after each heating period. In the regions of the peaks for both the fusion of water and the transition, temperature drifts were present after equilibration for as long as 24 hours.

Energy values for the fusion of ice and for the transition peak were determined by heating from a reproducible state below the peak to a reproducible state above the peak with appropriate integration of an equation for the "normal" heat capacity. A cubic equation for "normal" heat capacity was derived by the method of least squares from 80 points measured between 238° and 280° K. and 5 points above the transition peak between 312.5° and 318.9° K. The average deviation between the observed values and those calculated from the equation was 0.16%. The average of three measurements of the heat of fusion of ice (3.18, 2.79, 2.86) was 2.94 calories per sample. Only one measurement was made of the transition peak energy before the sample decomposed—141.2 calories per sample or 583 cal. mole^{-1}

In a final series of measurements of the heat capacity in the region above the transition peak, an exothermic reaction began spontaneously at 311.5° K. Two attempts to measure the heat capacity were unsuccessful, and the heating effect persisted and was greater at 318° K. Adiabatic conditions were maintained by automatic shield control and the self-heating rate was measured over 26 hours. The calorimeter was then cooled to 298° K. and the rate of heating was measured over 23 hours, then for 16 hours at 273° and at 251° K. The rate of heating was quite low at 273° and 251° K., but increased when the sample was warmed, indicating that, after initiation, the reaction could be slowed at low temperatures but would resume its original rate upon warming. From the known heat capacity of the calorimeter and the measured self-heating rates, values were calculated for the rate of heat generation as a function of temperature on the assumption that the rate of heat generation was proportional to the rate of reaction. With these values (cal. min.$^{-1}$) as specific rate constants, an Arrhenius plot indicated the energy of activation to be about 17 kcal. mole^{-1}.

When the heating-rate measurements were completed, the calorimeter was cooled to 77° K. The heat capacity was then significantly different from that of the original sample. The exothermic reaction was assumed to be hydrolysis of the hexaamide by the hydration water to phosphoryl triamide and its degradation products, ammonium orthophosphates.

In an effort to define the exothermic reaction in which NH_3, and almost certainly water, would be released, the calorimeter was cooled to 150° K. to freeze any possible combination of NH_3 and H_2O (*4*). The heat capacity of the altered material, measured from 150° to 279° K., was lower below 193° K. than that of the original material, moderately higher above 193° K., and showed a large fusion peak (251 cal. per sample or 1037 cal. per mole) extending from about 250° to 281° K., with a maximum at 263° K. Taking the peak maximum of 263° K. as the fusion temperature of a mixture of H_2O and NH_3, the phase diagram (*4*) indicates the composition to be 90% water and 10% ammonia, corresponding to 2.84 grams of water and 0.32 gram of ammonia liberated by the exothermic reaction. The corresponding quantities, determined later by chemical analysis, were in reasonably good agreement, 2.47 grams of H_2O and 0.60 gram of NH_3.

When the calorimeter was opened the sample was moist, had a strong odor of NH_3, and was blue-green from reaction of the liberated NH_3 and H_2O with exposed surfaces of the copper calorimeter. A portion of the sample material was washed with anhydrous methanol to remove surface NH_3, H_2O, and Cu salts. The washed solids contained 39.1% P and 52.8% N, close to the composition of the anhydrous hexaamide.

Petrographic and x-ray examinations of the material before and after washing with anhydrous methanol showed that it was no longer the monohydrate, but the anhydrous material. Paper chromatography showed the presence of a significant amount of phosphoryl triamide, indicating that the reaction was hydrolysis of the hexaamide by the freed hydrate water, as reported by Dostal *et al.* (*1*). The reaction is of interest in the chemistry of the phosphonitrilic hexaamide, but does not affect the results obtained for thermal values of the monohydrate, because all heat capacity measurements reported were measured before the reaction occurred.

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RECEIVED for review September 10, 1969. Accepted December 8, 1969.

Solubility of C_9 and Two C_{10} Aromatic Hydrocarbons in Liquid CO_2

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Solubilities of all C_9 and two C_{10} aromatic hydrocarbons in liquid CO_2 have been measured at temperatures from –25° to –65° C. Most of the binary systems studied exhibit a region where two immiscible liquid phases are formed with an upper critical solution temperature.

