Extraction of Mixed Solutes:

I. Separation of Formic and Hydrochloric Acids
II. Separation of Acetic and Sulfuric Acids

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In many complex systems in solvent extraction a second solute is often present or is added to promote extraction of the first solute. Previous studies showed that the electrolyte sulfuric acid can be considered as a salting-out agent for extraction of formic acid from water by methyl isobutyl ketone.

In the present work two systems were studied: (I) hydrochloric acid-formic acid-water-methyl isobutyl ketone and (II) sulfuric acid-acetic acid-water-methyl isobutyl ketone. Selectivities of over 200 were found favoring the extraction of formic over hydrochloric acid, and values of over 6,000 favoring the acetic over the sulfuric acid were found. The data for extraction of formic acid were correlated by the Setschenow equation. A similar type of equation was found for extraction of acetic acid in system II.

The results indicate that the electrolyte hydrochloric acid can also be considered as a salting-out agent for formic acid. The data show that sulfuric is more effective than hydrochloric acid in salting-out the formic acid. This is in qualitative agreement with experimental data in other systems employing sulfate and chloride electrolytes and with the theoretical equation derived by Debye and McAuley. About 28% less sulfuric acid is needed to salt-out a given amount of acetic acid when compared with salting-out the same amount of formic acid.

The changes in activity coefficient of the acetic acid in the aqueous phase with additions of sulfuric acid were measured in system II. These activity coefficient changes could account for only about 39% of the increase in distribution ratio of the acetic acid. A possible explanation for this is that the molecular species of the acetic acid in the organic and aqueous phases changed when sulfuric acid was added to the water phase.

A large amount of data are present in the literature for the liquid-liquid extraction of more than one solute from an aqueous solution. In many cases a second solute is added to a solute to enhance the extraction of the first solute. Whitehead and Geankoplis (*28*) and Seaton and Geankoplis (*23*) give a detailed discussion and summary of cases in extraction where two or more solutes are present and of the effects of activity coefficients, complex formation, and salting-out. Many such double solute systems have been studied (*7, 8, 11, 13, 18, 19, 21, 22, 27*). The system sulfuric acid-formic acid-water-methyl isobutyl ketone was studied by Whitehead and Geankoplis, and they found that the sulfuric acid can be considered as a salting-out agent and the data correlated by the Setschenow equation (*24, 25*).

The present work is essentially a continuation of the work of Whitehead and Geankoplis (*28*) and Seaton and Geankoplis (*23*) on the study of the effects of activity coefficients and salting-out and is divided into two parts, system I and system II. In system I hydrochloric acid was used instead of sulfuric acid as the salting-out electrolyte with formic acid-water-methyl isobutyl ketone.

In system II acetic acid was substituted for the formic acid and used with sulfuric acid-water-methyl isobutyl ketone. The results were then compared with the previous systems (*23, 28*).

THEORY

In extraction the simple distribution law

$$K = C_o/C_W \qquad (1)$$

is usually employed in expressing the experimental results. Seaton and Geankoplis (*23*) have summarized the relations between the distribution coefficient K and association, ionization, pH, etc.

Setschenow (*24*) proposed an empirical equation for the effect of an added electrolyte or salting-out of the solute:

$$\log (C^*_W/C_W) = kC_e \qquad (2)$$

Butler (*4*) modified Equation (2) to

$$(C^*_W - C_W)/C_W = kC_e \qquad (3)$$

This Equation (2) is discussed in detail elsewhere (*4, 5, 28*).

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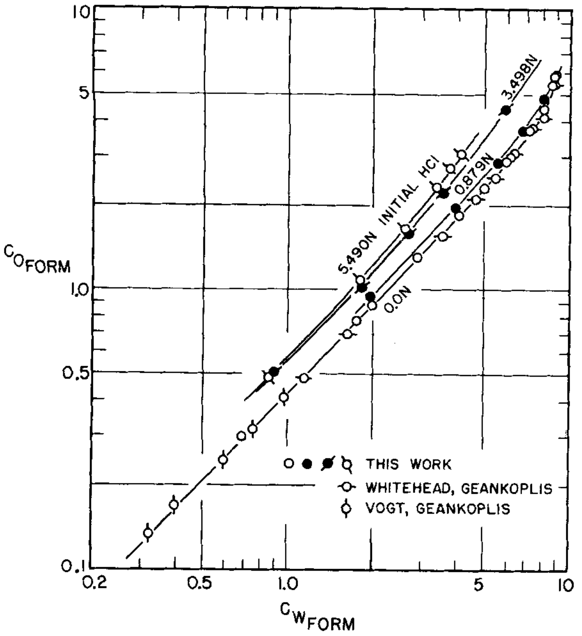

Fig. 1. Equilibrium data for water-hydrochloric acid-formic acid-methyl isobutyl ketone system at 25°C.

