[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Polymorphism of Solid Acetic Acid in the Acetic Acid–Benzene System[1]

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The freezing point curve for solutions of benzene in acetic acid has a pronounced nick in the region of 80% acetic acid by weight. This nick has been shown to result from a polymorphism of crystalline acetic acid. The polymorphism can be detected by X-ray diffraction and by dilatometry. The freezing point curve for the acetic acid–benzene system shows positive deviation from ideality over the entire range of concentrations.

Introduction

The solid–liquid relations of the acetic acid–benzene system have been studied by several investigators.[3] Close examination of their results reveals with striking consistency a marked deviation or nick in the freezing point curve at a concentration in the neighborhood of 80% by weight of acetic acid. Since there is poor agreement among the data of the individual investigators, the present study was undertaken to establish the freezing point curve of this system and to investigate the nick in it. Our experiments show that the nick is not due to a compound formation, as was first suspected, but to polymorphism of the solid acetic acid.

Experimental

Purification of Materials.—Eastman Kodak Co. acetic acid (99.9%, m.p. 16.6°) was purified by the procedure of Orton and Bradfield.[4] The purity of the acetic acid was then tested by taking its melting point according to the method of Harvey[5]; the melting point was found to be 16.60°.

Benzene was purified according to the procedure of Kraus and Fuoss[6] and the test of purity was a determination of its melting point by the method employed for acetic acid. The melting point was found to be 5.49°.

Spectroscopically pure hexane was prepared by the method of Castille and Henri.[7] This hexane was found to be nearly of the same transparency as distilled water in the range 2400–2700 Å.

Description of Apparatus.—The sensitivity of the freezing point of acetic acid to the presence of moisture[8] required the use of a special apparatus for the storage of the pure components and their low-pressure distillation into the ampoules in which the mixtures were prepared. Graduated pipets in the distillation train allowed close measure of the amounts of the components to be transferred to the ampoules.

Freezing Point Curve Determination.—The solubility curve of the system was obtained by determining the freezing points of an extensive series of mixtures covering the whole range of compositions, each mixture being prepared in a separate sealed ampoule. This determination was carried out in a bath with rising temperature; the temperature rise in the bath was controlled to approximately 0.001° per second. The ampoules were frozen and attached to a mechanical shaker and then immersed in this bath; the freezing point of the sample in the ampoule was the temperature at which no more solid could be observed. The temperature was recorded with a platinum resistance thermometer (N.B.S. certificate /986).

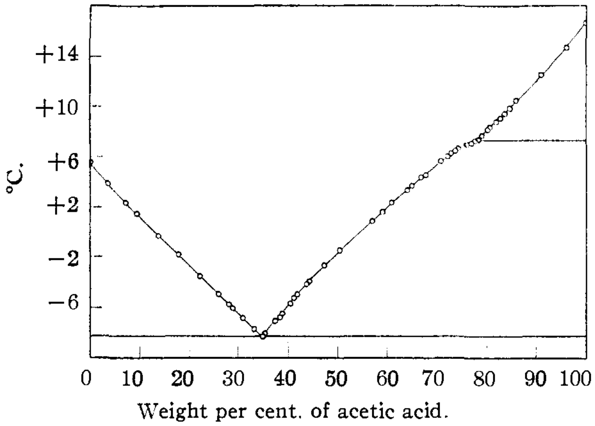

Fig. 1.—Freezing point diagram of the acetic acid–benzene system.

The ampoules were analyzed for acetic acid with carbonate-free sodium hydroxide; the benzene content of the sample

TABLE I

FREEZING POINTS OF THE ACETIC ACID–BENZENE SYSTEM[a]

