone, but little water. Sometimes two immiscible liquids are used. For example, a solution of acetone and acetic acid may be separated by distributing the components between water and chloroform. In this case, the acetone preferentially enters the chloroform while the acetic acid preferentially enters the water. Separations of this sort are essentially physical in character, and the various components are unchanged chemically. Nevertheless, the chemical nature of the liquids strongly influences the extent of separation possible, since the distribution of a solute depends on the extent of non-ideality of the solutions involved. Furthermore, the non-ideality may be altered in order to influence the distribution favorably, for example, by changing the temperature, by addition of salt to "salt out" an organic solute from a water solution, or by adjusting the pH of the solution or the state of oxidation of a metallic solute. In other cases, chemical reaction in the extracting liquid is actually resorted to, as in the extraction of phenol from light oil by aqueous caustic solutions.

Fields of Usefulness. Because liquid extraction results in a new solution which in turn must be separated, the more direct method of separation by distillation is usually considered first. However, liquid extraction separates primarily according to chemical type, and is therefore capable of separations which are impossible by ordinary distillation means. Thus, aromatic and paraffinic hydrocarbons of the same boiling range may be separated by liquid extraction with diethylene glycol or sulfolane as extractants for the aromatics. Even solutions which can be separated by distillation,

but which are expensive to deal with in this manner, may frequently be separated better by liquid extraction. For example, distillation of a dilute solution of acetic acid in water involves the vaporization of large amounts of water at high reflux ratio, and is expensive because of the high latent heat of vaporization of water. Extraction of the acid into ethyl acetate, followed by distillation of the new solution thus formed, provides a cheaper process. Similarly, costly evaporation of water from a non-volatile solute may sometimes be circumvented by extraction of the solute into a solvent of small latent heat. Costly fractional crystallization may be avoided, as in the separation of tantalum and columbium in solution by liquid extraction, which is relatively easy. In this case, even chemical methods of separation are impractical. Extensive application in the field of process metallurgy has been made, as in the separation of uranium-vanadium, hafnium-zirconium, recovery of copper from dilute solutions, and many other examples. Heat-sensitive substances, such as penicillin, may be separated from the mixtures in which they are formed by extraction into a suitable solvent at low temperature. While liquid extraction involves transfer of *matter* between two immiscible liquids, the transfer of *heat* may be done by the same techniques, and direct contact of two immiscible liquids for this purpose provides a non-fouling heat exchanger of increasing interest in recent years.

Definitions. The solution whose components are to be separated is the feed to the process. Liquid added to the feed for purposes of extraction is the solvent. If the solvent consists primarily of one substance (aside from small amounts of residual feed material which may be present in a recycled, recovered solvent), it is a single solvent. A solvent consisting of a solution of one or more substances chosen to provide special properties is a mixed solvent. The solvent-lean, residual feed solution, with one or more constituents removed by extraction, is the raffinate. The solvent-rich solution containing the extracted solute(s) is the extract. Two immiscible solvents between which the feed constituents distribute is a *double solvent*, in which case the terms extract and raffinate no longer apply.

The minimum requirement for liquid extraction is the intimate contact of two immiscible liquids for the purpose of mass transfer of constituents from one liquid (or phase) to the other, followed by physical separation of the two immiscible liquids. Any device

or combination of devices which accomplishes this once is a stage. If the effluent liquids are in equilibrium, so that no further change in concentration would have occurred within them after longer contact time, the stage is a theoretical or ideal stage. The approach to equilibrium actually attained is the stage efficiency. A multistage cascade is a group of stages, arranged for countercurrent or other type of flow of liquids from one to the other for purposes of enhancing the extent of separation.

In countercurrent flow particularly, the liquids are frequently contacted without repeated physical separation and recontacting in discrete stages. Such methods are known as differential- or continuous-contacting methods.