THE SOLUBILITY of the C_6-C_8 aromatic hydrocarbons in liquid CO_2 has been described (*2*). The same apparatus and measurement technique are used. Measurements are carried out in a calibrated 7.5-inch-long, 1-inch-i.d. Lab Crest glass pressure reaction vessel (Fischer and Porter Co., Warminster, Pa.), connected to a manifold and immersed in an acetone bath. Mixing of the contents of the tube is facilitated by a magnetic stirring bar in the tube. The temperature of the solution is measured by a thermocouple immersed in the liquid mixture. CO_2 can be introduced into and vented out of the system by opening the appropriate valves. The data are, therefore, obtained with the solution in equilibrium with the vapor phase. Because of the very low partial pressure of the hydrocarbons

Table I. Solubility of Aromatic Hydrocarbons in Liquid CO_2

Compound	Purity by GLC	Melting Pt. (3), ° C.	Temp., ° C.	Solubility, G. Hydrocarbon/ Ml. Solution	Second Phase on Cooling	Critical Solution Temp., ° C.
Cumene	99.93	−96.0	Miscible in all proportions			
n-Propylbenzene	98.6	−99.5	Miscible in all proportions			
1-Methyl-2-ethylbenzene	99.7	−80.8	−44.7	0.423	Liquid	
			−45.3	0.391	Liquid	
			−46.9	0.325	Liquid	
			−47.6	0.305	Liquid	
			−50.1	0.241	Liquid	
			−52.3	0.208	Liquid	
			−53.3	0.196	Liquid	
			−53.4	0.195	Liquid	
			−54.4	0.182	Liquid	
			−57.6	0.105	Solid	
			−57.7	0.126	Solid	
			−57.8	0.147	Solid	
1-Methyl-3-ethylbenzene	99.89	−95.6	−57.9	0.666	Solid	−49.8
			−57.6	0.653	Solid	
			−57.4	0.631	Solid	
			−55.8	0.616	Liquid	
			−53.6	0.579	Liquid	
			−51.3	0.520	Liquid	
			−50.2	0.381	Liquid	
			−50.8	0.296	Liquid	
			−52.9	0.227	Liquid	
			−55.0	0.201	Liquid	
			−55.8	0.186	Liquid	
			−57.7	0.100	Solid	
			−57.2	0.076	Solid	
			−56.9	0.061	Solid	
1-Methyl-4-ethylbenzene	99.41	−62.35	−62.6	0.789	Solid	−50.2
			−58.7	0.668	Solid	
			−54.6	0.528	Liquid	
			−50.3	0.425	Liquid	
			−51.3	0.338	Liquid	
			−53.2	0.278	Liquid	
			−54.3	0.241	Liquid	
			−54.2	0.239	Liquid	
			−56.9	0.192	Liquid	
			−57.9	0.156	Liquid	
1,2,3-Trimethylbenzene	99.75	−25.4	−46.4	0.747	Liquid	−37.2
			−37.2	0.454	Liquid	
			−39.2	0.304	Liquid	
			−39.5	0.279	Liquid	
			−39.4	0.278	Liquid	
			−40.9	0.223	Liquid	
			−49.2	0.177	Solid	
			−44.8	0.174	Liquid	
			−48.5	0.165	Liquid	
			−50.9	0.124	Solid	
			−54.0	0.088	Solid	
			−54.3	0.073	Solid	
			−56.7	0.037	Solid	
			−56.7	0.021	Solid	
1,2,4-Trimethylbenzene	99.00	−43.8	−49.0	0.515	Liquid	−48.1
			−48.3	0.352	Liquid	
			−49.2	0.283	Liquid	
			−50.5	0.220	Liquid	
			−52.0	0.171	Liquid	
			−57.3	0.152	Solid	
1,3,5-Trimethylbenzene	99.28	−44.7	−57.7	0.686	Solid	−48.1
			−53.6	0.625	Liquid	
			−58.0	0.611	Solid	
			−50.2	0.524	Liquid	
			−48.7	0.452	Liquid	
			−48.4	0.348	Liquid	
			−53.0	0.216	Liquid	
			−55.0	0.186	Liquid	
			−54.9	0.185	Liquid	
			−57.5	0.166	Liquid	
			−59.1	0.146	Liquid	

Table I. Solubility of Aromatic Hydrocarbons in Liquid CO_2 (*Continued*)

