# CHAPTER 15

# Separation Processes Based on Reversible Chemical Complexation

C. JUDSON KING

Department of Chemical Engineering University of California Berkeley, California

# SUMMARY

Separation processes based on reversible chemical complexation can have high capacities for dilute solutes and also high selectivities. In these processes the mixture is contacted with a second phase containing a complexing agent that reacts reversibly with the solute(s) of interest. In a second part of the process the reaction is reversed and the solute is recovered. Complexation is used commonly on very large scales for gas absorption and hydrometallurgical refining, and such applications are discussed in Chapters 6 and 8, respectively. This chapter is limited to the application of these chemical complexations to the separation of polar organic solutes from aqueous solutions.

For this purpose, complexation reactions can be implemented in many different ways, including solvent extraction, distillative processes, adsorption, liquid membranes, and foam or bubble fractionation. A solute suitable for separation by complexation usually has Lewis-acid and/or Lewis-base functional groups, low concentration, low volatility relative to water, and a low activity coefficient in water. The complexing agent is chosen so as to give a strong, specific, yet reversible reaction with the solute. Frequently, the complexing agent is dissolved in a diluent. The diluent can improve the equilibrium through solvation of the complex and can affect the process in other ways.

The specific cases of separation of acetic acid, phenol, and ethanol from aqueous solution are considered in some detail. Complexation proves to be very effective for acetic acid, leading to several promising new processing approaches. It is less attractive for phenol, primarily because phenol is extracted readily with conventional solvents; the benefits of complexation are more important for polyhydroxy benzenes. For ethanol, it is difficult to identify extractants giving strong complexation. However, the effects of weaker complexation generate important differences among solvents. Lewis acidity and branching give improved selectivity for ethanol over water at a given solvent capacity.

Complexation also offers attractive possibilities for selective recovery of dicarboxylic acids, hydroxycarboxylic acids (lactic, citric, etc.), phenolic carboxylic acids (gallic, vanillic, caffeic, etc.), amino acids, quinolines, and alkaloids from aqueous solution.

#### **15.1 INTRODUCTION**

The principal separation methods used in classical analytical chemistry are based on chemical reactions. These methods are attractive because many chemical reactions are specific for an individual component of a mixture, and the reactants frequently react completely to the desired products.

Chemical reactions are used far less frequently for separations in the chemical process industries. One reason for this is that processes employing chemical reactions often consume large amounts of expensive reactants, and the reaction product is usually less valuable than the original compound.

These disadvantages can be overcome by using a readily reversible chemical reaction to separate the component of interest from the feed mixture. In a second step of the process, the reaction can be reversed to regenerate the added reactant and recover the desired component in its original form. In order for the reaction to be reversible in an economically attractive process, it must have a relatively low bond energy. Such reactions are known as complexation or association reactions. Figure 15-1.1 shows some reactions of this type along with the bond energies typically involved. Complexation reactions with bond energies less than 10 kJ/mol are similar to ordinary associations by van der Waals forces in the condensed state, and reactions with bond energies above 50 kJ/mol tend to be difficult to reverse without undue expense.

#### 15.1-1 Equilibria

A simple complexation reaction gives an equilibrium of the form:

solute + 
$$n \cdot$$
 complexing agent  $\rightleftharpoons$  complex

described by an equilibrium constant,

$$K_{c} = \frac{[\text{complex}]}{[\text{solute}][\text{complexing agent}]^{n}}$$
(15.1-1)

If n = 1 and the uncomplexed solute assumes a linear distribution between one phase and a second phase containing the complexing agent, then Eq. (15.1-1) leads to a nonlinear equilibrium of the form shown in Fig. 15.1-2. This relationship shows that a complexation separation can give very high equilibrium distri-

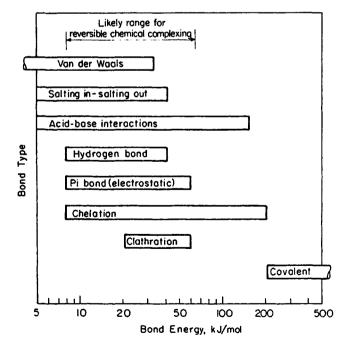
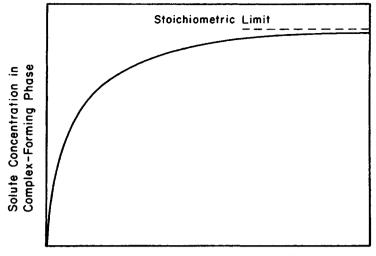


FIGURE 15.1-1 Bond energies most suited for chemically complexing separation processes. (From King;<sup>1</sup> courtesy of Dr. G. E. Keller.)



# Solute Concentration in Feed Phase

FIGURE 15.1-2 Shape of typical phase-equilibrium relationship for chemical complexation.

bution coefficients at low solute concentrations, but that the distribution becomes less favorable at higher solute concentrations where stoichiometric saturation of the complexing agent is approached. Thus, one important conclusion is that separations based on chemical complexation tend to be *more attractive for cases of relatively low solute concentration*.

In addition to high capacity at low solute concentration, the other major potential advantage of separation processes based on chemical complexation is *selectivity*. Since the complexation reaction can be selective for solutes with particular functional groups, these processes have the potential to separate only certain solutes from a complex mixture. They also can give less coextraction of water than separations with more conventional solvents.

These advantages of chemical complexation for separations are offset by some important potential disadvantages. These separations necessarily employ a mass separating agent rather than an energy separating agent.<sup>1</sup> Therefore, regeneration is required to isolate the product and allow recycle of the separating agent. The expense of regeneration must be taken into account, and the complexation equilibria must have satisfactory properties for the regeneration. Finally, the rate of the complexation reaction may be slow compared to the mass transfer rates in the contactor. This increases the size and cost of the contacting equipment.

# 15.1-2 Process Characteristics

Chemical complexation already has become well established as a separation method in analytical chemistry and on a large scale in the applications of gas absorption and metals extraction. The ethanolamine and carbonate systems for removal of  $CO_2$  and  $H_2S$  from gas streams are classic examples of complexation. Practical aspects of these systems are discussed in Chapter 6 and by Kohl and Riesenfeld,<sup>2</sup> and the more theoretical aspects are discussed by Danckwerts,<sup>3</sup> Danckwerts and Sharma,<sup>4</sup> and Astarita et al.<sup>5</sup> In the metals industry, complexation is used extensively in the hydrometallurgical production of copper and uranium and in the refining of nickel, molybdenum, cobalt, and other metals: for examples see Chapter 8 or the *Proceedings* of the triennial International Conferences on Solvent Extraction.

