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HYDRATE FORMATION IN PARTITION EQUILIBRIA OF CARBOXYLIC ACIDS

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HYDRATE FORMATION IN PARTITION EQUILIBRIA OF CARBOXYLIC ACIDS

CHAPTER I

INTRODUCTION

If a solute is distributed between two immiscible solvents, W and Q, the molar Gibbs free energies of the solute in dilute solution are

$$G^W = G^{o,W} + RT\ln c^W$$
$$G^Q = G^{o,Q} + RT\ln c^Q$$

where c^W and c^Q are the concentrations of the solute in the respective solvents. At equilibrium the Gibbs free energy of the solute must be equal in the two solvents; hence,

$$\frac{c^W}{c^Q} = \exp\left[-(G^{o,W} - G^{o,Q})/RT\right] = K$$

This result is the distribution law generally credited to W. Nernst(1). The derivation clearly limits its applicability to a single solute distributed between two immiscible solvents in dilute solution. Departures from this law frequently arise where the solute exists in different molecular forms in the two solvents. Thus, if a solute forms a double molecule, or dimer, in one phase but is largely monomeric in the other solvent, the ratio of its formal concentrations in the two solvents will

not be constant. Using this departure from constancy, Nernst showed that benzoic acid must self-associate in benzene since the ratio of the formal concentration of benzoic acid in benzene to that in water varied. Nernst assumed that the equilibrium involved was 2A (water) = A_2 (benzene). If we symbolize the formal concentration of benzoic acid in benzene as $f_A^b = 2C_{A_2}^b$ and that in water as C_A^W, then the equilibrium constant for the process is

$$K = \frac{C_{A_2}^b}{(C_A^W)^2} = \frac{f_A^b}{2(C_A^W)^2} \quad .$$

As Nernst found, the ratio $\sqrt{(f_A^b)}/C_A^W$ was approximately constant for benzoic acid distributed between benzene and water. This supported his assumption that benzoic acid dimerized in benzene.

One could assume also that the monomeric species distributes between the two solvents and exists in equilibrium with dimeric molecules in the organic solvent. Hendrixson (2), a pupil of Nernst, utilized this viewpoint to compute equilibrium constants of dimerization in the organic phase.

The following method, differing from that of Hendrixson, is now widely used in computing dimerization constants (3,4). Assume that the simple, or monomeric, species distributes itself between two immiscible solvents (water and an organic solvent) as expressed by the equation

$$A \text{ (water)} = A \text{ (organic)}.$$

The distribution law for the monomer requires

$$K_D = \frac{C_A^o}{C_A^W} ,$$

where C_A^o is the concentration of A in the organic phase and C_A^W the concentration in the water phase. In the organic phase a dimerization equilibrium exists,

$$2A = A_2$$

for which the equilibrium constant is

$$K_2 = \frac{C_{A_2}^o}{(C_A^o)^2} .$$

While strictly speaking, activities of the solute species are required in the equilibrium equation it is assumed here that in dilute solution the concentrations of the solutes are nearly equal to their activities. The experimentally determined, or formal, concentration of solute A based on its monomeric molecular weight in the organic phase is given by

$$f_A^o = C_A^o + 2C_{A_2}^o \qquad 1)$$

Substitution of the above equilibrium constants into equation 1) and division by C_A^W leads to

$$\frac{f_A^o}{C_A^W} = K_D + 2K_D^2 K_2 C_A^W \qquad 2)$$

If, as is frequently assumed, the solute is monomeric in water then the formal concentration of A in water is equal to C_A^W. The experimentally determined formal concentrations can be plotted as the ratio of f_A^o/C_A^W versus C_A^W, yielding a straight line whose intercept is K_D. Thus, the dimerization constant is obtained by,

$$K_2^{\text{apparent}} = \frac{\text{slope}}{2(\text{intercept})^2} \quad .$$

It is well to recall at this point that the above treatment assumes immiscibility of the two solvents. In particular, if the solubility of water in the organic phase should be increased by the solute, one might suspect the occurrence of a solute-water interaction in the organic phase in competition with the dimerization reaction. For this reason the constant, K_2, above has been labelled apparent.

If the solute chosen for study is a carboxylic acid, alcohol, or other substance capable of forming self-associated species through hydrogen bonding, the determination of dimerization constants becomes useful in interpreting the strength of the hydrogen bond involved. Measurements of dimerization constants at several temperatures allow computation of the enthalpy change on dimerization by use of the van't Hoff isochores. Then the free energy, enthalpy, and entropy change are available for the process. However, if a competitive hydration reaction occurs, these thermodynamic properties calculated from apparent dimerization constants will not reflect the true state of the dimerization reaction in the organic solvent. It seems useful to analyze the evidence for the existence of solute hydrates (particularly carboxylic acid hydrates) in organic solvents.

Cohen had observed in 1925 (5) that small quantities of water increased the solubility of salicylic acid and nitrobenzoic acid in benzene and chloroform. Bohdan von Szyszkowski (6) attributed this increase in solubility to the formation of a solute hydrate in the organic phase. By measurements of the distribution constant and the equilibrium

solubility of the organic acids in water saturated and in dry benzene he computed the apparent dimerization constant, true dimerization constant (extent of dimerization of unhydrated monomers), and degree of hydration at 25°C. Szyzkowski did not compute the hydrate equilibrium constant as he said he had no assurance that the water molecules were not polymerized in benzene (a matter that will be discussed later). He compared the acids studied as to the degree of hydration, defined as the ratio of hydrated monomers to the total of all monomers, hydrated or not. The m-nitrobenzoic acid showed the highest degree of hydration (0.80), salicylic acid the lowest (0.494), with benzoic acid (0.575), and o-nitrobenzoic acid (0.573) intermediate.

The influence of hydration on the calculated dimerization constant is illustrated in the following table (see also ref. 7). The symbol K'

TABLE 1

DISSOCIATION CONSTANTS OF AROMATIC ACIDS FROM DISTRIBUTION RATIOS AT 25°C (6)

Acid	K' molal	K molal
Benzoic	2.63×10^{-3}	4.74×10^{-4}
Salicylic	3.30×10^{-3}	8.45×10^{-3}
o-Nitrobenzoic	4.60×10^{-2}	8.38×10^{-3}
m-Nitrobenzoic	1.15×10^{-2}	2.49×10^{-4}

is the apparent dimer dissociation constant (hydration ignored), and K is the dissociation constant corrected for hydration, both in units of

moles per kilogram of benzene. Note that the dissociation constants are the reciprocals of dimerization constants. The effects of hydration on the value of K is most noticeable in the case of m-nitrobenzoic acid. For this acid the value of the apparent dimer dissociation constant might lead one to conclude that it is the most dissociated of the four acids studied. Upon correction for hydration, the m-nitrobenzoic acid dimer becomes the least dissociated.

Bell (8) took Szyszkowski's assumption further by assuming that other degrees of hydration were possible--dimer monohydrate, and dimer dihydrate. To demonstrate their presence Bell needed to determine the total water concentration in the organic phase. This was measured by weighing the water and then adding the minimum quantity of anhydrous benzene solution of the chloracetic acids required to dissolve the water at 15°C. Although the data indicated the presence of hydrated species other than monomer hydrate, there still was not sufficient information to compute the indicated equilibrium constants. The solubility of water in benzene at 15°C determined in this way was much too low, 0.018 moles per liter, compared to measurements reported here of 0.0260 moles of water per liter of solution.

Later Bell and Arnold (9) performed a cryoscopic study of trichloroacetic acid in wet and dry benzene. Unfortunately a phase study showed that a small amount of trichloroacetic acid was contained in the solid phase. Though no quantitative interpretation of this data could be made, Bell and Arnold were able to show that the monohydrate was present in the most dilute solutions and that the dimer dihydrate was apparently present at higher concentrations in benzene.

Cryoscopic measurements on solutions of associating solutes, obtained by the equilibrium method, had been reported earlier by Peterson and Rodebush (10). Bell, et al (11) attempted to calculate a dimerization constant for acetic acid from their data, but the "constant" varied by a factor of five no matter what cryoscopic constant of benzene was used between 5.10 and 5.23. The experimental technique given by Peterson and Rodebush appears to exclude water contamination. The equilibrium cryoscopic method is now preferred since the older Beckmann method gives values of the cryoscopic constant that vary with the instrument used and freezing temperatures that vary with the degree of super-cooling. Careful work by Barton and Kraus (12), using the equilibrium cryoscopic technique on benzoic acid in benzene, did yield a dimerization constant regarded by many authors as reliable for 5.5°C.

Mindful of possible competition of water for the carboxylic acid in non-polar solvents, Brown and Mathieson (13) compared cryoscopic measurements for acetic acid and the three chloroacetic acids in wet and dry styrene and α-methylstyrene. Their data showed that apparent dimerization of these acids was decreased by the presence of water in the organic phase. The moles of water dissolved in these solvents per mole of acid was determined also by turbidity titration at 25°C. Their data combined with Bell's (8) for benzene illustrate the relative extent of hydration of these acids.

The increase in solubility of water in a non-polar solvent caused by a third component caught the attention of Stavely, Jeffes, and Moy (14). They measured the water solubility in benzene solutions by observing the temperature at which opalescence appeared when the solution

TABLE 2

MOLE RATIO, WATER/ACID AT 25°C

Solvent	CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
Benzene (15°C)	0.15	0.20	0.60	1.07
Styrene	0.25	0.51	1.25	1.30
α-methylstyrene	0.20	0.54	1.30	1.11

containing a weighed amount of water was cooled. By interpolation of these data values for the solubility of water at 25° could be calculated. The following table, prepared by combining their data with that of others, illustrates the effect of a third component on water solubility. The greatest increases in solubility of water in benzene are due to the presence of hydroxylic compounds and aniline. One could interpret the increased solubility of water as being due to an association of water with these substances rather than to a mere increase in the polarity of the solvent, since there is no apparent correlation of the solubility effect with dipole moment. For example, the dipole moments of phenol and nitrobenzene are, respectively, 1.6 and 3.98 debye.