Compound	Purity by GLC	Melting Pt. (3), ° C.	Temp., ° C.	Solubility, G. Hydrocarbon/ Ml. Solution	Second Phase on Cooling	Critical Solution Temp., ° C.
1,4-Diethylbenzene	97.63	−42.85	−50.0	0.711	Liquid	−36.8
			−44.5	0.601	Liquid	
			−40.5	0.504	Liquid	
			−36.8	0.371	Liquid	
			−37.7	0.309	Liquid	
			−38.3	0.272	Liquid	
			−38.7	0.258	Liquid	
			−39.8	0.210	Liquid	
			−42.2	0.160	Liquid	
			−46.0	0.122	Liquid	
			−50.7	0.093	Liquid	
			−57.2	0.086	Solid	
n-Butylbenzene	99.9	−88.0	−43.3	0.554	Liquid	−40.2
			−40.5	0.413	Liquid	
			−40.9	0.296	Liquid	
			−43.5	0.232	Liquid	
			−48.4	0.160	Liquid	
			−52.7	0.118	Liquid	
			−54.8	0.095	Liquid	

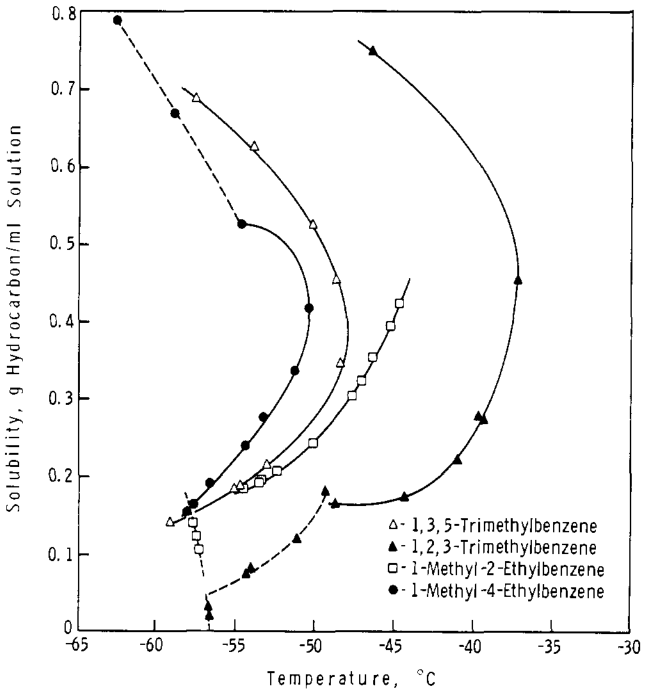

Figure 1. Solubility of C_9 aromatic hydrocarbons in liquid CO_2

under the conditions of the experiment, the total pressure of the system is approximately equal to the partial pressure of the CO_2. Volumetric measurements are always carried out with the liquid-gas interface in the middle region of the tube. At smaller volumes, the relative error becomes large; at higher levels, there may be insufficient mixing in the vertical axis. To cover the different concentration regions, several determinations are carried out for each compound with varying absolute amounts of the hydrocarbon. This approach also yields an internal check on the accuracy of the measurements. Determined volumes range from 15 to 60 ml. with a standard error of 0.11 ml. The thermocouple was calibrated against a platinum resistance thermometer calibrated by the National Bureau of Standards. The observed temperatures have a standard deviation of 0.13° C.

The aromatic hydrocarbons for this work were obtained commercially and used without further purification. Their purity was checked by gas chromatography using a 100-foot by 0.02-inch SCOT column packed with an MBM-Apiezon-Igepal liquid substrate in a Perkin-Elmer 900 gas chromatograph.

RESULTS AND DISCUSSION

Results are given in Table I and in Figures 1 and 2. As far as can be ascertained, there are no comparable data in the literature. Both *n*-propyl and isopropyl benzene are miscible in all proportions with liquid CO_2 above its triple point. All the other aromatic hydrocarbons studied show a region where two immiscible liquid phases are formed with an upper critical solution temperature. The reported