Solvent Recovery. It is usually desired that the extracted solutes be ultimately obtained free of solvent. In any case, cost considerations almost always require that the solvent be recovered for reuse, not only from the extract but in most cases from the raffinate as well even though the solvent content of the latter may be relatively small. Solvent recovery is usually accomplished by distillation, as in Fig. 15-1a, which is typified by the recovery of acetic acid from a dilute aqueous feed with ethyl acetate as solvent. The distillation operations are shown only schematically, and will vary considerably in detail depending upon whether the solvent is higher low-boiling, whether azeotropes (ordinary or heterogeneous two-liquid phase) form with the solvent, and relative solubility and volatility of the solvent. The details are discussed by Treybal ("Liquid Extraction," 2d ed., McGraw-Hill, New York, 1963). Sometimes the extracted solute is desired in solution form. Figure 15-1b schematically represents such a process, using liquid extraction for solvent recovery, typified by the recovery of uranium from an ore leach-liquor feed. Here the feed, containing uranium together with undesired metals, is extracted with a uranium-complexing solvent such as tributyl phosphate dissolved in kerosene, under such conditions of pH and state of oxidation that only uranium is extracted. The raffinate contains so little solvent that it needs no treatment for solvent recovery. The extract is contacted in the solvent stripper (by liquid extraction methods) with aqueous acid, whereupon the uranium enters the acid and the solvent is restored to its original condition for reuse. In this way, the uranium is concentrated several-hundred-fold, as well as separated from impurities.
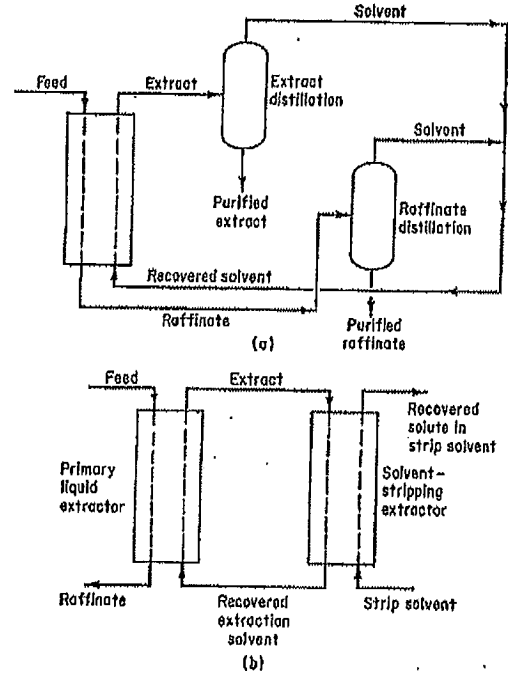

Fig. 15-1. Schematic flow sheets of liquid-extraction processes with associated solvent recovery by (a) distillation and (b) liquid extraction.

PHASE EQUILIBRIUMS

Accurate knowledge of phase-equilibrium relationships is vital for quantitative considerations of extraction processes. The required quantities of solvent (and reflux, if used) are set by these data. Also, the driving forces determining rates of mass transfer are governed by these thermodynamic considerations. Since formation of two stable liquid phases in contact with each other is an essential requirement, at least one phase is almost certain to be one in which solute components behave thermodynamically in a strongly non-ideal way. In fact, a solvent having a high selectivity for one component must be a material in which the other components have large activity coefficients and from which these other components are consequently excluded when phase equilibrium has been achieved. The quantitative expression of liquid-liquid phase-equilibrium relationships therefore unavoidably involves the use of methods for representing thermodynamic properties of non-ideal solutions. In the simplest case these solutions are composed of three components: the two comprising the feed solution (A, the feed solvent, and B, the solute) and solvent S. Only if the solvent and component A are completely immiscible—a condition which can occur only if the system remains very dilute in B—can simple relations applicable to two-component mixtures be employed, except as a rough approximation.

In what follows, only the simplest and most commonly occurring systems are described. For more complete discussion of the many possibilities, see Francis, "Liquid-Liquid Equilibriums," Interscience, New York, 1963; Ricci, "The Phase Rule and Heterogeneous Equilibrium," Van Nostrand, Princeton, N.J., 1951; Dover, New York, 1966; and Treybal, "Liquid Extraction," 2d ed., McGraw-Hill, New York, 1963.