In view of the above evidence, it would seem unjustified to assume that a solute such as acetic acid distributed between benzene and water would not associate with water present in the benzene phase. Investigators using the distribution method for the determination of dimerization constants have often stated the reservation that mutual solubility of the solvents may be a "disturbing factor" in the determination. It has been tempting to assume the disturbance small. Davies and Hallam (20)

TABLE 3

INCREASE IN SOLUBILITY OF WATER IN BENZENE AT 25°C
DUE TO PRESENCE OF A THIRD SUBSTANCE[a]

Added Solute	Moles of Water per Mole of Added Solute
Trichloroacetic acid, 15°C[b]	1.07
Phenol[c]	.20
Acetic Acid[d]	.15
Ethyl Alcohol[e]	.13
Methyl Alcohol[f]	.08
Aniline[g]	.04
Nitrobenzene[g]	.009
Anisole[g]	.005
Bromobenzene[g]	.000
Chloroform[g]	.000

[a] A similar table in ref. 15 reports values 1,000 times too large.

[b](8); [c](16); [d](17); [e](18); [f](19); [g](14).

have assembled five examples in which the solute dimerization constant is virtually the same whether determined by distribution or by another method in which the anhydrous solvent is used.

These examples have been cited by Davies (20, 21, 22) as justification for assuming the influence of water on the dimerization of acetic and benzoic acid to be insignificant. There are, however, several examples in which the results are not concordant as shown in Table 4.

TABLE 4

DIMERIZATION CONSTANTS BY DISTRIBUTION METHOD COMPARED WITH ANHYDROUS METHODS

Substance Forming Dimer in Solvent Given	Dimerization Constant, $(m/l)^{-1}$ By Distribution	Anhydrous
Acetic acid in CCl_4	282[a] at 25°	2370[b] at 24°
Benzoic acid in benzene	176[c] at 20°	787[d] at 20°
Propionic acid in CCl_4	674[a] at 25°	2480[b] at 24°
p-methoxybenzoic acid	85[e] at 60°	122[f] at 60°

[a](22); [b](23); [c](24); [d](25); [e](26); [f](27).

These lead one to conclude that Davies' examples may be the result of:

a) fortunate coincidences of values due to large errors,

b) careful selection of systems for comparison, or

c) water in solvents purportedly anhydrous.

The purpose of this dissertation will be to show not only that water is an important competitor for associating solutes, but that the distribution method is a valuable one for studying solute association, providing accurate water concentrations in the organic phase are determined so that the nature and significance of the various hydrated species can be inferred.

CHAPTER II

EXPERIMENTAL PROCEDURE

Introduction

Benzene-water systems were equilibrated with various concentrations of acetic or benzoic acids in a thermostatic bath. Samples of the benzene layer were titrated for water content with Karl Fischer reagent using the dead-stop back titration. The acid content of aqueous and benzene layers was determined by titration with standard base.

Materials

Reagent grade benzene was used directly from the container, since no difference in results was detected using redistilled benzene. The aqueous phase was prepared from distilled water. The solutes consisted of reagent grade glacial acetic acid or benzoic acid. The latter gave a neutral equivalent of 99.95±0.01% benzoic acid.

Partition Experiments

The solute acid was distributed between the benzene and water layers in 500 ml. glass stoppered Erlenmeyer flasks by adding the pure acid to about 150 ml. of distilled water and 250 ml. benzene. The flasks were shaken vigorously by hand for about one-half minute and placed in the thermostatic bath. The shaking was repeated at odd intervals for a

total of four to six times. The partition systems were equilibrated in the thermostat for at least 24 hours and often longer than 48 hours at a temperature controlled to 0.1°C.

A sample of the benzene layer was removed in a calibrated 50 ml. volumetric pipet by forcing the liquid into the pipet with air pressure. The glass stopper on the Erlenmeyer flask was replaced at the time of sampling by a cork fitted with a long glass tube that passed into the benzene layer and a shorter tube connected to a rubber blow tube and pipe stem. The pipet was attached to the sampling tube with a short piece of rubber hose. Air pressure was applied by blowing into the rubber tube with pipe stem.

The aqueous layer was sampled by thrusting a pipet through the benzene layer while blowing air through the pipet. Once the agitated layers had reformed, the pipet was filled by suction.

Preparation of Karl Fischer Reagent

The Karl Fischer reagent was prepared according to the proportions used by Mitchell and Smith (28) although the actual quantities used were based on 946 ml. (two pints) of Mallincrodt Analytical Reagent pyridine containing less than 0.1% water.

To 300 gm. of resublimed iodine in a one gallon brown bottle was added 946 ml. of pyridine. The contents were shaken until the iodine dissolved. Then 2365 ml. of methanol redistilled through a 30 plate Oldershaw column was added. One liter of this stock solution was transferred under pressure of dry air to the dry two liter reservoir for the automatic buret. This bottle was placed in a slurry of crushed ice and water. To its contents was added 60 ml. of liquid sulfur dioxide which had been

condensed in a calibrated cold trap immersed in a methanol-dry ice bath. The liquid sulfur dioxide was added slowly, five to ten milliliters at a time, with shaking to minimize splattering due to the vigorous reaction with the stock solution. The resulting Karl Fischer reagent was diluted with 750 ml. of redistilled methanol and set aside to age for two days. The titer of the reagent was about 2.0 mg. of water per milliliter of reagent.

Titration Vessel and End Point Detection

The titration vessel was a 250 ml., Pyrex, round bottomed, three necked flask with 24/40 standard tapers at the necks. The Karl Fischer buret tip was inserted in a cork and mounted in one neck. The buret tip from the water in methanol buret was attached to the center neck by a rubber sleeve connected to a shortened male 24/40 joint. This buret tip could be seen through the standard taper joint made translucent by a light coat of grease. Two platinum wire spirals, each mounted in a 6 mm. soft glass tube, were inserted in a cork to fit the third neck. The electrodes were positioned to fit near the bottom of the flask but out of reach of the magnetic stirring bar. Electrical contact with the platinum wire was achieved with a copper wire thrust into a pool of mercury in the bottom of the electrode tube. Samples to be titrated were added by pipet through a glass stoppered tube (formerly the neck of a 25 ml. volumetric flask) fused to the side of the flask.

The end point of the back titration was detected by the dead stop method. The electrodes were connected through a Leeds and Northrup 2420C galvanometer according to the diagram in Figure 20, page 87 of reference 28. The potentiometer resistor of 70,000 phm was connected in

series to the 1.5 volt battery with a fixed resistor of 20,000 ohm. The potentiometer resistor was adjusted so that the galvanometer deflected to the far right end of the scale when the electrodes were in contact with excess Karl Fischer reagent in 50 ml. of methanol. The galvanometer was adjusted to read zero current at the left hand end of the scale.

During the back titration of excess Karl Fischer reagent with water in methanol, the galvanometer remained deflected to the right until the end point was approached. Then with each addition of titrant the galvanometer became unstable, drifting to lower readings. The last drop of titrant caused a definite decline in reading which took ten seconds or longer to reach zero. The end point was most clearly detected when methanol solutions of water were titrated and less clearly detected when benzene solutions of water were titrated in an equal volume of methanol. In order to duplicate the conditions for standardization and for sample titration the Karl Fischer reagent was standardized in a 50/50 mixture by volume of methanol and benzene. This mixture was pretitrated to the end point before a weighed quantity of water was titrated.

Standardization of Karl Fischer Reagent

To the titration vessel was added 100 ml. of 50/50 methanol-benzene mixture and excess Karl Fischer reagent. The buret tip of the Karl Fischer reagent buret was disconnected from the titration flask and the neck stoppered before the solution was back titrated with the standard water in methanol solution. The stopper was removed to introduce one drop of water from a weight buret. The Karl Fischer buret was again connected to the flask, excess reagent added and back titrated. Duplicate

water samples were determined. The contents of the titration flask were removed between determinations by water aspirator into a filtration flask. Pressure equalization in the flask was achieved through a drying tube of magnesium perchlorate.

The water in methanol solution was standardized by comparison with the Karl Fischer reagent. To the titration flask was added 50 ml. of methanol and the contents pretitrated. Then slightly more than 10 ml. of Karl Fischer reagent was added and back titrated with water in methanol solution. The ratio, milliliters of Karl Fischer reagent per milliliter of water in methanol, was determined in this way three or more times. Since the Karl Fischer reagent changed titer slowly with time, the titer determined in this way was used only for titrations performed that day. The following day the titer was based on a redetermination of the above ratio assuming that the concentration of water in methanol was unchanged. On the second day after standardization the Karl Fischer reagent was again standardized against a weighed quantity of water.

Fifty milliliter samples of the benzene layer from the partition flasks were delivered into 50 ml. of pretitrated methanol, excess Karl Fischer reagent added and back titrated with standard water in methanol immediately.

Acid Titrations

The acid concentration of aqueous and benzene layers was titrated with standard sodium hydroxide (carbonate free) to the phenophthalein end point. In the case of the benzoic acid systems, the acid-rich benzene layer was sampled with a calibrated 10 ml. pipet in duplicate as previously

described and titrated with 0.05 N base. The aqueous sample was obtained in duplicate in a calibrated 10 ml. pipet as previously described and titrated with 0.01 N base. In the acetic acid systems, duplicate 50 ml. samples were taken in a calibrated pipet and titrated with 0.05 N base. Pipets used in sampling the benzene layer were rinsed and dried before obtaining each sample. The aqueous acetic acid layer was sampled with a calibrated 10 ml. pipet, diluted to 100 ml. and 10 ml. aliquots titrated with 0.05 N base.

