Theory of Solvent Extraction of Phosphoric and Hydrochloric Acids

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Mixtures of hydrochloric and phosphoric acids were extracted from aqueous solution by organic solvents in a study to advance the theories of solvent extraction.

Four solvents, t-amyl alcohol, n-butanol, cyclohexanol, and 2-hydroxyethyl, n-hexyl ether, were found to give high distribution coefficients of 0.1 to 0.5 for both acids. In studies using the ether type of solvent an increase of the *p*H of the aqueous phase from 0 to 10 reduced the distribution ratio of phosphoric acid by a factor of 1,100.

The substitution of hydriodic acid for hydrochloric caused a 42% increase in the *K* of phosphoric acid, which could indicate the importance of internal pressure of the additive in extraction. Measurements of activity coefficients of the hydrochloric acid in aqueous solution showed only a 1% increase in its activity coefficient with addition of large amounts of phosphoric acid. This could not be sufficient to cause up to a 40% increase in the distribution coefficient of the hydrochloric acid with the addition of the phosphoric acid.

In extraction of inorganic acids from aqueous solutions little has been published concerning the effects of such properties as *p*H, activity coefficient, and internal pressure on the distribution coefficients of acids between organic solvents and water. A few qualitative observations have been reported (*9, 23*) on the extraction of acids by control of *p*H. The effects of activity coefficients on the distribution coefficients of inorganic acids have been discussed by various investigators (*4, 17, 18*), but little actual data are available. Hildebrand and others (*8, 13*) have shown the role of internal pressure in extraction.

For the study of some of these factors in extraction a four-component system containing water, an organic solvent, and two solutes was used. Phosphoric acid was used as one solute, since very little is known about its extraction and its compounds are becoming increasingly important; hydrochloric acid was chosen as the second solute, to be used with phosphoric acid, because extraction of hydrochloric acid solutions has been extensively studied (*2, 13, 14, 19, 22*). Also, activity coefficients for hydrochloric acid are available (*6, 16, 18, 21*) for finding its effect on extraction of phosphoric acid and for comparisons between this research and that of others.

The choice of organic solvent was determined by an evaluation of different types of solvents. *N*-butanol, cyclohexanol, and 2-hydroxyethyl *n*-hexyl ether (2-HEHE) were found to be the best solvents for extraction of both hydrochloric and phosphoric acids. Quantitative equilibrium-extraction data were obtained on three complex systems containing water and hydrochloric and phosphoric acids, and each of the above three solvents.

More detailed studies were made with 2-HEHE as a solvent, and the effects of temperature, concentration, *p*H, solubility parameter, and the activity coefficient of hydrochloric acid as affected by phosphoric acid were studied.

THEORY

Distribution Coefficients and pH

In solvent extraction one is usually interested in the fraction of total solute in the organic phase as compared with that in the aqueous phase, regardless of the mode of dissociation, association, or interaction of the solute with other molecules. This is defined as

$$K = C_0/C_w \qquad (1)$$

This distribution ratio may not be constant, since the distribution law (*5*) is applicable only to the molecular species common to both phases. Hence the *K* will be affected by ionization, association, etc. The relationship between these factors can be derived for various cases.

1. *No association of the acid in the organic phase and ionization in the aqueous phase:*

For a monobasic acid HA, Golumbic (*7*) derived

$$K = K^1_{\mathrm{HA}}/(1 + B_1/[H^+]_w) \qquad (2)$$

If $[H^+]_w \ll B_1$,

$$\log K = \log K^1_{\mathrm{HA}} - \log B_1 - p\mathrm{H} \qquad (3)$$

Hence a plot of log *K* vs. *p*H should have a slope of −1. Golumbic (*7*) showed that this held for extraction of phenols. If $[H^+]_w \gg B_1$, log *K* is constant and independent of *p*H.

For a dibasic acid H_2A

$$K = K^1_{\mathrm{H_2A}}/(1 + B_1/[H^+]_w + B_1B_2/[H^+]_w^2) \qquad (4)$$

A plot of log K vs. *p*H should have a slope of −2 to 0 depending on the *p*H range.

2. *Association of the acid in the organic phase and ionization in the aqueous phase*:

For HA when one uses a derivation similar to Golumbic's (*7*)

$$n(\mathrm{HA})_0 \leftrightarrows ((\mathrm{HA})_n)_0 \qquad (5)$$

$$K = K^1_{\mathrm{HA}}\,(1 + nK_a[\mathrm{HA}]_0^{n-1})/(1 + B_1/[H^+]_w) \qquad (6)$$

Hence *K* depends on the concentration of HA as well as on *p*H. If $[H^+]_w \ll B_1$ and a very slight amount of association occurs, the slope of log *K* vs. *p*H is approximately −1.