Ternary Phase Diagrams. In the chemical literature, the phase equilibriums are usually displayed on an equilateral triangular graph, as in Fig. 15-2. These graphs represent isotherms, at sufficient pressure to maintain the system entirely liquid. Type I (Fig. 15-2a), in which the region of immiscibility touches only one side of the triangle, is the more common. The liquid pairs A-B and B-S are completely miscible; A and S dissolve to a limited extent, providing the mutually saturated solutions at G, and H.
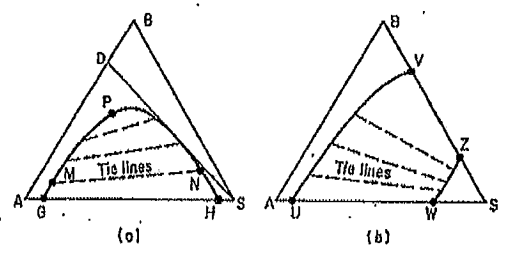

Fig. 15-2. Triangular phase diagrams. (a) Type I. (b) Type II.

FIG. 15-3. Effect of temperature on ternary liquid-liquid equilibrium.

FIG. 15-5. Distribution of solid B between liquids A and S.

Addition of B to such a mixture tends to make A and S become more soluble. At the plait point P, the two phases become one. Solute B distributes between the saturated phases, providing equilibrium liquids such as those at M and N, joined by a tie line. For such a tie line, the distribution coefficient K is defined as

$$K = \frac{X_{BN}}{X_{BM}} \quad \text{or} \quad K' = \frac{x_{BN}}{x_{BM}} \quad (15\text{-}1)$$

where X_{BN} indicates *weight fraction* and x_{BN} the *mole fraction*, of B in the solution at N. Tie lines usually, but not always, change their slope continually in one direction, as shown. Systems where the slope changes in sign with B concentration are *solutropes* [Francis, "Liquid-Liquid Equilibriums," Interscience, New York, 1963; Smith, *Ind. Eng. Chem.*, 42, 1206 (1950)]. In any event, the value of K (or K') ordinarily changes with B concentration, eventually becoming unity at the plait point (see below). Feed solutions lie on the line AD; feeds in the range DB cannot be processed with S since addition of S to such liquids will not produce a two-phase mixture. Raffinates will lie on the curve GMP, extracts on HNP. In type II systems (Fig. 15-2b) S is only partially miscible with both A and B, and a feed of any proportions of A and B may be processed. Raffinates lie on curve UV, extracts on WZ.

The two principal types of phase diagrams of interest for solvent-extraction operations, shown in Fig. 15-2, actually may represent two aspects of the same ternary system. Figure 15-3 shows how a ternary system may behave as the temperature is changed. (Pressure changes ordinarily have a negligible effect on liquid-liquid equilibriums because of the small partial volumes of the components.)
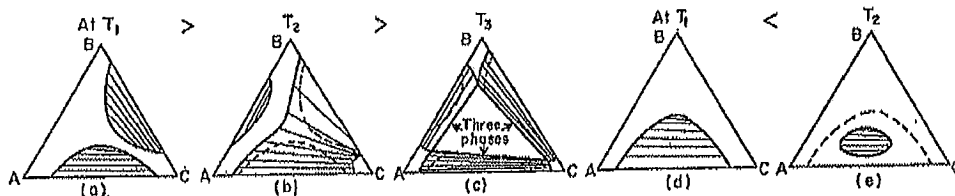
At a sufficiently high temperature all binary pairs are above their critical solution temperatures. As the temperature is reduced at T_{AS} the binary pair AS begins to form two phases. Below T_{AS} the isothermal (horizontal) section of the three-dimensional figure shows phase behavior of type I. Further reduction in temperature enlarges the two-phase region, and when T_{BS}, the binary critical solution temperature for components B and S, is reached the two-phase ternary region touches line BS. Upon further reduction in temperature the system exhibits type II characteristics.

Figure 15-3 shows why the experimental observation of binary critical solution temperatures of mixtures of pure components with prospective solvents is a good guide to solvent selection. As brought out by Treybal ("Liquid Extraction," 2d ed., McGraw-Hill, New York, 1963) and as employed by Francis [*Ind. Eng. Chem.*, 36, 764, 1096 (1944)] for aniline and by Drew and Hixson [*Trans. Am. Inst. Chem. Engrs.*, 40, 675 (1944)] and Hixson and Bockelmann [*Trans. Am. Inst. Chem. Engrs.*, 38, 891 (1942)] for propane as solvents, the solvent S having the lower critical solution temperature with solute B will be better able to select it preferentially during extraction of A-B mixtures. When both A-S and B-S are below their critical temperatures, the solvent will tend to select that component with which it has the lower critical temperature. Francis (Critical Solution Temperatures, *Advan. Chem.*, 31, Washington, D.C., 1961) has compiled a very large list of data.