CHAPTER III

EXPERIMENTAL RESULTS

Introduction

The solutes, acetic and benzoic acids, were distributed between benzene and water at temperatures of 15°, 20°, 25°, and 35°C according to methods described in Chapter II. The concentrations of solute acid in each phase and the concentration of water in the benzene phase were determined. The increased solubility of water in benzene was interpreted as the result of acid hydrate formation. The data allowed computation of monomer acid distribution, dimerization and acid hydration equilibrium constants. Before these calculations were performed the aqueous acetic acid concentration was reduced by the amount of aqueous dimer formed and the data smoothed by requiring a linear relation between the logarithm of equilibrium constants and reciprocal of temperature. Enthalpies of reaction were computed from the resulting equilibrium constants.

Distribution Data

The distribution data are displayed in Tables 5 and 6. The symbols f_A^w, f_A^o, f_w^o refer to the formal concentration in moles per liter of acid in the water phase, acid in the organic phase, and water in the organic phase, respectively.

TABLE 5

PARTITION AND WATER SOLUBILITY DATA FOR
ACETIC ACID-BENZENE-WATER SYSTEM

f_A^W	f_A^o	f_w^o
moles/liter	moles/liter	moles/liter
	15°C	
0.0000	0.0000	0.0260
0.8902	0.02206	0.0280
1.032	0.02869	0.0286
1.383	0.04784	0.0292
1.513	0.05577	0.0296
	20°C	
0.0000	0.0000	0.0305
0.6612	0.01412	0.0335
0.7328	0.01659	0.0326
0.7677	0.01818	0.0324
1.423	0.05232	0.0346
1.465	0.05530	0.0357
1.941	0.09066	0.0370
2.774	0.1716	0.0411
	25°C	
0.0000	0.0000	0.0365
0.5100	0.00987	----
0.7463	0.01787	----
0.8924	0.02396	----
1.086	0.03360	0.0390
1.316	0.04811	0.0415
1.570	0.06448	0.0416
1.654	0.07114	0.0445
1.684	0.07299	0.0421

TABLE 5--Continued

f^{W}_{A} moles/liter	f^{o}_{A} moles/liter	f^{o}_{w} moles/liter
	25°C	
1.719	0.07418	0.0421
1.961	0.09720	0.0471
2.230	0.1193	0.0460
2.380	0.1333	0.0470
	35°C	
0.0000	0.0000	0.0478
0.5364	0.01204	0.0503
0.7045	0.01869	----
0.7386	0.01998	0.0509
0.8396	0.02479	----
0.8456	0.02489	----
1.019	0.03392	0.0521
1.053	0.03547	----
1.211	0.04343	0.0527
1.367	0.05491	---

TABLE 6

PARTITION AND WATER SOLUBILITY DATA FOR
BENZOIC ACID-BENZENE-WATER SYSTEM

f_A^W moles/liter	f_A^O moles/liter	f_W^O moles/liter
	15°C	
0.0000	0.0000	0.0260
0.00481	0.03094	0.0292
0.00526	0.03609	0.0290
0.00765	0.07650	0.0319
0.00943	0.1153	0.0335
0.0115	0.1692	0.0374
	20°C	
0.0000	0.0000	0.0305
0.004511	0.02549	0.0336
0.004859	0.0291	0.0343
0.007363	0.0647	0.0364
0.008171	0.0804	0.0384
0.01031	0.126	0.0393
0.01309	0.0202	0.0442
	25°C	
0.0000	0.0000	0.0365
----	0.0321	0.0405
----	0.0499	0.0422
0.006719	0.04996	0.0416
0.008030	0.0705	0.0433
----	0.0722	0.0434
0.01114	0.1329	0.0467
0.01361	0.1951	0.0512
----	0.3033	0.0583
	35°C	
0.0000	0.0000	0.0478
0.005311	0.02877	0.0537
0.006845	0.04391	0.0542
0.008053	0.05865	0.0555
0.01140	0.1145	0.0607
0.01323	0.1503	0.0633

Comparison with Literature

The distribution data have been compared with those of other workers in Figures 1, 2, and 3 by plotting the Z-function, f_A^o/c_A^w, versus f_A^w. At 25°C the distribution data obtained in this work compare very well with values obtained by Moelwyn-Hughes (24) and Davies and Griffiths (21). The agreement is not so good at 35°C with Davies, et al (22). The only reference to distribution data for benzoic acid at the temperatures used in this study was the classic work of Nernst (1) at 20°C. As seen in Figure 3 the values obtained by Nernst do not agree with those in this study. Three of the points in Figure 3 were obtained by titration with a different solution of standard base than that used for the other points; hence no error from incorrect base normality seems likely in this work.

The solubility of water in benzene at 20° and 25°C determined in this work is compared with the work of others in Table 7. There, as in Figure 4, it is seen that the water solubilities are all higher than values previously reported. The values at the four temperatures are consistent with a linear relation between the logarithm of the solubility and reciprocal of the temperature as shown in Figure 4. Since the sampling and analysis of water was done in the same way for all systems, the differences $f_w^o - c_w^o$, which are important here, are assumed to be unaffected by apparent high values of water solubility.

Interpretation of Results

The data in Tables 5 and 6 reveal an increasing water solubility in benzene with increasing solute acid concentration. In order to account