For H_2A

$$K = K^1_{\mathrm{H_2A}}\,(1 + nK_a[\mathrm{H_2A}]_0^{n-1})/(1 + B_1/[H^+]_w + B_1B_2/[H^+]_w^2) \qquad (7)$$

Irving and coworkers (*10*), Tribalat (*23*), and Glasstone (*5*) also derived equations for other special cases.

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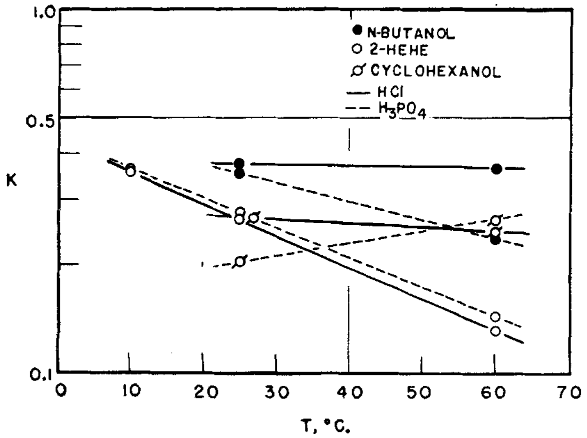

Fig. 1. Effect of temperature on distribution ratios.

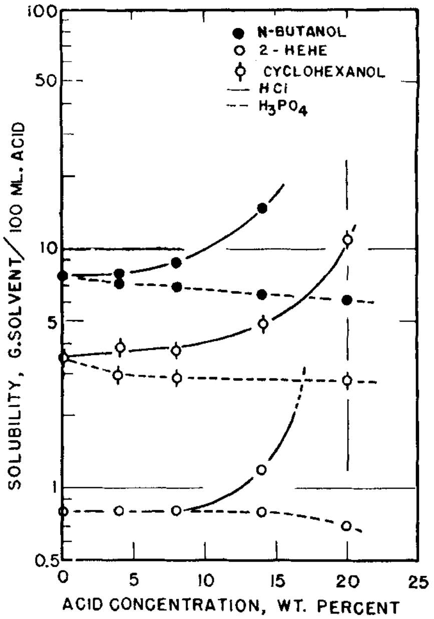

Fig. 3. Solubility of solvents in aqueous acids at 25°C.

Solubility Parameters and Extraction

Hildebrand (*8*) states that two liquids will be immiscible when their internal pressures are sufficiently different so that the molecules of one liquid may force out those of another. Using the thermodynamic equation of state and the fact that the energy of vaporization is equal to the internal pressure, he defines a solubility parameter,

$$\delta = \left(\frac{\Delta H - RT}{V}\right)^{\frac{1}{2}} \qquad (8)$$

Hildebrand derives theoretically most of the thermodynamic properties of solutions using δ values.

Hence an organic solvent which is highly selective for the solute should have a value similar to that of the solute. Highly polar ionic compounds tend to have high δ values; for water the δ value is 23.4. Most paraffinic hydrocarbons have values of 6 to 9 and organic solvents values of 7 to 14. Irving and coworkers (*10*) report that the extraction of dithizone from water by organic solvents decreases in the order chloroform (δ = 9.3), *o*-dichlorobenzene (9.9), chlorobenzene (9.5), benzene (9.2), toluene (8.9), carbon tetrachloride (8.6), cyclohexane (8.2), and hexane (7.3). Since dithizone should have a high δ value of approximately 9 to 10, solvents of high δ values should favor the extraction as shown above.

The δ values could be used to screen solvents in a preliminary way for extraction of a given solute. However chemical interactions, such as hydrogen bonding, association, complex formation, etc., may appreciably affect the extraction, and so solubility parameters may not always be valid criteria of extraction.

Activity Coefficients and Extraction

Garwin and Hixson (*4*) found that certain inorganic additives enhanced, while others hindered, the extraction of aqueous cobalt-chloride solutions by organic solvents. They observed that the additive enhanced the extraction when its activity coefficient increased with concentration in a manner similar to the cobalt salt, and when its activity coefficient decreased, the additive had no effect or hindered the extraction. Schlea (*17*) in the extraction of cobalt sulfate found contradicting effects of activity coefficients of the additives. However activity coefficients of the solute have not been measured when both the solute and additive are present in the solution in order to find the actual effect of the additive on the activity coefficient of the solute.