The ionic strength of a solution is defined as (9)

$$\mu = \frac{1}{2}\,(C_1z_1 + C_2z_2 + \ldots.) \qquad (4)$$

Here the actual concentrations of the ions must be known for a weak electrolyte, or the degree of ionization must be calculated. The activity coefficient of an ion species i in dilute solution is related to the physical properties of the solution as given by Debye and Hückel (9):

$$-\ln\gamma_i = \frac{\epsilon^3 z_i^{\,2}}{(DbT)^{3/2}}\sqrt{\frac{2\pi N'\mu}{1{,}000}} \qquad (5)$$

If an electrolyte has two kinds of ions and the solvent is water at 25°C., the mean activity coefficient is (9, 16)

$$-\ln\gamma_m = 0.509\,z_1z_2\sqrt{\mu} \qquad (6)$$

Glasstone (10) and others (23) discuss in detail the true thermodynamic distribution coefficient:

$$K_t = \frac{a_O}{a_W} = \frac{\gamma_O C_O}{\gamma_W C_W} = \frac{\gamma_O}{\gamma_W}K \qquad (7)$$

The separation factor or selectivity is used when two solutes distribute themselves between two relatively immiscible solvents and is defined as

$$\beta = K_{FORM}/K_{HCl} \qquad (8)$$

EXPERIMENTAL PROCEDURE

All chemicals used were reagent grade except the methyl isobutyl ketone. Equal volumes of 100 ml. of aqueous and organic solutions were pipetted into 250-ml. glass-stoppered flasks. The solutions were equilibrated with magnetic stirrers and sampled by the method described by Whitehead and Geankoplis (28).

The analytical methods were similar to those used before (28) except that when small amounts of sulfuric acid were present in the organic phase, the acid was analyzed by a modification of the barium sulfate precipitation method (14). A sample of 50 or 75 ml. was pipetted to a 600-ml. beaker. Then 350 ml. of water and 2 ml. of concentrated hydrochloric acid were added. The methyl isobutyl ketone phase was vaporized with a gentle air stream over the surface. Then the solution was heated and hot barium chloride solution added. The precipitate was filtered, dried, and weighed. The average error was less than 0.8% for weights of 100 mg. and the maximum error 4.6% for weights of 5 mg. The chloride was analyzed by the Volhard method (14).

Activity coefficients of the acetic acid in the acetic acid-sulfuric acid aqueous solutions were determined by the isopiestic method described by Robinson and Sinclair (20) and Seaton and Geankoplis (23). Activity coefficients for acetic acid in water at 25°C. were obtained from the literature (12).

In the sulfuric-acid side of the cell the mole fraction of acetic acid was calculated from the density, molarity of acetic acid, and molarity of sulfuric acid. The activity coefficient times mole fraction of the acetic acid in the water side was equated to the activity coefficient times mole fraction of the acetic acid in the sulfuric-acid side. Then the unknown activity coefficient of acetic acid in the sulfuric-acid side was solved for the equation.

DISCUSSION OF SYSTEM I: FORMIC ACID-HYDROCHLORIC ACID-WATER-METHYL ISOBUTYL KETONE

Ternary Equilibrium Data

The experimental data for the distribution ratios and densities for the

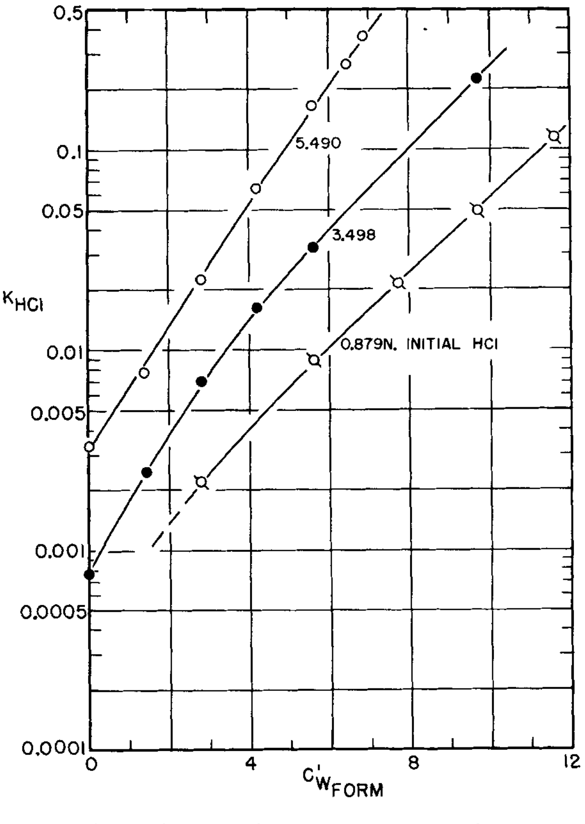

Fig. 2. Effect of formic acid concentration on distribution ratio of hydrochloric acid at 25°C.