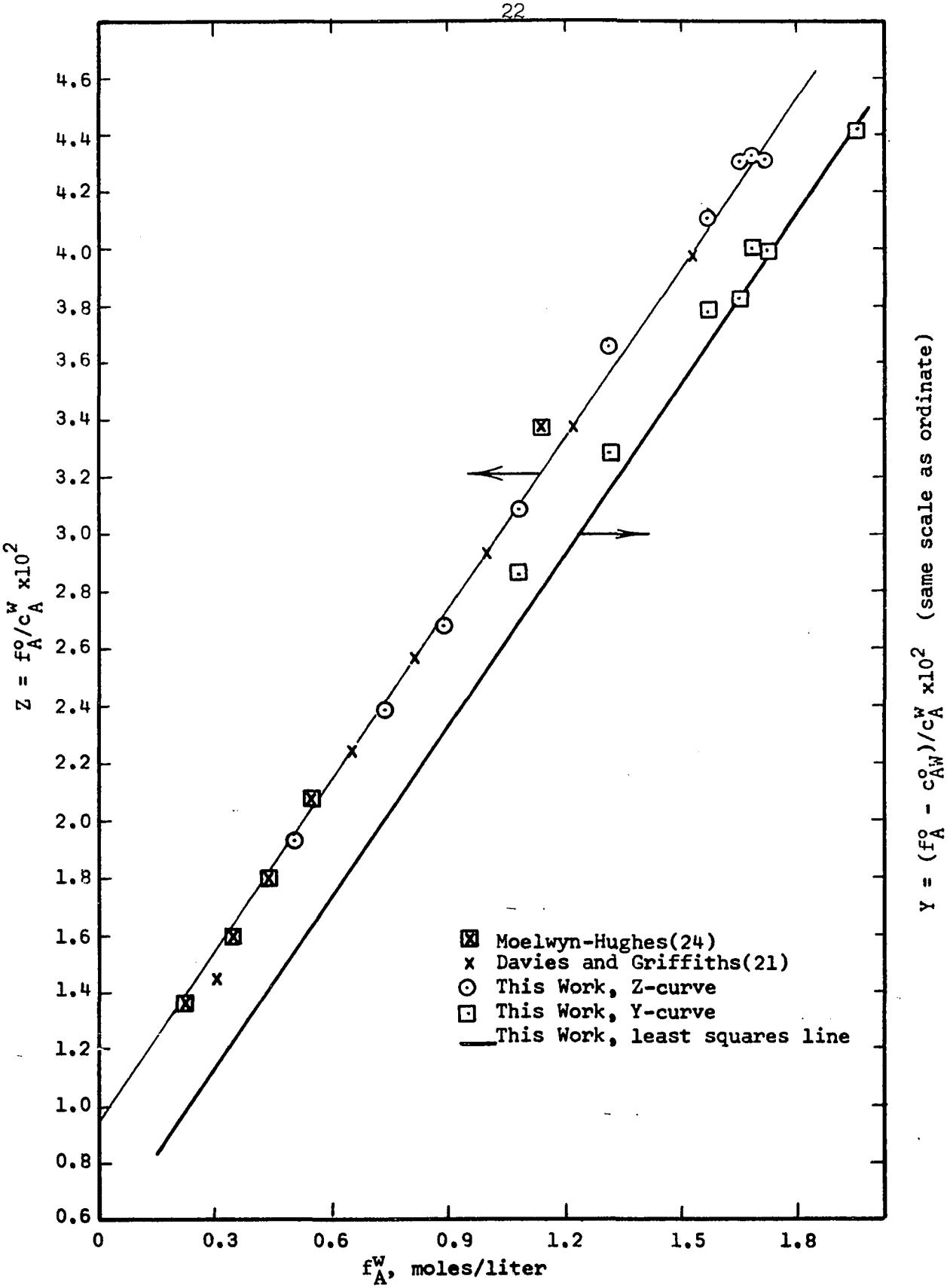

Fig. 1.--Dependence of Z and Y on f_A^w for acetic acid, 25°C

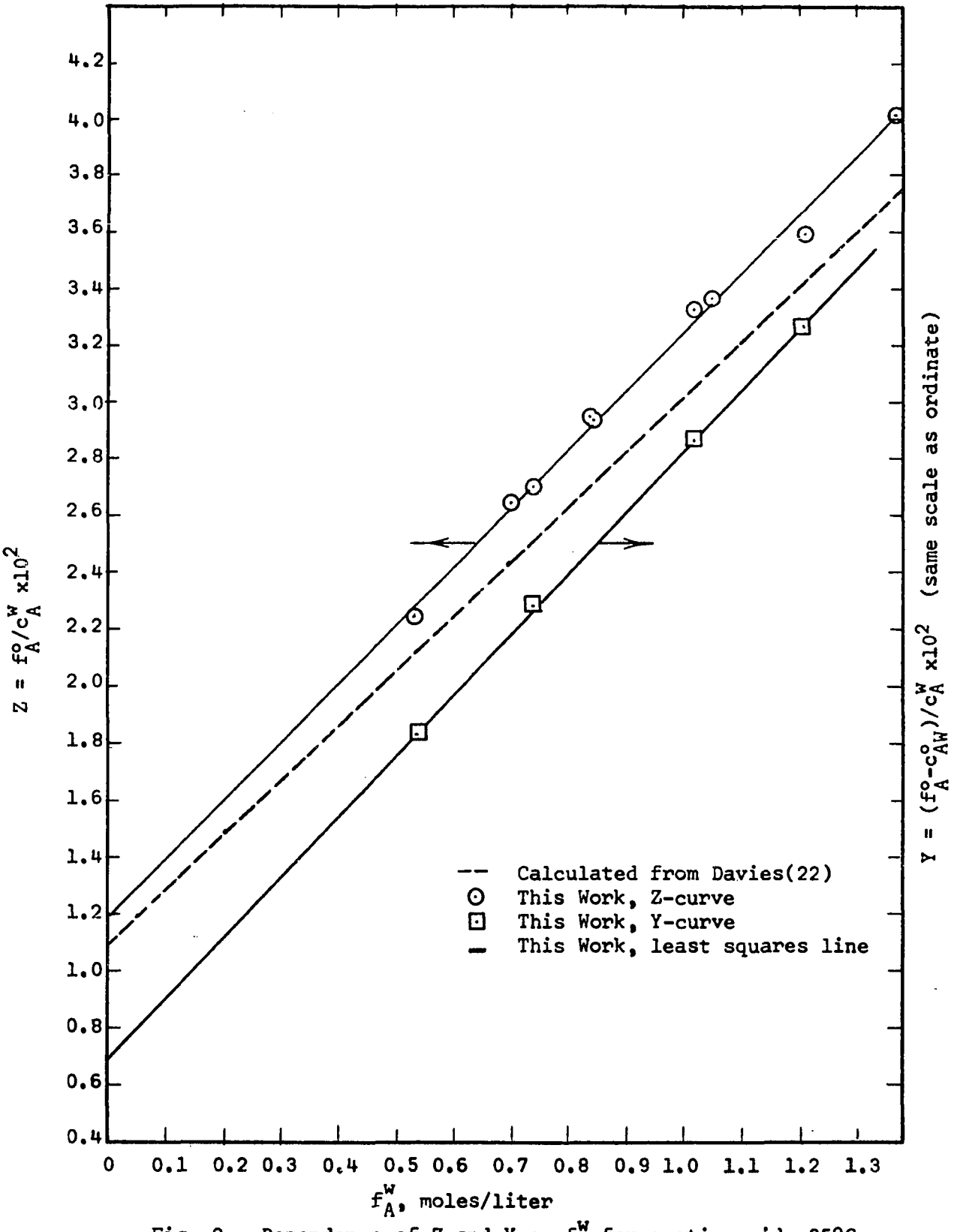

Fig. 2.--Dependence of Z and Y on f^w_A for acetic acid, 35°C

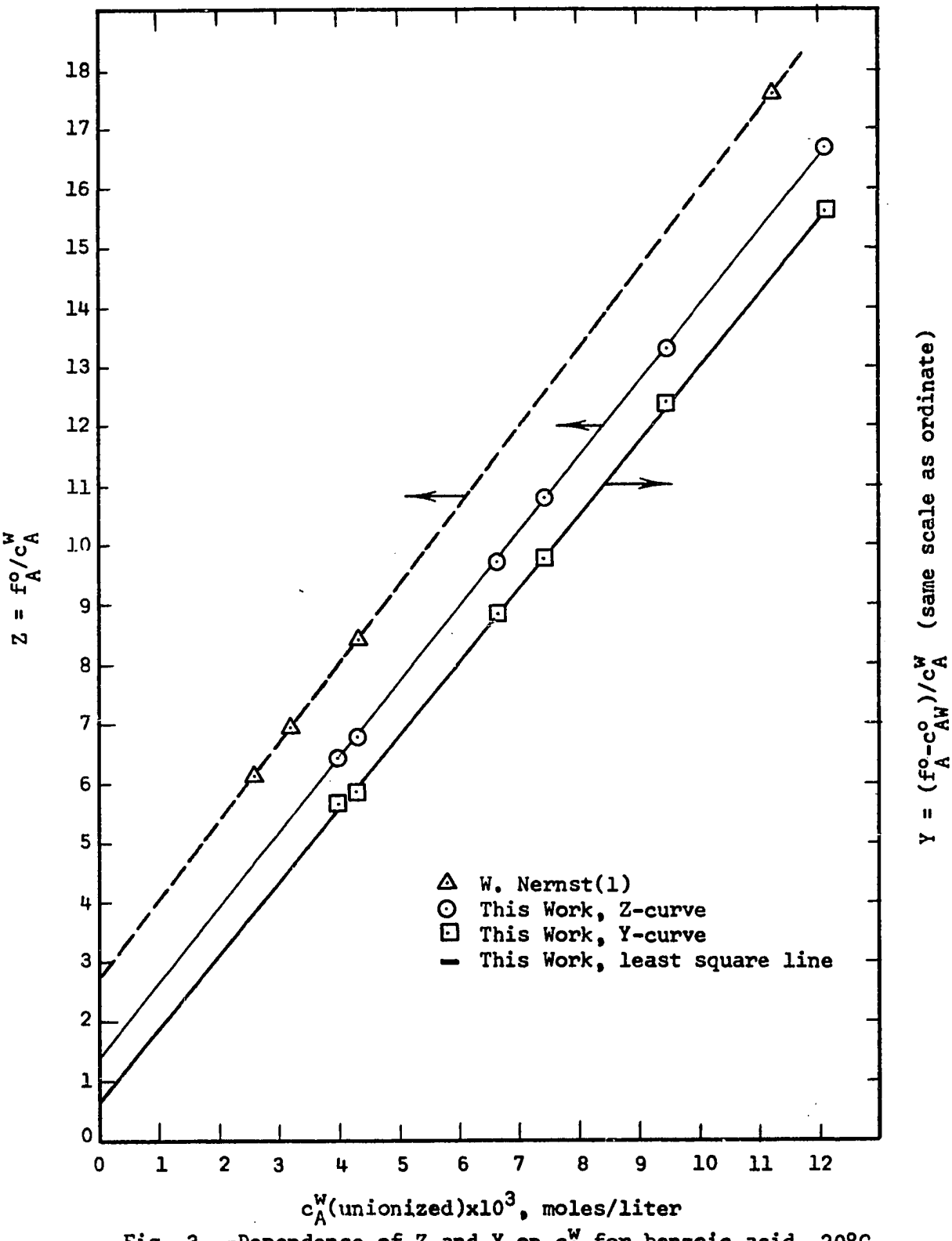

Fig. 3.--Dependence of Z and Y on c^w_A for benzoic acid, 20°C

TABLE 7

SOLUBILITY OF WATER IN BENZENE

$c_w^o \times 10^2$, molar 20°C	25°C	Reference	Analysis Method
2.7	3.3	(29)	Cloud point
3.0	3.5	(29)	Solubility of $AgClO_4$
---	2.6	(31)	Water displaced by dry air and absorbed in $CaCl_2$
2.8	3.3	(32)	Gasometric with CaH_2
2.6	3.1	(33)	Cloud point
2.8	3.3	(14)	Cloud point
2.6	3.3	(34)	Karl Fischer
2.1	2.5	(35)	Tritium tracer
2.82±0.05	3.07±0.03	(36)	Tritium tracer
2.60±0.01	---	(37)	Karl Fischer
---	3.2±0.1	(38)	Karl Fischer
2.54	---	(39)	Tritium tracer
---	3.49	(40)	Karl Fischer
3.05±0.01[a]	3.65±0.02[a]	This work	Karl Fischer

