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Studies of Liquid-Liquid Partition Systems. V. The Formation of Mixed Dimers with Two Carboxylic Acids in Carbon Tetrachloride

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The distribution of acetic, propionic and butyric acids, or of mixtures of two of these acids, between carbon tetrachloride and aqueous solutions has been studied at 25°C. The distribution data have been explained in terms of the partition of the acid monomer molecules and the dimerization of the monomer molecules in the organic phase. A salting-out effect has been observed upon additions of sodium perchlorate to the aqueous phase; this salting-out effect is larger in the order butyric>propionic>acetic acid. From the distribution data, the equilibrium constants for the distribution and the dimerization have been determined, and the formation constants for the mixed-dimer molecules have been compared with the statistical values. It has been concluded that the mixed-dimer molecules are equally stable or only a little less stable than had been statistically expected.

The polymerization of carboxylic acids in various organic solvents has been repeatedly studied by many authors.[1] Most of the previous work has studied the polymerization of one sort of carboxylic acid, but some authors have also paid attention to the heterodimerization of two different carboxylic acids, for example, salicylic and *o*-nitrobenzoic acids or acetic and trichloroacetic acids.[2-5]

In the present study, the authors will determine the liquid-liquid distribution of mixtures of two of the following acids; acetic, propionic and butyric acids, and they will determine the hetero-dimerization constants for these acids in carbon tetrachloride using the homo-dimerization constants and the distribution data.

Statistical Treatment

In this paper, HA or HB denotes a monobasic carboxylic acid; the subscript "*org*" denotes a chemical species in an organic phase, while the subscript "*aq*" or no subscript denotes that in an aqueous phase.

To make the statistical treatment simpler, the following assumptions will always be made for the distribution of a weak carboxylic acid between water and an immiscible organic solvent: (i) the change in the activity coefficients of the chemical species is negligible, and the concentration units can be used in the equilibrium constants; (ii) the dissociation of the weak acid in the aqueous phase is negligible, and (iii) in the aqueous phase, the acid exists only as the monomer, while in the organic phase it exists both as the monomer and the dimer.

Simple Acid Distribution Systems. The distribution of an acid between the organic and the aqueous phase may be described as:

$$\mathrm{HA} \rightleftarrows \mathrm{HA}_{(org)} \tag{1}$$

and

$$K_D = [\mathrm{HA}]_{org}/[\mathrm{HA}] \tag{2}$$

The dimerization of the acid molecules in the organic phase may be described as:

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[1] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco (1960).

[2] B. V. Szyskowski, *Z. physik. Chem.*, **131**, 175 (1927).

[3] K. L. Wolf and R. Wolf, *Angew. Chem.*, **61**, 191 (1949).

[4] S. D. Christian, *J. Phys. Chem.*, **61**, 1441 (1957).

[5] H. E. Affsprung, S. D. Christian and A. M. Melnick, *Spectrochim. Acta*, **20**, 285 (1964).

$$2\mathrm{HA}_{(org)} \rightleftarrows (\mathrm{HA})_{2(org)} \tag{3}$$

$$K_2 = [(\mathrm{HA})_2]_{org}/[\mathrm{HA}]^2_{org} \tag{4}$$

The net distribution ratio of the acid may be defined as:

$$D = C_{org}/C_{aq} \tag{5}$$

where C_{org} and C_{aq} are the acid concentrations in the organic and in the aqueous phases, which may be determined by the acid-base titration.

When the acid molecules polymerize in the organic phase, the total acid concentration may be described as:

$$C_{org} = [\mathrm{HA}]_{org} + 2[(\mathrm{HA})_2]_{org} \tag{6}$$

From the assumption iii, the total acid concentration in the aqueous phase may be described as:

$$C_{aq} = [\mathrm{HA}] \tag{7}$$

The net distribution ratio may then be described from Eqs. (2), (4), (5), (6) and (7) as:

$$D = K_D + 2K_D{}^2K_2[\mathrm{HA}] \tag{8}$$

One can determine the K_D and K_2 values by introducing the distribution data of the acid at different concentrations into Eq. (8).

