Solid–Liquid Phase Equilibria in Binary Mixtures of Silicon Tetrachloride, Silicon Tetrabromide and Tin Tetrachloride with Benzene, p-Xylene, and p-Dioxane

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Solid-liquid phase diagrams have been obtained from time-temperature cooling curves for the binary systems of $SiCl_4$ with benzene and p-xylene, and for $SiBr_4$ with p-dioxane. Unlike CCl_4, $SiCl_4$ does not form solid compounds with either benzene or p-xylene, but rather forms liquid solutions that are nearly ideal over the whole range of composition. The $SiBr_4$-dioxane system also shows no compound. The 1:4 compound described in the earlier literature was not verified. Correlations between the capacity to form intermolecular compounds and the ability of the tetrahalides of C, Si, and Sn to act as electron acceptors are discussed.

PREVIOUS WORK has shown that CCl_4 forms solid compounds with benzene and a number of its derivatives (1, 2, 5, 6, 9, 10, 12). Other work (8, 11) has shown that CCl_4 also forms solid compounds with p-dioxane.

The similarities in the tetrahalides of C, Si, and Sn suggested the present investigation of the solid-liquid phase properties of $SiCl_4$, $SiBr_4$, and $SnCl_4$ with benzene, p-xylene, and p-dioxane. Furthermore, the temperature of the meritectic halt for the 1:4 solid compound of $SiBr_4$ with p-dioxane described by Kennard and McCusker (7) coincides closely enough with the solid phase transition in p-dioxane described in previous reports (11, 4) that we felt it advisable to reinvestigate the phase equilibria in this system.

EXPERIMENTAL

The method for purification of the aromatic compounds and the dioxane have been previously described (10, 11). The $SiCl_4$ was fractionally distilled in a 170 cm. vacuum jacketed distillation column at a reflux ratio of 100:1. The center third cut was used in the measurements. The $SiBr_4$ was prepared by passing N_2 gas saturated with Br_2 vapor over hot silicon in a manner similar to that described by Kennard and McCusker (7). The $SiBr_4$ formed was partially purified by shaking with a zinc-mercury amalgam to remove the small amount of bromine in the product. The material was then filtered and distilled in a 40 cm. distillation column at a 25:1 reflux ratio. The $SnCl_4$ was Matheson, Coleman, and Bell-"Purified" grade material, and was used without further purification. Calculations made on the change of the melting point with fraction melted showed the liquid soluble-solid insoluble impurities to be 0.04 mole % in benzene, 0.05 mole % in p-xylene, 0.02 mole % in stannic chloride, and 0.01 mole % in silicon tetrachloride and silicon tetrabromide.

All the solutions were prepared in a drybox to prevent hydrolysis of the $SiCl_4$ and $SiBr_4$ by moisture in the air. The solutions were volumetrically made to their approximate concentration by dispensing the chemical constituents from automatic burettes equipped with teflon stopcocks and protected with drying tubes at the openings. The actual concentrations were determined by weighing the amount of each component.

Freezing points were measured immediately after preparation of the solutions. Successive freezing point determinations on the same sample over a time period of several hours did not change. This indicated that no change occurred in the composition of the solutions because of chemical reactions during the time period necessary to make the freezing point measurements.

Freezing points accurate to ±0.1° were determined from time-temperature cooling and warming curves. The apparatus has been described previously (3). The temperature measurements on the $SiBr_4$-dioxane system and the $SiCl_4$-dioxane system were made with a strain-free platinum resistance thermometer of laboratory designation T-2. All other measurements were made with strain free platinum thermometer T-1. The calibration of these thermometers is described in earlier papers (4, 3). The absolute temperature scale is estimated to be accurate to within ±0.05° K. over the temperature range of the measurements.

In order to ensure that thermal equilibrium was established, each sample was successively frozen, slowly cooled to low temperatures, slowly warmed, and melted. This procedure was repeated at least once over a period of several hours.