[a]average deviation from average

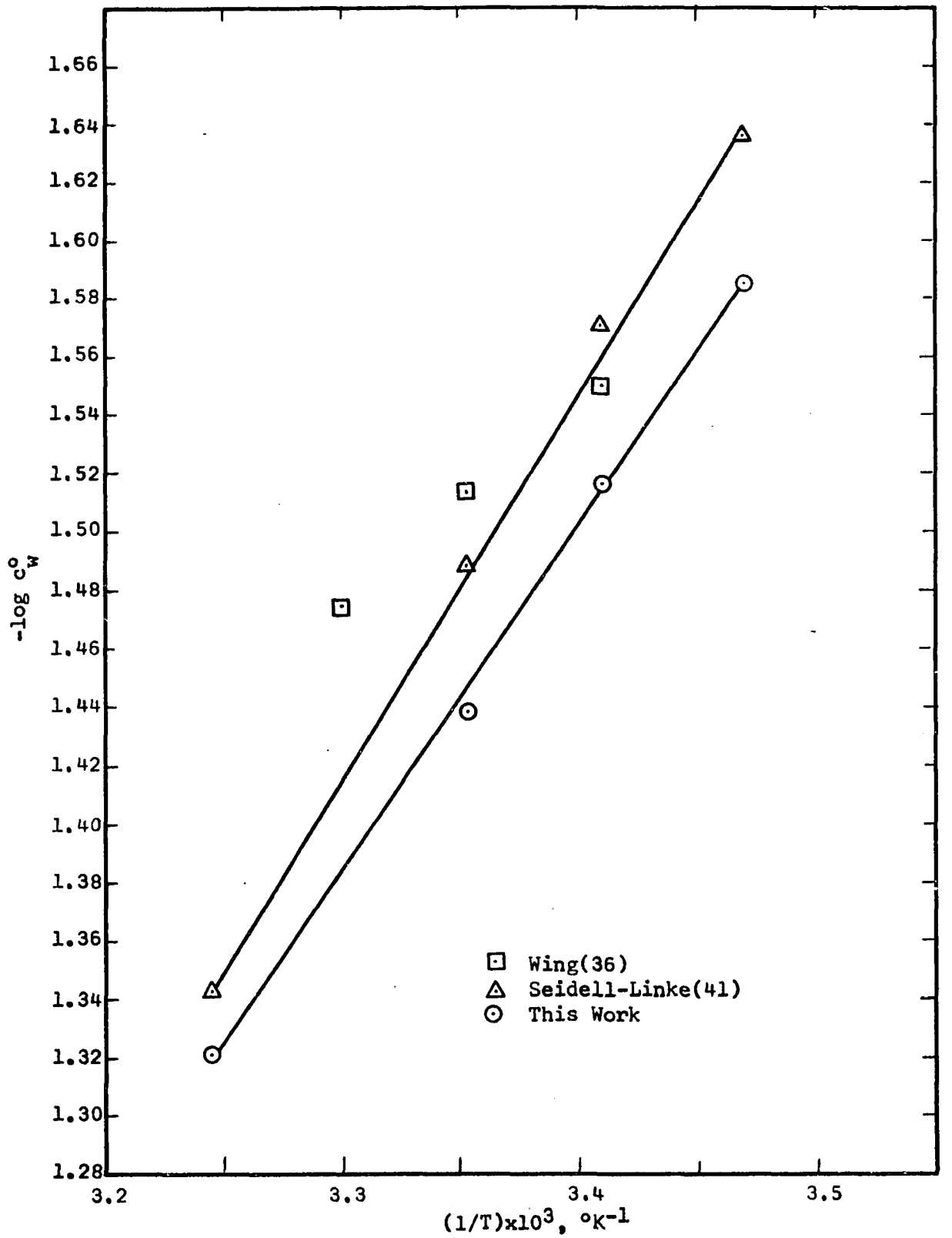

Fig. 4.--Log solubility of water in benzene versus 1/T

for this increased solubility it was assumed in the early stages of this work that the dissolved water reacts with the acid monomer to form a monohydrate. Thus, the species present in the benzene phase were assumed to be acid monomer (RCOOH), acid dimer $(RCOOH)_2$, monomer hydrate ($RCOOH \cdot H_2O$), and water monomer. The formal concentration of acid in the organic layer could be written as

$$f_A^o = c_A^o + 2c_{A_2}^o + c_{AW}^o \tag{3}$$

and the formal concentration of water in the organic phase as,

$$f_w^o = c_{AW}^o + c_w^o \tag{4}$$

where c_A^o, $c_{A_2}^o$, c_w^o, and c_{AW}^o represent molarities of the species RCOOH $(RCOOH)_2$, H_2O, and $RCOOH \cdot H_2O$ respectively. The equilibrium constants in dilute solution would be

$$K_2 = c_{A_2}^o/(c_A^o)^2, \qquad K_h = c_{AW}^o/c_A^o \cdot c_w^o, \qquad K_D = c_A^o/c_A^w \tag{5}$$

where c_A^w is the concentration of acid monomer in the water phase, K_2 and K_h are the acid dimerization and acid monomer hydration constants in the organic phase, and K_D is the distribution constant for the acid monomer.

Combination of equations 3, 4, 5 leads to

$$\frac{f_A^o - f_w^o + c_w^o}{c_A^w} = Y = K_D + 2K_D^2 K_2 c_A^w \tag{6}$$

and

$$f_A^o/c_A^w = Z = K_D + K_h c_w^o K_D + 2K_D^2 K_2 c_A^w \tag{7}$$

where Y and Z are defined in terms of measurable concentrations.[1] Thus, the assumption of hydrate formation should lead to linear plots of Y versus C_A^w and Z versus c_A^w. Figures 1, 2, and 3 show that the data for acetic and benzoic acids do indicate a linear relationship and that Y and Z curves are very nearly parallel as predicted in equations 6 and 7. For the purpose of illustration Figures 1 and 2 have been drawn from values of the formal aqueous acid concentration.

Equations 6 and 7 show that the equilibrium constants of equation 5 can be evaluated from the slope and intercept of the Y and Z functions. Thus, the value of K_2 can be obtained from the Y plot by

$$K_2 = \frac{\text{slope}}{2(\text{intercept})^2} .$$

The value of K_h can be obtained from the intercept of the Z plot using the value of K_D obtained above. The reader is referred to equation 2 in the introduction of this dissertation where the traditional method of evaluating dimerization constants is discussed. If competition by water in the organic phase for the acid monomer is ignored, the intercept of the function Z plotted versus c_A^w will be K_D. However, equation 7 shows the intercept to be larger by the term $K_h c_w^o K_D$. If hydration occurs, the apparent dimerization constant determined by the traditional method will be too small.

An extension of this interpretation has been proposed by Christian, Affsprung, and Taylor (42) for cases in which more complex hydrates may form.

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[1] In dilute solutions c_w^o is equal to the solubility of water in the pure organic phase at the given temperature. Also, c_A^w is equal to the concentration of undissociated monomer acid molecules in water.

Method of Computation

The computation of equilibrium constants (equation 5) from equations 6 and 7 requires a knowledge of the aqueous acid monomer concentration. The formal benzoic acid concentration in the aqueous phase was corrected for the extent of ionization of the acid but in the acetic acid system a correction was not required, since neglect of ionization led to an error of only one-half of one per cent at the concentrations studied. The thermodynamic acid dissociation constant of benzoic acid at each temperature was computed from the formula tabulated by Robinson and Stokes (43),

$$pK_a = \frac{1590.2}{T} - 6.394 + 0.01765T,$$

The mean ionic activity coefficients of benzoic acid were estimated from the following formula for 1:1 electrolytes by Davies (44),

$$\log \gamma_{\pm} = \frac{-A\sqrt{\mu}}{1+\sqrt{\mu}} + 0.1\mu,$$

where μ is the ionic strength and A is a function of temperature whose values are tabulated by Robinson and Stokes (op.cit., p. 468).

Several authors (21, 45, 46, 47, 48, 49, 50, 51, 52) have given evidence for dimerization of acetic acid in water. Table 8 presents the acetic acid dimer dissociation constant in water as determined by several methods. Since Davies and Griffiths (21) took no account of the water interaction with acetic acid in the benzene phase it was felt that their computation based on the distribution method was less reliable than the other methods cited in Table 8. This investigator, therefore, has arbitrarily selected a dimer dissociation constant K_{12}^{w} equal to 20 to reduce the formal acetic acid concentration to aqueous monomer concentrations.

TABLE 8

DIMER DISSOCIATION CONSTANT OF ACETIC ACID IN WATER

Method	K_{12}^{W} molal
Conductivity at 25°C[a]	19±2
Distribution at 25°C[b]	28
Freezing Point at 0°C[b]	28
Vapor pressure at 25°C[c]	20±3
Electromotive force at 25°C[d]	18±1.6

[a](50); [b](21); [c](21, 45); [d](51)

The authors cited above also find that K_{12}^{W} is insensitive to temperature; hence this same constant was used at all temperatures in this dissertation. No evidence has been found that benzoic acid is dimerized in water.

The interpretation of the data also assumes that water exists as a monomer in benzene solution. This assumption has been verified by Christian, Affsprung, and Johnson (40).

Because of a natural scatter in experimental results the data have been smoothed before calculation of equilibrium constants. The smoothing process was based on the validity of a linear relation between the natural logarithm of an equilibrium constant and the reciprocal of the temperature (the van't Hoff relation). Furthermore, the slopes of the Z and the Y data plotted against c_{A}^{W} are essentially equal, as

predicted by equations 6 and 7; hence these two slopes are set equal in the computations.

The equilibrium between dissolved acid, A; water, w; and acid hydrate, AW, is

$$A\ (\text{aqueous}) + W\ (\text{aqueous}) \rightleftharpoons AW\ (\text{organic})$$

with its equilibrium constant

$$K_1 = \frac{C^o_{AW}}{C^w_A}$$

in dilute solution where the activity of water was assumed to be unity. The constant K_1 is just the difference Z-intercept minus Y-intercept (cf. equation 6 and 7). For each partition experiment the difference $f^o_w - c^o_w = c^o_{AW}$ is obtained and the logarithm K_1 calculated. Since the relative error in the water determination is lower at higher water concentrations the values of log K_1 have been weighted to reflect the greater importance attached to values at higher water concentrations in benzene. The weighting factor chosen was $(c^w_A)^2$ (where c^w_A refers to the concentration of aqueous acid monomer) since c^o_{AW} is linearly related to C^w_A. The smoothing process is outlined as follows:

1. Each log K_1 was weighted by $(c^w_A)^2$ and the best straight line found for weighted log K_1 versus 1/T by method of least squares. K_1 at each temperature is equal to Z-intercept minus Y-intercept.
2. The raw data $f^o_A/c^w_A = Z$ versus c^w_A were smoothed by least squares method to obtain Z-intercept at each temperature.
3. The difference,

   Z-intercept (step 2) - (Z-intercept - Y-intercept) (step 1)

   equal to Y-intercept, was obtained at each temperature.

