Extraction of Mixed Solutes

Separation of Propionic and Sulfuric Acids

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IN LIQUID-LIQUID EXTRACTION systems described in the literature a second solute is often present or is added to modify the extraction of the first solute. As yet no general theory can explain and predict the effect of one solute upon the distribution ratio of another solute in a four-component system which includes two immiscible solvents.

Often a large change in the distribution coefficient of one solute will occur because of complex formation, salting out, hydrogen bonding, internal pressure differences, and other phenomena (*3, 4, 8, 10, 13*). It appears that each case must be studied individually.

In some cases the change in distribution coefficient of a solute may be due to the salting-out effect of the added solute or electrolyte. This effect was studied by Swabb and Mongan in the system water-isopropyl ether-acetic acid-sodium sulfate (*12*). Their data were correlated by the Setschenow equation (*11*), which considers the sodium sulfate to be a salting-out agent.

Using the solvents water and methyl isobutyl ketone (4-methyl-2-pentanone) Whitehead and Geankoplis (*14*) found that when the solutes formic acid and sulfuric acid are used, the sulfuric acid can be considered as a salting-out agent for the formic acid. McAteer, Cox, and Geankoplis (*7*) used the same solvents and studied the solute systems acetic-sulfuric and formic-hydrochloric acids. The data of these three systems were also correlated by the Setschenow equation (*11*).

The present research is a continuation of the study of double-solute systems using water and methyl isobutyl ketone as solvents and propionic and sulfuric acids as solutes. The purpose of the study was to see what differences are encountered when propionic acid, the next higher member of the homologous series of carboxylic acids, is used. The distribution coefficients of these two solutes were systematically studied and the data correlated and compared to the previous three systems.

The effects of sulfuric acid on the activity coefficient of propionic acid were determined experimentally and compared to the changes in distribution coefficient of the propionic acid and to similar data on the acetic acid-sulfuric acid system (*7*).

THEORY

Seaton and Geankoplis (*10*) and others (*7*) have given detailed discussions and literature surveys of the theory of extraction when two solutes are extracted by immiscible solvents. The following simple distribution law is usually employed in expressing the data in extraction:

$$K = C_O/C_W \tag{1}$$

When association, dissociation, or other interactions occur, the value of K may not be constant, since the distribution law is applicable only to the molecular species common to both phases (*5*). These relations have been summarized (*10*).

The equation of Setschenow (*11*) derived theoretically by Debye and others (*1, 2*) gives the effect of an added electrolyte or second solute in salting out the first solute.

$$\log (C_W^*/C_W) = kC_e \tag{2}$$

Butler (*1*) modified this to

$$(C_W^* - C_W)/C_W = kC_e \tag{3}$$

The two equations have been discussed in detail (*7*).

The true thermodynamic distribution coefficient, K_t, of a solute (*10*) is a constant and equal to 1.0, since a_O equals a_w.

$$K_t = \frac{a_O}{a_W} = \frac{\gamma_O C_O}{\gamma_W C_W} = \frac{\gamma_O}{\gamma_W}\ (K) \tag{4}$$

If a second solute which is an electrolyte is added to the aqueous phase, it could affect the activity coefficient of the first solute in the aqueous phase. If this electrolyte increases the ionic strength of the solution and decreases the value of γ_W, then by Equation 4, C_W would increase and K decrease. This assumes that the addition of the electrolyte to the aqueous phase does not affect the activity coefficient or molecular species of the solute in the organic phase. In actual practice some of the electrolyte dissolves in the organic phase and the solubility of the water in the organic phase may change.

When two solutes distribute themselves between two relatively immiscible solvents, the selectivity is defined as

$$\beta = K_{\text{prop}}/K_{\text{sulf}} \tag{5}$$

EXPERIMENTAL

The experimental techniques are very similar to those employed in previous studies (*7*). A volume of 100 ml. of aqueous solution containing propionic and/or sulfuric acids and 100 ml. of methyl isobutyl ketone was pipetted into glass-stoppered flasks. The sealed flasks were agitated at 25.00° ± 0.05° C. and samples removed for analyses as before (*7*).