RESULTS

The freezing point data for silicon tetrachloride with benzene and with p-xylene are summarized in Table I and

Table I. Freezing Points[a]

SiCl₄–Benzene		SiCl₄–p-Xylene		SiBr₄–p-Dioxane	
Mole fraction SiCl₄	Freezing point, ° K.	Mole fraction SiCl₄	Freezing point, ° K.	Mole fraction dioxane	Freezing point, ° K.
0.0000	278.66	0.0000	286.38	0.0000	278.54
0.0622	274.83	0.0650	283.87	0.0577	275.55
0.1212	271.47	0.1592	280.07	0.1202	272.54
0.2060	267.15	0.2521	276.29	0.2196	268.21
0.2903	263.08	0.3309	272.87	0.3223	264.12
0.3762	258.94	0.4033	269.70	0.3677	262.47
0.4646	254.54	0.4870	265.84	0.4164	263.54
0.5323	250.81	0.5670	261.61	0.4578	265.22
0.6268	244.97	0.6568	256.22	0.5093	267.16
0.6958	239.51	0.7082	252.29	0.5955	270.03
0.7542	234.31	0.7705	246.70	0.6841	272.54
0.8171	226.85	0.8160	241.95	0.7101	273.30
0.8823	215.65	0.8862	231.43	0.7498	274.66
0.9042	210.48	0.9476	214.71	0.8036	276.54
0.9275	204.16	0.9638	207.61	0.8688	279.03
0.9428	202.00	0.9717	203.06[b]	0.9293	281.55
0.9616	202.67	0.9799	203.47		
0.9801	203.51	0.9926	204.05		

[a] 0° C. = 273.150° K. [b] Unstable phase crystallizing below the eutectic.

Figure 1. The compositions and temperatures of the eutectics are 0.935 mole fraction $SiCl_4$ and 201.63 ±0.1° K. for the system containing benzene, and 0.973 mole fraction $SiCl_4$ and 203.11 ± 0.1° K. for the p-xylene system. Unlike the analogous carbon tetrachloride systems, there is no evidence for compound formation in either of these systems. The coincidence of the liquidus lines for the two systems
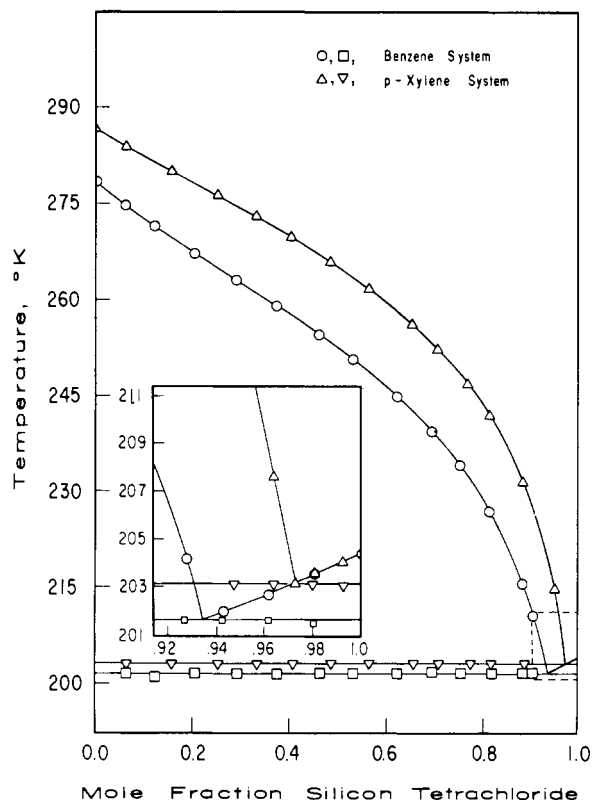

Figure 1. Solid-liquid phase diagram of silicon tetrachloride–benzene and silicon tetrachloride–p-xylene

Figure 2. Solid-liquid phase diagram of silicon tetrabromide–p-dioxane

on the right of the eutectics and almost parallel lines on the left suggest close to ideal behavior. Calculation of the activity coefficients from the freezing point data show these solutions to be ideal (activity coefficients of unity to four significant figures) on the right hand side of the eutectic, and only slightly nonideal over the whole range of composition.