4. The Y-intercepts from step 3 were smoothed by least squares of log (Y-intercept) versus 1/T.
5. The sum,

   (Z-intercept - Y-intercept) (step 1) + Y-intercept (step 4)

   equal to Z-intercept, was obtained at each temperature.
6. The Z-slope was computed using Z-intercept from step 5 and least squares parameters in step 2 and set equal to Y-slope.
7. The Y-slope was smoothed by requiring straight line for log (Y-slope) versus 1/T.

From the smoothed parameters one can obtain a consistent set of equilibrium constants by means of the following relations:

$$\text{(Z-intercept - Y-intercept) (step 1)} = K_h c_w^{\circ} K_D$$

$$\text{Y-intercept (step 4)} = K_D$$

$$\text{Y-slope (step 7)} = 2K_D^2 K_2$$

It is true that a least squares treatment of the experimental data would give the linear equation of Z and Y as functions of c_A^w from which Z-intercepts and Y-intercepts could be obtained. Because of the long extrapolation to $c_A^w = 0$ the Y-intercepts (equal to K_D) do not satisfy closely the van't Hoff isochore. Since the Z data are more accurately determined than Y data the Z-intercepts should be more reliable; hence step 3 of the smoothing process above should give a better set of Y-intercepts for smoothing in step 4. These smoothed Y-intercepts were used to get an improved set of Z-intercepts in step 5. Step 6 and 7 yielded a Z-slope (equal to Y-slope) consistent with the intercepts and the van't Hoff isochore. The data used in step 1 of the computation are

displayed in Table 9 and 10 with the linear equation established by the method of least squares. Tables 11 and 12 show the linear equation parameters for the Y and Z functions obtained by a least square fit through the experimental data with the standard deviations in these parameters.

Equilibrium constants computed from the smoothed data are given in Tables 13 and 14.

TABLE 9

DATA SMOOTHING FOR ACETIC ACID SYSTEM
STEP 1

f_A^w molar	$c_A^{w\,a}$ molar	w^b (molar)^2	$-\log K_1$	$c^o_{AW} \times 10^3$ molar exp't.	$\Delta \times 10^{3c}$
		15°C			
0.8902	0.8564	0.7334	2.6308	2.0	-0.6
1.032	0.987	0.9742	2.5800	2.6	-0.4
1.383	1.307	1.7082	2.6108	3.2	-0.8
1.513	1.424	2.0278	2.5968	3.6	-0.7
		20°C			
0.6612	0.6418	0.4119	2.3307	3.0	+0.7
0.7328	0.7090	0.5027	2.5287	2.1	-0.4
0.7677	0.742	0.5506	2.5918	1.9	-0.7
1.423	1.343	1.8036	2.5157	4.1	-0.7
1.465	1.381	1.9072	2.4237	5.2	+0.3
1.941	1.802	3.2472	2.4425	6.5	+0.1
2.774	2.518	6.3403	2.3757	10.6	+1.7
		25°C			
1.087	1.037	1.0754	2.6180	2.5	-1.8

TABLE 9--Continued

f^w_A molar	c^{wa}_A molar	w^b (molar)^2	-log K_1	$c^o_{AW} \times 10^3$ molar expt.	$\Delta \times 10^{3c}$
		25°C			
1.316	1.246	1.5525	2.3969	5.0	-0.2
1.570	1.475	2.1756	2.4609	5.1	-1.0
1.654	1.549	2.3994	2.2874	8.0	+1.6
1.684	1.576	2.4838	2.4498	5.6	-0.9
1.719	1.607	2.5824	2.4584	5.6	-1.1
1.961	1.820	3.3124	2.2351	10.6	+3.1
2.230	2.054	4.2189	2.3344	9.5	+1.0
2.380	2.183	4.7655	2.3179	10.5	+1.5
		35°C			
0.5364	0.5234	0.2739	2.3206	2.5	-0.4
0.7386	0.7147	0.5108	2.3625	3.1	-0.8
1.019	0.975	0.9506	2.3556	4.3	-1.1
1.211	1.151	1.3248	2.3706	4.9	-1.5

Linear equation by least squares method,

$$\log K_1 = -1.1536 \times 10^3 \, (1/T) + 1.4852$$

$$\sigma_{c^o_{AW}} = 1.2 \times 10^{-3}$$

[a] aqueous monomeric acid concentration

[b] weighting factor = $(c^w_A)^2$

[c] c^o_{AW} (experimental) - $K_1 c^w_A = \Delta$

TABLE 10

DATA SMOOTHING FOR BENZOIC ACID SYSTEM
STEP 1

$f_A^w \times 10^3$ molar	$c_A^w \times 10^{3a}$ molar	w^b $(\text{molar})^2$	$-\log(K_1 \times 10)$	$c_{AW}^o \times 10^3$ molar exp't.	$\Delta \times 10^{3c}$
			15°C		
4.81	4.26	18	0.8758	3.2	-0.8
5.26	4.68	22	0.8069	3.0	-1.4
7.65	6.93	48	0.9301	5.9	-0.5
9.43	8.62	74	0.9396	7.5	-0.5
11.5	10.60	112	0.9917	10.4	+0.6
			20°C		
4.511	3.97	16	0.8926	3.1	-0.9
4.859	4.30	18	0.9463	3.8	-0.5
7.363	6.657	44	0.9475	5.9	-0.8
8.171	7.422	55	1.0269	7.9	+0.4
10.31	9.455	89	0.9688	8.8	-0.7
13.09	12.11	146	1.0535	13.7	+1.5
			25°C		
----	4.69[d]	22	0.9309	4.0	-1.1
----	6.02[d]	36	0.9763	5.7	-0.8
6.719	6.04	36	0.9266	5.1	-1.4
8.030	7.28	53	0.9701	6.8	01.1
----	7.38[d]	54	0.9708	6.9	-1.1
11.14	10.24	105	0.9983	10.2	-0.9
13.61	12.61	159	1.0667	14.7	+1.1
----	15.88[d]	252	1.1377	21.8	+4.6

TABLE 10--Continued

$f_A^W \times 10^3$ molar	$c_A^W \times 10^{3a}$ molar	w^b $(\text{molar})^2$	$-\log(K_1 \times 10)$	$c_{AW}^o \times 10^3$ molar exp't.	$\Delta \times 10^{3c}$
		35°C ,			
5.311	4.724	22	1.0966	5.9	0.0
6.845	6.172	38	1.0158	6.4	-1.3
8.053	7.304	53	1.0228	7.7	-1.4
11.40	10.46	109	1.0910	12.9	-0.15
13.23	12.24	149	1.1024	15.5	+0.2

Linear equation by least squares method,

$$\log (K_1 \times 10) = -0.56795 \times 10^3 \, (1/T) + 2.9392$$

$$\sigma_{c_{AW}^o} = 1.3 \times 10^{-3}$$

[a] concentration of unionized benzoic acid

[b] weighting factor $= (c_A^W)^2$

[c] $\Delta = c_{AW}^o$ (Experimental) $- K_1 c_A^W$

[d] value of c_A^W calculated from least squares equation for a measured value of f_A^o.

TABLE 11

LINEAR EQUATION PARAMETERS BY LEAST SQUARES METHOD
FOR ACETIC ACID SYSTEM, AQUEOUS DIMER ASSUMED
STEP 2

	Z-		Y-	
T°C	slope $\times 10^2$	intercept $\times 10^2$	slope $\times 10^2$	intercept $\times 10^2$
15	2.431±0.030	0.501±0.035	2.419±0.023	0.267±0.027
20	2.462±0.009	0.602±0.012	2.428±0.039	0.292±0.056
25	2.495±0.029	0.695±0.043	2.301±0.073	0.593±0.120
35	2.448±0.059	1.051±0.054	2.515±0.025	0.551±0.021

TABLE 12

LINEAR EQUATION PARAMETERS BY LEAST SQUARES METHOD
FOR BENZOIC ACID SYSTEM
STEP 2

	Z-		Y-	
T°C	slope $\times 10^{-3}$	intercept	slope $\times 10^{-3}$	intercept
15	1.396±0.014	1.275±0.10	1.351±0.009	0.772±0.065
20	1.226±0.006	1.350±0.045	1.232±0.010	0.653±0.076
25	1.097±0.009	1.675±0.080	1.052±0.005	1.099±0.050
35	0.845±0.017	1.981±0.15	0.829±0.015	0.942±0.13

TABLE 13

SMOOTHED EQUILIBRIUM CONSTANTS FOR ACETIC ACID SYSTEM

T°C	$K_1 \times 10^3$ (mole/liter)$^{-1}$	$K_D \times 10^2$	Y-slope $\times 10^2$	K_h (mole/liter)$^{-1}$	$K_2 \times 10^{-3}$ (mole/liter)$^{-1}$
15	3.0±0.6	1.9±1.3	2.4±0.1	61±42	3.3±3.1
20	3.6±0.7	2.4±0.6	2.46±0.04	48±15	2.1±0.7
25	4.1±1.0	3.1±1.6	2.47±0.09	37±21	1.3±0.9
35	5.5±1.1	4.8±1.5	2.51±0.17	24± 9	0.6±0.2