The topic of this chapter is the application of reversible chemical complexation for removal and recovery of polar organic solutes from aqueous solution. There are some current examples of such separations, and many more are subjects of active research. One of the most important applications is the recovery of products of biochemical synthesis processes, such as fermentation and enzymatically catalyzed reactions. These separation problems range from recovery of commodity chemicals or fuel substances such as acetic acid and ethanol to isolation of much more complex pharmaceuticals and compounds produced by recombinant DNA and other recently developed biological techniques. Another important application is removal and recovery of polar organics from effluent or recycle water streams.

Chemical complexation has been implemented most often in absorption, extraction, and gas and liquid chromatography. A more comprehensive list of alternative processes where chemical complexation could be employed for the recovery of polar compounds from aqueous solution is shown in Table 15.1-1. In

<b>TABLE 15.1-1</b>	Alternatives for Removing Polar-Organic
Solutes from A	queous Solution by Chemical Complexation

Solvent extraction Extractive distillation Azeotropic distillation Adsorption Solid-infusion processes Emulsion liquid membranes Solid-supported liquid membranes Foam fractionation Bubble fractionation

extraction, extractive distillation, and azeotropic distillation, the complexing agent is added to modify liquid-phase activity coefficients and thereby establish more favorable phase equilibrium and selectivity. In adsorption, the adsorbent has functional groups on the surface of the solid which form a complex with the solute. An alternative related to adsorption is a solid-infusion process, such as "adsorption" with a polymer gel. In this process the solute can have sufficient mobility in the solid phase to allow transport to complexation sites in the interior of the solid. In an emulsion liquid membrane process, the complexing agent could be present in the outer-emulsion phase to provide facilitated transport of a solute into the inner-emulsion phase, or the complexing agent could be in the inner-emulsion phase where it would have a high capacity for the solute. In the latter case, the complexing agent would have to be regenerated after the emulsion was broken apart. In a solid-supported liquid-membrane process, the complexing agent would be in the liquid impregnated into a polymeric support and would facilitate transport of the solute. In a foam-fractionation<sup>6</sup> or bubble-fractionation<sup>7</sup> process the complexing agent would be surface active or attached to a surfactant and would attract the solute to the gas-liquid interface.

# 15.1-3 Solute Characteristics

Chemical complexation is most useful for the separation of organic solutes from water when the solute has certain physical properties. Some of the most important criteria favoring the use of complexation are the following:

1. Lewis-Acid or Lewis-Base Functional Groups. The solute(s) of interest should have one or more functional groups that can participate in moderately strong complexation. Since most complexation processes involve interactions of Lewis acids with Lewis bases, acidic and basic functional groups are useful.

2. Low Solute Concentration. Since complexing agents provide particularly high equilibrium distribution coefficients for low solute concentrations and tend to saturate stoichiometrically at high concentrations (Fig. 15.1-2), complexation is most attractive for relatively dilute aqueous solutions. It is difficult to generalize, but a solute concentration of 5 wt.% is an approximate upper limit beyond which complexation becomes less attractive.

3. Low Activity Coefficient in Water. Complexation separation processes are useful for hydrophilic solutes, because these solutes are difficult to recover from aqueous solution by most other means. Complexation is capable of providing a very low organic-phase activity coefficient and hence an acceptable phase-distribution coefficient, even though the activity coefficient in the aqueous phase is low.

4. Low Solute Volatility. Solutes that are less volatile than water are good candidates for separation by complexation, because they cannot be separated by steam stripping. Solutes in this category include acetic acid, dicarboxylic acids (succinic, malonic, etc.), glycols, glycol ethers (Cellosolves), lactic acid, and polyhydroxybenzenes (catechol, pyrogallol, etc.), among others. Stripping is also expensive if the solute has a relative volatility close to 1 with respect to water (e.g., ethanol) or if it forms a low-concentration heterogeneous azeotrope with water (e.g., phenol).

# 15.1-4 Characteristics of the Complexing Agent

There also are a number of criteria by which potential chemical-complexation agents can be evaluated:

- 1. The complexation bond energy should be great enough to give a substantial improvement over conventional mass separating agents, which usually are less expensive.
- 2. The complexation bond energy should be low enough so that the complex can be regenerated easily and completely.

- 3. Coextraction of water can be an important economic disadvantage. The complexing agent should be selected to minimize coextraction of water and/or facilitate subsequent removal of that water.
- 4. There should be *no side reactions*, and the complexing agent should be *thermally stable*, to avoid irreversible loss.
- 5. The complexation reaction should have sufficiently fast kinetics in both directions so that equipment sizes do not become prohibitively large.

In a number of processes it is either necessary or desirable to use a cosolvent or diluent with the complexing agent. For example, if the complexing agent is a solid—such as trioctyl phosphine oxide—the diluent is needed to form a liquid solution for extraction or liquid-membrane processes. In an extraction process the diluent controls the viscosity, density, and interfacial tension of the mixed solvent. With a relatively nonvolatile complexing agent, the diluent volatility also determines the temperature in the reboiler of a distillation column in a regeneration process. In a liquid-membrane process the diluent may increase the transport rates in the liquid phase.

Two other important functions of a diluent are more subtle:

- 1. The complexing agent itself may be a poor solvating medium for the complex, in which case an effective diluent can solvate the complex and thereby encourage its formation. Very large changes in equilibrium distribution coefficients can be achieved by changing the diluent.
- 2. When coextraction of water is an important consideration, the diluent can have a large effect on the amount of water coextracted and also can improve the separation of water in a subsequent distillation step. It can be worthwhile to choose a diluent with a lower equilibrium distribution coefficient for the solute, if the ratio of solute to water extracted is increased.

#### 15.1-5 Regeneration Methods

Any complexation separation process requires a regeneration scheme to recover the complexation agent. In some unusual cases the reaction product can be discarded, but then an inexpensive reactant and an irreversible reaction would be desirable. The following list gives some alternatives for regeneration processes:

1. If the solute is volatile, it can be taken overhead in a distillation or stripping process. The volatility of the solute may be suppressed by the complexation equilibrium. In cases of nonvolatile solutes and sufficiently volatile complexing agents, the complexing agent can be taken overhead.

2. If the equilibrium constant of the complexation reaction is sufficiently sensitive to temperature, back-extraction into water at a different temperature can give an overall concentration of the solute. Even if the resulting solution were not more concentrated, this process can isolate one solute from other solutes.