Concn. of acetic acid, %	Freezing point, °C.	Concn. of acetic acid, %	Freezing point, °C.
0.0	5.49	63.9	3.35
3.6	3.94	65.0	3.75
7.3	2.32	65.1	3.75
9.3	1.54	66.7	4.37
13.8	−0.24	67.6	4.50
17.7	−1.74	70.8	5.60
22.6	−3.55	72.1	6.04
26.0	−4.87	72.2	6.12
27.9	−5.59	72.8	6.30
28.7	−5.88	73.4	6.45
31.0	−6.76	74.1	6.72
33.0	−7.66	76.2	6.94
34.7	−8.20	77.0	7.16
34.9	−8.13	78.1	7.25
37.4	−7.04	78.4	7.28
38.2	−6.78	78.8	7.66
38.7	−6.45	80.3	8.17
40.4	−5.68	80.6	8.36
41.2	−5.13	81.8	8.80
41.7	−4.90	82.6	9.14
43.6	−4.09	83.6	9.48
44.1	−3.96	84.6	9.89
47.2	−2.64	84.6	9.92
49.0	−1.92	85.9	10.51
50.4	−1.42	91.0	12.53
56.7	0.83	96.2	14.62
59.0	1.63	100.00	16.60
60.8	2.35		

[a] The concentrations are expressed in weight per cent. acetic acid.

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[1] Based on a dissertation submitted in April, 1952, by Willy Tan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Harrison Scholar, 1951–1952.

[3] "International Critical Tables of Numerical Data," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 108.

[4] J. P. Orton and H. F. Bradfield, *J. Chem. Soc.*, **125**, 960 (1924).

[5] C. O. Harvey, *Analyst*, **51**, 238 (1926).

[6] C. A. Kraus and R. M. Fuoss, THIS JOURNAL, **55**, 21 (1933).

[7] A. Castille and V. Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

[8] W. R. Bousfield and T. M. Lowry, *J. Chem. Soc.*, **99**, 1432 (1911).

was estimated by difference. To avoid loss during the operation, the samples were solidified before the ampoules were broken.

The temperature–composition diagram of the system is shown in Fig. 1 and the data for this freezing point curve are given in Table I.

Investigation of Compound Formation.—For detection of compound formation by the thaw-point values, a series of mixtures was prepared, ranging from 80–90% by weight of acetic acid. Capillaries open on both ends were filled with the mixtures, the capillaries were then sealed in the middle and separated. The mixtures in the capillaries were frozen and the thaw-point of each was determined.

The method of analyzing the solid by the addition of a third component[9] was adopted to determine the composition of the solid which separates out in the region where the nick in the freezing point curve was observed. Hexene-1 and *n*-hexane were used as third components. The system which had hexene-1 as third component was analyzed for both acetic acid and hexene-1, the Koppeschaar solution[10] being used in the latter determination; the system with *n*-hexane was examined for its benzene content by ultraviolet spectroscopy using a Beckman Model DU spectrophotometer and the amount of acetic acid was measured by titration with sodium hydroxide.

A modified Seemann–Bohlin X-ray camera was used for study of the several solid phases encountered. The specimen holder was a copper bar with a drilled hole for a chromel–alumel thermocouple whose junction was located close to the focal circle of the camera. The copper bar was cooled by a jacket, temperature control being obtained by regulation of the flow of refrigerant through this jacket.

Thin layers of pure acetic acid and benzene as well as mixtures of acetic acid and benzene with compositions in the critical region were frozen on the specimen holder at 1–2° and exposed to the X-ray beam for 40 minutes.

Detection of Polymorphism in Solid Acetic Acid.—X-Ray diffraction patterns[11] of solid acetic acid were taken above and below the temperature at which the nick in the freezing point curve was observed.

In the dilatometric study, the bulb was partially filled with solid acetic acid and the remaining space was occupied by triple distilled mercury; in order to bring the mercury to a convenient starting place in the capillary, a mercury levelling device was connected to the dilatometer between the bulb and the capillary. The rate of temperature increase or decrease in the bath surrounding the bath was regulated to about 0.05° per minute. The mercury level in the capillary and the bath were recorded at frequent intervals and the experiments were carried out with both rising and falling temperatures.

Results and Discussion

The freezing point curve in Fig. 1 shows a pronounced nick at 7.28° and a concentration of 78.4% by weight of acetic acid. It was thus established that this phenomenon is a characteristic property of the system and was not caused by impurities. Normally a behavior such as this may be due either to formation of a compound with an incongruent melting point or to the existence of polymorphism in the solid component.