In addition to triangular diagrams of types I and II other kinds of phase equilibriums are known. While these are not always desirable for the operation of extraction systems, their appearance needs to be recognized because they are sometimes obtained at extreme temperatures in a ternary system that behaves normally at other temperatures. Figure 15-4 shows several ways in which a hypothetical three-component mixture can change progressively as the temperature is reduced. In Fig. 15-4c all three binary pairs are below their critical solution temperatures, and a three-phase region forms in the center of the diagram. In Fig. 15-4e the binary pair A-C becomes completely miscible as the temperature is raised, but a two-phase region persists inside the triangular region.

Figure 15-5 shows a common case of distribution of a solid solute B between liquids A and S, where solute-solvent compounds such as hydrates are not formed. The solubility of B in A is shown at

FIG. 15-4. Unusual phase behavior in ternary systems as affected by temperature.

A and S.

pairs are above their
erature is reduced to
hases. Below T_{A6} the
mensional figure shows
n in temperature en-
s the binary critical
S, is reached the two-
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observation of binary
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t selection. As brought
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propane as solvents, the
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are below their critical
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s I and II other kinds of
are not always desirable
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aves normally at other
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nge progressively as the
three binary pairs are
and a three-phase region
g, 15-4e the binary pair
mperature is raised, but
agular region.
tribution of a solid solute
solvent compounds such
y of B in A is shown at

(e)

in S at J. Tie lines UB and VB show equilibrium between solid
B and the saturated solutions at U and V. Mixtures within triangle
KL are three phase, of compositions B, K, and L. MN is a typical
liquid-liquid tie line and liquid extraction processes are confined to
the region below the last of these, KL.

Distribution Diagrams. Figure 15-6 shows typical distribution
diagrams on the right, corresponding to the systems (on the left)
thus far discussed. The slope of a chord from a point on the distribu-
tion curve to the origin provides the distribution coefficient K.
Treybal ("Liquid Extraction," 2d ed., McGraw-Hill, New York,
1963) has outlined the computations which may be made to predict
the variation of the distribution coefficient with B concentration,
for cases where B associates or dissociates in the two immiscible
solvents.

Tie-line Correlations. Direct interpolation of experimentally
observed tie lines is difficult on a triangular diagram, yet closely
spaced tie lines are needed for design computations of extractors.
Interpolation may be done with the help of a distribution diagram
(Fig. 15-6), but some method of linearizing this is greatly to be
desired. This reduces the number of experimental data required,
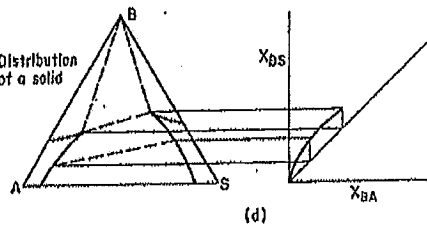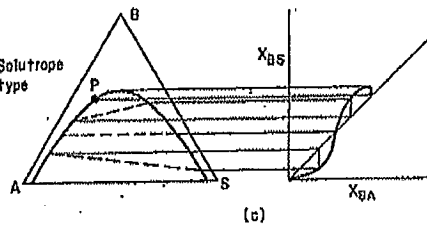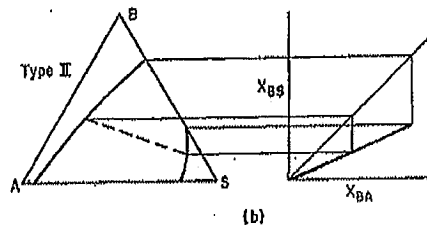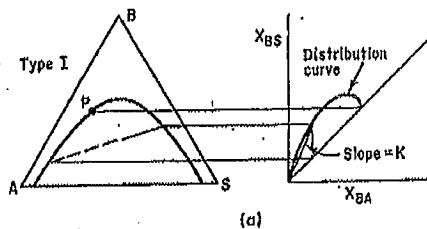and moreover permits extrapolation of data beyond the range of