Mixed Acid Distribution Systems. In the following sentences, the subscripts A and B denote a term concerning the HA acid and the HB acid respectively. When the two acids, HA and HB, co-exist in an organic phase, they will form one kind of mixed dimer:

$$\mathrm{HA}_{(org)} + \mathrm{HB}_{(org)} \rightleftarrows \mathrm{HAHB}_{(org)} \tag{9}$$

$$K_{\mathrm{AB}} = [\mathrm{HAHB}]_{org}/[\mathrm{HA}]_{org}[\mathrm{HB}]_{org} \tag{10}$$

From the titration of the two phases, one may obtain the following total acid concentrations:

$$\mathrm{C}_{org} = [\mathrm{HA}]_{org} + 2[(\mathrm{HA})_2]_{org} + [\mathrm{HB}]_{org} + 2[(\mathrm{HB})_2]_{org} + 2[\mathrm{HAHB}]_{org} \tag{11}$$

$$C_{aq} = [\mathrm{HA}] + [\mathrm{HB}] \tag{12}$$

The net distribution ratio may be described from Eqs. (2), (4) and (10) as:

$$D = (K_{\mathrm{DA}}[\mathrm{HA}] + 2K^2{}_{\mathrm{DA}}K_{2\mathrm{A}}[\mathrm{HA}]^2 + K_{\mathrm{DB}}[\mathrm{HB}] + 2K^2{}_{\mathrm{DB}}K_{2\mathrm{B}}[\mathrm{HB}]^2 + 2K_{\mathrm{DA}}K_{\mathrm{DB}}K_{\mathrm{AB}}[\mathrm{HA}][\mathrm{HB}])/([\mathrm{HA}]+[\mathrm{HB}]) \tag{13}$$

When the volumes of the two phases are the same, one may make the following definitions:

$$C_{\mathrm{T,A}} = [\mathrm{HA}] + [\mathrm{HA}]_{org} + 2[(\mathrm{HA})_2]_{org} + [\mathrm{HAHB}]_{org} \tag{14}$$

$$C_{\mathrm{T,B}} = [\mathrm{HB}] + [\mathrm{HB}]_{org} + 2[(\mathrm{HB})_2]_{org} + [\mathrm{HAHB}]_{org} \tag{15}$$

From Eqs. (2), (4) and (10), the difference between $C_{\mathrm{T,A}}$ and $C_{\mathrm{T,B}}$ can be described as:

$$C_{\mathrm{T,A}} - C_{\mathrm{T,B}} = [\mathrm{HA}](1+K_{\mathrm{DA}}) - [\mathrm{HB}](1+K_{\mathrm{DB}}) + 2K_{\mathrm{DA}}{}^2K_{2\mathrm{A}}[\mathrm{HA}]^2 - 2K_{\mathrm{DB}}{}^2K_{2\mathrm{B}}[\mathrm{HB}]^2 \tag{16}$$

One can determine the $C_{\mathrm{T,A}}$ and the $C_{\mathrm{T,B}}$ from the amount of the acid initially added to the system, and the C_{aq} in Eq. (12), by the titration of the aqueous phase.

One can obtain the [HA] and [HB] values from Eqs. (12) and (16); the K_{DA}, K_{DB}, $K_{2\mathrm{A}}$ and $K_{2\mathrm{B}}$ values can be determined from separate experiments using Eq. (8) and from the $C_{\mathrm{T,A}}$, $C_{\mathrm{T,B}}$ and C_{aq} values. Finally, one may obtain the formation constant for the K_{AB} mixed dimer in Eq. (10) from these values and Eq. (13).

One may also determine the following equilibrium constant from Eqs. (4) and (10):

$$(\mathrm{HA})_{2(org)} + (\mathrm{HB})_{2(org)} \rightleftarrows 2(\mathrm{HAHB})_{(org)} \tag{17}$$

$$K = [(\mathrm{HAHB})]^2{}_{org}/[(\mathrm{HA})_2]_{org}[(\mathrm{HB})_2]_{org} = K^2{}_{\mathrm{AB}}/K_{2\mathrm{A}}K_{2\mathrm{B}} \tag{18}$$

The statistical value for the K constant in Eq. (18) has been shown to be (4)[6,7]; thus one may calculate the statistical value of the formation constant for the mixed dimer from the experimentally determined dimerization constants for the separate acids as:

$$K_{\mathrm{AB,\ stat}} = 2\sqrt{K_{2\mathrm{A}}K_{2\mathrm{B}}} \tag{19}$$

The stabilization factor, *SF*, for the mixed dimer may be difined as the ratio of the constants statistically calculated to those experimentally determined:

$$SF = K_{\mathrm{AB}}/K_{\mathrm{AB,stat}} \tag{20}$$

Experimental

Reagents. All of the reagents were of the C. P. grade. The carbon dioxide in the water was driven out by boiling it for half an hour. The carbon tetrachloride was washed three times by shaking it with the same volume of carbon dioxide-free water.