ΔH_2 = -16 kcal./mole dimer

ΔH_h = -8.2 kcal./mole hydrate

TABLE 14

SMOOTHED EQUILIBRIUM CONSTANTS FOR BENZOIC ACID SYSTEM

T°C	K_1 (mole/liter)$^{-1}$	K_D	Y-slope $\times 10^{-3}$	K_h (mole/liter)$^{-1}$	$K_2 \times 10^{-3}$ (mole/liter)$^{-1}$
15	0.93±0.16	0.3±0.5	1.45±0.07	109±167	6.7±23
20	1.01±0.13	0.4±0.1	1.27±0.02	80±29	3.8±2.5
25	1.08±0.18	0.5±0.1	1.11±0.03	59±36	2.2±2.6
35	1.25±0.13	0.8±0.2	0.86±0.03	34±11	0.8±0.5

ΔH_2 = -9.4 kcal./mole dimer

ΔH_h = -10.2 kcal./mole hydrate

Validity of Equilibrium Constants

The uncertainty in each equilibrium constant shown in Tables 13 and 14 was calculated as the standard deviation. From the smoothing process a Y-slope and a Y-intercept (equal to K_D) were obtained at each temperature which defined a Y function linear with c_A^w,

$$Y = mc_A^w + b.$$

From the least square analysis of the experimental data the standard deviation in K_D was computed from the variance (53),

$$\sigma_b^2 = \frac{\sigma^2 \sum x_i^2}{\Delta}$$

in the Y-intercept (here equal to b) where

$$x_i = (c_A^w)_i$$

$$\Delta = N\sum_i x_i^2 - (\sum_i x_i)^2$$

N = number of determinations

and σ^2 equals the variance of experimental Y_i from the calculated Y. This method assumed the c_A^w were more reliably known than the Y_i.

The standard deviation in K_1 at each temperature was computed from the variance

$$\sigma_{K_1}^2 = \sum_i \left[K_1(\text{obs.}) - K_1(\text{calc.}) \right]_i^2 / N$$

Since the hydrate equilibrium constant, K_h, is related to the other constants by

$$K_1 = K_h c_w^o K_D$$

the fractional standard deviations, σ/K, are related by

$$(\sigma_{K_h}/K_h)^2 = (\sigma_{K_1}/K_1)^2 + (\sigma_{K_D}/K_D)^2$$

assuming that c_w^o is more reliably known than the K's. Thus, the standard deviation in K_h was obtained from the standard deviation in K_1 and K_D as described in the preceding paragraphs. The uncertainty in K_D made the largest contribution to the uncertainty in K_h.

The dimerization constant, K_2, is related to the other equilibrium constants by the relation

$$\text{Y-slope} = 2K_D^2K_2,$$

hence the fractional standard deviations are related by

$$(\sigma_{\text{Y-slope}}/\text{Y-slope})^2 = 2^2(\sigma_{K_D}/K_D)^2 + (\sigma_{K_2}/K_2)^2$$

The standard deviation in Y-slope (here = m) was obtained from the variance of m by

$$\sigma_m^2 = \frac{N\sigma^2}{\Delta}$$

where the symbols have the same meaning as in the first paragraph of this section. The fractional standard deviation in Y-slope made a very small contribution to the uncertainty in K_2 compared to the fractional standard deviation in K_D.

CHAPTER IV

DISCUSSION

The dimerization constants for acetic acid given in Table 13 are much larger than those obtained by the classical distribution method as anticipated. For example, Davies and Griffiths (21) obtained a value of K_2 = 151 (liter/mole) at 25°C compared to K_2 = 1300 (liter/mole) in this work. There are no reliable determinations of the dimerization constant of acetic acid in anhydrous benzene with which to make further comparisons.[1] The magnitude of the dimerization constants calculated here and the indicated uncertainties in these values illustrate the difficulties in obtaining reliable equilibrium constants by the distribution method unless accurate water solubility data at low concentrations are available.

The extent of dimerization of benzoic acid in apparently anhydrous benzene has been investigated by several methods. These results have been recomputed on a molar concentration basis and collected in Table 15. It is apparent that the dimerization constants reported here are much larger than is consistent with the van't Hoff isochore through the other values. If one assumes that the dimer hydrate as well as the

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[1]The dimerization constants obtained by Nagai and Simamura (54) by infrared spectroscopy in benzene are much too low.

TABLE 15

DIMERIZATION CONSTANTS FOR BENZOIC ACID IN BENZENE

T°C	Original Values		Association Constant, K_2	Method[h]
	Dissociation Constant, K,	Units[g]	(liter/mole)	
80.11	13.0×10^{-4}	mf	73.9[a]	bpe
65.36	8.04×10^{-4}	mf	117[a]	bpe
53.9	5.19×10^{-4}	mf	179[a]	bpe
56.5	6.33×10^{-3}	m/l	158[b]	vp
43.3	3.69×10^{-3}	m/l	271[b]	vp
32.5	2.30×10^{-3}	m/l	435[b]	vp
30.0	4.8×10^{-4}	mol/mv	190[c]	dc
33	------	---	524[d]	IR
80	-----	---	65.6[d]	bpe
35.0	-----	---	750[e]	D
25.0	-----	---	2200[e]	D
20.0	-----	---	3800[e]	D
15.0	-----	---	6700[e]	D
5.5	6.4×10^{-4}	molal	1750[f]	fpl

[a](27); [b](25); [c](58); [d](59);

[e]This work, assuming monomer monohydrate in organic phase;

[f](12);

[g]mf = mole fraction, m/l = mole/liter, mol/mv = mole/ molar volume solvent;

[h]bpe = boiling point elevation, vp = isopiestic, dc = dielectric constant, IR = infrared spectroscopy, D = distribution, fpl = freezing point lowering.

monomer hydrate of benzoic acid forms in benzene phase then smaller values of dimerization constants would result. This assumption finds some support in the observation that the Y-slope is always slightly less than the Z-slope. This effect would be the result of dimer monohydrate formation as pointed out by Christian, et al (42). If monomer and dimer monohydrates are formed the Z-slope becomes

$$K_D^2(2K_2 + 2K_{h2}c_w^o)$$

and the Y-slope becomes

$$K_D^2(2K_2 + K_{h2}c_w^o)$$

where K_{h2} is the dimer monohydrate formation constant. Thus, the dimer formation constant K_2 would be evaluated from the relation

$$2Y\text{-slope} - Z\text{-slope} = 2K_2K_D^2.$$

If Z-slope is greater than the Y-slope by a quantity d then,

$$2Y\text{-slope} - Z\text{-slope} = Y\text{-slope} - d.$$

However, if only the acid monomer monohydrate is formed

$$Y\text{-slope} = 2K_2K_D^2.$$

As a result, the value of K_2 obtained by assuming presence of both monomer and dimer monohydrates must be smaller than K_2 calculated by assuming only acid monomer monohydrate species. From unsmoothed data for benzoic acid a calculation of the dimerization constant assuming the formation of a dimer hydrate yields at 15°, 20°, 25°, and 35° the values 1680, 1390, 417, and 459 (liter/mole), respectively, and an enthalpy of dimerization of -17 kcal./mole. Although these values appear in better agreement with the work of others, the standard deviation in c_{AW}^o shown at the

base of Table 10 indicates that these data will not support a reliable calculation of dimer hydration constants. The difference between Z-slope and Y-slope is small and nearly equal to the uncertainty in the slopes. A more sensitive method for water solubility, or a solvent with higher water solubility, would be needed to investigate the existence of a benzoic acid dimer hydrate.

The heats of dimerization, ΔH_2, for both acetic and benzoic acids recorded here are more negative than most determinations in the literature. Pimentel and McClellan (55) tabulate values of $-\Delta H_2$ determined for acetic acid in the gas phase from 13.8 to 16 kcal./mole dimer with 14 kcal. indicated as the most reasonable value. If benzene behaves as an inert solvent for carboxylic acids one might expect the heat of dimerization to be close to the vapor phase value. That benzene is an inert solvent for carboxylic acids seems unlikely in view of heat of mixing data for hydroxylic and carbonyl compounds with benzene. The excess heat of mixing of benzene with methanol or ethanol is larger (more positive) than the excess heat of mixing of a hydrocarbon or carbon tetrachloride with the alcohol (56). This behavior has been interpreted as due to a more favorable interaction between the hydroxyl group of the alcohol and the pi-electrons of the benzene molecule than with the less polarizable electrons of the hydrocarbon. Thus, more hydrogen bonds are broken in the alcohol by dilution with benzene than with hydrocarbon resulting in a greater positive excess heat of mixing for the benzene-alcohol system. Similar results and interpretations for the acetone-benzene and acetone-carbon tetrachloride or cyclohexane systems are reviewed by Rowlinson (56) and by McGlashan (57). It seems likely from this evidence

that the carboxylic acid group must interact with benzene. Thus, the heat of dimerization should be slightly more positive than the heat of dimerization measured in the vapor phase, rather than nearly equal as found here. Similarly, Pimentel and McClellan (55) have tabulated $-\Delta H_2$ for benzoic acid in benzene and find values between 8 and 16 kcal./mole dimer compared to 19 kcal./mole computed here for monomer monohydrate assumption or about 17 kcal./mole if a dimer hydrate also is assumed. On the other hand, enthalpies of dimerization for acetic acid reported by Davies, et al (22) with the partition method in several solvents are rather small and thereby imply large interactions of the solvent with the acid. They reported $-\Delta H_2$ values for acetic acid of 8.98, 8.19, 7.56, 7.05, 5.02 and 5.25 kcal./mole of dimer in normal hexane, benzene, carbon tetrachloride, carbon disulfide, chlorobenzene, and nitrobenzene, respectively. Let the difference between 14 kcal./mole (gas phase value) and each of these represent twice the enthalpy change for solute interaction with the solvent. These heats of interaction, 2.5 to 4.5 kcal., seem unexpectedly large for such poor electron donors as hexane, carbon tetrachloride and carbon disulfide as solvents. The results of this dissertation indicate the assumption of Davies, et al (22) that water does not compete with the acetic acid in the organic phase is wrong and that conclusions based on their distribution data are probably in error for that reason.