Fig. 15-6. Typical distribution diagrams for ternary systems.
X_{BS} = weight fraction B in S-rich solution, X_{BA} = weight frac-
tion B in A-rich solution.

measurement. Such methods have been proposed by Brancker,
Hunter, and Nash [Ind. Eng. Chem., Anal. Ed., 12, 35 (1940)],
Bachman [Ind. Eng. Chem., Anal. Ed., 12, 38 (1940)], Campbell
[Ind. Eng. Chem., 36, 1158 (1944)], Hand [J. Phys. Chem., 34, 1960
(1930)], Ishida [Bull. Chem. Soc. Japan, 33, 693 (1960)], Othmer and
Tobias [Ind. Eng. Chem., 34, 693 (1942)], and Treybal et al. [Ind.
Eng. Chem., 38, 817 (1940)].

Figure 15-7 shows how the data for two tie lines may be plotted
on Hand-type coordinates. The tie-line correlation will usually be
excellently straight, except for solutropic systems which produce
two straight lines. The solubility curve is only slightly curved.
Extrapolation of the tie-line correlation line produces the plait point
P [see also Boberg and White, Ind. Eng. Chem. Fundamentals, 1,
40 (1962)]. Treybal ("Liquid Extraction," 2d ed., McGraw-Hill,
New York, 1963) shows that such a plot may be used not only to
interpolate and extrapolate for tie lines, but also to predict reasona-
bly well the entire diagram from the data of only two tie lines.

Quaternary systems may be displayed on an isothermal regular
tetrahedron, with the equilateral triangles of the faces representing
the four constituent ternaries [Brancker, Hunter, and Nash, J. Phys.
Chem., 44, 683 (1940); Ind. Eng. Chem., 33, 880 (1941)]. Such
diagrams are difficult to work with, however, and it is usually
possible to display the solute distributions, at least, on plane distribu-
tion diagrams of the sort shown on the right of Fig. 15-6 (Treybal,
"Liquid Extraction," 2d ed., Chap. 7, McGraw-Hill, New York,
1963). Thus, if B and C are solutes which distribute between
immiscible solvents A and D, the B distribution may be shown on
a plot of X_{BA} vs. X_{BD} with curves of constant X_{CD} as parameter.
In some systems, particularly if the total concentration of solute
is low, the distributions of B and C are independent of each other,
and only one such curve for each will then appear.

Multicomponent systems containing more than four components
become generally impractical to display graphically. For such
complex systems as those involving petroleum oils, where the vari-
ous components are frequently individually unidentifiable, attempts
have been made to describe the oil-solvent system as a pseudoter-
nary, with some significant physical property of the oils such as
viscosity-gravity constant replacing the A-B axis of a triangular
diagram [Hunter and Nash, Proc. World Petrol. Congr., London, 2,
340 (1933). Hill and Coats, Ind. Eng. Chem., 20, 641 (1928). Thomp-
son and Dunstan, "Science of Petroleum," vol. 3, p. 1829, Oxford,
New York, 1938. For vegetable oils, Ruthruff and Wilcock, Trans.
Am. Inst. Chem. Engrs., 37, 649 (1941)]. Alders [J. Inst. Petrol., 42,
228 (1956)] has shown that use of such diagrams to compute the
characteristics of multistage countercurrent extractors can lead to
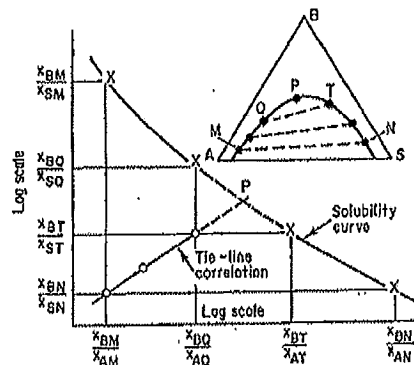considerable error. A method of dealing with this problem practi-
cally is discussed later.