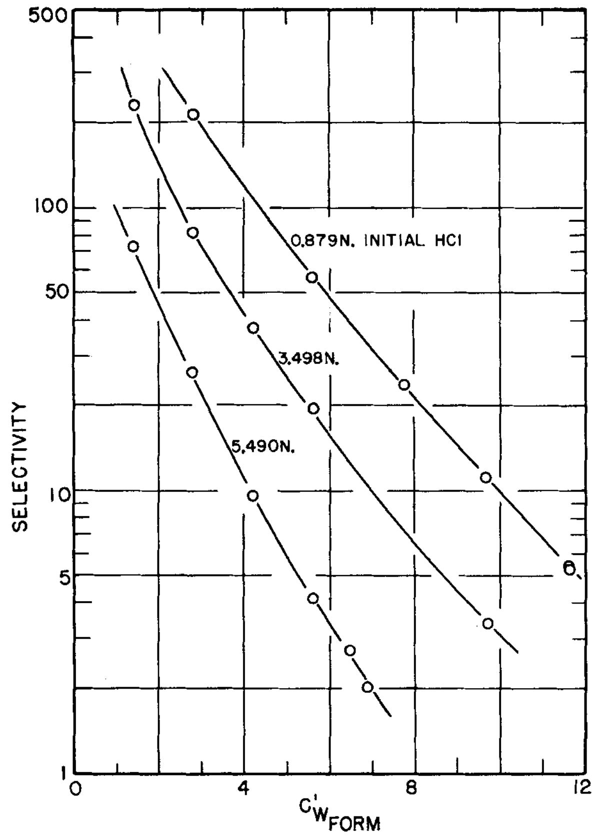

Fig. 3. Effect of formic acid concentration on selectivity at 25°C.

ternary systems of formic acid-water-methyl isobutyl ketone and hydrochloric acid-water-methyl isobutyl ketone are given elsewhere (*1*). Whitehead and Geankoplis (*28*) and Vogt and Geankoplis (*26*) also obtained data for the ternary system with formic acid, and their data are compared in Figure 1. The *K* for formic is shown to rise slightly as the concentration of formic in the aqueous phase is increased.

The *K* for hydrochloric acid (*1*) increases by almost thirtyfold as the concentration of hydrochloric acid in the water phase is increased from 3.5 to 6.7 normal. This is in contrast to the sulfuric-acid system (*28*), where the *K* value increases only about threefold over a similar concentration range. In both ternary systems containing the electrolytes the *K* values are quite low compared with those of formic.

A plot was made (*1*) showing the effect of temperature on the *K* value for hydrochloric acid. In going from 0° to 55°C. the distribution coefficient of hydrochloric acid decreased by 60%. From Whitehead's data (*28*) the *K* of formic acid also decreases as temperature increases. The apparent separation factor, on the assumption that the *K* values would not be affected by the presence of both solutes, is about 500 at 25°C. and increases to 570 at 55°C. For the formic acid-sulfuric acid-water-methyl isobutyl ketone system the apparent separation factor decreases with increase in temperature.

Quaternary Equilibrium Data

The equilibrium data for the two-solute system formic acid-hydrochloric acid-water-methyl isobutyl ketone are tabulated elsewhere (*1*). The effect of hydrochloric acid on the distribution coefficient of formic acid is shown in Figure 1. The lines of constant initial hydrochloric-acid concentration are approximately parallel, and the distribution coefficient of formic acid increases with addition of hydrochloric acid. Very similar trends were obtained by Whitehead (*28*) using sulfuric acid as the electrolyte.

A plot was made (*1*) showing the effect of hydrochloric acid on increasing the distribution coefficient of formic acid. At the highest hydrochloric-acid concentration used the distribution coefficient of formic acid is increased by about 60% over the value obtained when no hydrochloric acid is present.

TABLE 1. CORRELATION OF MIXED SOLUTE EQUILIBRIUM DATA ACCORDING TO THE SETSCHENOW EQUATION

$$\log(C^*_{W_{FORM}}/C_{W_{FORM}}) = 0.03215\, C_{W_{HCl}}$$

Equil. conc., $C_{O_{FORM}}$	Initial conc., $C'_{W_{HCl}}$	Equilibrium conc., $C_{W_{FORM}}$ Exp. (Figure 1)	Calc.	% error	Equil. conc., (HCl = 0) $C^*_{W_{FORM}}$ (Figure 1)	$\log(C^*_{W_{FORM}}/C_{W_{FORM}})$ Exp.	Calc.	Equil. conc., $C_{W_{HCl}}$ (Figure 4)
0.50	3.498	0.88	0.89	1.1	1.16	0.1200	0.1149	3.57
0.50	5.490	0.86	0.78	−9.4	1.16	0.1300	0.1750	5.45
1.00	0.879	2.08	2.10	1.0	2.26	0.0360	0.0305	0.95
1.00	3.498	1.72	1.72	0	2.26	0.1183	0.1176	3.66
1.00	5.490	1.65	1.51	−8.5	2.26	0.1367	0.1750	5.44
2.00	0.879	4.04	4.05	0.2	4.37	0.0341	0.0328	1.02
2.00	3.498	3.25	3.30	1.5	4.37	0.1284	0.1221	3.80
2.00	5.490	3.00	2.93	−2.3	4.37	0.1632	0.1734	5.39
2.50	0.879	4.93	4.95	0.4	5.34	0.0347	0.0341	1.06
2.50	3.498	3.93	4.03	2.5	5.34	0.1335	0.1237	3.85
2.50	5.490	3.57	3.62	1.4	5.34	0.1749	0.1697	5.28
3.00	0.879	5.74	5.75	0.2	6.21	0.0342	0.0347	1.08
3.00	3.498	4.55	4.69	3.1	6.21	0.1351	0.1240	3.86
3.00	5.490	4.06	4.29	5.7	6.21	0.1850	0.1610	5.01
4.00	0.879	7.06	7.08	0.3	7.65	0.0349	0.0363	1.13
4.00	3.498	5.50	5.76	4.7	7.65	0.1433	0.1230	3.83