When either phase contained a single acid, it was analyzed by titration with sodium hydroxide. When either phase contained both propionic and sulfuric acids, the solution was analyzed first for total acid by titration and then for sulfate by the barium sulfate method (*7, 14*). In some cases the weight of barium sulfate precipitate obtained from the organic layer was very small. Knowns simulating these conditions and containing the equivalent of 6 mg. of precipitate were analyzed; the average error was ±5.3%. Since the accuracy of two weighings is ±0.4 mg. or ±7%, this method is within the accuracy of weighing.

Activity coefficients of the propionic acid in the propionic-sulfuric acid solutions were determined by the isopiestic cell method (*7, 9, 10*). From the cell, samples of the propionic acid-water side and of the mixed-acid side of propionic acid-sulfuric acid-water were obtained and analyzed. Activity coefficients for propionic acid in water at 25° C. were obtained from the experimental data of Hansen, Miller, and Christian (*6*).

In the mixed-acid side of the cell, the mole fraction of the propionic acid was calculated from the density and molarities of propionic and sulfuric acids. The known activity coefficient times the mole fraction of the propionic

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acid in the water side was then equated to the unknown activity coefficient times the mole fraction of the propionic acid in the sulfuric acid side.

RESULTS AND DISCUSSION

Ternary and Quaternary Equilibrium Data. The experimental data for the ternary systems propionic acid–water–methyl isobutyl ketone and sulfuric acid–water–methyl isobutyl ketone are given in Table I and plotted in Figure 1. They show that the sulfuric acid is almost insoluble in the organic phase, while the propionic acid is extracted to a large extent.

Equilibrium data for the quaternary system propionic acid–sulfuric acid–water–methyl isobutyl ketone are tabulated in Table II. The effect of sulfuric acid on the distribution of propionic acid is shown in Figure 1. The curves are very similar to those of the formic-sulfuric and acetic-sulfuric acid systems (*7, 14*).

The effect of the initial aqueous sulfuric acid concentration on increasing the distribution coefficient of the propionic acid is shown in Figure 2. In general, the *K* of propionic acid increases slightly as the aqueous concentration increases, regardless of the sulfuric acid concentration. For the formic and acetic acid systems the increase in *K* is much greater.

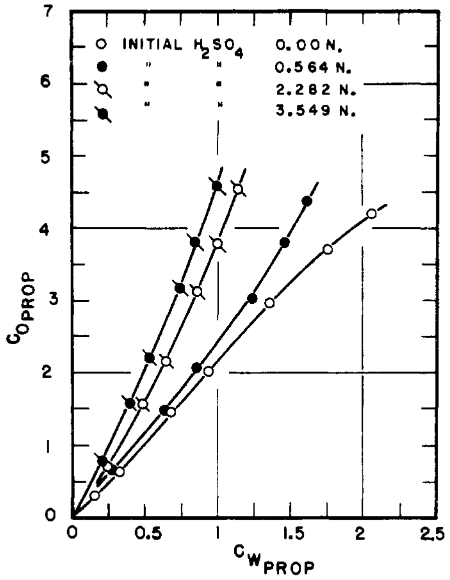

Figure 1. Equilibrium data for propionic acid–sulfuric acid–water–methyl isobutyl ketone system at 25° C.

The *K* values for propionic acid are three to five times greater than the *K* values for acetic acid at all sulfuric acid concentrations. The highest concentration of sulfuric acid increases the *K* of propionic acid by about 70 to 110%. For acetic acid the increase is about 50%. Hence, the sulfuric acid is more effective in salting out the propionic acid.

In Figure 3 the effect of adding propionic acid to a sulfuric acid solution is shown. Similar trends were found for acetic and formic acids (*7, 14*). If 8*N* propionic acid is added to an aqueous 3.5*N* solution of sulfuric acid, the *K* of sulfuric acid is increased 300-fold. If 8*N* acetic acid is used instead of propionic, the increase is only 45-fold. Hence, propionic is more effective in increasing the distribution coefficient of sulfuric acid. These increases may be due to increasing phase solubilities.

At low propionic acid concentrations the selectivity factor of propionic acid compared to sulfuric acid is over 15,000 but decreases to about 300 at high propionic acid concentrations (Figure 4). These high values mean that quantitative separations of solutions of propionic and sulfuric acids are possible in two or three stages. Similar trends are shown for the acetic–sulfuric acid system in Figure 4 (*7*). The selectivities for propionic acid are from two to nine times higher when compared to the acetic-sulfuric acid system.