The true distribution coefficient of a solute is a constant and is equal thermodynamically to its activity in the organic over its activity in the aqueous phase (*5*):

$$K_t = a_0/a_w = \gamma_0 C_0/\gamma_w C_w = (\gamma_0/\gamma_w)K$$

Increasing the activity coefficient of the solute in the water phase with an additive should decrease its concentration and increase the distribution ratio. Glasstone (*5*) also shows that the ratio of the saturation solubilities of the pure solute in the two layers is approximately equal to *K*. Hence a compound which is slightly soluble in the organic phase will have a low *K* value.

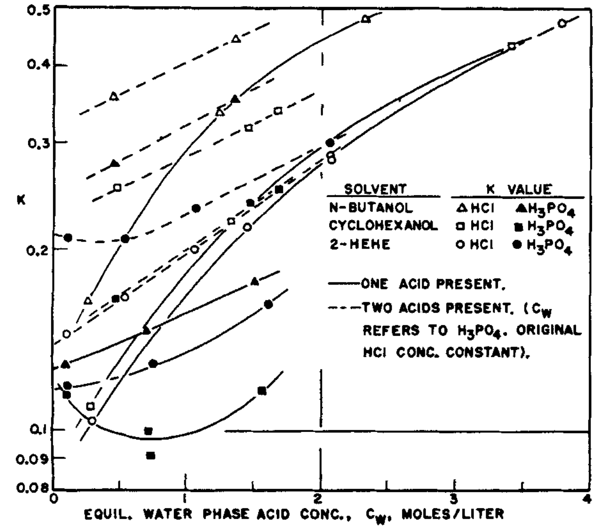

Fig. 2. Effect of concentration on distribution ratios at 25.0°C.

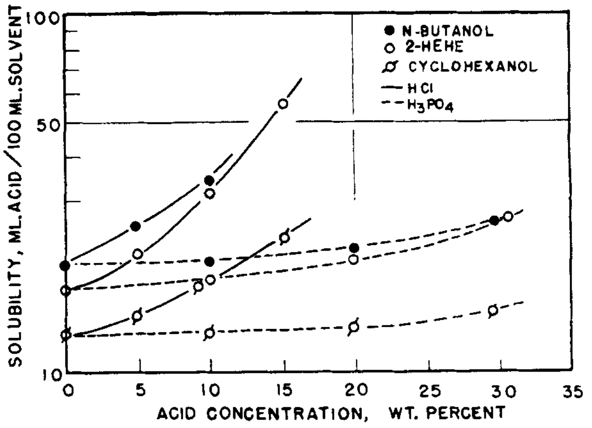

Fig. 4. Solubility of acid solutions in solvents at 25.0°C.

TABLE 1. DISTRIBUTION-RATIO DATA FOR VARIOUS SOLVENTS AT 25.00 ± 0.05°C. (Each acid equilibrated separately)