Fig. 15-7. Tie-line and solubility correlation, after Hand
[J. Phys. Chem., 34, 1960 (1930)] and Treybal et al. [Ind. Eng.
Chem., 38, 817 (1940)]. X_{AM} = weight fraction A in the solution
at M, X_{BQ} = weight fraction B in the solution at Q, etc.

Experimental Equilibrium Data. Table 15-1 lists data for four typical ternary systems, corresponding to those of Fig. 15-6. Table 15-2 is a selected list of ternary systems for which similar, reasonably complete, numerical values of the distribution of all three components have been published. The total list probably numbers four or five times as many systems, with partially complete data for many more. Additional compilations of data may be found in "International Critical Tables," vol. 3, McGraw-Hill, New York, 1928; Francis, in Seidell and Linke (eds.), "Solubilities of Inorganic and Organic Compounds," supplement to 3d ed., Van Nostrand, Princeton, N.J., 1952 (4th ed. in preparation); Linke, "Solubilities," American Chemical Society, Washington, D.C. Additional listings of sources of data may be found in Francis, "Liquid-Liquid Equilibriums," Interscience, New York, 1963; Himmelblau, Brady, and McKetta, *Bur. Eng. Res. Spec. Publ.* 30, University of Texas, Austin, Tex., 1959; the Solvent Extraction Annual Reviews of Elgin and Treybal listed under General Reviews at the beginning of this section; the Annual Thermodynamics Reviews, Smith et al., *Ind. Eng. Chem.*, 47, 664 (1955); 48, 676 (1956); 49, 583 (1957); 50, 561 (1958); 51, 473 (1959); 56(9), 41 (1964); 57(12), 44 (1965). Francis [*Ind. Eng. Chem.*, 47, 230, 1033 (1955); *J. Phys. Chem.*, 58, 1099 (1954); 60, 20 (1956); 62, 579 (1958); *J. Chem. Eng. Data*, 10, 45, 145, 280, 327 (1965); 11, 234 (1966)] has published ternary diagrams, without numerical data, for hundreds of systems.

Table 15-2 may be used as a source of data for *preliminary screening* of solvents. Thus [see Eq. (15-29) and definitions follow-

Table 15-1. Some Ternary Liquid Equilibriums

Equilibrium tie-line concentrations in weight percent. The concentration of component S is found by difference from 100. Reprinted with permission from the indicated sources.

A = water, B = acetic acid, S = methylisobutyl ketone, 25°C.
Sherwood, Evans, and Longcor, *Ind. Eng. Chem.*, 31, 599 (1939)

A	B	A	B
98.45	0	2.12	0
95.45	2.85	2.80	1.87
85.8	11.7	5.4	8.9
75.7	20.5	9.2	17.3
67.8	26.2	14.5	24.6
55.0	32.8	22.0	30.8
42.9	34.6	31.0	33.6

A = ethylbenzene, B = styrene, S = ethylene glycol, 25°C.
Boobar et al., *Ind. Eng. Chem.*, 43, 2922 (1951)

A	B	A	B
90.56	8.63	9.85	1.64
80.40	18.67	9.31	3.49
70.49	28.51	8.72	5.48
60.93	37.98	8.07	7.45
52.96	45.84	7.31	9.49
53.55	45.25	7.35	9.25
41.51	57.09	6.06	12.54
43.29	55.32	6.30	12.00
21.60	76.60	3.73	18.62

A = water, B = pyridine, S = benzene, 25°C.
Vriens and Medcalf, *Ind. Eng. Chem.*, 45, 1098 (1953)

A	B	A	B
94.7	5.1	0.75	13.9
87.2	12.2	1.8	27.0
71.6	25.9	3.1	35.3
54.5	41.7	4.8	38.4
36.3	53.7	5.8	43.8

A = water, B = cupric sulfate, S = n-butanol, 30°C.
Blumberg, Cejtlin, and Fuchs, *J. Appl. Chem.*, 10, 407 (1960). Hill and Malisoff, *J. Am. Chem. Soc.*, 48, 918 (1926).