The data for the $SiBr_4$–p-dioxane system are also summarized in Table I and in Figure 2. The single eutectic occurs at 261.89° K. and 0.384 mole fraction dioxane. The invariant point at 272.79° K. is of particular interest since it was described by Kennard and McCusker (7) as being due to the formation of a 1:4 solid compound. However, the temperature for this invariant point corresponds very closely to the solid phase transition temperature in dioxane observed in a number of other systems (11, 4). The graph of the length of invariant halt $vs.$ mole fraction shown at the top of Figure 2 shows no maximum corresponding to a 1:4 compound but instead increases smoothly to pure dioxane. Careful cooling and warming in this region showed only one invariant temperature. Therefore, it must be concluded that no solid compounds exist between silicon tetrabromide and dioxane.

During the course of our measurements, we observed at several compositions the unstable melting point of $SiBr_4$ described by Kennard and McCusker (7). However, it was difficult to make accurate measurements of its melting point in our apparatus as the unstable phase rapidly converted to the stable form. For this reason, this information is not included on the phase diagram.
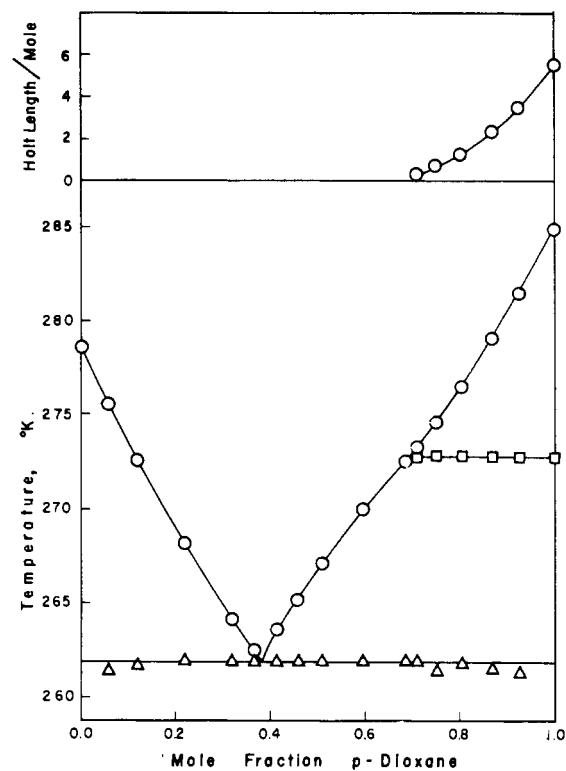
Exploratory measurements were made on mixtures of $SnCl_4$-C_6H_6, $SnCl_4$-p-$C_6H_4(CH_3)_2$, and $SiCl_4$-p-dioxane. Several measurements in the mole fraction range of about 0.3 to 0.7 showed only one invariant temperature in each system. From this it is concluded that, again unlike the analogous carbon tetrachloride systems, no 1:2, 1:1, or 2:1 compounds are formed between stannic chloride and benzene, stannic chloride and p-xylene, or silicon tetrachloride and p-dioxane. The $SiCl_4$-dioxane results are in agreement with the more extensive work of Kennard and McCusker (7).

In the course of this study, measurements were made of the freezing points of pure $SiCl_4$, $SiBr_4$, and $SnCl_4$. These temperatures, corrected for liquid soluble–solid insoluble impurities, are 204.36 ± 0.05° K. for $SiCl_4$, 278.54 ± 0.05° K. for $SiBr_4$, and 239.00 ± 0.05° K. for $SnCl_4$, with 0° C. taken as 273.150° K.

