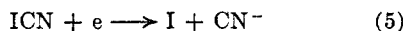


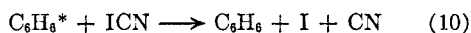
then would arise since at low concentrations of ICN the reaction



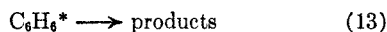
could not compete so effectively with the reaction



If processes of energy transfer are involved, then this implies that the reaction



is in competition with a reaction

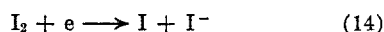


It is difficult to state with precision the processes responsible for I_2 production. The results obtained in this work do indicate, however, that reactions other than those normally invoked in the radiation chemistry of benzene must be taking place. It then would appear that the degree of radiation inertness of benzene is very dependent on the nature of the scavenger used.

Since the ionization potential of benzene is not very different from that of hexane, it might be expected that the radiation yields of primary products, *e.g.*, ions and excited molecules, are not very different in the two species. That there is considerable difference in the net decomposition has been attributed to the fact that energy can be distributed readily throughout the benzene ring, thus reducing the localization of energy in any particular bond, and hence the possibility of rupture of that bond. In principle, it ought to be possible,

by the choice of suitable scavengers, to measure the yield of primary products.

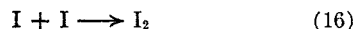
It is unlikely that iodine would be suitable in detecting ionic precursors since even if an electron were captured



charge neutralization with the benzene ion would lead to



In so far as the iodine atom is chemically fairly unreactive, dimerization to give I_2 would occur



so that no net decomposition would be observed. The effect of high concentrations of iodine has been examined but little published data are available. The system appears to be complex.¹⁰

It has been claimed that CF_4 reacts with some ionic intermediate in the radiolysis of benzene- CF_4 solutions,¹¹ and this might be a promising system for further investigation. The essential characteristic of a suitable scavenger, as ICN, is that processes of charge capture, etc., should lead to the formation of a reactive radical which results in some net decomposition.

Thanks are due to the Bio-organic chemistry group of the Lawrence Radiation Laboratory, University of California, for the irradiation facility and to Dr. W. M. Garrison for valuable discussion during the course of this work.

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SOLID-LIQUID PHASE EQUILIBRIA AND SOLID COMPOUND FORMATION IN ACETONITRILE-AROMATIC HYDROCARBON SYSTEMS

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Solid-liquid phase diagrams were obtained from time-temperature cooling curves for the binary systems containing acetonitrile with benzene, toluene and *p*-xylene. A solid phase compound with an incongruent melting point and a composition of one acetonitrile to two benzene molecules was identified in the first of these systems. A number of other acetonitrile-aromatic compounds were screened for possible compound formation. No evidence for 1:2, 1:1 or 2:1 solid compounds was found for acetonitrile with *o*-xylene, *m*-xylene, pseudocumene, anisole, chlorobenzene, nitrobenzene or α, α, α -trifluorotoluene. A solid phase transition in acetonitrile is reported, and the freezing point of acetonitrile is compared with a wide range of values found in the literature.

Prausnitz and Anderson¹ have measured volume changes on mixing for the system acetonitrile-benzene and found an "S" shaped volume change *vs.* composition curve, typical of systems that form stable complexes in the liquid state. They also pointed out that the freezing point measurements of Joukovsky² indicate that a solid phase compound may form in this system. Although Joukovsky reported no compound, peculiarities in the graph of his freezing point *vs.* composition data suggest that had the data been more detailed a compound might have been found.

These results suggested an investigation of

compound formation in acetonitrile-aromatic compound systems in general. This paper reports the results of an investigation of the solid-liquid phase equilibrium properties of several such systems.

Experimental

Chemicals.—Reagent grade benzene and *p*-xylene were rapidly distilled over sodium metal. The center third cut of each distillation then was fractionally crystallized several times. Phillips Petroleum research grade toluene and Eastman spectro grade acetonitrile were used without special purification. Calculations made on the change of the melting point with fraction melted showed the liquid soluble-solid insoluble impurities to be 0.03 mole % in the benzene, 0.05 mole % in the *p*-xylene, 0.05 mole % in the toluene and 0.20 mole % in the acetonitrile.

A number of other chemicals were used in only a few ex-

(1) J. M. Prausnitz and R. Anderson, private communication.

(2) N. I. Joukovsky, *Bull. soc. chim. Belges*, **43**, 397 (1934).

ploratory measurements to check on the presence or absence of compound formation. These were either reagent or research grade chemicals that were used without further purification.