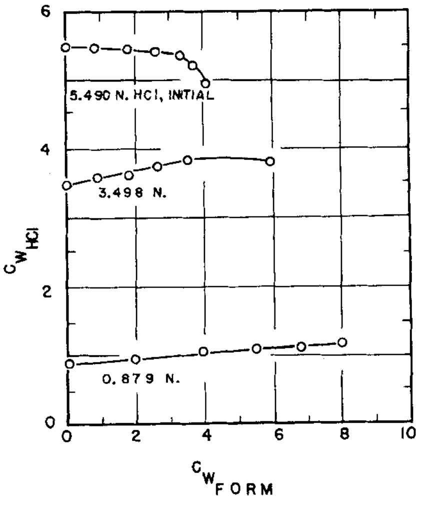

Fig. 4. Relation between aqueous equilibrium acid concentrations at 25°C.

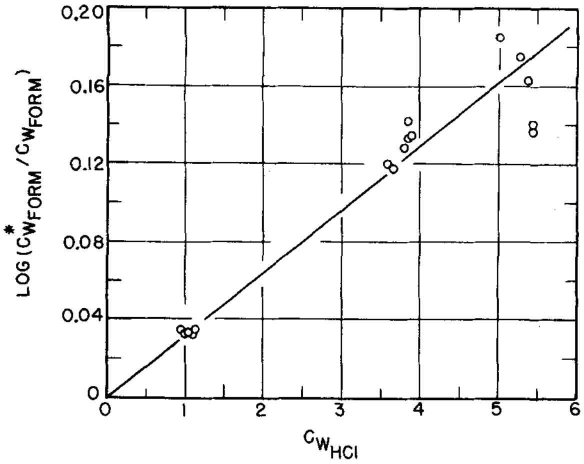

Fig. 5. Correlation of data with the Setschenow equation.

Similar trends and shapes of curves were found by Whitehead (*28*) when using sulfuric instead of hydrochloric acid.

As shown in Figure 2 the addition of formic acid to a hydrochloric-acid solution greatly increases the distribution coefficient of hydrochloric acid. Adding 10 normal formic acid to an aqueous solution having an initial hydrochloric-acid concentration of about 3.6 normal increases the distribution coefficient of hydrochloric acid over 300 fold. Adding the same amount to 3.6 normal sulfuric acid increases the distribution coefficient over 100 fold (*28*). This increase in *K* value may be due to increasing phase solubilities.

Selectivity Factors

At low formic acid concentrations the selectivity of formic acid compared with hydrochloric acid is very high and over 200 (Figure 3). This means that in a mixture of hydrochloric-formic acids a quantitative separation of the two solutes could be obtained in several stages. The selectivity decreases with increasing concentration of either solute. Similar trends were found for the mixture of sulfuric-formic acids (*23*).

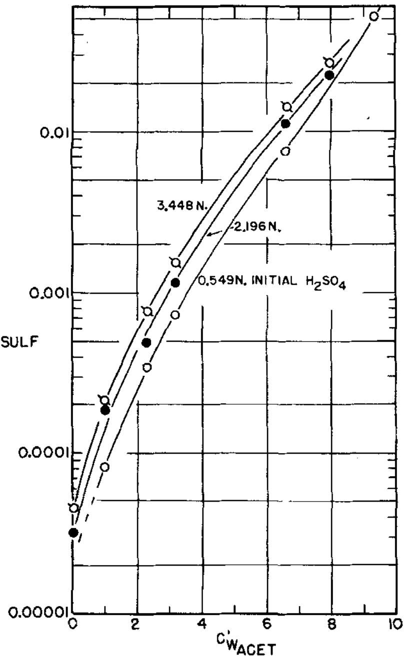

Fig. 6. Effect of acetic acid concentration on distribution ratio of sulfuric acid at 25°C.

Correlation Equations

In Figure 4 the aqueous equilibrium concentration of hydrochloric acid is plotted vs. that of formic acid with the parameter being initial hydrochloric acid concentration. This plot and Figure 1 were used for the determination of experimental values tabulated in Table 1 and used in Equation (2). The details of this calculation procedure are discussed elsewhere (*28*).

A plot of the data from Table 1 is given in Figure 5. A straight line through the data gives the Setschenow equation

$$\log(C^*_{W_{FORM}}/C_{W_{FORM}}) = 0.03215\, C_{W_{HCl}} \quad (9)$$

The equation represents the data with an average deviation of ± 2.6% and a maximum of 9.4%. Hence the fact that some hydrochloric acid is extracted does not invalidate the use of the equation derived on the basis of the electrolyte salting-out the formic acid. The errors for this Equation (9) with hydrochloric acid as the electrolyte are fairly small and of the same order of magnitude as the Setschenow equation with sulfuric acid as the electrolyte (*28*).