3. Back-extraction of the solute into a strong base or a strong acid can be used for acidic or basic solutes, respectively. In this case a high degree of concentration may be achieved, but the chemical form of the solute will be changed. A change in the solution pH also may affect the solute in other ways so as to facilitate regeneration. These regeneration methods can consume large quantities of chemicals.

### 15.2 SPECIFIC EXAMPLES

The recovery of three solutes—acetic acid, phenol, and ethanol—from aqueous solution is considered in detail to illustrate the important factors in these separations. Then separation by chemical complexation is evaluated from some other classes of organic solutes.

# 15.2-1 Acetic Acid

Acetic acid often is found in dilute solution from processes that use it as a raw material or solvent. Fermentation processes also produce acetic acid in dilute solution. In many of these cases the solution pH is high enough so that the acetic acid is ionized partially or completely. The present discussion is restricted to the recovery of un-ionized acetic acid. At a pH below the  $pK_a$ , all the acetic acid can be removed in the un-ionized form. At a higher pH the acetate ion does not distribute into the second phase, and a large distribution coefficient is required for the un-ionized form to shift the equilibrium and obtain an attractive removal capacity.

Acetic acid is less volatile than water, and the relative volatility is close enough to unity so that simple distillation is not the process of choice for recovery of acetic acid, except possibly at extremely high concentrations in aqueous solution.<sup>1</sup> For the past 30 or more years, azeotropic distillation has been the conventional technology for recovering acetic acid from feeds having greater than 35-45% w/w acetic acid in water. For more dilute feeds the favored process has been extraction with solvents such as ethyl acetate, mixtures of ethyl acetate and benzene, and isopropyl acetate.<sup>1.2</sup> These solvents give values of the equilibrium

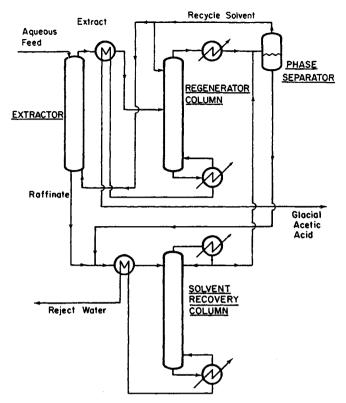


FIGURE 15.2-1 Conventional process for recovery of acetic acid by solvent extraction, followed by azeotropic distillation.<sup>1,2</sup>

distribution coefficient<sup>\*</sup>  $K_D$  less than 1.0. An example of such a process is shown in Fig. 15.2-1. An important property of these solvents is their ability to improve the separation of the coextracted water from the acetic acid. The extract is fed to the regeneration column where the solvent modifies the vapor-liquid equilibria and acts as an entrainer for an azeotropic distillation. The distillate, which contains the solvent and the coextracted water, splits into two liquid phases—a solvent-rich stream suitable for recycle to the extractor and a water-rich stream that is combined with the raffinate and sent to a solvent stripping column. The bottom product from the regeneration column is glacial acetic acid.

The lowest feed concentration allowing economical recovery with these conventional processes is 3-5% w/w acetic acid, depending on the value accorded to recovered acetic acid. For more economical processing of dilute feed streams, a solvent giving a higher value of  $K_D$  is needed. This leads to chemical complexation. Acetic acid in these aqueous streams meets all the criteria listed above (Lewis-acid functional group, low concentration, low volatility, and low activity coefficient in water) for solutes which are good candidates for separations based on chemical complexation.

Since acetic acid is a Lewis acid, it is appropriate to study solvents that are moderately strong Lewis bases. Complexing agents that have received the most investigation to date incorporate either phosphoryl or amine groups. Tributyl phosphate (TBP) gives a  $K_D$  of about 2.3 for acetic acid at high dilution and a somewhat lower value at higher concentrations of acetic acid.<sup>3-5</sup> When TBP is mixed with hydrocarbon diluents, the resulting  $K_D$  is approximately a mass-weighted average of the values for the pure solvents.<sup>4</sup> Stronger Lewis bases that have received attention are tertiary amines and trioctyl phosphine oxide (TOPO). All these extractants are used in the hydrometallurgical industry. They are available commercially; therefore, operating experience has been gained with them.

With these more basic extractants the nature of the diluent becomes quite important. Blumberg and Gai<sup>6</sup> have interpreted diluent effects in terms of Lewis acidity and basicity for extraction of mineral acids by tertiary amines. Frolov et al.<sup>7</sup> interpreted diluent effects for extraction of acetic acid by amines in terms

 ${}^{*}K_{D}$  is the weight fraction solute in organic phase per weight fraction solute in aqueous phase, at equilibrium. All equilibrium distribution coefficients reported here are defined in this way unless otherwise noted.

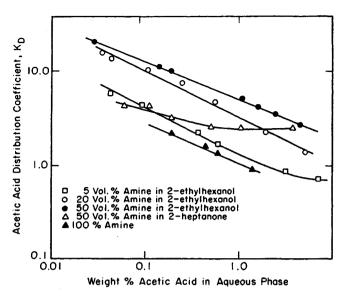


FIGURE 15.2-2 Equilibrium distribution coefficients for solvent extraction of acetic acid from aqueous solution into solvent mixtures containing Alamine 336.<sup>8</sup>

of empirical polarity parameters. Wardell and King,<sup>4</sup> Ricker et al.,<sup>8</sup> and Spala and Ricker<sup>9</sup> have observed very pronounced maxima in  $K_D$  at intermediate solvent compositions for extraction of acetic acid by mixtures of tertiary amines or TOPO with diluents such as alcohols, ketones, and chlorinated hydrocarbons. These maxima have been interpreted in terms of the ability of the diluent to solvate the complex formed by acetic acid and the Lewis-base extractant. An example of the behavior of  $K_D$  is shown in Fig. 15.2-2, where the intermediate compositions of a mixture of Alamine 336 (a commercial tertiary amine mixture, Henkel Corp.) and 2-ethylhexanol give values of  $K_D$  as much as a factor of 5 greater than either the undiluted amine or the alcohol without amine. It is interesting to note in Fig. 15.2-2 that  $K_D$  decreases with increasing concentration of acetic acid in the raffinate. This is due to the effect of stoichiometry on the complexation equilibrium [Eq. (15.1-1)]. The ketone diluent, 2-heptanone, also increases  $K_D$  as compared to the undiluted amine, but the increase is not very large at low acetic acid concentration. Spala and Ricker<sup>9</sup> interpret that behavior in terms of the lack of an electron acceptor group in the ketone to hydrogen bond with the electronegative carbonyl oxygen in the complex. The ketone diluent becomes more favorable than the alcohol diluent at higher raffinate concentrations of acetic acid because the ketone itself has an appreciable solvent capacity for the uncomplexed carboxylic acid through hydrogen bonding. Sakai et al.<sup>10</sup> measured degrees of extraction of acetic acid from water using solvent mixtures composed