Correlation of Data. In Figure 5 the aqueous equilibrium concentration of sulfuric acid is plotted against that of propionic acid. Using Figures 1 and 5, the experimental

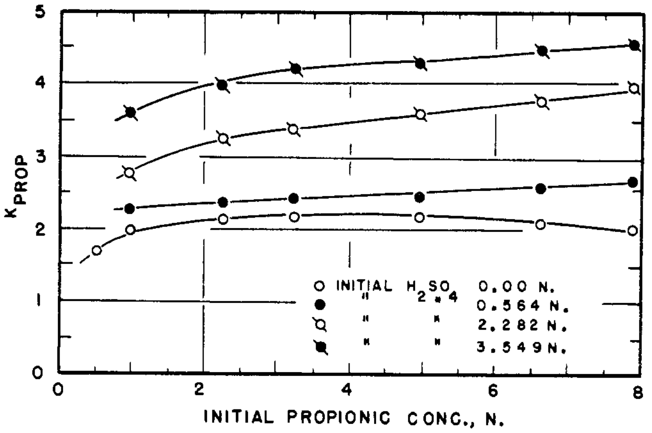

Figure 2. Effect of sulfuric acid concentration on distribution ratio of propionic acid at 25° C.

Table I. Effect of Concentration upon Distribution Ratios of Propionic or Sulfuric Acids between Water and Methyl Isobutyl Ketone at 25° C.

Initial Aqueous Acid Concn., C'_W	Concn. of Equilibrium Solutions		K, C_O/C_W	Density of Equilibrium Solutions	
	C_O	C_W		d_O	d_W
		Propionic Acid–Water–Methyl Isobutyl Ketone System			
0.4857	0.2828	0.1692	1.672	0.8048	0.9960
0.9911	0.648	0.3268	1.984	0.8147	0.9976
2.258	1.456	0.6792	2.144	0.8301	0.9976
3.242	2.020	0.9354	2.160	0.8418	0.9994
4.952	2.970	1.371	2.167	0.8648	1.005
6.632	3.709	1.776	2.088	0.8826	1.003
7.900	4.211	2.067	2.037	0.8954	0.9997
		Sulfuric Acid–Water–Methyl Isobutyl Ketone System			
0.576	0.000017	0.5748	0.0000296	0.7982	1.019
2.258	0.000102	2.255	0.0000452	0.7983	1.025
3.535	0.000159	3.525	0.0000451	0.7974	1.100

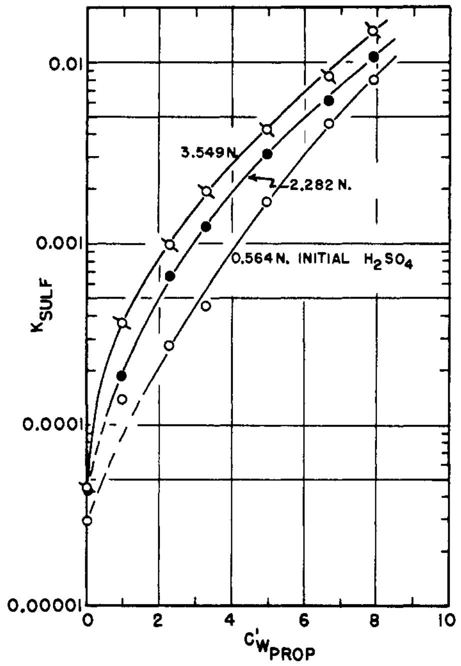

Figure 3. Effect of propionic acid concentration on distribution ratio of sulfuric acid at 25° C.

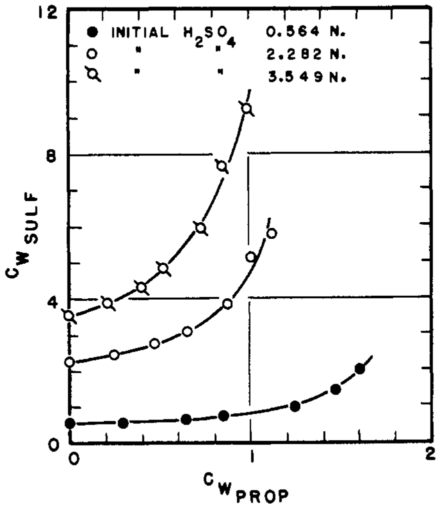

Figure 5. Relation between aqueous equilibrium acid concentrations at 25° C.

values for Equation 2 were obtained and tabulated in Table III. Using the method described in detail previously (*7*, *14*), these data were plotted in Figure 6. A straight line through the data gives the Setschenow equation

$$\log (C^*_{W_{prop}}/C_{W_{prop}}) = 0.0590C_{W_{sulf}} \qquad (6)$$

The average deviation of the data from the equation is ±4.0% and the maximum is −11.6%. The data were also correlated by Equation 3, giving a constant of 0.1742 and deviations of the same order of magnitude.