Temperature Scale.—Temperatures were measured with a Leeds and Northrup calibrated strain-free platinum resistance thermometer in combination with an L. & N. high precision resistance recorder. The calibration was checked against the ice point (273.150°K.); the freezing points of toluene (178.16°K.), mercury (234.29°K.), *o*-xylene (247.97°K.), benzene (278.683°K.) and *p*-xylene (286.41°K.); the transition point of sodium sulfate decahydrate (305.534°K.); and two Bureau of Standards calibrated mercury thermometers (298.15 and 323.15°K.). All melting points were corrected for impurities by using the intercept of the plot of temperature of melting *vs.* the reciprocal of the fraction melted as the true melting point of the compound.

On the basis of these measurements a small linear correction was made on the calibration, after which the Callendar equation gave the correct temperature at the previously mentioned points to within 0.01° , with the exception of *o*-xylene and toluene, which were within 0.05° . On the basis of these checks, the thermometer calibration is considered accurate to at least 0.05° over the range of 175 – 325°K.

The calibration was rechecked periodically at the mercury freezing point, ice point, and sodium sulfate transition temperature. No changes were found in the resistance of the thermometer even after six months of almost constant cooling and warming.

Apparatus.—The freezing point apparatus was for the most part conventional. Essentially it consisted of a 2.5×28 cm. Pyrex tube sealed inside a 5×30 cm. tube, with the outer jacket thus formed connected to a 10^{-6} mm. pressure vacuum line. Provision was made to introduce varying amounts of nitrogen gas into the jacket to act as a heat exchanger when desired.

The resistance thermometer sat in a well that went down through the center of the freezing tube. The lower four inches of the well were made of gold-plated copper tubing for rapid heat exchange between the sample and the thermometer; the upper part of the well was made of glass to slow down exchange of heat between the room and the thermometer, and also to allow the upper end of the well to be sealed into a ground glass cap that topped the freezing tube. The exchange fluid in the freezing tube was 2-methylpentane.

Stirring was accomplished with a motor-driven stainless steel coil that moved vertically in the freezing tube at approximately 100 strokes per minute. The stirring wire entered the freezing tube through a section of glass capillary tube sealed into the cap. A flexible plastic sleeve was used to seal the opening between the cap and stirrer, preventing evaporation of sample from, and condensation of moisture into, the sample.

Liquid nitrogen was used as the coolant. Time-temperature cooling curves and occasionally time-temperature melting curves were measured. The solutions generally supercooled, and their freezing points were obtained by extrapolation of the time-temperature curves back across the super-cooled region.

The accuracy of the freezing points of the solutions are estimated to be within $\pm 0.1^{\circ}$. Several of the points along the invariant temperature lines—those with compositions that differed greatly from the eutectic or meritectic composition—had to be obtained without stirring; the uncertainty in such points is considered to be $\pm 1^{\circ}$.

Results

Acetonitrile - Aromatic Systems.—Solid - liquid equilibria data were obtained over the entire range of composition for the three binary systems acetonitrile-benzene, acetonitrile-toluene and acetonitrile-*p*-xylene. The freezing point data for the acetonitrile-benzene system are recorded in Table I, and the phase diagram for this system is shown in Fig. 1. The significant feature in the phase diagram is the meritectic line at $249.15 \pm 0.10^{\circ}\text{K.}$, indicating the presence of a solid phase compound with an incongruent melting point.