Procedures. All of the experiments were carried out in a thermostatted room at 25±0.5°C. Phenolphthalein was always used as the indicator of the acid-base titrations, while potassium hydrogen carbonate was used to standardize the standard hydrochloric acid solutions.

Stock solutions of acetic, propionic and butyric acids were prepared by dilutions of the acids with water. The concentrations of the acid in the stock solutions were then titrated with standard barium hydroxide solutions. Stoppered Erlenmeyer flasks (volume: 120 m*l*) were used as the vessels. A 50.0 m*l* portion of the aqueous solution of an acid or of a mixture of acids at one of several concentrations and a 50.0 m*l* portion of carbon tetrachloride were placed in the flasks. The flasks with the two phases were then tightly stoppered and shaken mechanically for three hours. In the preliminary experiments, it was observed that

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6) R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," University Press, Cambridge (1952), p. 167.

7) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 2013 (1964).

shaking for over two hours always gave the same distribution ratio as that obtained by shaking for three hours.

After the shaker had been stopped, the two phases were allowed to stand overnight to get a complete separation. Ten to twenty milliliter-portions were then pipetted from each phase and transferred into 100 m*l* Erlenmayer flasks; the acid concentrations were titrated with standard barium hydroxide solutions under a nitrogen atomosphere. The recovery of the acid from both the phases was found to be quantitative.

Results

Table 1 gives the distribution ratios of acetic, propionic, and butyric acids as a function of acid concentration in the aqueous phase. The distribution constant of acid monomer molecules, K_D, and the formation constants of the dimer, K_2, of these acids were calculated from the distribution data in Table 1 by a least-squares method using Eq. (8). The constants thus obtained are given in Table 2.

Some experiments were also carried out on the distribution of valeric acid between carbon tetrachloride and water. It was found that most of the valeric acid in the organic phase was in the form of a dimer; it was concluded from the analysis of the distribution data that more than 99.7% of the acid in the organic phase exists as the dimer in the acid concentration range from 0.006 M to 0.18 M. It seemed to be difficult to determine the K_D and the K_2 of valeric acid accurately from the distribution data; only the plot of log D *vs.* log[HA] is given in Fig. 1, together with the plots of the other three acids.

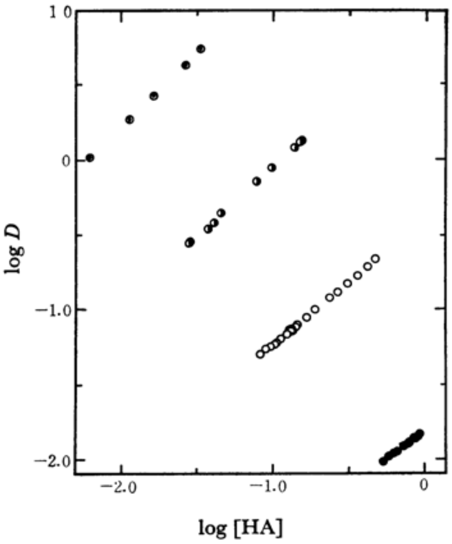

Fig. 1. The distribution ratios of acetic, propionic, butyric and valeric acids between carbon tetrachloride and water at 25°C as a function of the acid concentration in the aqueous phase. ●: acetic acid, ○: propionic acid, ◑: butyric acid, ◎: valeric acid

Some experiments were also carried out in order to observe the effect of electrolytes in the aqueous phase. Table 3 gives the changes in the net distribution ratios of these acids when the aqueous phases contained different amounts of sodium perchlorate.