Comparison of Formic, Acetic, and Propionic Acids. The Setschenow constants for the three systems formic-sulfuric, acetic-sulfuric, and propionic-sulfuric acids in water–methyl isobutyl ketone are 0.0282, 0.0392, and 0.0590, respectively. These constants show that it requires 32% less sulfuric acid to salt out a given amount of propionic acid than to salt out the same amount of acetic acid. It requires 28% less sulfuric acid to salt out a given amount of acetic acid than to salt

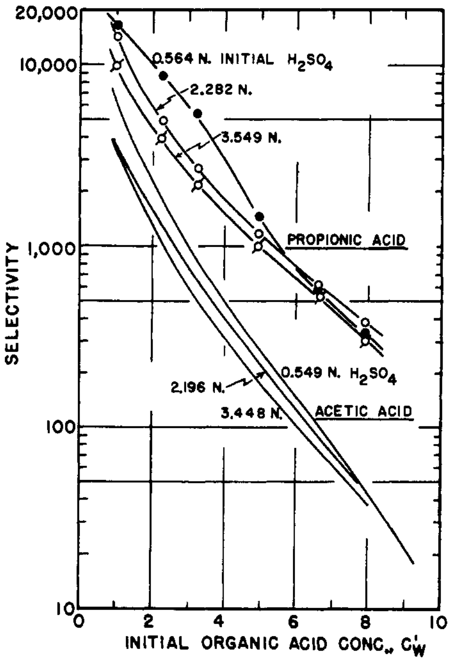

Figure 4. Comparison of selectivity of propionic acid–sulfuric acid system and acetic acid–sulfuric acid system of McAteer, Cox, and Geankoplis (7)

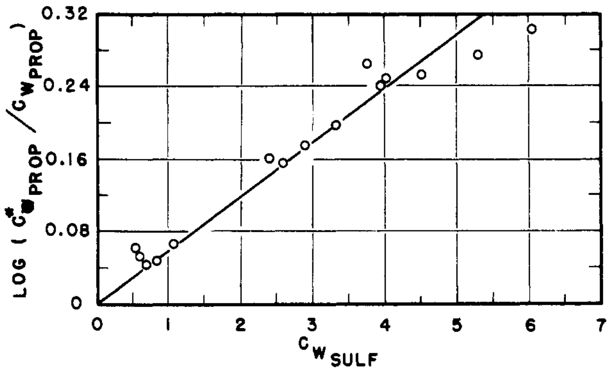

Figure 6. Correlation of data using the Setschenow equation

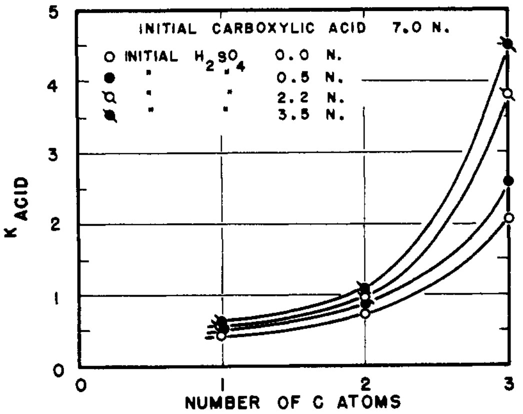

Figure 7. Effect of number of carbon atoms in carboxylic acid upon distribution ratios of the acid

Data for formic and acetic acids from (*7*, *14*)

Table II. Equilibrium Data for Quaternary System Propionic Acid–Sulfuric Acid–Methyl Isobutyl Ketone–Water at 25° C.