The data were also correlated with Equation (3), and the following was obtained:

$$(C^*_{W_{FORM}} - C_{W_{FORM}})/C_{W_{FORM}} = 0.0896\, C_{W_{HCl}} \quad (10)$$

Similar per cent deviations were obtained with this Butler equation when compared with Equation (9).

Salting-Out Effects of Hydrochloric and Sulfuric Acids

When sulfuric acid was used as the salting-out electrolyte, the following was obtained (*28*):

$$\log(C^*_{W_{FORM}}/C_{W_{FORM}}) = 0.0282\, C_{W_{SULF}} \quad (11)$$

Hence for the same salting-out effect on the left side of Equations (9) or (10) a 14% higher normality is required of the sulfuric acid than for the hydrochloric acid. Hence it would appear that hydrochloric acid is more

TABLE 2. CORRELATION OF MIXED SOLUTE EQUILIBRIUM DATA ACCORDING TO THE SETSCHENOW EQUATION $\log(C^*_{W_{ACET}}/C_{W_{ACET}}) = 0.0392\, C_{W_{SULF}}$

Equil. conc., $C_{O_{ACET}}$	Initial conc., $C'_{W_{SULF}}$	Equilibrium conc., $C_{W_{ACET}}$ Exp.	Calc.	% error	Equil. conc., (SULF = 0) $C^*_{W_{ACET}}$	$\log(C^*_{W_{ACET}}/C_{W_{ACET}})$ Exp.	Calc.	Equil. conc., $C_{W_{SULF}}$ (Figure 8)
0.50	0.549	0.87	0.88	1.1	0.94	0.0335	0.0227	0.58
0.50	2.196	0.73	0.76	4.1	0.94	0.1096	0.0902	2.30
0.50	3.448	0.64	0.68	6.2	0.94	0.1662	0.1412	3.60
1.00	0.549	1.59	1.65	3.8	1.72	0.0341	0.0239	0.61
1.00	2.196	1.36	1.39	2.2	1.72	0.1020	0.0933	2.38
1.00	3.448	1.22	1.23	0.8	1.72	0.1491	0.1470	3.75
2.00	0.549	2.78	2.82	1.4	3.00	0.0331	0.0267	0.68
2.00	2.196	2.38	2.37	—0.4	3.00	0.1005	0.1019	2.60
2.00	3.448	2.10	2.08	—1.0	3.00	0.1549	0.1599	4.08
2.50	0.549	3.29	3.32	0.9	3.54	0.0318	0.0282	0.72
2.50	2.196	2.82	2.76	—2.1	3.54	0.0988	0.1078	2.75
2.50	3.448	2.51	2.40	—4.4	3.54	0.1493	0.1693	4.32
3.00	0.549	3.78	3.80	1.1	4.07	0.0310	0.0302	0.77
3.00	2.196	3.22	3.12	—3.1	4.07	0.1006	0.1156	2.95
3.00	3.448	2.92	2.68	8.2	4.07	0.1401	0.1811	4.62

effective as a salting-out electrolyte. However the comparison can be made on the basis of the number of electrolyte ions as predicted in the derivation of Equation (2) and that of Butler *(4)*.

If 1 normal electrolyte is taken as a basis and 100% ionization is assumed, hydrochloric acid contains 2.0 ions and sulfuric acid 1.5 ions. Then on the basis of the number of ions and the same salting-out effect sulfuric acid ions would be 17% more effective in salting-out formic acid. Sulfuric acid is not considered 100% ionized, and the first ionization constant for sulfuric acid is about 1 x 10^3 and the second is 1.2 x 10^{-2} (*3*, *15*). The first or primary ionization is virtually complete, but very little of the secondary occurs. Using an experimental activity coefficient for sulfuric acid (*9*) one calculates the total number of ions of 1 normal sulfuric acid to be 1.058. If an activity coefficient of 1.0 is assumed, this calculated value drops to only 1.006 ions.

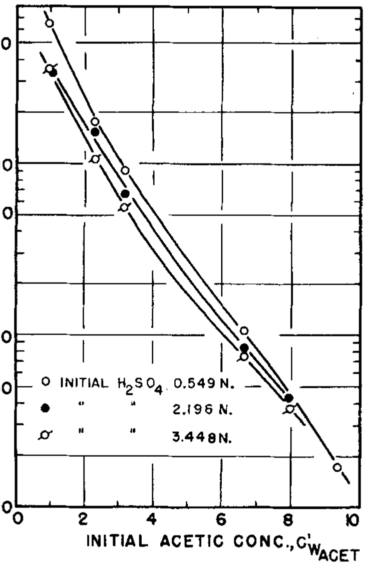

Fig. 7. Effect of acetic acid concentration on selectivity at 25°C.

With the value of 1.058 sulfuric acid ions would be 65% more effective than hydrochloric acid ions in salting-out. Doubling the concentration of sulfuric acid essentially doubles the number of ions, since the first ionization is virtually complete. Hence the apparent number of ions in solution is not the whole effect which determines the amount of salting-out of solute. The type of electrolyte is also important.