A better interpretation of the water solubility and distribution data than that given above can be made if one assumes that a monomer dihydrate species is formed in benzene. The species present in benzene would be acid monomer (RCOOH), acid dimer $(RCOOH)_2$, acid monomer dihydrate

($RCOOH \cdot 2H_2O$), and water monomer. A plausible picture of the dihydrate might be a cyclic structure held together by hydrogen bonds between the two water molecules and the carboxylic group of the acid. Thus, the formal concentration of acid in the organic layer can be written with previously defined symbols of

$$f_A^o = c_A^o + 2c_{A_2}^o + c_{AW_2}^o \tag{8}$$

and the formal concentration of water in the organic layer can be written as

$$f_w^o = 2c_{AW_2}^o + c_w^o \tag{9}$$

where $c_{AW_2}^o$ represents the molarity of the acid monomer dihydrate. The equilibrium constants in dilute solution are

$$K_2 = \frac{c_{A_2}^o}{(c_A^o)^2}, \quad K_{AW_2} = \frac{c_{AW_2}^o}{c_A^o (c_w^o)^2}, \quad K_D = \frac{c_A^o}{c_A^w} \tag{10}$$

Combination of equations 8, 9, 10 leads to

$$Z = \frac{f_A^o}{c_A^w} = K_D + K_{AW_2} K_D (c_w^o)^2 + 2K_D^2 K_2 c_A^w \tag{11}$$

$$Y = \frac{f_A^o - (f_w^o - c_w^o)}{C_A^w} = K_D - K_{AW_2} K_D (c_w^{o2}) + 2K_D^2 K_2 c_A^w \tag{12}$$

where Z and Y functions are defined in terms of measurable concentrations. The assumption of acid monomer dihydrate species also yields a linear relationship between Y or Z functions and c_A^w as illustrated in Figures 1, 2, and 3. The slopes of the Y and Z plots are parallel as was the case

in the previous assumption. The equilibrium constants are evaluated from equations 11 and 12 by the relations

$$\text{Z-intercept} + \text{Y-intercept} = 2K_D$$

$$K_2 = \frac{2(\text{slope})}{(\text{Z-intercept} + \text{Y-intercept})^2}$$

$$(\text{Z-intercept} - \text{Y-intercept}) = 2K_{AW_2}K_D(c_w^o)^2$$

The distribution and water solubility data were smoothed in much the same manner as in the previous computations. The equilibrium between acid in the aqueous phase, A; water, W; and acid monomer dihydrate is

$$A(\text{aqueous}) + 2W(\text{aqueous}) = AW_2(\text{organic})$$

with the equilibrium constant,

$$K_3 = \frac{c_{AW_2}^o}{c_A^w}$$

in dilute solution where the activity of water was assumed to be unity. The numerator of K_3 is obtained from equation 9,

$$f_w^o - c_w^o = 2c_{AW_2}^o$$

just as for K_1 previously. Thus, the previously smoothed log K_1 values were reused since $2K_3 = K_1$.

However, the Y-intercept is no longer equal to an equilibrium constant or a product of equilibrium constants, hence it cannot be smoothed by the van't Hoff relation. The following outline indicates the steps in smoothing the data:

1. K_3 smoothed by use of linear relation between log K_3 and 1/T using weighted least square method previously given.

$$K_3 = \frac{\text{Z-intercept - Y-intercept}}{2}$$

2. From least squares line fit to raw data of Z versus c_A^w the Z-intercept at each temperature was obtained.
3. At each temperature a Y-intercept was obtained,
   Z-intercept (step 2) - (Z-intercept - Y-intercept) (step 1).
4. The sum Z-intercept (step 2) + Y-intercept (step 3) was smoothed by least square fit of the logarithm of this sum versus 1/T.
5. The sums at each temperature
   (Z-intercept - Y-intercept)(step 1) + (Z-intercept + Y-intercept) (step 4) = 2Z-intercept,
   and (Z-intercept + Y-intercept) (step 4) = 2Y-intercept were obtained.
6. A Z-slope at each temperature was computed from the least square parameters consistent with Z-intercept (step 5) and set equal to Y-slope.
7. The above slope was smoothed by least squares line through logarithm slope versus 1/T.

From these smoothed parameters a consistent set of equilibrium constants was obtained for the acetic acid and benzoic acid systems. These constants are displayed in Tables 16 and 17. The uncertainty in each constant tabulated is the standard deviation computed by the method described previously.

The attractiveness of the monomer dihydrate assumption should be noted. The uncertainties in computed equilibrium constants shown in

TABLE 16

SMOOTHED EQUILIBRIUM CONSTANTS FOR ACETIC ACID SYSTEM ASSUMING ACID MONOMER DIHYDRATE

T°C	Y-slope $\times 10^{-3}$	$K_D \times 10^3$	K_{AW_2} $(mole/liter)^{-2}$	$K_2 \times 10^{-3}$ $(mole/liter)^{-1}$
15	2.44±0.14	3.42±0.66	656±311	1.04±0.41
20	2.46±0.04	4.21±0.29	453± 81	0.69±0.10
25	2.47±0.09	5.16±0.81	310±130	0.46±0.15
35	2.50±0.17	7.55±0.79	160± 49	0.22±0.05

ΔH_2 = -13.8 kcal./mole dimer

ΔH_{AW_2} = -12.4 kcal./mole hydrate

TABLE 17

SMOOTHED EQUILIBRIUM CONSTANTS FOR BENZOIC ACID SYSTEM ASSUMING ACID MONOMER DIHYDRATE

T°C	Y-slope $\times 10^{2}$	K_D	K_{AW_2} $(mole/liter)^{-2}$	$K_2 \times 10^{-3}$ $(mole/liter)^{-1}$
15	1.421±0.034	0.79±0.14	870±210	1.13±0.39
20	1.243±0.026	0.92±0.11	590±100	0.74±0.17
25	1.089±0.052	1.06±0.25	400±110	0.49±0.23
35	0.851±0.018	1.38±0.11	200± 25	0.22±0.04

ΔH_2 = -14.3 kcal./mole dimer

ΔK_{AW_2} = -13.1 kcal./mole hydrate

Tables 16 and 17 are lower than those in Tables 13 and 14. The enthalpies of dimerization for acetic and benzoic acids are consistent with the expected interaction between the solvent and solute acids. The magnitudes of the benzoic acid dimerization constants compare better with the results of others found in Table 15. The benzoic acid dimer formation constants would not be improved by an additional assumption that an acid dimer monohydrate species is present. For the same reason given on page 43 of this dissertation the values of K_2 would be lowered further; hence they would diverge more from the values reported by others (collected in Table 15). In all, the data fit the assumption that an acid monomer dihydrate is formed in benzene better than the earlier interpretation.

CHAPTER V

CONCLUSIONS

The increase in solubility of water in benzene with concentration of carboxylic acids partitioned between water and benzene has been interpreted as the result of acid hydrate formation in benzene. The pertinent equilibrium constants have been calculated in two different ways: one assuming presence of acid monomer monohydrate as well as acid monomer, dimer, and water monomer, the other assuming the presence of acid monomer dihydrate as well as acid monomer, dimer, and water monomer. The experimental data give more consistent results if the dihydrate is assumed.

If the competition of water for the acid monomer is ignored, it is not possible to infer the extent of carboxylic acid dimerization in the organic phase. However, if hydration is assumed, the extent of solute association can be calculated from measurements of the total water in the organic phase and acid concentration in aqueous and organic phases for each partition experiment. As expected, acid dimer formation constants reported here are larger than those obtained by the traditional treatment of distribution data. However, there are no reliable values reported elsewhere for the association of acetic acid in anhydrous benzene for comparison. Dimer association constants of benzoic acid in benzene

computed on the assumption that an acid monomer monohydrate forms were very much larger than values obtained by other methods in anhydrous benzene. In principle, the values of these constants would become smaller if an acid dimer monohydrate also formed. However, the experimental data were not precise enough to permit this calculation. Dimer association constants for benzoic acid in benzene computed on the assumption that the only hydrate was the acid monomer dihydrate are comparable to values obtained by other methods. These constants cannot be improved by the concomitant formation of an acid dimer monohydrate. It does seem clear that the distribution method is a difficult technique for determining association constants unless all species in the organic phase can be determined.

Due to a large body of evidence that acetic acid dimerizes in water, it was necessary to correct formal aqueous acetic acid concentrations for dimer present. This has not been done before in distribution studies with the exception of Davies and Griffiths' work (21). The assumption of aqueous dimerization of acetic acid had a marked influence on the thermodynamic values computed from the data. If aqueous dimerization is ignored, the values of K_2 computed by the same method shown in Chapter III for 15°, 20°, 25°, and 35° are 490, 390, 314, and 208, respectively, and the resulting enthalpy change is $\Delta H_2 = -7.6$ kcal./mole. These values should be compared with those in Table 13. Acetic acid is not the only carboxylic acid to dimerize in water as has been shown by Davies and Griffiths (60) and Cartwright and Monk (50). If the distribution method is to be used to study association equilibria, the extent of solute association in the aqueous phase must be known.

The existence of carboxylic acid hydrates in wet benzene reported here has wider implications for other methods of measuring solute association. Meaningful self-association constants can be obtained only after detailed attention to the exclusion of water from such systems. It may be that unexpected water contamination is the major reason for the variable results reported throughout the literature by authors studying the same system.

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