A	B	A	B
92.9	0	20.6	0
95.59	2.45	19.6	0.00123
72.9	14.7	16.3	0.00425*

*In equilibrium with solid phase.

ing], assuming that solutions remain dilute and that, for two different solvents 1 and 2, the same number of stages and the same extent of extraction are desired, then the extraction factors for the solvents must be the same. Then $(S_1/H)/(S_2/H) = K_2/K_1$, where S/H = solvent/feed ratio. For example, suppose acetic acid is to be extracted from dilute solution in water. If benzene (1) and butyl acetate (2) are to be compared as possible solvents, Table 15-2 shows $K_1 = 0.0984$ and $K_2 = 0.705$ at 30°C. Then $(S_1/H)/(S_2/H) =$ (lb. benzene/lb. feed)/(lb. butyl acetate/lb. feed) = 0.705/0.0984 = 7.16. This means that seven times as much benzene would be required as would butyl acetate. The distribution coefficients are only one of the solvent properties which must be considered, however (see Desirable Solvent Properties).

Thermodynamic Basis of Liquid-Liquid Equilibriums. In ternary systems of the sort shown in Fig. 15-2, all three substances are present in both phases. For equilibrium phases, the activity a of each substance must be the same in both phases, provided that the reference state chosen is the same throughout. This is assured by choosing as reference state the pure components at the temperature and pressure of the system. Then, if the phases are A-rich and S-rich, respectively,

$$a_{AA} = a_{AS} \qquad a_{BA} = a_{BS} \qquad a_{SA} = a_{SS} \qquad (15-1)$$

where a_{BA} = activity of B in the A-rich phase, etc. If the activities can be expressed as functions of concentration correctly, through consideration of data other than the liquid equilibriums, then the equilibriums can be predicted. With our present state of knowledge, it is not generally possible to do this well enough to rely upon the predicted equilibriums for purposes of extractor design, but it is possible nevertheless to make useful predictions of the general trend of the equilibriums, for purposes of choosing possible solvents in the absence of data.

Provided the concentrations of B are taken as very small and the mutual solubility of pure A and S may be neglected, the initial distribution of B may often be estimated quickly. Introducing the definition of activity coefficient for B, $\gamma_B = a_B/x_B$, Eq. (15-2) for B provides the distribution coefficient for B:

$$K' = \frac{x_{BS}}{x_{BA}} = \frac{\gamma_{BA}}{\gamma_{BS}} \qquad (15-3)$$

where γ_{BS} = activity coefficient of B in the B-S binary, γ_{BA} = activity coefficient of B in the A-B binary. Here, $\log \gamma_{BA} = A_{BA}$ and $\log \gamma_{BS} = A_{BS}$, where the A's are the Margules or van Laar constants for the binaries (see Sec. 13) or, more generally, the logarithm of the activity coefficient of substance B in infinitely dilute solution in A or S, respectively. Thus,

$$\log K'_{B, x_B = 0} = A_{BA} - A_{BS} \qquad (15-4)$$

Values of the A's may be obtained from vapor-liquid data generally and many are listed (Kux, in Landolt-Bornstein, "Zahlenwerte und Funktionen," vol. II, Part 2a, Springer, Berlin, 1960; binary systems, pp. 336-711; ternary systems, pp. 712-767). They may be estimated in the absence of data through such correlations as that of Pierotti, Deal, and Derr [*Ind. Eng. Chem.*, 51, 95 (1959)] or, when applicable, through the regular-solution theory of Hildebrand and Scott ("The Solubility of Nonelectrolytes," 3d ed., Reinhold, New York, 1950; "Regular Solutions," Prentice-Hall, Englewood Cliffs, N.J., 1962. See also Hildebrand, Prausnitz, and Scott, "Regular and Related Solutions," Van Nostrand Reinhold, New York, 1970.

Example 1. Estimate the distribution coefficient for acetone between two liquid phases composed of water and chloroform. The end values of the activity coefficients from measurements of vapor-liquid equilibriums are

System	van Laar constant	Reference
Acetone (B)-water (A)	$A_{BA} = +0.79$	Beare, McVicar, and Ferguson, *J. Phys. Chem.*, 34, 1310 (1930)
Acetone (B)-chloroform (S)	$A_{BS} = -0.57$	Mueller and Kearns, *J. Phys. Chem.*, 62, 1441 (1958)