Solvent	Acid	Concentrations, mole/liter C_o	C_w	Distribution ratio K	Solubility parameter δ
t-Amyl alcohol	HCl	0.4971	1.178	0.4218	
t-Amyl alcohol	H_3PO_4	0.1127	0.6837	0.1648	
n-Butanol	HCl	0.4201	1.241	0.3386	11.3
n-Butanol	H_3PO_4	0.1036	0.7085	0.1462	
Cyclohexanol	HCl	0.3037	1.332	0.2280	11.1
Cyclohexanol	H_3PO_4	0.0663	0.7307	0.0908	
2-Hydroxyethyl, *n*-hexyl ether	HCl	0.3152	1.45	0.2173	9.6
2-Hydroxyethyl, *n*-hexyl ether	H_3PO_4	0.0987	0.7624	0.1294	
Octylene glycol	HCl	0.2661	1.327	0.2007	
Octylene glycol	H_3PO_4	0.0510	0.7564	0.0674	
Cyclopentanone	HCl	0.1217	0.8705	0.1398	10.2
Cyclopentanone	H_3PO_4	0.1110	0.4680	0.2371	
iso-Amyl alcohol	HCl	0.1811	1.396	0.1297	
iso-Amyl alcohol	H_3PO_4	0.0351	0.7450	0.0471	
n-Amyl alcohol	HCl	0.1752	1.422	0.1230	10.7
n-Amyl alcohol	H_3PO_4	0.0355	0.7438	0.0478	
2-Hydroxyethyl, phenyl ether	HCl	0.1252	1.512	0.0828	
2-Hydroxyethyl, phenyl ether	H_3PO_4	0.0330	0.7532	0.0437	
n-Hexyl alcohol	HCl	0.1119	1.473	0.0760	10.4
n-Hexyl alcohol	H_3PO_4	0.0237	0.7589	0.0312	
Benzyl alcohol	HCl	0.0947	1.479	0.0640	11.7
Benzyl alcohol	H_3PO_4	0.0200	0.7581	0.0264	
Tri-*n*-butyl phosphate	HCl	0.0893	1.525	0.0586	
Tri-*n*-butyl phosphate	H_3PO_4	0.0816	0.710	0.1149	
n-Octanol	HCl			0.0417	10.0
2-Ethyl-1-butanol	HCl	0.0573	1.487	0.0385	
2-Ethyl-1-butanol	H_3PO_4	0.0112	0.7513	0.0149	
o-Chlorophenol	HCl	0.0227	1.669	0.0136	
o-Chlorophenol	H_3PO_4	0.0042	0.8522	0.0050	
Isophorone	HCl	0.0103	1.530	0.0067	9.2
n-Butyl ether	HCl	0.0010	1.498	0.0007	7.6
n-Butyl ether	H_3PO_4	0.00002	0.7385	0.00003	
Tri-perfluorobutyl amine	HCl	0.0009	1.503	0.0006	
Tri-perfluorobutyl amine	H_3PO_4	0.0000	0.7411	0.0000	
Acetophenone	HCl	0.0005	1.517	0.0003	10.2
Acetophenone	H_3PO_4	0.0004	0.751	0.0005	
Ethylene glycol dibutyl ether	HCl	0.0004	1.512	0.003	
Ethylene glycol dibutyl ether	H_3PO_4	0.0000	0.7430	0.000	
Thiophene	HCl	0.0003	1.499	0.0002	9.6
Thiophene	H_3PO_4	0.0000	0.7370	0.0000	
Methyl isobutyl ketone	HCl	0.0002	1.548	0.0001	8.4
Methyl isobutyl ketone	H_3PO_4	0.0002	0.7402	0.0003	
Chloroform	HCl	0.00008	1.487	0.00005	9.3
Chloroform	H_3PO_4	0.00005	0.7344	0.00007	
4-Heptanone	HCl	0.00005	1.509	0.00003	8.3
Carbon tetrachloride	HCl	0.00002	1.509	0.00001	8.6
Carbon tetrachloride	H_3PO_4	0.00005	0.7449	0.00007	
n-Hexyl ether	HCl	0.000	1.506	0.0000	7.5
n-Hexyl ether	H_3PO_4	0.0025	0.7386	0.0034	
1-Pentanethiol	HCl	0.0000	1.506	0.0000	
1-Pentanethiol	H_3PO_4	0.0003	0.7433	0.0004	

EXPERIMENTAL METHODS

When hydrochloric acid was alone in the aqueous solution, it was analyzed by titration with 0.1 to 0.5 *N* sodium hydroxide solutions. When in the organic phase, distilled water was added and the two-phase layer was titrated with sodium hydroxide solutions. Phosphoric acid alone in the aqueous solution was titrated by means of glass and calomel electrodes to a *p*H of 9.2 according to the method of Dijksman (*3*). Thymol blue was used in some cases. Both methods gave results to ±0.5%. Analysis of the organic phase was carried out as above after the addition of distilled water.

Several methods of analyzing mixtures containing both hydrochloric and phosphoric acids in solution were tried and discarded; two methods were employed. When the ratio of moles of hydrochloric acid to moles of phosphoric acid was in the range of 1/5 to 20/1, the sample was titrated to a phenolphthalein end point which gave total moles of sodium chloride and sodium phosphate, dibasic (*20*). Then the total chlorides were determined by the addition of excess silver nitrate solution and back titration by the Volhard procedure (*11*). The maximum deviation when knowns were used was −1.3% for hydrochloric acid and −2.1% for phosphoric acid; the average devia-

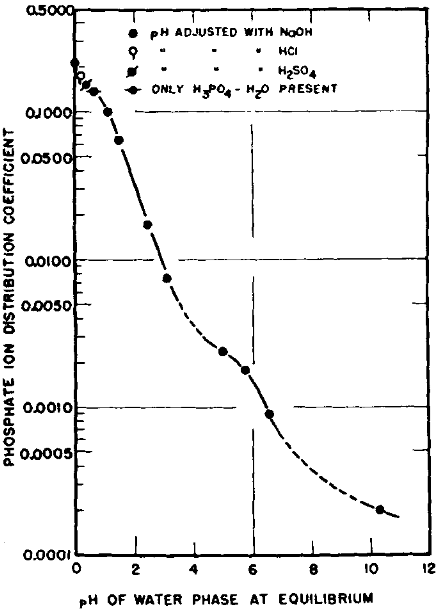

Fig. 5. Distribution ratio of phosphate vs. hydrogen ion concentration at 25.0°C.