The results of the thaw-melt method, the analyses of the solid phase and X-ray diffractions indicate the absence of compound formation. In the thaw-melt method the thaw point was the same as the eutectic temperature for all the different mixtures. The composition of the solid in the critical region was found to be pure acetic acid within the experimental error. The results of these analyses are shown in Tables II and III. The X-ray patterns of the different mixtures correspond to those of the pure acid at the same temperature. The data obtained in this study are recorded in Table IV. The similarity between the X-ray diffraction patterns of acetic acid and benzene is striking.

TABLE II

ANALYSIS OF THE SOLID MATERIAL WITH HEXENE-1 AS THE THIRD COMPONENT

Solid composition, 99.8% acetic acid by weight

Initial liquid weight ratios		Final liquid weight ratios	
Acetic acid	4.712	Acetic acid	4.136
Benzene	1.317	Benzene	1.316
Hexene-1	1.000	Hexene-1	1.000

TABLE III

ANALYSIS OF THE SOLID MATERIAL WITH *n*-HEXANE AS THE THIRD COMPONENT

Solid composition, 98.8% acetic acid by weight

Initial liquid weight ratios		Final liquid weight ratios	
Acetic acid	3.203	Acetic acid	2.955
Benzene	0.538	Benzene	0.535
n-Hexane	1.000	*n*-Hexane	1.000

TABLE IV

X-RAY SPECTRA OF ACETIC ACID AND BENZENE

Acetic acid				Benzene at 1–2°			
Observed at 1–2°		Observed at 8–9°		Observed		Calculated[a]	
d/n	Intensity	*d/n*	Intensity	*d/n*	Intensity	*d/n*	*n*
1.412	m	1.412	w	1.412	m	1.420	4
1.341	w	1.341	ww	1.216	s	1.215	2
1.270	w	1.270	ww	1.163	s	1.167	6
1.246	w	1.246	ww	0.918	w	0.915	2
1.216	s	1.216	ww	.895	w	.904	5
1.163	m	1.163	ww	.815	w	.810	3
1.142	w	1.142	ww				
1.126	ww	1.126	ww				
0.918	w	0.815	ww				
.895	w						
.815	w						

[a] E. D. Eastman, THIS JOURNAL, **46**, 917 (1924).

In the X-ray studies of pure acetic acid at temperatures above and below the nick, it was observed that in the higher temperature pattern the lines corresponding to *d/n* 0.895 and 0.918 were missing even though the exposure times were made 50% greater for these crystals. The graphical representations of the dilatometric studies in Figs. 2 and 3 show an inflection point at 7.4° with rising temperature and 7.3° with falling temperature.

The discrepancies between the present freezing point curve and that given in the "International Critical Tables of Numerical Data" can be explained by improved methods of preparation and purification of the components and also by minimizing the effect of moisture in the system.

If a comparison is made between our experimental data and theoretical values it can be shown that the experimental solubility curve exhibits a positive deviation with respect to the ideal behavior if the concentrations are expressed in mole per cent, and the assumption is made that the acetic acid exists

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(9) W. D. Bancroft, *J. Phys. Chem.*, **6**, 178 (1902).

(10) H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

(11) With the assistance of Dr. E. R. Nixon the possibility of examining the polymorphism of solid acetic acid by its infrared spectrum was also attempted. Unfortunately it was discovered that this substance absorbs too strongly in the region 3–15μ, and was thus unsuitable for a study of this nature with the apparatus available.

as double molecules.[12] From molecular weight determinations for acetic acid by the cryoscopic method with benzene as solvent[13,14] and the study of the Raman spectra of aqueous acetic acid solutions,[15] it is apparent that acetic acid at concentrations higher than 20% exists as dimers.

Compound formation between solvent and solute is the only cause of negative deviation from ideality and since a positive deviation was observed, this evidence also favors the absence of compound formation.

Recent studies of the polymorphism of stearic acid[16] and palmitic acid[17] show a similarity of the polymorphism of those acids to that revealed here for acetic acid. In fact, a plot of the dilatometric data of Ward and Singleton[17] for palmitic acid gives a curve similar to those of Figs. 2 and 3 for acetic acid, and shows a transition point in the neighborhood of 25.5°.