Glasstone (*10*) presents data for salting-out gases from solution by lithium chloride and sodium sulfate. These are both strong electrolytes. The sodium sulfate is about 100% more effective than lithium chloride in salting-out when the comparison is made on the basis of the same number of ions in solution. He observes that the smaller the size of ion and/or the larger the charge the greater the salting-out effect. This also follows from equations of others (*4*, *5*).

TABLE 3. EFFECT OF SULFURIC ACID ON ACTIVITY COEFFICIENT OF ACETIC ACID AT 25 ±0.05°C.

Run no.	Nominal original concentrations, g. eq./liter: Acetic side, Acetic	Mixed acid side, Acetic	Mixed acid side, Sulfuric	Equilibrium compositions, g. eq./liter: Acetic side, Acetic conc.	Mixed acid side, Acetic conc.	Mixed acid side, Sulfuric conc.	Mole fraction activity coefficient of acetic acid: Acetic side* γ_1	Mixed acid side γ_2	Ratio γ_1/γ_2
1	1	1	1	0.7966	0.7761	0.9669	2.967	3.052	1.030
2	2	2	2	2.370	2.200	2.189	2.570	2.750	1.071
3	2†	2†	2	2.357	2.160	2.156	2.571	2.780	1.081
4	5	5	1	4.752	4.531	1.090	2.082	2.158	1.036

* Calculated from equation of Hansen, Miller, and Christian.
† 1.5% methyl isobutyl ketone added to each side.

For a 1 normal solution of hydrochloric acid the ionic strength was calculated to be 1.0 and 0.62 for the sulfuric acid. Hence the sulfuric acid is still more effective when compared on the basis of equal ionic strengths.

The fact that large amounts of formic acid are present in the solution should have little effect on suppressing the ionization of sulfuric acid, since the first ionization constant of sulfuric acid is so large. Approximate calculations on lowering of the dielectric constant of the solution by addition of 1 normal formic, sulfuric, or hydrochloric acid showed less than 5% decrease in this constant.

DISCUSSION OF SYSTEM II: ACETIC ACID-SULFURIC ACID-WATER-METHYL ISOBUTYL KETONE

Ternary Equilibrium Data

The experimental data for the ternary systems acetic acid-water-methyl isobutyl ketone and sulfuric acid-water-methyl isobutyl ketone are given elsewhere (*1*). The data for acetic acid were plotted (*1*), and for comparison the data of Bak and Geankoplis (*2*) were plotted and shown to correspond closely to the present data.

Quaternary Equilibrium Data

The data for the system acetic acid-sulfuric acid-water-methyl isobutyl ketone are given elsewhere (*1*). Plots were made (*1*) showing the effect of sulfuric acid on the distribution coefficient of acetic acid. These trends are very similar to those obtained by Whitehead and Geankoplis (*28*) using formic instead of acetic acid and similar to those using hydrochloric and formic acids with the same two solvents.

The effect of the initial aqueous sulfuric acid concentration on increasing the distribution coefficient of acetic acid was determined in a plot (*1*). With no sulfuric acid present the values of the distribution coefficient of acetic acid are on the average about 35% higher than those for formic acid (*28*) in a similar system. This is expected, since the higher the molecular weight of the acid the more soluble is the acid in the organic phase. The general shape and trends of the curves are similar to the previous solute-electrolyte systems (*28*).

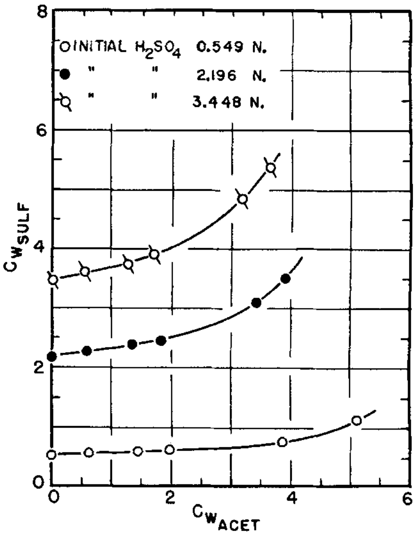

Fig. 8. Relation between aqueous equilibrium acid concentrations at 25°C.

In Figure 6 the effect of adding acetic acid to a sulfuric acid solution is shown. When 8 normal acetic acid is added to an aqueous solution containing 3.5 normal sulfuric acid, the distribution coefficient of the sulfuric acid is increased by 600 fold. Adding 8 normal formic acid to the same solution of sulfuric acid increases the dis-

TABLE 4. COMPARISON OF EFFECT OF SULFURIC ACID ON ACTIVITY COEFFICIENTS OF ACETIC ACID AND ON DISTRIBUTION COEFFICIENTS

Run	Equilibrium compositions									Mole fraction ratios	
	No H_2SO_4 Present				H_2SO_4 Present						
no.	$C_{O_{ACET}}$	$C_{W_{ACET}}$	K_2	γ^*_{W2}	$C_{W_{SULF}}$	$C_{O_{ACET}}$	$C_{W_{ACET}}$	K_1	γ_{W1}	γ_{W1}/γ_{W2}	$K^{\dagger}_1/K_2$
1	0.487	0.922	0.528	2.925	0.9669	0.487	0.7761	0.627	3.052	1.043	1.180
2	1.80	2.75	0.655	2.475	2.189	1.80	2.200	0.820	2.750	1.111	1.261
3	1.77	2.72	0.652	2.479	2.156	1.77	2.160	0.820	2.780	1.120	1.266
4	4.15	5.08	0.818	2.028	1.090	4.15	4.531	0.916	2.158	1.061	1.131

* Mole fraction activity coefficients.