Table 4 to 6 give the net distribution ratios of the acids when the systems contained two kinds of the carboxylic acids at different concentrations and different mixing ratios. The formation constants for the mixed-dimers were calculated from these data using Eqs. (12), (13) and (16). The constants thus obtained are listed in Table 2.

Discussion

The dissociation constants for acetic, propionic, and butyric acids in water at 25°C have been reported to be as follows;[8,9]

TABLE 1. DISTRIBUTION RATIOS OF THE CARBOXYLIC ACIDS BETWEEN CARBON TETRACHLORIDE AND WATER AT 25°C AS A FUNCTION OF ACID CONCENTRATION IN THE AQUEOUS PHASE

(A) Acetic acid

[HA]	D	]HA]	D
5.33×10^{-1}	9.57×10^{-3}	7.81×10^{-1}	1.26×10^{-2}
5.75×10^{-1}	1.03×10^{-2}	7.85×10^{-1}	1.26×10^{-2}
6.35×10^{-1}	1.08×10^{-2}	8.51×10^{-1}	1.36×10^{-2}
6.55×10^{-1}	1.11×10^{-2}	8.91×10^{-1}	1.40×10^{-2}
7.28×10^{-1}	1.21×10^{-2}	9.31×10^{-1}	1.45×10^{-2}

(B) Propionic acid

[HA]	D	[HA]	D
8.21×10^{-2}	5.00×10^{-2}	1.43×10^{-1}	7.84×10^{-2}
9.05×10^{-2}	5.36×10^{-2}	1.66×10^{-1}	8.79×10^{-2}
9.58×10^{-2}	5.56×10^{-2}	1.89×10^{-1}	9.89×10^{-2}
1.00×10^{-1}	5.79×10^{-2}	2.36×10^{-1}	1.19×10^{-1}
1.05×10^{-1}	5.92×10^{-2}	2.65×10^{-1}	1.31×10^{-1}
1.14×10^{-1}	6.30×10^{-2}	3.09×10^{-1}	1.50×10^{-1}
1.23×10^{-1}	6.78×10^{-2}	3.59×10^{-1}	1.69×10^{-1}
1.30×10^{-1}	7.14×10^{-2}	4.19×10^{-1}	1.94×10^{-1}
1.33×10^{-1}	7.18×10^{-2}	4.70×10^{-1}	2.17×10^{-1}
1.40×10^{-1}	7.48×10^{-2}		

(C) Butyric acid

[HA]	D	[HA]	D
2.79×10^{-2}	2.68×10^{-1}	7.78×10^{-2}	7.09×10^{-1}
2.84×10^{-2}	2.80×10^{-1}	9.68×10^{-2}	8.74×10^{-1}
3.73×10^{-2}	3.45×10^{-1}	1.38×10^{-1}	1.21
4.08×10^{-2}	3.80×10^{-1}	1.50×10^{-1}	1.31
4.51×10^{-2}	4.39×10^{-1}	1.54×10^{-1}	1.35

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[8] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.*, **55**, 65 (1933).

[9] H. S. Harned and R. O. Sutherland, *ibid.*, **56**, 2039 (1934).

	Acetic acid	Propionic acid	Butyric acid
pK_a	4.76	4.87	4.82

As the lowest concentration of the acids in the aqueous phase was 3×10^{-2} M or more, the degrees of ionization of the acid in the aqueous phase were in the ranges from 1 to 2%, from 0.4 to 0.5%, and from 0.4 to 0.6% respectively for butyric, propionic, and acetic acid. The dissociation of the acids in the aqueous phase may be negligible within the range of experimental accuracy.

The Distribution of One Kind of Acid. Table 7 summarizes some previous data in the

TABLE 2. EQUILIBRIUM CONSTANTS FOR DISTRIBUTION AND FORMATION OF MIXED-DIMERS IN CARBON TETRACHLORIDE AT 25°C

(A) Simple acid systems

$K_D=[\mathrm{HA}]_{org}/[\mathrm{HA}]$ $K_2=[(\mathrm{HA})_2]_{org}/[\mathrm{HA}]^2_{org}$

HA	K_D	K_2	HA	K_D	K_2
Acetic acid	3.20×10^{-3}	5.92×10^{2}	Propionic acid	1.51×10^{-2}	9.40×10^{2}
Butyric acid	3.83×10^{-2}	2.91×10^{3}			