The composition of the compound was deter-

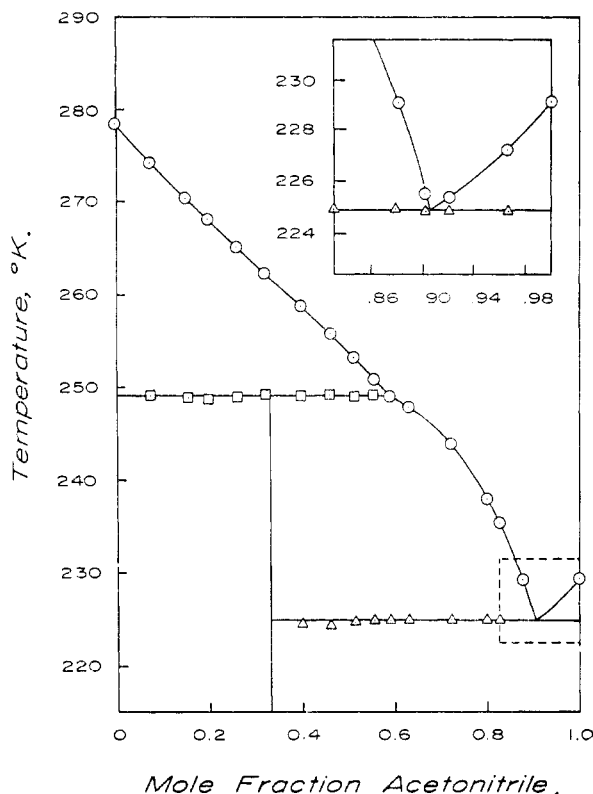


Fig. 1.—Phase diagram of acetonitrile-benzene.

TABLE I
EQUILIBRIUM TEMPERATURES FOR PHASE CHANGES IN THE
SYSTEM ACETONITRILE-BENZENE

Mole fraction acetonitrile	Freezing point, $^{\circ}\text{K.}$	Meritectic point, $^{\circ}\text{K.}$	Eutectic point, $^{\circ}\text{K.}$
0.0000	278.66
.0746	274.38	249.27 ^a	...
.1541	270.55	248.95 ^a	...
.2009	268.08	248.81 ^a	...
.2626	265.15	248.97 ^a	...
.3231	262.28	249.19	...
.3993	258.58	249.19	224.48 ^a
.4607	255.73	249.16	224.25 ^a
.5134	253.14	249.05	224.70
.5574	250.77	249.10	224.73
.5933	249.12	...	224.83
.6305	247.49	...	224.81
.7204	243.80	...	224.83
.8008	237.75	...	224.82
.8256	235.28	...	224.83
.8786	229.09	...	224.83
.8983	225.48	...	224.82
.9200	225.35	...	224.80
.9612	227.18	...	224.72
1.0000	229.30
0.903 = Eutectic composition	Best 249.15 value: $\pm 0.1^{\circ}\text{K.}$	224.82	$\pm 0.1^{\circ}\text{K.}$

^a Less accurate values obtained without stirring.

mined by plotting the length of the meritectic halt *vs.* mole fraction and extrapolating the two straight lines obtained to their point of intersection. The composition at this point, which is the composition of the compound, is 0.336 mole fraction acetonitrile, or on a molecular ratio basis, two molecules of benzene to one of acetonitrile.

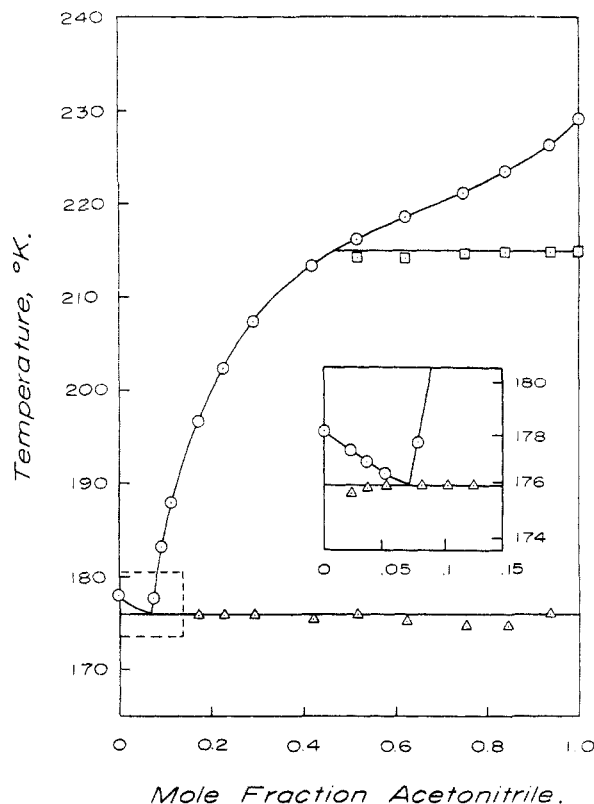
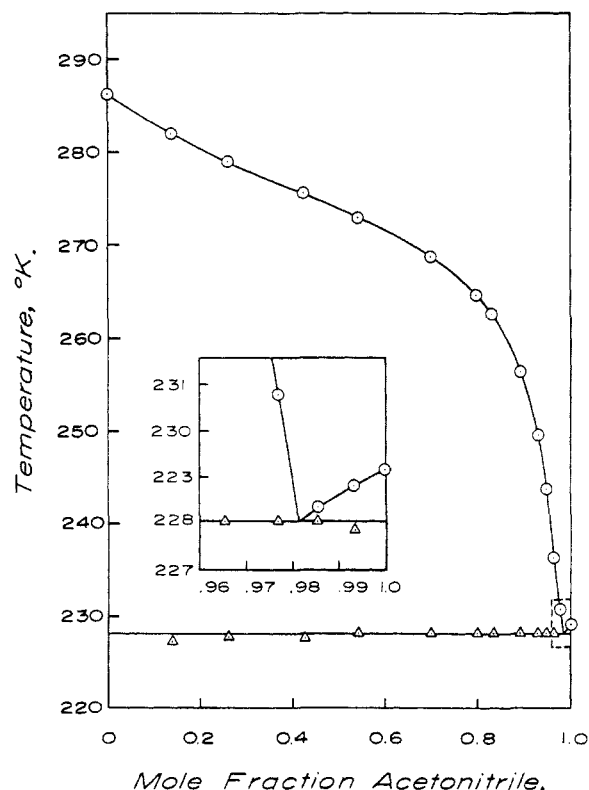