Acid Solute	Initial Acid Concn., C'_W	Concn. of Equilibrium Solutions		K, C_O/C_W	Density of Equilibrium Solutions		Separation Factor, β
		C_O	C_W		d_O	d_W	
Propionic	0.9911	0.6561	0.2872	2.285	0.8133	1.016	16,559
Sulfuric	o.5642	0.0000854	0.6186	0.000138			
Propionic	0.9911	0.6988	0.2532	2.758	0.8144	1.071	14,766
Sulfuric	2.282	0.000461	2.468	0.000187			
Propionic	0.9911	0.7951	0.2211	3.600	0.8138	1.111	9,988
Sulfuric	3.549	0.00140	3.881	0.000361			
Propionic	2.258	1.484	0.6299	2.357	0.8319	1.018	8,613
Sulfuric	0.5642	0.000188	0.6863	0.000274			
Propionic	2.258	1.558	0.4775	3.260	0.8312	1.080	4,965
Sulfuric	2.282	0.00183	2.775	0.000658			
Propionic	2.258	1.593	0.4050	3.930	0.8307	1.125	3,960
Sulfuric	3.549	0.00434	4.366	0.000993			
Propionic	3.242	2.069	0.8526	2.426	0.8434	1.025	5,361
Sulfuric	0.5642	0.000341	0.7543	0.000453			
Propionic	3.242	2.157	0.6499	3.318	0.8445	1.089	2,687
Sulfuric	2.282	0.00379	3.068	0.00124			
Propionic	3.242	2.202	0.5209	4.228	0.8443	1.142	2,184
Sulfuric	3.549	0.00932	4.814	0.00194			
Propionic	4.952	3.026	1.247	2.426	0.8637	1.034	1,418
Sulfuric	0.5642	0.00171	0.9976	0.00171			
Propionic	4.952	3.147	0.8697	3.618	0.8619	1.115	1,159
Sulfuric	2.282	0.01207	3.865	0.00312			
Propionic	4.952	3.182	0.7437	4.279	0.8598	1.172	1,003
Sulfuric	3.549	0.02523	5.912	0.00427			
Propionic	6.632	3.803	1.454	2.610	0.8793	1.047	574.2
Sulfuric	0.5642	0.00644	1.415	0.00455			
Propionic	6.632	3.790	1.008	3.759	0.8762	1.153	615.5
Sulfuric	2.282	0.03155	5.166	0.00611			
Propionic	6.632	3.809	0.8427	4.520	0.8766	1.219	537.3
Sulfuric	3.549	0.06410	7.620	0.00841			
Propionic	7.900	4.372	1.616	2.706	0.8911	1.061	337.8
Sulfuric	0.5642	0.01649	2.059	0.00801			
Propionic	7.900	4.549	1.135	4.008	0.8836	1.197	377.6
Sulfuric	2.282	0.06094	5.741	0.01061			
Propionic	7.900	4.579	1.006	4.550	0.8833	1.257	306.0
Sulfuric	3.549	0.1374	9.240	0.01487			

out the same amount of formic acid. The ionic concentrations of the formic, acetic, or propionic acids should have no effect, since all are ionized to a very small percentage.

A semilog plot of the Setschenow constants for the three systems *vs.* the number of carbon atoms in the carboxylic acid yields approximately a straight line. Hence a k value of 0.082 is predicted for butyric acid and 0.118 for pentanoic acid.

In Figure 7 the K data are compared for the three systems at an initial carboxylic acid concentration of 7.0N. The K of the acid increases markedly as the chain length of the acid increases.

Activity Coefficients. Seven separate experiments were performed to obtain activity coefficients of the propionic acid in the aqueous mixed-acid side containing sulfuric and propionic acids (Table IV). The molar concentrations were converted to mole fractions to obtain the activity coefficients based on mole fractions.

In run 3, 1.5% of methyl isobutyl ketone was added to each side of the activity cell; this had a negligible effect (1.5%) on the activity coefficient compared to run 2. The saturation solubility of the methyl isobutyl ketone is 2.1%, but only 1.5% was used, to ensure that two phases did not form.

In Figure 8 the activity coefficient of propionic acid in aqueous solutions of sulfuric acid is plotted against the concentration of propionic acid. The line for 0.0N sulfuric acid was taken from the literature (*6*) and the other experimental data are from Table IV. Adding 2.10N sulfuric acid to a solution containing 1.0N propionic acid raises the activity coefficient of the propionic acid from 8.85 to 9.93, an increase of 12%. In all cases the sulfuric acid increased the activity coefficient. Similar results were obtained in the acetic-sulfuric acid system (*7*).