DISCUSSION

The lack of compound formation in the $SiCl_4$ and $SnCl_4$–aromatic hydrocarbon systems ($SiCl_4$–anisole excepted) supports the explanation given in an earlier paper (5) for the bonding in the CCl_4–aromatic systems. In those systems the evidence suggested that CCl_4 was accepting electrons from the aromatic nucleus to form a charge-transfer bond. In the case of $SiCl_4$ and $SnCl_4$, one would predict that the smaller electronegativity of silicon and tin as compared with carbon would make these molecules weaker electron acceptors, perhaps to the degree that no stable solid compounds would form. It is significant that the one carbon compound that $SiCl_4$ does form a compound with is anisole (13), which is, of those studied, the carbon compound with the highest electron density in the ring.

The lack of compound formation in the $SiCl_4$ and $SiBr_4$–dioxane systems in a like manner supports the explanation given in a previous paper (10) that CCl_4 is an electron acceptor and p-dioxane an electron donor in the stable solid compound formed between these materials. The behavior of $SnCl_4$ and $SnBr_4$, however, is anomalous in

that both form 1:1 and 1:2 solid compounds with dioxane (14). It is possible, however, that the bonding in these compounds is quite different from that in the analogous CCl_4 system. The very much greater stability of the former as evidenced by their high heats of reaction and high melting points suggests a different type of bonding. The relatively large size of the Sn atom may allow it to assume a coordination number of five or six, in which case either one or two dioxane molecules might conceivably be bonded directly to the Sn atom.

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Thermodynamic Functions of Aqueous Hydrochloric Acid at Various Concentrations and Temperatures

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The values of the mean molal activity coefficients of aqueous hydrochloric acid have been calculated from e.m.f. measurements of the cell:

Pt/H₂/HCl/AgCl/Ag/Pt

over a HCl concentration range that includes the highest concentrations (from 0.00555 to 9.251 molal), and covering a temperature range from 20° to 50° C. Moreover the values of the thermodynamic functions of aqueous hydrochloric acid at 25° C. have been obtained over the same concentration range as stated above, and the values of the potential of the saturated calomel electrode for a temperature range from 20° to 50° C. have been redetermined.

THIS INVESTIGATION has been carried out as a preliminary contribution to researches on the electrochemical processes concerning the Cl_2/Cl^- redox system. Redetermination of the mean molal activity coefficients and the thermodynamic functions of aqueous hydrochloric acid over a wide range of concentrations and temperatures, on the basis of electromotive force measurements is reported.

Bates and Kirschman (3), Harned and Ehlers (7), and Akerlöf and Teare (2) have calculated such coefficients and functions over different HCl concentration ranges.

Study of the lowest HCl concentrations have been reconsidered recently by Hills and Ives (8) and Gupta, Hills, and Ives (5).

EXPERIMENTAL

The measurement apparatus included a Type K3 Leeds and Northrup potentiometer and a high-impedance electronic millivoltmeter, Type Philips GM 6010, as a null-point detector.

The silver–silver chloride electrode was prepared according to Gordon (10) and the hydrogen electrode according to Hills and Ives (9): characteristics and performances of both of them are described in detail and discussed in the recent book by Ives and Janz on reference electrodes (11).

The temperature of the cell was regulated to $\pm 0.01°$ C. by means of an air-thermostat. All e.m.f. values were corrected to 760 mm. Hg pressure of hydrogen.

The solutions were made up with doubly distilled water and Merck reagents, reagent grade. Analysis and checking of solutions and of other substances involved in the cell were carried out according to commonly used techniques.

RESULTS AND DISCUSSION

Mean Molal Activity Coefficients of Aqueous HCl. The measurements of the e.m.f. E of the cell:

$$- Pt/H_2/(1 \text{ atm.})/HCl(m)/AgCl/Ag/Pt + \qquad (1)$$
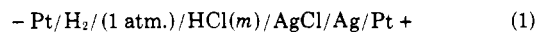
allowed us to calculate the mean molal activity coefficients