(B) Mixed acid systems

$K_{\mathrm{AB}}=[\mathrm{HAHB}]_{org}/[\mathrm{HA}]_{org}[\mathrm{HB}]_{org}$ $K_{\mathrm{AB,stat}}=2\sqrt{K_{2\mathrm{A}}\times K_{2\mathrm{B}}}$ $SF=K_{\mathrm{AB}}/K_{\mathrm{AB,stat}}$

HA	HB	K^*_{AB}	$K_{\mathrm{AB,stat}}$	SF
Acetic	Propionic	$(1.52\pm0.17)\times10^{3}$	1.49×10^{3}	1.02
Acetic	Butyric	$(2.18\pm0.33)\times10^{3}$	2.62×10^{3}	0.83
Propionic	Butyric	$(2.95\pm0.57)\times10^{3}$	3.30×10^{3}	0.89

* The limit of error is 3σ.

TABLE 3. DISTRIBUTION RATIOS AND DISTRIBUTION CONSTANTS FOR CARBOXYLIC ACIDS BETWEEN CARBON TETRACHLORIDE AND SODIUM PERCHLORATE SOLUTIONS AT 25°C

$K_D=[\mathrm{HA}]_{org}/[\mathrm{HA}]$ $K_2=[(\mathrm{HA})_2]_{org}/[\mathrm{HA}]^2_{org}$ $D=K_D+2K^2_DK_2[\mathrm{HA}]$

$K_{D,0}$; Distribution constant when the aqueous phase contains no perchlorate.

(The values K_2 used are taken from Table 2.)

(A) Acetic acid

[NaClO$_4$]	[HA]	D	K_D	$K_D/K_{D,0}$
0	—	—	3.20×10^{-3}	1.0
0.1	5.48×10^{-1}	9.82×10^{-3}	3.20×10^{-3}	1.0
1.0	5.46×10^{-1}	11.38×10^{-3}	3.49×10^{-3}	1.1
2.0	5.46×10^{-1}	12.95×10^{-3}	3.77×10^{-3}	1.2
3.0	5.48×10^{-1}	15.65×10^{-3}	4.20×10^{-3}	1.3
4.0	5.42×10^{-1}	18.40×10^{-3}	4.63×10^{-3}	1.5

(B) Propionic acid

[NaClO$_4$]	[HA]	D	K_D	$K_D/K_{D,0}$
0	—	—	1.51×10^{-2}	1.0
1.0	1.78×10^{-1}	1.17×10^{-1}	1.73×10^{-2}	1.2
3.0	1.65×10^{-1}	2.00×10^{-1}	2.48×10^{-2}	1.6
4.0	1.55×10^{-1}	2.68×10^{-1}	3.00×10^{-2}	2.0
5.0	1.44×10^{-1}	3.79×10^{-1}	3.73×10^{-2}	2.5

(C) Butyric acid.

[NaClO$_4$]	[HA]	D	K_D	$K_D/K_{D,0}$
0	—	—	3.83×10^{-2}	1.0
1.0	9.69×10^{-2}	1.20	4.52×10^{-2}	1.2
2.0	8.39×10^{-2}	1.56	5.55×10^{-2}	1.5
3.0	6.91×10^{-2}	2.08	7.07×10^{-2}	1.9
4.0	5.61×10^{-2}	2.77	9.08×10^{-2}	2.4
5.0	4.35×10^{-2}	3.85	12.13×10^{-2}	3.2

TABLE 4. NET DISTRIBUTION RATIOS OF ACETIC ACID (HA)-PROPIONIC ACID (HB) MIXTURE BETWEEN CARBON TETRACHLORIDE AND WATER AT 25°C

C_{TA}	C_{TB}	C_{aq}	D_{AB}
5.70×10^{-1}	1.20×10^{-1}	6.63×10^{-1}	3.16×10^{-2}
6.16×10^{-1}	1.31×10^{-1}	7.18×10^{-1}	3.37×10^{-2}
6.65×10^{-1}	1.41×10^{-1}	7.75×10^{-1}	3.56×10^{-2}
7.13×10^{-1}	1.52×10^{-1}	8.30×10^{-1}	3.77×10^{-2}
7.50×10^{-1}	1.63×10^{-1}	8.83×10^{-1}	3.99×10^{-2}
8.55×10^{-1}	1.84×10^{-1}	9.90×10^{-1}	4.37×10^{-2}