† Distribution coefficients corrected and based on mole fractions in both phases.

tribution coefficient of sulfuric acid by 45 fold (*28*). Hence acetic acid is much more effective than formic acid in increasing the distribution coefficient of sulfuric acid.

The selectivity factor of acetic acid compared to sulfuric acid is plotted in Figure 7. At an initial acetic-acid concentration of 2 normal the selectivity factor is 1,500 and decreases rapidly to a value of 10 at 10 normal acetic-acid concentration. The selectivity factor decreases slightly with an increase in sulfuric-acid concentration. At dilute concentrations the selectivity factor is over 6,000. These general trends are very similar to the system where formic acid is used instead of acetic acid (*28*).

Correlation of Data

In order to use Equation (2) for correlation of the quaternary data the aqueous equilibrium concentration of sulfuric acid was plotted vs. the aqueous equilibrium concentration of acetic acid for constant initial sulfuric-acid concentrations (Figure 8). With Figure 8 and one given elsewhere (*1*) the data needed for Equation (2) were obtained and tabulated in Table 2.

With the method described previously (*28*) these data were plotted (*1*) and the straight line through the data gives the Setschenow equation:

$$\log(C^*_{W_{ACET}}/C_{W_{ACET}}) = 0.0392\, C_{W_{SULF}} \tag{12}$$

The maximum deviation of the data from the equation is 8.2%, and the average is 2.6%. The data were also correlated with the Butler equation:

$$(C^*_{W_{ACET}} - C_{W_{ACET}})/C_{W_{ACET}} = 0.1004\, C_{W_{SULF}} \tag{13}$$

Comparison of Acetic and Formic Acids

In the system formic acid-sulfuric acid-water-methyl isobutyl ketone Whitehead (*28*) obtained a constant of 0.0282 for Equation (12). A comparison of the two constants shows that it requires 28% less sulfuric acid to salt-out a given amount of acetic acid than to salt-out the same amount of formic acid; hence the acetic is easier to salt-out. This difference in salting-out cannot be attributed to changes or large differences in ionic concentrations, since both 1 normal acetic and formic acids are less than 2% ionized and are present in aqueous solution mainly as un-ionized molecules. Because of this small ionization of acetic or formic acids the total ionic strengths of an aqueous sulfuric-formic or sulfuric-acetic acid solution are the same.

Activity Coefficients

Four separate experiments were performed obtaining activity coefficients, and the data are given in Table 3. The concentrations of acetic and sulfuric acids were varied in three out of the four runs. In run number 3, 1.5% methyl isobutyl ketone was added to each side of the activity cell to see if this had any effect on the activity coefficient of the acetic acid. The saturation solubility of methyl isobutyl ketone in the solutions is 1.9%, but only 1.5% was used to insure that two phases did not form in either side of the apparatus. The activity coefficients were affected by only 1% because of the presence of the organic solvent.

In all four of the runs the concentration of acetic acid in the sulfuric acid-acetic acid-water (mixed acid) side was always less in concentration than the acetic acid in the acetic acid-water side. Since the activity of acetic acid in both sides of the apparatus is equal, the activity coefficient of acetic acid in the sulfuric-acid side increased. The ratio γ_1/γ_2 shows the relative increase (Table 3).

In accordance with Equation (7) for extraction, if the concentration C_W of acetic acid in the aqueous phase drops because of sulfuric-acid addition, both the distribution coefficient K and the activity coefficient γ_W of acetic acid in the water phase should increase by the same percentages. This assumes that the concentration C_0 and hence the activity of acetic acid in the methyl isobutyl ketone layer is held constant. If substantially no sulfuric acid enters the organic phase, the activity coefficient γ_o of the acetic acid should remain constant.

A comparison of the actual experimental data was made similar to the above discussion. In run number 1 (Table 3) for a concentration C_W of acetic acid of 0.7966 normal and no sulfuric acid present, the concentration C_o of acetic acid in equilibrium in the organic phase is 0.420 normal (*1*). The value of K is then 0.527. For 0.9669 normal sulfuric acid present and the same concentration C_o of acetic acid in the organic phase of 0.420 normal the value of C_W of acetic acid in the water phase in equilibrium is 0.690 normal as obtained from a plot of C_o vs. C_W (*1*). This value of K is 0.609. The change or ratio of K values because of the addition of sulfuric acid to the aqueous phase is 0.609/0.527 or 1.155. Hence the value of K increased 15.5%. Since mole fraction activity coefficients are used, the above concentrations were converted to mole fractions and the ratio of K values based on mole fractions was calculated to be 1.150. The solutions are dilute, and mole fraction ratios are approximately equal to concentration ratios.