Sakai et al.<sup>10</sup> measured degrees of extraction of acetic acid from water using solvent mixtures composed of a secondary amine mixture, Amberlite LA-2 (Rohm & Haas Corp.), with diluents such as hexane, CCl<sub>4</sub>, CHCl<sub>3</sub>, or methyl isobutyl ketone (MIBK). The ketone and CHCl<sub>3</sub> diluents gave the highest values of  $K_D$ , consistent with the results for the extraction of acetic acid with tertiary amines. A weak effect of temperature on  $K_D$  was observed for LA-2 with CHCl<sub>3</sub> diluent. Tertiary amines probably are better extractants because primary and secondary amines can react irreversibly when heated with acetic acid to form amides.

Process aspects for extraction of acetic acid with amines are discussed by Ricker et al.<sup>11</sup> Alcohol diluents gave the highest values of  $K_D$ , but the alcohols were subject to esterification with acetic acid upon regeneration by distillation. Ketones appeared to be satisfactory diluents from the standpoint of high  $K_D$ . Chloroform is a superior diluent because it is a Lewis acid and can interact with the complex.<sup>9</sup> However, chloroform is toxic, and this fact may limit its use.

Process aspects for extraction by TOPO are discussed by Helsel,<sup>12</sup> Ricker et al.,<sup>11</sup> and Golob et al.<sup>13</sup> Among hydrocarbons, aromatics are better diluents since they have higher solvent capacities for TOPO. Alcohol diluents appear to interact preferentially with the phosphoryl group and thereby give values of  $K_D$  even lower than found with aromatic hydrocarbon diluents. Ketone diluents cannot interact with the phosphoryl group, and they solvate the acetic acid-TOPO complex to some extent; hence, they give higher values of  $K_D$  when used as diluents than do aromatics.<sup>8</sup>

In these extractant-diluent systems for acetic acid, the optimal molecular weight for the extractant reflects a compromise between high  $K_D$  (low molecular weight) and low enough solubility of the extractant or the complex in the aqueous phase (high molecular weight). TOPO and Alamine 336 (tri-octyl/decyl amines) appear to be near optimal in this sense. The optimum diluent molecular weight reflects a compromise between high  $K_D$  (low molecular weight) and either low solubility in water or low enough volatility

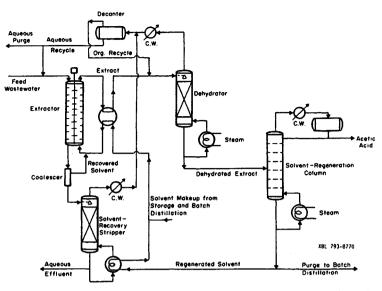


FIGURE 15.2-3 Extraction process for recovery of acetic acid from aqueous solution using a heavy solvent.<sup>11</sup>

relative to acetic acid for solvent regeneration to be carried out in the presence of the extractant (high molecular weight). Among the ketones, diisobutyl ketone (DIBK) or a decanone seem to be an effective compromise in that regard. Values of  $K_D$  for extraction of acetic acid (1% w/w in raffinate) are about 2.5 for both 50% Alamine 336 in DIBK and 40% TOPO in 2-heptanone.<sup>8</sup>

TBP, TOPO, and the amines are all higher-boiling solvents than acetic acid. This reduces steam costs for regeneration as compared to low-boiling solvents, but it can lead to higher reboiler temperatures in the regenerator and accumulation of nonvolatile impurities in the solvent. A portion of the solvent might have to be discarded or processed further to remove these impurities. The complexing extractants tend to be more expensive than conventional solvents; TBP and amines are in the range of \$2.2-3.3/kg, while TOPO costs about \$17/kg. Losses are therefore important. Assuming that extractant losses will be about the same in either case, amines are probably more attractive than TOPO because they are less expensive.

Chemically complexing extractants can be much more selective than conventional solvents and therefore can reduce the amount of coextracted water. On a solvent-free basis, the extract in equilibrium with a 6.6% w/w aqueous acetic acid solution contains about 84% acetic acid<sup>8</sup> for extraction with Alamine 336–DIBK. The selectivity for acetic acid over water is lower for extraction with TBP,<sup>5</sup> but is still substantially higher than with conventional solvents such as acetates or ketones. Coextracted water can be removed in an extractive distillation column located before a solvent regeneration column, as shown in Fig. 15.1-2.

Jagirdar and Sharma<sup>14</sup> have employed tertiary amine extractants to recover and fractionate among several carboxylic acids in aqueous solution by means of dissociation extraction, in which a stoichiometrically deficient amount of extractant is used. Comparative equilibria for different carboxylic acids also are given by Niitsu and Sekine<sup>15</sup> for TOPO-based solvents and by Wardell and King<sup>4</sup> for TBP, TOPO, and amines.

Extractive distillation was used in the past in the Suida process for recovery of acetic acid from pyroligneous acid, with recycle wood oils used as the extractive agent.<sup>16</sup> Although this process has long since been discontinued, it is possible that extractive distillation could become attractive again for more concentrated acetic acid feeds if a water-soluble complexing agent were used, such as one of the lower molecular weight phosphates, amines, or phosphine oxides.

Chemical complexing can be used for recovery of acetic acid in process configurations other than extraction, as listed in Table 15.1-1. Smith<sup>17</sup> reports studies using solid-supported liquid membranes, where the impregnating agents are solvents containing amines or TOPO. The acetic acid permeate is taken up by a solution of an aqueous base, such as  $Ca(OH)_2$ , thereby converting the acetic acid to a salt. TOPO was found to give better sustained performance and a more plasticized polyvinyl chloride membrane than either primary or secondary amines. Kuo and Gregor, <sup>18,19</sup> also have studied TOPO-impregnated membranes for removal of acetic acid from dilute aqueous feeds by facilitated transport. They have modeled factors influencing transport rates, explored effects of different diluents for TOPO, and investigated ways of sustaining the membrane strength.