In Equation 4 if the C_W of propionic acid drops because of sulfuric acid addition, both the distribution coefficient, K, and the activity coefficient, γ_W, in the water phase should increase by the same percentages. This is based on the assumption that the concentration, C_O, and the activity coefficient of the propionic acid, γ_O, in the organic layer are held constant. This method of analysis is discussed in detail elsewhere (*7*).

Table III. Correlation of Mixed Solute Equilibrium Data According to the Setschenow Equation

$$\log(C^*_{W_{prop}}/C_{W_{prop}}) = 0.0590\ C_{W_{sulf}}$$

Equil. Concn., $C_{O_{prop}}$	Initial Sulfuric Concn., $C_{W_{sulf}}$	Equilibrium Concn., $C_{W_{prop}}$		% Error	Equil. $C^*_{W_{prop}}$ (Initial Sulf. = 0) (Fig. 1)	$\log(C^*_{W_{prop}}/C_{W_{prop}})$		Equil. Concn. C_W (Fig. 5)
		Exptl. (Fig. 1)	Calcd.			Exptl.	Calcd.	
0.50	0.5642	0.225	0.241	+7.1	0.260	0.0626	0.0325	0.55
0.50	2.282	0.180	0.188	+4.5	0.260	0.1596	0.1416	2.40
0.50	3.549	0.140	0.156	+11.4	0.260	0.2688	0.2210	3.75
1.00	0.5462	0.430	0.448	+4.2	0.487	0.0539	0.0354	0.60
1.00	2.282	0.340	0.344	+1.2	0.487	0.1556	0.1505	2.55
1.00	3.549	0.275	0.282	+2.5	0.487	0.2484	0.2360	4.00
1.75	0.5642	0.750	0.750	0	0.825	0.0414	0.0413	0.70
1.75	2.282	0.550	0.559	+1.6	0.825	0.1761	0.1693	2.87
1.75	3.549	0.460	0.446	−3.0	0.825	0.2536	0.2678	4.53
2.50	0.5642	1.030	1.029	−0.1	1.150	0.0481	0.0490	0.83
2.50	2.282	0.730	0.732	+0.3	1.150	0.1981	0.1958	3.32
2.50	3.549	0.625	0.559	−10.6	1.150	0.2648	0.3140	5.32
3.25	0.5642	1.300	1.316	+1.2	1.525	0.0697	0.0631	1.08
3.25	2.282	0.890	0.891	+0.1	1.525	0.2340	0.2335	3.96
3.25	3.549	0.750	0.663	−11.6	1.525	0.3081	0.3620	6.13
Maximum absolute error.		−11.6%.						
Average absolute error.		±4.0%.						

Table IV. Effect of Sulfuric Acid on Activity Coefficient of Propionic Acid at 25° C.

Run No.	Nominal Original Concns.			Equilibrium Compositions			Mole Fraction Activity Coefficient of Propionic Acid		Ratio γ_1/γ_2
	Propionic side,	Mixed-Acid Side		Propionic side,	Mixed-Acid Side		Propionic side[a], γ_2	Mixed-acid side, γ_1	
	Prop.	Prop.	Sulf.	prop. concn.	Prop. concn.	Sulf. concn.			
	Gram Equivalents per Liter								
1	1	1	1	0.9942	0.9455	1.0453	8.835	9.200	1.043
2	2	2	2	2.026	1.833	2.105	7.221	7.813	1.082
3[b]	2	2	2	2.037	1.832	2.096	7.201	7.906	1.098
4	5	5	5	5.960	3.366	4.962	3.326	6.820	2.055
5	0.5	0.5	2	0.4588	0.3824	2.100	9.804	11.55	1.178
6	1	1	2	1.0287	0.8686	2.094	8.771	10.25	1.167
7	1.3	1.3	1	1.2954	1.232	1.049	8.329	8.689	1.043

[a] Calculated from equation of Hansen, Miller, and Christian (*6*).
[b] 1.5% methyl isobutyl ketone added to each side. Saturation solubility determined to be 2.1%.