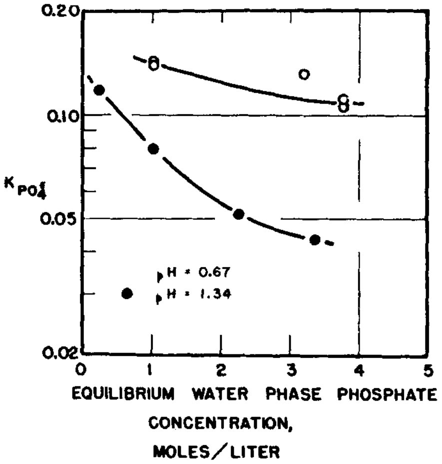

Fig. 6. Phosphate distribution ratio vs. phosphate concentration at constant hydrogen ion concentration values (25.0°C).

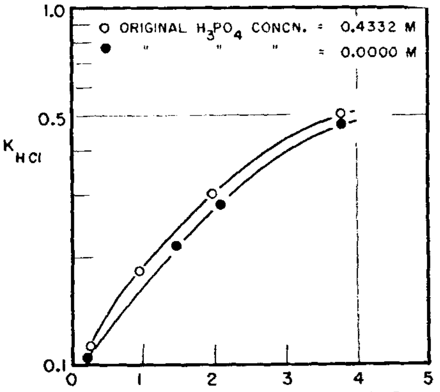

Fig. 7. Effect of hydrochloric acid concentration on distribution ratio of hydrochloric acid in phosphoric acid solutions at 25.0°C.

Table 2. Influence of H_3PO_4 on Activity Coefficient of HCl at 25.0°C. in Aqueous Solution

Nominal original concentrations			Equilibrium compositions			Molal activity*-coefficient of HCl		
HCl side	H_3PO_4 side		HCl side	HCl-H_3PO_4 side				
HCl, wt %	HCl, wt %	H_3PO_4, wt %	HCl concentration, moles/liter	HCl concentration, moles/liter	H_3PO_4 concentration, moles/liter	Actual, (γ_1)	Corresponding to HCl molality in HCl-H_3PO_4 solution, (γ_2)	γ_1/γ_2
2	2	5	0.698	0.6831	0.5276	0.773	0.773	1.000
5	5	1	1.397	1.400	0.1073	0.884	0.885	0.999
5	5	5	1.459	1.398	0.5130	0.896	0.892	1.004
5	5	10	1.478	1.365	1.108	0.899	0.891	1.009

*From data of Robinson and Stokes.

tion was ±0.6% for hydrochloric acid and ±1.0% for phosophoric acid. For extreme ranges of moles hydrochloric acid to phosphoric acid of 1.4/100 to 41/1, or in basic solution, a method depending on silver precipitation of hydrochloric acid and phosphoric acid was developed and used (*20*). Similar accuracies were also obtained.

The equilibrium extractions were performed in glass-stoppered Erlenmeyer flasks sealed on the outside by rubber stalls. Fifty- to one hundred-milliliter samples of aqueous phase and organic solvent were added to the flasks, which were totally immersed in the bath at 25.00 ± 0.05°C. and agitated by magnetic stirrers. After equilibration and settling, samples were pipetted for chemical analysis and density determinations.

Solubility determinations of the solvent in the aqueous phase or the aqueous phase in the solvent were made by the titration of one phase with another until a permanent turbidity appeared.

Activity measurements were made by an isopiestic method similar to that used by others (*15*). An aqueous solution of hydrochloric acid was placed in one leg of a glass container and hydrochloric acid–phosphoric acid solution in another leg. The only contact between the two legs of the container was through the vapor space. Three identical samples were placed in a constant-temperature bath. The first sample was analyzed after 10 days and the second 6 days later. These samples always checked; hence equilibrium was reached in 10 days. Only the hydrochloric acid and the water were able to migrate in the vapor space. Analyses showed that no phosphoric acid ever reached the hydrochloric acid side. Details are given elsewhere (*20*).