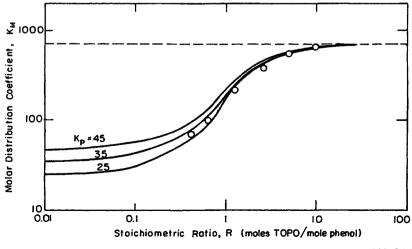
#### 15.2-2 Phenol

Phenol meets several of the criteria for a desirable solute for complexation separations. Phenol is a Lewis acid due to the hydroxyl group. It often is present in dilute aqueous solutions from industrial processes. Although it is more volatile than water in dilute aqueous solutions, it is difficult to separate by stripping because it forms a heterogeneous azeotrope at low concentration (9.2% w/w in water). However, an essential difference in contrast with acetic acid is that phenol has a substantially higher activity coefficient in aqueous solution, and therefore it is extracted much more readily by conventional solvents. For example, diisopropyl ether (DIPE) and methyl isobutyl ketone (MIBK) provide  $K_D$  values of about 37 and 100, respectively, for phenol at high dilution.<sup>20</sup> This means that extraction processes with either of these solvents can operate at relatively low solvent-to-feed ratios, and there is therefore less incentive to gain the still higher values of  $K_D$  which should be provided by complexing extractants. It might be noted, however, that DIPE and MIBK provide substantially higher values of  $K_D$  hand on many other solvents of comparable molecular weight. That fact can be attributed to their Lewis basicity, although they are substantially weaker bases than amines or phosphoryl compounds. One disadvantage of conventional solvents is that residual dissolved solvent must be recovered from the aqueous raffinate.

Despite the advantages of conventional solvents, some work has been done with chemically complexing extractants for phenol. Amines have been studied as extractants for phenol by Wolf and Fuertig,<sup>21</sup> Pollio et al.,<sup>22</sup> Pittman,<sup>23</sup> and Inoue et al.<sup>24</sup> These researchers found that diluents such as benzene and 2-ethyl-hexanol provide substantially higher values of  $K_D$  than does CCl<sub>4</sub>, and that CCl<sub>4</sub> provides higher  $K_D$  values than do alkane diluents. Nonetheless, the values of  $K_D$  realized are not high enough to warrant the use of the more expensive extractant rather than DIPE, MIBK, or similar solvents. The amine group, which is a stronger Lewis base, might be expected to give very high  $K_D$  values compared to conventional solvents. However, if the complexation occurs through a proton transfer to the amine, it must be recognized that phenol has a relatively high value of  $pK_a$ .

Phosphoryl solvents also have been studied for extraction of phenol. Tricresyl phosphate has a  $K_D$  of about 72 for phenol.<sup>25</sup> This value is comparable to those for DIPE and MIBK, an important difference being that the phosphate is a high-boiling solvent, whereas DIPE and MIBK are low-boiling solvents. The Lewis basicity increases in the order: phosphates [PO(OR)<sub>3</sub>] < phosphonates [PO(OR)<sub>2</sub>R] < phosphine oxides [POR<sub>3</sub>]. Complexes formed by phenol with these compounds have been studied extensively by spectroscopic, dielectric, and equilibrium measurements.<sup>26-32</sup> Complexes formed with phosphine oxides are particularly strong, reflecting the hydrogen bond.

Figure 15.2-4 shows measured equilibrium data for extraction of phenol from an aqueous feed containing 5000 ppm phenol at 22.5 °C into a solvent composed of 25% w/w TOPO in diisobutyl ketone (DIBK).<sup>33</sup> Here the data are expressed as  $K_{\mu}$ , the concentration (mass or moles/volume) in the solvent divided by the concentration of phenol in the equilibrium aqueous phase. Predicted curves are drawn for a theoretical model, in which fitted parameters are  $K_{\rho}$ , the physical (or unreacted) distribution coefficient, and  $K_{R}$ , the equilibrium constant of a complexation reaction with one-to-one stoichiometry. The curves are drawn for



XBL822-5/98

FIGURE 15.2-4 Concentration-based equilibrium distribution coefficients for extraction of phenol from dilute aqueous solution into a solvent mixture composed of 25% w/w TOPO in DIBK.<sup>33</sup>

1000

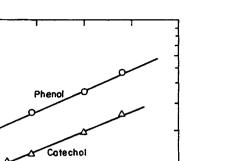
Distribution Coefficient, K<sub>D</sub>

10

4

3.0

3.1



XBL822-5201

3.5

3.4

**FIGURE 15.2-5** Equilibrium distribution coefficients vs. temperature for extraction of phenol and catechol from dilute aqueous solution into a solvent mixture of 25% w/w TOPO in DIBK. Stoichiometric ratio =  $2.5 \text{ mol TOPO/mol solute.}^{33}$ 

3.2

3.3

 $1/T \times 10^{-3} (K^{-1})$ 

 $K_P = 25$ , 35, and 45, and for  $K_P K_R T_{io} = 700$ , where  $T_{io}$  is the initial molar concentration of TOPO in the organic phase. From these results,  $K_R$  is in the range of 40-50 L/mol.

One possible regeneration method, mentioned above, is temperature-swing back-extraction. Figure 15.2-5 shows measured values of  $K_D$  as a function of temperature for extraction of phenol and catechol individually from water into 25% w/w TOPO in DIBK with feed concentrations of 5000 ppm and a molar TOPO solute ratio of 2.5.<sup>33</sup> There is a substantial change of  $K_D$  with temperature but probably not enough to support this method of regeneration.

An alternative is to regenerate by distilling phenol overhead from the solvent, in which case a diluent much heavier than DIBK is needed. Tests by Bixby<sup>34</sup> have shown that the volatility of phenol is reduced by the complexation reaction even at temperatures above 200°C. Even though pure phenol boils at 182°C, it is desirable to use a diluent boiling at 250°C or higher to achieve economical regeneration.

From these results it appears that the more conventional "physical" solvents, such as DIPE or MIBK, have more advantages for phenol removal than the more common Lewis-base complexing extractants. However, complexing extractants may be advantageous for feed solutions containing di- and trihydoxy benzenes. Dihydroxy benzenes have sufficiently low values of  $K_D$  into DIPE<sup>20</sup> that solvent-to-water mass phase ratios of about 1.0 would be required. Phase ratios required to remove trihydroxy benzenes would be prohibitively high. MIBK performs significantly better, but TOPO-based extractants give considerably higher values of  $K_D$ . A comparison is made in Table 15.2-1 of measured values of  $K_D$  for extraction of phenol and di- and trihydroxy benzenes from dilute aqueous solution at ambient temperature using DIPE, MIBK, and 25% w/w TOPO in MIBK (molar ratio of TOPO to solute is about 2.5). All measurements are at low enough pH so that the solutes are not ionized.