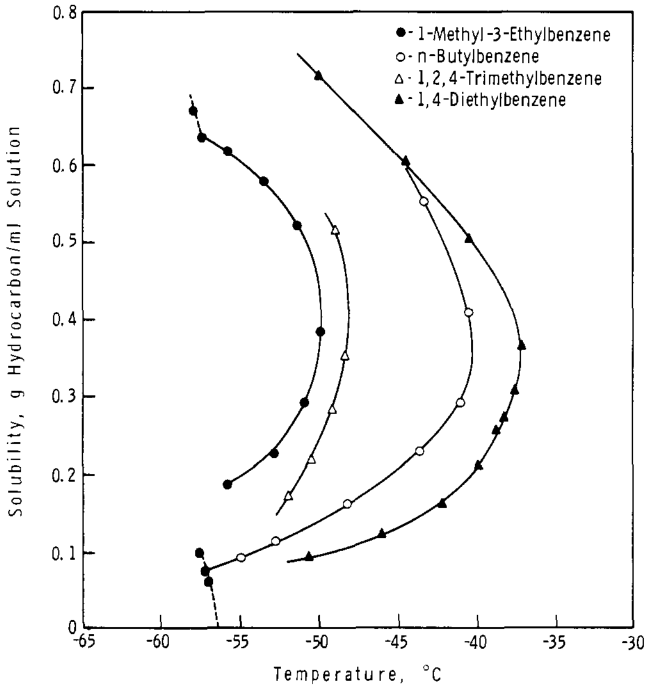

Figure 2. Solubility of C_9 and C_{10} aromatic hydrocarbons in liquid CO_2

critical solution temperatures are determined visually from the drawn solubility curves. They range from −36.8° C for 1,4-diethylbenzene to −50.2° C for 1-methyl-4-ethylbenzene. The standard deviation of these temperatures is probably equivalent to the standard deviation of the observed data points—i.e., 0.13° C (*2*).

The transition from a clear solution to two immiscible liquids can be observed very clearly if the temperature of the bath is slowly decreased. At this transition point, the well-stirred mixture is no longer optically uniform; and because of the amount of light scattered, the result is a clearly observable opalescence (*1, 4*).

If the temperature is maintained just below the transition point, the mixture will separate into two phases in a few minutes after stirring is discontinued. The lower CO_2-rich phase is usually clear, but the lighter hydrocarbon-rich phase is often opaque. For practical reasons, temperature and volume observations are taken with rise in temperatures just before the point where the cloudy emulsion changes into a clear solution. The rate of change of the temperature is maintained at 0.5° C a minute or less during these transitions. Further cooling of the mixture will result in an intersection with the solidus line. At this point the solids formed can usually be observed in the form of platelets. In many cases there are only a few degrees difference between these two transitions. Solidus lines are not reported in this communication. The accurate determination of these curves by the present method is not feasible, because the liquid-solid transition is masked by the opalescence of the two immiscible liquid phases.

The region where the hydrocarbon solidifies in equilibrium with liquid CO_2 without going through a liquid-liquid region is very small in some and virtually nonexistent in the majority of the systems studied. The crystal forms of the hydrocarbons are markedly different from that of CO_2. The solid-liquid equilibrium lines are shown dashed in Figures 1 and 2. In the region of high hydrocarbon concentration, the solid which crystallizes out should contain considerable amounts of the hydrocarbon (as in 1-methyl-3-ethyl- and in 1-methyl-4-ethylbenzene). In the region of low hydrocarbon concentration, where the solid-liquid phase equilibrium lines originate at −56.6°C, the melting point of pure CO_2, the crystalline phase consists mainly of CO_2.

The only hydrocarbon which could be observed to crystallize at low concentrations without being obscured by the region of two immiscible liquid phases is 1,2,3-trimethylbenzene. This solid-liquid curve is shown dashed in the region of −49° to −57° C and 0.05 to 0.2 gram per ml of solution. From the slope of the curve and the crystal form, which was markedly different from that of CO_2, it appears that the solid which crystallizes in this region should contain appreciable amounts of 1,2,3-trimethylbenzene. At still lower hydrocarbon concentrations, below the eutectic, the crystallizing solid is, of course, predominantly CO_2.

Table I lists the results of these measurements. The melting points given in the second column are those reported in the literature, included to indicate the relative position of the equilibrium lines in respect to the melting point of the constituents of the mixtures.

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Received for review September 25, 1969. Accepted February 6, 1970.

Vapor Pressures of Liquid Alkaline Earth Bromides and Iodides

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The vapor pressures of the bromides and iodides of calcium, strontium, and barium in the liquid range were measured by a Knudsen effusion method. Equations for the vapor pressures as a function of temperature were determined and the enthalpies of vaporization at temperature were calculated from these equations.

THE VAPOR PRESSURE and heats of vaporization of the alkaline earth bromides and iodides have been estimated by a number of authors (*2, 3, 4, 7, 8*). However, there have been very few experimental measurements of these vapor pressures on which to base and confirm the estimates. The anhydrous salts were prepared by direct union of the elements and purified by vacuum sublimation. The vapor pressures were measured by observing the rate of weight loss from a Knudsen diffusion cell.

EXPERIMENTAL PROCEDURE

The salts were prepared by direct union because alkaline earth metals of high purity with respect to other metals were available and because the hydrated salts are difficult to dehydrate without hydrolysis. The method was similar to one described in the literature (*1*).

Five to 10 grams of the pure metal crystals were placed in a quartz boat in a quartz reaction tube. An amount