The main solvent was 2-HEHE, known as *n*-hexyl Cellosolve. The solvent was redistilled, and the portion boiling at 95.5°C. at 11 mm. was retained with only 2% boiling below 95.5°C. and 2% over 95.5°C. The hydrochloric acid and phosphoric acid used were reagent grade. Other solvents were research grade or the purest obtainable.

DISCUSSION OF SOLVENT SEARCH

The experimental data using various solvents (Table 1) show that, as found by Crittenden and Hixson (*2*), alcohols are the best solvents for extracting hydrochloric acid; however, ketones and ethers show some ability to extract it. Those solvents which are best for hydrochloric acid are also best for phosphoric acid extraction. The K_{HCl} is greater than the $K_{H_3PO_4}$ for the same solvent. Cyclopentanone is an exception, but unfortunately this solvent is excessively soluble in the aqueous phase. The two solvents 2-hydroxyethyl *n*-hexyl ether and 2-hydroxyethyl phenyl ether were also studied, since each compound includes functional groups of the alcohol and the ether.

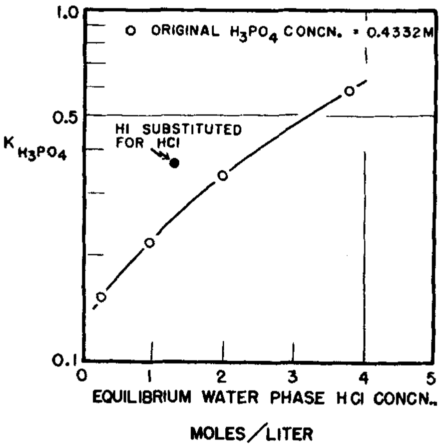

Fig. 8. Effect of hydrochloric acid concentration on distribution ratio of phosphoric acid in phosphoric acid solutions at 25.0°C.

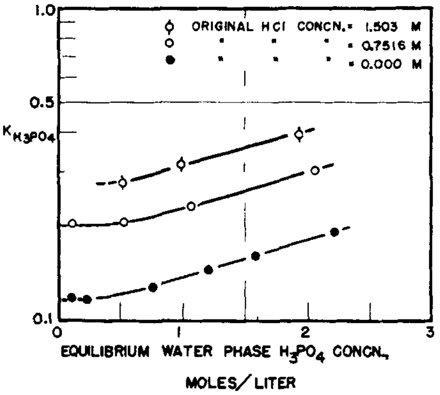

Fig. 9. Effect of phosphoric acid concentration on distribution ratio of phosphoric acid in hydrochloric acid solutions at 25.0°C.

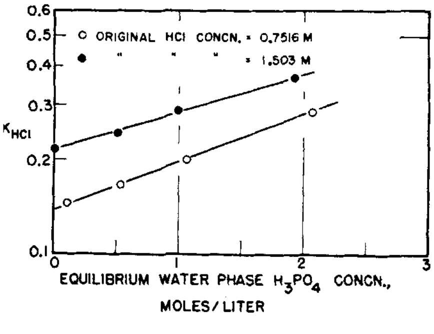

Fig. 10. Effect of phosphoric acid concentration on distribution ratio of hydrochloric acid in hydrochloric acid solutions at 25.0°C.

Generally in a given family or homologous series of solvents the higher the solubility parameter, δ, the higher the extraction. The high distribution ratios for the 2-HEHE with respect to its δ value may be due to the oxonium type of complex. For all the alcohols the $K_{HCl}/K_{H_3PO_4}$ was approximately constant at 2.55 ± 0.2.

Four solvents, *t*-amyl alcohol, *n*-butanol, cyclohexanol, and 2-HEHE, which gave the highest distribution ratios, were selected for further study at different temperatures. At 60°C. and in contact with acidic solutions *t*-amyl alcohol decomposed and was eliminated from further study. The temperature data are tabulated elsewhere (*1*) and are plotted in Figure 1. The hydrochloric and phosphoric acids were equilibrated together. In all cases the K values decreased somewhat with increasing temperature except for the K_{HCl} with cyclohexanol. The separation factor $K_{HCl}/K_{H_3PO_4}$ changed greatly with temperature for *n*-butanol and cyclohexanol and, this fact could be used to separate hydrochloric from phosphoric acid.

The effects of concentration of hydrochloric or phosphoric acid on the distribution ratio were investigated, and the data, which are given elsewhere (*1*), are plotted in Figure 2. In all cases except one (phosphoric acid and cyclohexanol) the distribution ratio increased with increasing concentration. For phosphoric acid alone the $K_{H_3PO_4}$ values seem to approach the same value for all three solvents at dilute concentrations. It is apparent from the mixed-acid curves that each acid increases the distribution ratio of the other acid by an average of approximately 50%. The highest K values were obtained with *n*-butanol.