#### 15.2-3 Ethanol

Ethanol also has several desirable characteristics for separation by chemical complexation. Ethanol is produced in dilute aqueous solution by fermentation processes. Ethanol has a low activity coefficient in water; therefore, extraction with conventional solvents is difficult. Although ethanol is substantially more volatile than water in dilute solutions, it forms an azeotrope with water at high concentration, making distillation processes complicated and possibly expensive. However, chemically complexing extractants have not been identified that provide high values of  $K_D$  for ethanol. Measurements by Roddy,<sup>35</sup> Munson and King,<sup>36</sup> and others have shown that amines and phosphoryl compounds do not provide values of  $K_D$  appreciably greater than those provided by conventional solvents. Alcohols have both Lewis-acid and Lewisbase sites. One possible explanation for the low  $K_D$  values is that the association of hydroxyl groups with one another in the aqueous phase is significant compared to the association with the extractant in the organic phase. Although solvents with high capacity have not been identified, complexation effects can improve the selectivity of potential solvents.

Solute	Measured Value of $K_D$ for the Following Solvents			
	DIPE"	MIBK"	25% w/w TOPO in DIBK <sup>*</sup>	
Phenol	36.5	(100)	460	
Catechol (1,2)	4.9	18.7	200	
Resorcinol (1,3)	2.1	17.9	98	
Hydroquinone (1,4)	1.03	9.9	35	
Pyrogallol (1,2,3)		3.6	53	
Hydroxyquinol (1,2,4)	0.18	5.0	24	
Phloroglucinol (1,3,5)		3.9	21	

 Table 15.2-1 Equilibrium Distribution Coefficients for Extraction of

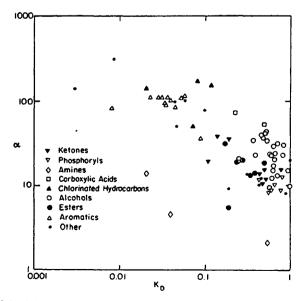
 Phenol and Higher Phenols from Water with Various Solvents

<sup>a</sup>Greminger, et al.<sup>20</sup>

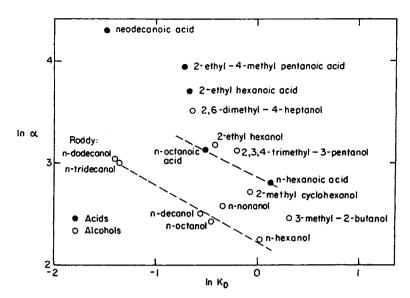
<sup>b</sup>MacGlashan et al.<sup>33</sup>

In the recovery of ethanol and many other organic solutes from aqueous solution, coextraction of water has a large effect on the process economics. Solvents may be compared by plotting the selectivity ( $\alpha$  = separation factor between ethanol and water) versus the solvent capacity for ethanol, expressed as  $K_D$ . Figure 15.2-6 is such a plot for extraction of ethanol from relatively dilute aqueous solution by many different solvents.<sup>36</sup> This figure includes data from Roddy,<sup>35</sup> Souissi and Thyrion,<sup>37</sup> and Munson and King.<sup>46</sup> It is apparent that the Lewis-acid solvents (alcohols, carboxylic acids, and chlorinated hydrocarbons) provide much better selectivity for a given capacity than do the Lewis-base solvents (ketones, esters, amines, phosphoryls). Furthermore, branching of the solvent molecule is important, as shown in Fig. 15.2-7. The dashed lines relate selectivity to  $K_D$  for normal carboxylic acids (solid points) and normal alcohols (open points). Branched carboxylic acids give substantially higher selectivities than do straight-chain acids for a given value of  $K_D$ . The same is true for alcohols.

Many investigations of the extraction of ethanol from water have postulated that a very high selectivity is needed to enrich the solvent-free extract to an ethanol content near or above the binary azeotrope with water. However, this degree of enrichment is not necessary. The extraction step can be followed by an extractive-distillation dewatering step similar to the process shown for acetic acid recovery in Fig. 15.2-3.



**FIGURE 15.2-6** Selectivity ( $\alpha$ ) for ethanol over water versus  $K_D$  for extraction of ethanol from dilute aqueous solution with various common solvents.<sup>36</sup>



**FIGURE 15.2-7** Effect of branching on relationship between  $\alpha$  and  $K_D$  for extraction of ethanol from dilute aqueous solution by carboxylic acid and alcohol solvents.<sup>36</sup>

#### 15.2-4 Solutes With Multiple Functional Groups

Separations based on reversible chemical complexation may be useful for recovery of many other organic solutes from dilute aqueous solution. Solutes that have multiple Lewis-acid or Lewis-base functional groups are particularly good candidates. Such solutes also have low activity coefficients in water and low relative volatilities with respect to water, thereby satisfying all the desirable criteria identified above. The results shown in Table 15.2-1 demonstrate that separation by complexation with the strong Lewis base TOPO is more attractive for polyhydroxybenzenes than for phenol, especially if the hydroxyl groups are located on adjoining carbon atoms of the aromatic ring.

#### DICARBOXYLIC ACIDS

Vieux et al.<sup>38,39</sup> have investigated extraction of oxalic, malonic, succinic, and glutaric acids from water, using triisooctyl amine in various diluents. The values of  $K_D$  are substantially lower than are found for extraction of acetic acid by similar amines—a result that could be anticipated because the two carboxylic acid groups decrease the solute activity coefficient in water. Vieux and coworkers also found substantial effects of the diluent on  $K_D$ , with chloroform and 1,2-dichloroethane giving higher values of  $K_D$  than 1,2-dichloroethane, which in turn gave higher values of  $K_D$  than benzene as diluent. These results are consistent with the results observed for extraction of acetic acid with amines (see above), where the stronger Lewis acids are more effective diluents because they solvate the carbonyl group of the complex better.

#### HYDROXYCARBOXYLIC ACIDS

Lactic acid is an important article of commerce. It is difficult to separate from aqueous solution because it has a strong affinity for water, resulting from the presence of a hydroxyl group and a carboxylic acid group. Solvent extraction of lactic acid from aqueous solution is discussed in detail by Short and Eaglesfield,<sup>40</sup> who report concentration-based equilibrium distribution coefficients ( $K_{M}$ ) for common alcohol, ketone, ether, and ester solvents ranging from 0.04 to 0.82. The stronger Lewis base TBP gives  $K_M$  values of 1.3-1.4.<sup>3</sup>

Citric acid contains three carboxylic acid groups and one hydroxyl group and is therefore even more hydrophilic. Common alcohol, ester, ketone, and ether solvents give values of concentration-based distribution coefficients  $(K_M)$  ranging from 0.1 to 0.3.<sup>41</sup>  $K_M$  ranges from 2.0 to 2.3 for TBP.<sup>3,42</sup> Wennersten<sup>42</sup> also found that  $K_D$  increased significantly from tributyl phosphate, to dibutyl phosphonate, to trioctyl phosphine oxide. This reflects increases in the basicity of the phosphoryl group. At 25 and 80°C, respectively, a solvent composed of 50% v/v triisooctyl amine in a hydrocarbon diluent (Shellsol H, 16% aromatics) gave  $K_D$  values of 6.5 and 0.33—different by a factor of nearly 20! It has been reported that a recent commercial process for extraction of citric acid uses trilauryl amine as extractant, with regeneration through a temperature change and back-extraction into water.