Fig. 2.—Phase diagram of acetonitrile-toluene.

Fig. 3.—Phase diagram of acetonitrile-*p*-xylene.

The freezing point data for acetonitrile-toluene and acetonitrile-*p*-xylene systems are recorded in Tables II and III. The phase diagrams for these systems are shown in Figs. 2 and 3. Both systems

were investigated very carefully around the compositions corresponding to 1:1 and 2:1 compounds. Very slow cooling, very rapid cooling, and vigorous stirring all were tried. No evidence of compound formation was observed in either system.

TABLE II
EQUILIBRIUM TEMPERATURES FOR PHASE CHANGES IN THE
SYSTEM ACETONITRILE-TOLUENE

Mole fraction acetonitrile	Freezing point, °K.	Solid phase transition in acetonitrile, °K.	Eutectic point, °K.
0.0000	178.09
.0220	177.30	...	175.6
.0317	176.92	...	175.8
.0481	176.39	...	175.8
.0757	177.65	...	175.8
.0953	183.13	...	175.9
.1157	187.78	...	175.9
.1708	196.57	...	175.9
.2297	202.37	...	175.9
.2929	207.40	...	175.9
.4199	213.29	...	175.5
.5180	216.12	214.0	175.8
.6221	218.52	214.1	175.1
.7510	221.16	214.5	174.6 ^a
.8405	223.23	214.9	174.6 ^a
.9357	226.18	214.8	175.9 ^a
1.0000	229.30	215	...
0.073 = Eutectic composition			
Best value:		215	175.8 ± 1 °K. 0.2° K.

^a Less accurate values obtained without stirring.

TABLE III
EQUILIBRIUM TEMPERATURES FOR PHASE CHANGES IN THE
SYSTEM ACETONITRILE-*p*-XYLENE

Mole fraction acetonitrile	Freezing point, °K.	Eutectic point, °K.
0.0000	286.39	...
.1437	282.11	227.39 ^a
.2608	278.96	227.75 ^a
.4278	275.36	227.69 ^a
.5407	272.92	228.07
.7015	268.80	228.10
.8020	264.60	228.10
.8336	262.54	228.10
.8930	256.39	228.10
.9313	249.46	228.09
.9492	243.72	228.10
.9655	236.25	228.09
.9770	230.8	228.09
.9852	228.38	228.04
.9935	228.81	227.87 ^a
1.0000	229.30	...
0.981 = Eutectic composition		Best value: 228.09 ± 0.10 °K.

^a Less accurate values obtained without stirring.

The acetonitrile-toluene system shows a solid transition in the acetonitrile at 215 ± 1 °K. The large uncertainty in the transition temperature occurs because the phase that is stable at the higher temperature supercooled considerably, and even after conversion to the second phase started the rate was slow, requiring several minutes for completion. To obtain a more accurate value, the transition temperature would need to be measured

in an apparatus in which the sample could be better thermally insulated from its surroundings.

Exploratory measurements were made on mixtures of several other aromatic hydrocarbons with acetonitrile to check on the possibility of compound formation. The procedure consisted of obtaining freezing curves at several compositions. If all curves showed the same eutectic temperature with no other temperature halts or irregularities, it was concluded that no solid compound existed in the range between the extreme compositions studied. The results are summarized in Table IV.