Solubilities of the solvents in the aqueous acid phase (Figure 3) and of the aqueous acid phase in the solvents (Figure 4) were studied. All solvents became completely miscible in the aqueous phase (Figure 3) at approximately 15 to 20 wt. % hydrochloric acid. The presence of phosphoric acid in the aqueous phase decreased all the solubilities slightly. The solvent 2-HEHE showed a small solubility of less than 1%. The solubilities of the aqueous solutions in the solvents (Figure 4) are quite high and all over 12%. The solubilities of the solvents in the aqueous acids (Figure 3) are much less and well below 10% in most cases. This would increase the internal pressure of the organic layer and cause a greater distribution coefficient of the acid (*2*). For the solvent 2-HEHE the increase of water solubility in the organic solvent phase due to the increase in acid concentration can only partially explain the increase in the K value. The solvent *n*-butanol was not considered for further research because of its excessive miscibility with aqueous solutions. Since cylcohexanol has a very high viscosity, it was decided to select 2-hydroxyethel *n*-hexyl ether as the solvent for further studies.

EXTRACTION WITH 2-HYDROXYETHYL *N*-HEXYL ETHER

Effect of pH

Hydrochloric acid has a great effect on increasing the $K_{H_3PO_4}$. This may be due to the hydrochloric acid lowering the internal pressure of the aqueous solution, the raising of the internal pressure of the organic by the solubility of water in the organic, or to the importance of pH. It seems that pH should play an important part in the extraction of a partly ionized acid like phosphoric acid as shown in Equations (2) to (7). To obtain the pH plot in Figure 5, a 1.003M phosphoric acid solution containing suitable amounts of sodium hydroxide or hydrochloric acid was equilibrated with 2-HEHE and the pH and concentrations determined. The data are tabulated elsewhere (*1*).

The pH does have a large effect on the distribution of the phosphate, since increasing the pH from 0 to 10 causes the distribution coefficient of the phosphate to drop by a factor of 1,100. This could offer a means of removing the phosphate from the solvent in an extraction porcess. The plot also shows that the pH is important to the distribution of phosphate even in the region where essentially all the phosphate is present as phosphoric acid. The acid ionization constants for phosphoric acid are $B_1 = 7.5 \times 10^{-3}$, $B_2 = 6.2 \times 10^{-8}$, $B_3 = 4.8 \times 10^{-13}$ (*12*).

The average slope of the log K vs. pH line in the region of 0 to 6 pH is approximately -0.4. For a pH range of about 3 to 6 and no association of the acid in the organic phase, the slope should be -1 to -2 as given by Equations (3) and (4). This may indicate association of phosphoric acid in the organic phase. Others (*10*) also indicate appreciable association for hydrochloric acid in similar solvents.

Data obtained by varying the phosphoric acid concentration while keeping the pH constant with addition of sodium hydroxide are plotted in Figure 6 and tabulated elsewhere (*1*). As the phosphate concentration increases at constant pH, the distribution ratio decreases. Equations (6) and (7) show that at constant pH the distribution coefficient should vary with concentration only if association occurs.

Effect of Concentration and Internal Pressure

Additional data on the four-component system water, hydrochloric acid, phosphoric acid, 2-hydroxyethel *n*-hexyl ether, which were obtained, are tabulated elsewhere (*1*) and are plotted in Figures 7 to 10. These show that the K_{HCl} as well as the $K_{H_3PO_4}$ are increased by the increase in concentration of hydrochloric acid in the aqueous phase or by the increase of phosphoric acid in this phase. This helps support the theory that since the hydrochloric acid lowers the internal pressure of water, it diminishes the advantage of water for the solutes. Hence the organic solvent is able to share in a greater amount of the solute.

Reburn and Shearer (*13*) reported that hydriodic acid has a greater ability to lower the internal pressure of water than has hydrochloric acid. Hence a higher $K_{H_3PO_4}$ would be obtained for phosphoric acid if it were extracted in the presence of hydriodic instead of hydrochloric acid. This experiment was performed, and the data point plotted in Figure 8 shows that substitution of hydriodic acid for hydrochloric acid resulted in a 42% increase in the $K_{H_3PO_4}$. However since the activity coefficient of hydriodic acid in pure water is about 22% higher than that of hydrochloric acid at the same concentrations (*16*), this could be a contributing factor.