#### CHROMATOGRAPHIC MEASUREMENTS

A number of studies of separations by means of liquid chromatography (HPLC), paper chromatography, and related laboratory techniques provide useful information on the utility of various complexing extractants for polyfunctional organic solutes. From such studies it is possible to obtain distribution coefficients, effects of diluents, and information on the complexation stoichiometry and bond strength. An example of such a study is the work of Stuurman et al.,<sup>32</sup> who used HPLC to study complexation of phenol, hydroxybenzoic acids, and other hydroxycarboxylic acids with TOPO in a diluent of *n*-hexane.

Soczewinski and coworkers have carried out an extensive series of measurements with paper chromatography to observe the characteristics of various complexing systems. These include extraction of various phenolic carboxylic acids (gallic acid, vanillic acid, caffeic acid, etc.) into TBP<sup>43</sup> and of polyhydroxybenzenes and naphthols into both TBP with various diluents and tributyl amine with various diluents.<sup>44</sup> Soczewinski and Rojowska<sup>45</sup> studied effects of pH on chromatographic extraction of several amino acids into di-2-ethyl hexyl phosphoric acid (D2EHPA), with ketones and ethers as diluents, and later extended these measurements to solvents using hexanol as the diluent for D2EHPA.<sup>46</sup> Mixed solvents composed of a Lewis acid (CHCl<sub>3</sub>) and a Lewis base (phosphate, ketone, or ether) were used for chromatographic extractions of polyfunctional solutes combining hydroxyl, amino, and nitro groups along with phenols, anilines and quinolines.<sup>47,48</sup> In earlier work, oleic acid and D2EHPA in various diluents were used for separations of various quinolines and alkaloids.<sup>49,50</sup>

#### COMPLEXING ADSORBENTS

Adsorbents, particularly those made from synthetic polymers, can be made to contain specified and controlled functional groups capable of complexation. In some cases the solute-uptake process is one of solid infusion (Table 15.1-1) or bulk absorption. As an example of such a system, Kawabata and Ohira<sup>51</sup> have used a Lewis-base resin made of cross-linked poly(4-vinyl pyridine) to separate phenol from water. Kawabata et al.<sup>52</sup> used this same polymeric material to separate various carboxylic acids from aqueous solution. For a complexing, regenerable absorbent it is important to have a complexation reaction which is strong enough to give a substantial increase in capacity due to complexation, but which is not so strong as to complicate regeneration. In a series of experiments with adipic acid as solute, Kawabata et al.<sup>52</sup> show that poly(4-vinyl pyridine) resin gives substantially greater capacities than the more common styrene-divinylbenzene copolymeric resins, presumably because of the greater basicity of the pyridyl group. A resin containing amine groups in a styrene-divinylbenzene matrix also gave high capacities for adipic acid, comparable to the pyridyl resin, but required more methanol for regeneration. This presumably reflects the much higher basicity of the amine groups compared to the pyridyl groups.

#### GENERAL REVIEWS

The extraction chemistry of carboxylic acids with both conventional and complexing extractants has been reviewed by Kertes and King.<sup>53</sup> A review of extraction chemistry of the low-molecular-weight chemistry of the low-molecular-weight alcohols has been prepared by the same authors.<sup>54</sup>

#### REFERENCES

# Section 15.1

- 15.1-1 C. J. King, Separation Processes, 2nd ed., McGraw-Hill, New York, 1980.
- 15.1-2 A. L. Kohl and F. C. Riesenfeld, Gas Purification, 4th ed., Gulf Publishing, Houston, 1985.
- 15.1-3 P. V. Danckwerts, Gas-Liquid Reactions, McGraw-Hill, New York, 1970.
- 15.1-4 P. V. Danckwerts and M. M. Sharma, The Chemical Engineer, No. 202, p. CE244 (1966).
- 15.1-5 G. Astarita, D. W. Savage, and A. Bisio, Gas Treating with Chemical Solvents, Wiley, New York, 1983.
- 15.1-6 R. Lemlich (Ed.), Adsorptive Bubble Separation Techniques, Academic Press, New York, 1972.
- 15.1-7 E. Valdes-Krieg, C. J. King, and H. H. Sephton, Sep. Purif. Methods, 6, 221 (1977).

# Section 15.2

- 15.2-1 C. J. King, Acetic Acid Extraction, in T. C. Lo, M. H. I. Baird, and C. Hanson (Eds.), Handbook of Solvent Extraction, Wiley-Interscience, New York, 1983.
- 15.2-2 P. Eaglesfield, B. K. Kelly, and J. F. Short, Ind. Chem., 29, 147, 243 (1953).
- 15.2-3 H. A. Pagel and F. W. McLafferty, Anal. Chem., 20, 272 (1948).
- 15.2-4 J. M. Wardell and C. J. King, J. Chem. Eng. Data, 23, 144 (1978).
- 15.2-5 D. J. Shah and K. K. Tiwari, J. Sep. Proc. Technol., 2, 1 (1981).