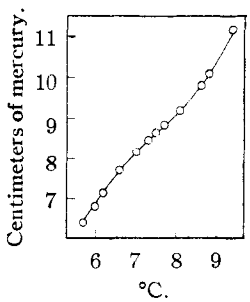

Fig. 2.—Dilatometry with rising temperature.

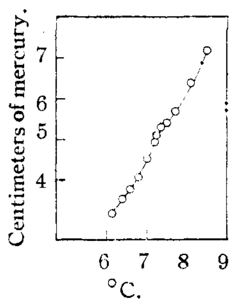

Fig. 3.—Dilatometry with falling temperature.

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[12] W. W. Lucasse, R. P. Koob and J. G. Miller, *J. Chem. Education*, **21**, 454 (1944).

[13] J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).

[14] C. R. Bury and H. O. Jenkins, *J. Chem. Soc.*, 688 (1934).

[15] S. I. Leitman and S. A. Ukholin, *J. Chem. Phys.*, **2**, 825 (1934).

[16] W. S. Singleton, T. L. Ward and F. G. Dollear, *J. Am. Oil Chemists' Soc.*, **27**, 143 (1950).

[17] T. L. Ward and W. S. Singleton, *J. Phys. Chem.*, **56**, 696 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN AND THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Diffusion Coefficients of Certain Metals in Mercury

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A discussion of the electrochemical methods of determining the diffusion coefficients of individual metals through mercury is presented. Diffusion coefficient data for the metals zinc, cadmium, lead, copper, thallium, tin and bismuth are presented. Diffusion coefficients for tin and bismuth, derived from polarographic data, were found to be 1.68×10^{-5} and 0.99×10^{-5} cm.^{2} sec.$^{-1}$, respectively. The nature of dilute amalgams is examined, and evidence of compound formation in dilute mercurial solution between mercury and the metals copper and bismuth is presented.

Introduction

One approach to a study of the diffusion of metals in mercury is through the measurement of diffusion coefficients. According to Smith[1] the diffusion coefficient D can be defined by the formula

$$dS = -Dq\frac{dc}{dx}\,dt$$

in which dS is the quantity of the diffusing substance which passes a given point in the time dt through a cross-section q of a diffusion cylinder under the influence of the concentration gradient dc/dx.[2]

All experimental methods used to determine diffusion coefficients hinge on the various possibilities for the determination of concentration changes. In the case of amalgams the possibilities are not so numerous as they are with aqueous solutions, since all the optical methods which have been applied successfully to such solutions cannot be used. Although chemical analysis and density determinations can be used for amalgams, the principal methods are electrochemical in nature. The purpose of this paper is to discuss briefly these electrochemical methods with particular emphasis on the polarographic method used by the authors and to examine the nature of dilute amalgams in the light of diffusion coefficient data.

Methods of Measuring Diffusion Coefficients

E.m.f. Methods.—The diffusion coefficients of cadmium, zinc and lead in mercury were determined by Meyer[3] who made the amalgam the anode of a small cylindrical cell. By electrolysis the metal in the amalgam was put into solution from the under base of the amalgam. The rate of diffusion of the metal atoms to the under surface of the amalgam was determined by measuring the potential between the upper region of the amalgam and a constant amalgam reference electrode at various time intervals. A disadvantage of Meyer's method is the fact that an accurate determination of the height of the small amalgam column is very difficult. Here is a serious source of error, since in the equation used for the calculation of D the height of the column appears as h^2.

Meyer's student von Wogau[4] determined the diffusion coefficients of a number of individual metals in mercury employing a method analogous to that of Graham.[5] A cylindrical column of mercury was covered over by the amalgam of the metal being investigated whereupon the diffusion

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[1] G. McP. Smith, THIS JOURNAL, **36**, 847 (1914).

[2] A more critical definition of diffusion coefficient is given by G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

[3] G. Meyer, *Ann. physik. Chem.*, **61**, 225 (1897).

[4] M. von Wogau, *Ann. physik*, **23**, 345 (1907).

[5] T. Graham, *Ann. chem. pharm.*, **121**, 1 (1862).