TABLE IV
ACETONITRILE-AROMATIC SYSTEMS SCREENED FOR SOLID PHASE COMPLEXES

Aromatic component	Range of composition investigated, mole fraction acetonitrile
<i>o</i> -Xylene	0.30-0.69
<i>m</i> -Xylene	.31- .70
Pseudocumene	.31- .94
Anisole	.37- .75
Chlorobenzene	.27- .66
Nitrobenzene	.25- .79
α,α -Trifluorotoluene	.25- .74

The hydrocarbons were chosen so as to have a variety of geometrical structures and both low and high electron density in the ring. The range in composition investigated included compositions corresponding to 1:2, 1:1 and 2:1 complexes.

No evidence for solid state compound formation was found in any of these mixtures.

Freezing Point of Acetonitrile.—We obtained a value for the freezing point of pure acetonitrile of 229.30 ± 0.05 °K. Eight measurements were made at varying rates of cooling and on samples of acetonitrile from two different lot numbers. The measurements all agreed within 0.02° . This freezing point may be compared with the following values found in the literature: 228.25 ,³ 228.15 ,² 227.95 ,⁴ 227.43 ⁵ and 229.28 .⁶

The agreement with the last value, obtained by Mathieu,⁶ is satisfying. The fact that some of the other values are more than a degree and a half lower is unusual. The solid transition at lower temperatures suggests the possibility that some of the others may have measured a metastable freezing point. However, all attempts by us to supercool the acetonitrile to obtain the metastable freezing point failed.

Acknowledgment.—The authors gratefully acknowledge the support given this project by the National Science Foundation and Research Corporation of America.

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(5) R. R. Dreisbach, "Physical Properties of Chemical Substances," Dow Chemical Co., Midland, Michigan, 1952.

(6) M. P. Mathieu, *Acad. roy. Belg., Classe sci. Mem. Collection in-8*, **28**, No. 2 (1953).

LEAST SQUARES COMPUTER CALCULATIONS OF CHLORIDE COMPLEXING OF TIN(II), THE HYDROLYSIS OF TIN(II), AND THE VALIDITY OF THE IONIC MEDIUM METHOD¹

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The stability constants of the chloro-complexes of Sn^{+2} have been redetermined at 25° for a perchlorate medium at an ionic strength of 3 by e.m.f. measurements using a cell with a tin amalgam electrode. A computer program which permits the assignment of weights to all experimentally determined quantities is outlined and applied to the computation of the constants. The values for the cumulative stability constants are $\beta_1 = 15.12 \pm 0.25 M^{-1}$, $\beta_2 = 54.9 \pm 2.1 M^{-2}$, $\beta_3 = 47.3 \pm 4.2 M^{-3}$ (standard errors). No evidence was found for mixed chlorohydroxo-complexes in solutions with $[\text{H}^+]$ from 0.05 to 0.50 M , nor was there any evidence for polynuclear complexes involving chloride bridges.

Introduction

Recently Rabideau and Moore² have presented results of least squares calculations of the stability constants of the chloro-complexes of Sn^{+2} using the data of Duke and Courtney³ and Vanderzee and Rhodes.⁴ The first set of data was satisfactorily fitted by three constants for the mono-, di- and trichloro-complexes instead of the four constants given in the original paper. These values apply to

(1) This work was supported, in part, by the United States National Science Foundation under grant NSF-14173.

(2) S. W. Rabideau and R. H. Moore, *J. Phys. Chem.*, **65**, 371 (1961).

(3) F. R. Duke and W. G. Courtney, *Iowa State Coll. J. Sci.*, **24**, 397 (1950).

(4) C. E. Vanderzee and D. E. Rhodes, *J. Am. Chem. Soc.*, **74**, 3552 (1952).

a medium 2 M in $[\text{H}^+]$ with an ionic strength of 2.03. The total tin(II) concentration was not held constant during the measurements. In the studies of Vanderzee and Rhodes, the total tin(II) concentration was held constant at approximately 0.01 M in a medium with an ionic strength of 3.00. The least squares fitting was carried out with data for solutions with 0.100 and 0.500 M $[\text{H}^+]$ and for measurements at four different temperatures. The data for each different temperature and $[\text{H}^+]$ were fitted with three parameters corresponding to the coefficients in the power series expansion

$$\exp(-nFE/RT) = 1 + A_1[\text{Cl}^-] + \cdots + A_n[\text{Cl}^-]^n$$

If only mononuclear chloro-complexes are formed, the parameters are the stability constants; how-