- 15.2-6 R. Blumberg and J. E. Gai, Proc. Int. Solvent Extr. Conf. (ISEC'77), Can. Inst. Metall., Spec. Vol. 21, pp. 9-16, (1977).
- 15.2-7 Yu. G. Frolov, A. A. Pushkov, and V. V. Segievsky, Proc. Int. Solv. Extr. Conf. (ISEC'77), Can. Inst. Metall., Spec. Vol. 21, pp. 1236-1242 (1977).
- 15.2-8 N. L. Ricker, J. N. Michaels, and C. J. King, J. Sep. Proc. Technol., 1, 36 (1979).
- 15.2-9 E. E. Spala and N. L. Ricker, Ind. Eng. Chem. Process Des. Dev., 21, 409 (1982).
- 15.2-10 W. Sakai, F. Nakashio, T. Tsuneyuki, and K. Inoue, Kagaku Kogaku, 33, 1221 (1969).
- 15.2-11 N. L. Ricker, E. F. Pittman, and C. J. King, J. Sep. Proc. Technol., 1, 23 (1980).
- 15.2-12 R. W. Helsel, Chem. Eng. Prog., 73, 55 (1977).
- 15.2-13 J. Golob, V. Grilc, and B. Zadnik, Ind. Eng. Chem. Process Des. Dev., 20, 433 (1981).
- 15.2-14 G. C. Jagirdar and M. M. Sharma, J. Sep. Proc. Technol., 1, 40 (1980).
- 15.2-15 M. Niitsu and T. Sekine, Bull. Chem. Soc. Jpn., 51, 705 (1978).
- 15.2-16 W. F. Schurig, Acetic Acid, in Kirk-Othmer Encyclopedia of Chemical Technology, 1st ed., Vol. 1, pp. 56-78, Interscience, New York, 1947.
- 15.2-17 B. R. Smith, "Organic Acid Recovery with Coupled-Transport Membranes," paper presented at the Engineering Foundation Conference on Advances in Fermentation Recovery Process Technology, Banff, Alberta, Canada, June 1981. See also Annual Reports for 1980 and subsequent, C.S.I.R.O., Division of Chemical Technology, South Melbourne, Victoria, Australia.
- 15.2-18 Y. Kuo, D. Eng. Sci. dissertation in Chemical Engineering, Columbia University, New York, 1980.
- 15.2-19 Y. Kuo and H. P. Gregor, paper presented at the American Chemical Society Meeting, Seattle, WA, March 1983.
- 15.2-20 D. C. Greminger, G. P. Burns, S. Lynn, D. N. Hanson, and C. J. King, Ind. Eng. Chem. Process Des. Dev., 21, 51 (1982).
- 15.2-21 F. Wolf and H. Fuertig, Chem. Technol., 18, 405 (1966).
- 15.2-22 F. X. Pollio, R. Kunin, and A. F. Preuss, Environ. Sci. Technol., 1, 495 (1967).
- 15.2-23 E. F. Pittman, M.S. Thesis in Chemical Engineering, University of California, Berkeley, 1979.
- 15.2-24 K. Inoue, K. Tsubonoue, and I. Nakamori, Sep. Sci. Technol., 15, 1243 (1980).
- 15.2-25 N. E. Bell, M.S. Thesis in Chemical Engineering, University of California, Berkeley, 1980.
- 15.2-26 G. Aksnes, Acta Chem. Scand., 14, 1475 (1960).
- 15.2-27 G. Aksnes and T. Gramstad, Acta Chem. Scand., 14, 1485 (1960).
- 15.2-28 G. Aksnes and P. Albriktsen, Acta Chem. Scand., 22, 1866 (1968).
- 15.2-29 D. Hadzi, H. Ratajczak, and L. Sobczyk, J. Chem. Soc. A, 48 (1967).
- 15.2-30 A. A. Shvets, E. G. Amarskii, O. A. Osipov, and L. V. Goncharova, Zh. Obshch. Khim., 46, 1701 (1976).
- 15.2-31 N. M. Karayannis, C. M. Mikulski, L. S. Gelfand, and L. L. Pytlewski, J. Inorg. Nucl. Chem., 40, 1513 (1978).
- 15.2-32 H. W. Stuurman, K.-G. Wahlund, and G. Schill, J. Chromatogr., 204, 43 (1981).
- 15.2-33 J. D. MacGlashan, J. L. Bixby, and C. J. King, Solvent Extr. Ion Exchange, 3, 1 (1985); J. D. MacGlashan and C. J. King, Report No. LBL-13963, Lawrence Berkeley Laboratory, Berkeley, CA, March 1982.
- 15.2-34 J. L. Bixby, M.S. Thesis in Chemical Engineering, University of California, Berkeley, 1983.
- 15.2-35 J. W. Roddy, Ind. Eng. Chem. Process Des. Dev., 20, 104 (1981).
- 15.2-36 C. L. Munson and C. J. King, Ind. Eng. Chem. Process Des. Dev., 23, 109 (1984).
- 15.2-37 A. Souissi and F. C. Thyrion, Proc. 2nd World Congr. Chem. Eng., 4, 443 (1981).
- 15.2-38 A. S. Vieux, N. Rutagengwa, J. B. Rulinda, and A. Balikungeri, Anal. Chim. Acta, 68, 415 (1974).
- 15.2-39 A. S. Vieux and N. Rutagengua, Anal. Chim. Acta, 91, 359 (1977).
- 15.2-40 J. F. Short and P. Eaglesfield, Trans. Inst. Chem. Eng., 30, 109 (1952).
- 15.2-41 C. S. Marvel and J. C. Richards, Anal. Chem., 21, 1480 (1949).
- 15.2-42 R. Wennersten, J. Chem. Tech. Biotechnol., 33B, 85 (1983); paper presented at the International Solvent Extraction Conference (ISEC'80), Liege, Belgium, 1980.
- 15.2-43 G. Matysik and E. Soczewinski, Sep. Sci., 12, 657 (1977).
- 15.2-44 E. Soczewinski and G. Matysik, J. Chromatogr., 48, 57 (1970).
- 15.2-45 E. Soczewinski and M. Rojowska, Rocz. Chem., 47, 1025 (1973).

- 15.2-46 E. Soczewinski and M. Rojowska, J. Chromatogr., 32, 364 (1978).
- 15.2-47 E. Soczewinski, G. Matysik, and W. Dumkiewicz, J. Chromatogr., 132, 379 (1977).
- 15.2-48 G. Matysik and E. Soczewinski, J. Chromatogr., 160, 29 (1978).
- 15.2-49 E. Soczewinski, G. Matysik, and H. Szumilo, Sep. Sci., 2, 25 (1967).
- 15.2-50 E. Soczewinski and G. Matysik, J. Chromatogr., 32, 458 (1968).
- 15.2-51 N. Kawabata and K. Ohira, Environ. Sci. Technol., 13, 1396 (1979).
- 15.2-52 N. Kawabata, J.-I. Yoshida, and Y. Tanigawa, Ind. Eng. Chem. Prod. Res. Dev., 20, 386 (1981).
- 15.2-53 A. S. Kertes and C. J. King, Biotechnol. Bioeng., 28, 269 (1986).
- 15.2-54 A. S. Kertes and C. J. King, "Extraction Chemistry of Low Molecular Weight Aliphatic Alcohols," Lawrence Berkeley Laboratory Report No. LBL-21210, March 1986.