The activity coefficient ratio or the ratio of the γ values (Table 2) shows an increase of only 3.0%. However this increase is strictly not the correct one to use for comparison, since the γ_1 value (Table 3) is the activity coefficient for a value of C_W of 0.7761 normal acetic acid and a sulfuric-acid concentration of 0.9669 normal. The number sought is the value of γ_1 at an equilibrium C_W value of 0.690 normal acetic acid. To obtain this interpolated value the values of γ_W were plotted vs. the $C_{W_{ACET}}$ with the data of Table 3. The data of Hansen (*12*) were available for the line of zero normality sulfuric acid. Two points from runs 1 and 4 were used to establish the line for 1.0 normal sulfuric acid, which was approximately parallel to the zero line, and one point (run number 2) for the 2.19 normal sulfuric-acid line

With this graph used the new value of γ_1 for run 1 was corrected to 3.075. This correction applied to the γ_1 value was small, since the two values of C_W used were close together. The corrected increase in activity coefficients was 3.7% as compared with the uncorrected value of 3.0%. This 3.7% increase is still appreciably less than the 15.0% increase in the mole fraction K value. For the runs 2, 3, and 4 the mole fraction K values increased by 25.6%, 25.6%, and 14.0% respectively, while the activity coefficients increased by 10.0%, 10.0%, and 6.6%.

Another possibly more accurate method to correct or interpolate the activity coefficients is to use the experimental values in the mixed-acid side as the starting point. In run 1 for a C_W value of acetic acid of 0.7761 normal and 0.9669 normal sulfuric acid the C_O of acetic acid in equilibrium is 0.487 normal (*1*). The experimental γ_{W1} value of acetic acid is 3.052. With this value of C_O of 0.487 normal used the concentration of acetic acid C_W in equilibrium is found to be 0.922 normal for zero sulfuric acid (*1*). The value of γ_{W2} for the acetic acid in water is 2.925 (*12*). Calculating and converting the K values to mole fractions one finds that the increase in K is 18.0% and the increase in γ is 4.3%. These results with this latter method of interpolation are given in Table 4. The ratio of the per cent increase in activity coefficient divided by the per cent increase in K values is 4.3/18.0 or 0.24, and the same ratio for the previous method is 3.7/15.0 or 0.25. Hence both methods give very similar results.

In summary the change or increase in activity coefficients of acetic acid because of sulfuric-acid addition can account for an average of only 39% of the change in the K values. Seaton (*23*) also found that the changes in activity coefficients of hydrochloric acid when phosphoric acid was added to the aqueous phase accounted for a small percentage of the change in K values of the hydrochloric acid. Other factors, such as internal pressure changes, hydrogen bonding, complexing, etc., may explain these discrepancies. If addition of sulfuric acid causes the acetic acid in the water phase to form a complex or to associate, then the molecular species of acetic acid in the methyl isobutyl ketone layer will change. This will change the assumption of constant activity coefficient and activity of the acetic acid in the organic layer.

In the experiments in Table 3 the concentration of sulfuric acid in the organic phase was always less than 0.006 normal. Even such a small concentration of a strongly polar compound might be expected to have an appreciable influence on the γ_O of the strongly polar acetic acid in the relatively nonpolar organic solvent.

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NOTATION

a_O = activity of solute in organic phase, $\gamma_O C_O$
a_W = activity of solute in aqueous phase, $\gamma_W C_W$
b = gas constant per molecule
C_1 = concentration of ion species 1, g. moles/liter
C_i = concentration of ion species i, g. moles/liter
C_O = equilibrium concentration of solute in organic phase, g. equiv./liter
C_W = equilibrium concentration of solute in aqueous phase, g. equiv./liter
C^*_W = concentration of solute in aqueous phase ($C_e = 0$) in equilibrium with the same solvent phase (C_O) as C_W, g. equiv./liter
C'_W = initial concentration of solute in aqueous phase, g. equiv./liter
C_e = equilibrium concentration of electrolyte in aqueous phase, g. equiv./liter
D_O = dielectric constant of pure solvent
D = dielectric constant of the solution = $D_O\ (1-\lambda n)$
d_O = density of equilibrium organic phase, g./ml.
d_W = density of equilibrium aqueous phase, g./ml.
k = constant
K = distribution ratio of solute between two solvent layers, C_O/C_W
K_t = true thermodynamic distribution ratio of solute between two solvent layers
N' = Avogadro's number
n = number of molecules of solute per unit volume solution
T = absolute temperature
z_1 = valence of ion species 1
z_i = valence of ion species i

Greek Letters

β = selectivity factor, $K_{\text{FORM}}/K_{\text{HCl}}$ or $K_{\text{ACET}}/K_{\text{SULF}}$
γ_O = activity coefficient of solute in organic phase
γ_W = activity coefficient of solute in aqueous phase
γ_i = activity coefficient of ion species i
γ_m = mean activity coefficient of an electrolyte
ϵ = charge of an electron
λ = related to lowering of dielectric constant of solution
μ = ionic strength of solution

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