Table V. Effect of Sulfuric Acid on Activity Coefficient of Propionic Acid and on Distribution Ratios

Run No.	Equilibrium Compositions							Mole Fraction Ratios	
	No H_2SO_4 Present			H_2SO_4 Present					
	$C_{O_{prop}}$	$C_{W_{prop}}$	γW_2[b]	$C_{W_{sulf}}$	$C_{O_{prop}}$	$C_{W_{prop}}$	γW_1[b]	γW_1[a] / γW_2[a]	K_1[b] / k_2[b]
1	2.36	1.090	8.68	1.0453	2.36	0.9455	9.200	1.060	1.151
5	1.090	0.525	9.69	2.100	1.090	0.3824	11.55	1.191	1.356
6	2.54	1.170	8.56	2.094	2.54	0.8686	10.25	1.197	1.341
7	3.10	1.44	8.12	1.049	3.10	1.232	8.689	1.070	1.170

[a] Mole fraction activity coefficients.
[b] Distribution coefficients corrected and based on mole fractions in both phases.

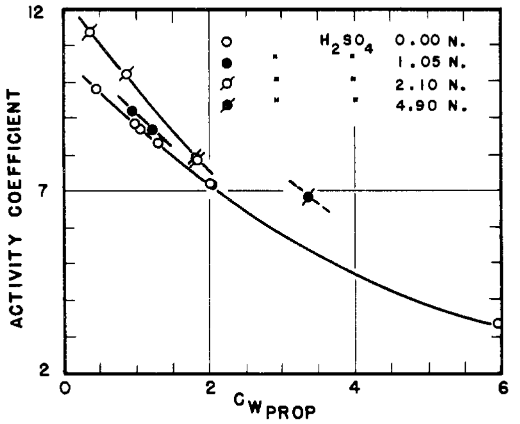

Figure 8. Effect of sulfuric acid concentration upon activity coefficient of propionic acid at 25° C.
Data for 0.00N sulfuric acid from (6)

To make these comparisons of distribution coefficients and activity coefficients the data have been calculated and compared in Table V. In run 1 (Table IV) for a concentration $C_{W_{\text{prop}}}$ of 0.9455N in the mixed-acid side containing 1.0453N sulfuric acid, the concentration $C_{O_{\text{prop}}}$ in equilibrium in the organic phase is 2.36N. This value was obtained by replotting and interpolating the data of Table II, so that the parameter was the aqueous equilibrium concentration of sulfuric acid and not the initial concentration as in Figure 1.

The value of K with the sulfuric acid present is then 2.36/0.9455 or 2.498 and the mole fraction activity coefficient of propionic acid, γ_{W_1}, is 9.200 (Table V). Using this value of $C_{O_{\text{prop}}}$ of 2.36N, the concentration of propionic acid, $C_{W_{\text{prop}}}$, in equilibrium is found to be 1.090N (Figure 1) for zero aqueous sulfuric acid concentration. The value of γ_{W_2} for propionic acid in water with zero sulfuric acid concentration is 8.680 (Figure 8). The value of K for no sulfuric acid present is 2.36/1.090 or 2.164.

Converting the K values based on concentrations to K values based on mole fractions, the increase in K because of the addition of sulfuric acid is 15.1% and the increase in activity coefficients is 6.0%. The ratio of the percentage increase in activity coefficients to the increase in K values is 6.0/15.1 or 40%.

Only four runs of Table IV were in the range of the variables covered in Figure 1. For these four runs in Table V the increase in activity coefficients of propionic acid because of the addition of sulfuric acid can account for an average of only 48% of the increase in K values. This compares closely to the 39% value found for the acetic-sulfuric acid system of others (7). They discuss in detail the reasons for these results. A major factor could be the change in activity coefficient of the propionic acid in the organic layer because of change of molecular species.

NOMENCLATURE

a_O = activity of solute in organic phase, $\gamma_O C_O$
a_W = activity of solute in aqueous phase, $\gamma_W C_W$
C_O = equilibrium concentration of solute in organic phase, gram equiv./liter
C_W equilibrium concentration of solute in aqueous phase, gram 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), gram equiv./liter.
C'_W = initial concentration of solute in aqueous phase, gram equiv./liter.
C_e = equilibrium concentration of electrolyte in aqueous phase, gram equiv./liter
d_O = density of equilibrium organic phase, grams/ml.
d_W = density of equilibrium aqueous phase, grams/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
β = selectivity factor, $K_{\text{prop}}/K_{\text{sulf}}$
γ_O = activity coefficient for propionic acid in organic phase
γ_W = activity coefficient of propionic acid in aqueous phase
γ_1 = activity coefficient of propionic acid in aqueous mixed-acid side
γ_2 = activity coefficient of propionic acid in aqueous side with no sulfuric acid

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