TABLE 5. NET DISTRIBUTION RATIOS OF PROPIONIC ACID (HA)-BUTYRIC ACID (HB) MIXTURE SYSTEM AT 25°C

C_{TA}	C_{TB}	C_{aq}	D_{AB}
4.15×10^{-2}	5.50×10^{-2}	7.52×10^{-2}	2.69×10^{-1}
4.24×10^{-2}	5.61×10^{-2}	7.66×10^{-2}	2.63×10^{-1}
6.29×10^{-2}	9.27×10^{-2}	1.11×10^{-1}	3.88×10^{-1}
6.42×10^{-2}	9.47×10^{-2}	1.14×10^{-1}	3.89×10^{-1}
8.45×10^{-2}	1.37×10^{-1}	1.46×10^{-1}	5.02×10^{-1}
8.61×10^{-2}	1.40×10^{-1}	1.50×10^{-1}	5.06×10^{-1}
1.08×10^{-1}	1.92×10^{-1}	1.84×10^{-1}	6.27×10^{-1}
1.31×10^{-1}	2.52×10^{-1}	2.19×10^{-1}	7.38×10^{-1}
1.54×10^{-1}	3.18×10^{-1}	2.53×10^{-1}	8.54×10^{-1}
1.78×10^{-1}	3.92×10^{-1}	2.86×10^{-1}	9.69×10^{-1}
2.01×10^{-1}	4.71×10^{-1}	3.19×10^{-1}	1.08

TABLE 6. NET DISTRIBUTION RATIOS OF ACETIC ACID (HA)-BUTYRIC ACID (HB) MIXTURE BETWEEN CARBON TETRACHLORIDE AND WATER AT 25°C

C_{TA}	C_{TB}	C_{aq}	D_{AB}
3.01×10^{-1}	4.18×10^{-2}	3.26×10^{-1}	4.88×10^{-2}
3.01×10^{-1}	5.75×10^{-2}	3.36×10^{-1}	6.89×10^{-2}
3.01×10^{-1}	6.17×10^{-2}	3.38×10^{-1}	7.58×10^{-2}
3.01×10^{-1}	7.56×10^{-2}	3.46×10^{-1}	9.41×10^{-2}
3.01×10^{-1}	9.44×10^{-2}	3.55×10^{-1}	1.21×10^{-1}
3.01×10^{-1}	1.06×10^{-1}	3.58×10^{-1}	1.37×10^{-1}

literature. The present value for K_D of acetic acid is somewhat larger than those given by Shikata⁽¹⁰⁾ or by Davies and his co-workers.⁽¹¹⁾

The present distribution data for acetic acid agree with those reported by Bhat, Benjamin, Lu and Johnson,⁽¹²⁾ who did not, however, derive the constants from their data. The distribution data reported by Shikata are slightly higher than the present data. Davies and his co-workers did not give any distribution data in their paper.

The dimerization constants determined from the infrared absorption are much larger than those determined from the liquid-liquid distribution data.[1,13-15)

The salting-out effect for acetic acid in aqueous electrolyte solutions has been studied by Rothmund and Wilsmore,⁽¹⁶⁾ by Sugden,⁽¹⁷⁾ and by Shikata.⁽¹⁸⁾ However, those previous authors discussed only the increase in the net distribution ratios with the increase in the electrolyte concentration in the aqueous phase. In the present paper. the authors have assumed that the organic phase is not influenced by the addition of electrolytes into the aqueous phase, and that the dimerization equilibrium, which is a phenomenon occuring only inside organic phase, will not be changed by additions of electrolytes. From this, the present authors have calculated the changes in the distribution constant for the acid monomer K_D and these changes are shown in Fig. 2 as a function of the electrolyte concentration. The salting-out effect is nearly negligible for the distribution of acetic acid; the effect appears in the other two acids, however, and it is much larger in butyric acid.