Effect of Activity Coefficients

The data on the effect of the presence of phosphoric acid on the activity coefficient of hydrochloric acid in aqueous solution are given in Table 2. The data show that the presence of approximately 1 to 10% phosphoric acid in aqueous solutions containing 2 to 5% hydrochloric acid raises the activity coefficient of the hydrochloric acid a maximum of only 0.9%. However in an aqueous solution of 2.8% hydrochloric acid (Figure 3) the presence of 1% phosphoric acid raises the K_{HCl} about 4%, and the presence of 10% phosphoric acid raises the K_{HCl} by 40%. Also in an aqueous solution of hydrochloric acid containing from 2 to 5% hydrochloric acid (Figure 7) the presence of about 4% phosphoric acid raised the K_{HCl} by an average of 13%.

Equation (9) shows that the K value is directly proportional to the activity coefficient. It appears inconceivable that a 0.9% increase in activity coefficient of the hydrochloric acid can increase the distribution coefficient by up to 40%. Hence the changes in internal pressure of the water or other factors are causing the increase in distribution coefficient. This small raising of the activity coefficient of hydrochloric acid by the addition of phosphoric acid is in contrast to the increase of 43% in the activity coefficient of hydrochloric acid having a concentration of 10% in aqueous solutions, when 10% sulfuric acid is added as reported by others (*18*). The data of Garwin and Hixson (*4*) and Schlea (*17*) do not answer this question of the effect of activity coefficient on K, since the activity coefficients of the solute were not measured when both solute and additive are present. In their discussions these investigators used the activity coefficients of the additives when the additives were alone in the aqueous solutions.

ACKNOWLEDGMENT

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NOTATION

a = molal activity of hydrochloric acid
a_0 = activity of solute in organic phase
a_w = activity of solute in aqueous phase
B = Brönsted dissociation contant
C_0 = equilibrium concentration of total solute in organic phase, g. mole/liter
C_w = equilibrium concentration of total solute in aqueous phase, g. mole/liter
ΔH = latent heat of vaporization at 25°C., cal./g. mole
2-HEHE = 2-hydroxyethyl *n*-hexyl ether
$[HA]_0$ = concentration in organic phase of molecular HA
K = C_0/C_w = distribution ratio of total solute
K^1 = distribution ratio of molecular solute
K_a = association constant of molecular HA or H_2A
K^1_{HA} = constant, distribution ratio of unionized, molecular HA in both phases
$K_t = a_0/a_w$ = true thermodynamic distribution ratio

n = number of molecules associating

R = gas constant

T = temperature, °K.

V = molar volume of the liquid, ml./g. mole

δ = solubility parameter

$$= \left(\frac{\Delta H - RT}{V}\right)^{1/2}$$

γ = molal activity coefficient of hydrochloric acid

γ_w = activity coefficient of solute in water phase

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Continuous Stirred Tank Reactors:

Designs for Maximum Conversions of Raw Material to Desired Product. Homogeneous Reactions

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It is shown in a series of illustrative examples how the conversion efficiency of many reactions can be markedly affected by the type of reactor used, even though the temperatures, catalyst. and basic kinetics are already fixed by the chemistry of the process.

For such purpose graphical and analytic criteria are developed which permit the selection of a continuous stirred tank or tubular reactor system to obtain the most advantageous conversion of raw material to desired product. When a continuous stirred tank reactor process is preferable, the optimum number of reactor stages for maximum conversion is one. An example is given of a case where a combination of a continuous stirred tank and a tubular reactor is advantageous.

A new graphical method of reactor design for simple or complex reactions is also introduced. This method utilizes continuous stirred tank reactor data directly rather than batch data or kinetics analyses.

Reactions are classified according to the kinetic and stoichiometric characteristics which determine the allowable design procedures and the differences in the composition paths occurring in batch, tubular, or continuous stirred tank reactors.

The mathematical analysis of continuous stirred tank reactor systems for complex reactions leads to a set of difference equations. For cases of zero- or first-order reactions these are readily solved as illustrated in examples, even when several independent components influence the reaction kinetics.

Even when identical feed compositions are used, the concentrations of the chemical components flowing from any one reactor of a continuous stirred tank reactor system may or may not be the same as the concentration obtainable from a batch process or from a tubular reactor design. Consequently in many cases the engineer can markedly improve the conversion efficiency of an important reaction by selecting the proper type and arrangement of reactor system. The possibility of effecting a gain, however, depends upon the characteristics of the reaction.

From the stoichiometric viewpoint a

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