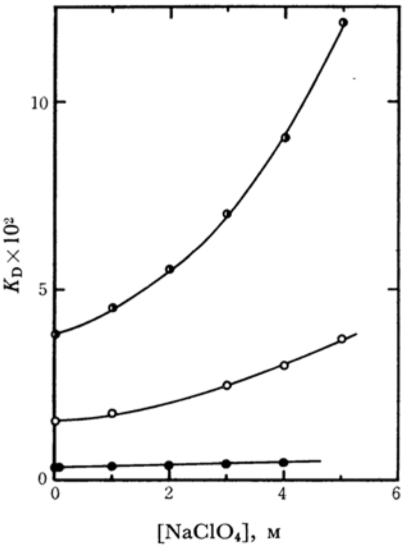

Fig. 2. The change in the distribution constants of acid monomers by additions of sodium perchlorate into the aqueous phase.
$K_D=[HA]_{org}/[HA]$
●: acetic acid, ○: propionic acid, ◑: butyvic acid.

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16) V. Rothmund and N. T. M. Wilsmore, *Z. physik. Chem.,* **40**, 611 (1902).

17) M. S. Sherrill and E. F. Izard, *J. Am. Chem. Soc.,* **53**, 1667 (1931).

18) K. Shikata, *J. Chem. Soc. Japan,* **52**, 332 (1931).

TABLE 7. DISTRIBUTION AND DIMERIZATION CONSTANT OF CARBOXYLIC ACIDS IN CARBON TETRACHLORIDE-WATER SYSTEMS

$K_D=[\mathrm{HA}]_{org}/[\mathrm{HA}]$ $K_2=[(\mathrm{HA})_2]_{org}/[\mathrm{HA}]^2_{org}$

Acetic acid Temp., °C	K_D	K_2	Method	Ref.
25	4.25×10^{-3}	347	dis.	6
25	3.55×10^{-3}	483	dis.	7
—	—	1000—2650	IR	8
25	—	4000	IR	9
24	—	2370	IR	10

Propionic acid Temp., °C	K_D	K_2	Method	Ref.
20	1.60×10^{-2}	800	dis.	7
30	2.01×10^{-2}	518	dis.	7
24	—	2480	IR	10

TABLE 8. FORMATION CONSTANTS OF MIXED CARBOXYLIC ACID DIMERS FROM PREVIOUS WORK

$K_{\mathrm{AB}}=[(\mathrm{HAHB})]_{org}/[\mathrm{HA}]_{org}[\mathrm{HB}]_{org}$ $K_{\mathrm{AB,stat}}=2\sqrt{K_{2\mathrm{A}}\times K_{2\mathrm{B}}}$ $SF=K_{\mathrm{AB}}/K_{\mathrm{AB,stat}}$

HA	HB	Temp., °C	K_{AB}	$K_{\mathrm{AB,stat}}$	SF	Remarks
Benzoic	Stearic	80	5.0×10	1.37×10^2	0.36	1
Salicylic	*o*-Nitrobenzoic	25	1.58×10^2	2.36×10^2	0.67	2
m-Nitrobenzoic	Salicylic	25	4.56×10^2	1.37×10^3	0.33	2
m-Nitrobenzoic	*o*-Nitrobenzoic	25	1.12×10^3	1.37×10^3	0.89	2
Acetic	Trichloroacetic	25	7.2×10^3	2.35×10^3	3.07	3

1) Boiling point elevation (Ref. 3)
2) Solubility measurement (Ref. 2)
3) Near IR absorption (Ref. 5)

The Distribution of Acid Mixtures. The constants for the mixed dimers of acetic-propionic acids, acetic-butyric acids, and propionic-butyric acids in Table 2 seem to indicate that the mixed dimers of these acids are equally stable or only a little less stable than statistically expected. Table 7 summarizes the formation constants for mixed dimers in several carboxylic acid mixture systems derived from previous data.

One may see in Table 8 that the mixed dimers of two carboxylic acids are less stable than statistically expected except in the case of the acetic-trichloroacetic acids dimer studeid by the infrared absorption method.

Affsprung and his co-workers[5] theorized that the mixed dimer of acetic-trichloroacetic acids is more stable than statistically expected as a results of a cooperative-interaction between the electric moment of the perhalogenated methyl or methylene groups and the carboxylic group. However, the constants in Table 2 and 8 for the mixed dimers which consisted of two non-halogenated carboxylic acids indicate that there is no special effect making the dimers more stable when the dimer is asymmetrical.