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Solid Compound Formation in the CCl_4 Mixtures of *p*-Dioxane with CCl_4, $CBrCl_3$, and $CFCl_3$. Solid-Liquid Phase Equilibria in Binary and $CFCl_3$ Systems

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Solid-liquid phase diagrams have been obtained from time-temperature cooling curves for the three binary systems formed from *p*-dioxane with CCl_4, $CFCl_3$, and $CBrCl_3$. Solid compounds with the empirical formulas of *p*-$C_4H_8O_2 \cdot (CCl_4)_2$ and *p*-$C_4H_8O_2 \cdot (CFCl_3)_2$ were formed. The system *p*-$C_4H_8O_2$–$CBrCl_3$ shows a maximum freezing point in a solid solution, but the evidence is against compound formation in that system. Exploratory measurements on the CH_3CCl_3–dioxane and $(CH_3)_3$–CCl–dioxane systems show that they do not form compounds. These results are in qualitative agreement with the concept that *p*-dioxane is acting as an electron donor and the halogenated molecules as acceptors in the intermolecular compounds.

PREVIOUS PHASE DIAGRAM studies have shown that CCl_4 forms solid compounds with benzene and several of its derivatives (*2, 3, 6, 7, 9, 11, 12*). Each of the aromatic substances that is known to form the CCl_4 addition compound is characterized by a high electron density in the benzene ring, which suggests that the aromatic compound acts as a donor in a charge-transfer process. This explanation is supported by x-ray diffraction work on the related CBr_4-*p*-Xylene system (*13*).

Other molecules capable of acting as electron donors might also form compounds with CCl_4. Dioxane appears to meet the requirements for a donor molecule; and it is known to form a compound with CCl_4 (*8*).

This paper reports a solid-liquid phase equilibria study of *p*-dioxane with CCl_4 (a more detailed study than the earlier work referred to above), $CBrCl_3$, and $CFCl_3$. The selection of the three halogen compounds, all of roughly the same shape and size, made possible a study of the effect of electronegativity of a substituent atom in CCl_4 on the ability to form the intermolecular compound.

EXPERIMENTAL

Chemicals. Starting materials were spectro-grade *p*-dioxane and reagent grade CCl_4, $CBrCl_3$, and $CFCl_3$. The dioxane, CCl_4, and $CFCl_3$ were purified by fractional distillation in a vacuum-jacketed 100-cm. column packed with glass helices and operated at a reflux ratio of approximately 50:1. The $CBrCl_3$, because it showed signs of some decomposition (yellow color) under the conditions that the other substances were distilled, was vacuum distilled at room temperature in a 170-cm. long, glass helices packed distillation column and then fractionally crystallized once. The entire distillation apparatus was shielded from light by wrapping it in aluminum foil, since there was evidence for photochemical as well as thermal decomposition of this material.

With the exception of the $CBrCl_3$, which is discussed below, the purity of the products was determined from their time-temperature freezing curves. Calculations of the change in melting point as a function of the fraction melted showed the following liquid soluble-solid insoluble impurities present: *p*-dioxane, 0.06 mole %; CCl_4, 0.02 mole %; and $CFCl_3$, 0.05 mole %. The CH_3CCl_3 and $(CH_3)_3CCl$ used in the exploratory measurements were also purified by fractional distillation.

Because of the physical properties of the $CBrCl_3$ (hard and massive crystals and small heat of fusion), it was difficult to obtain equilibrium conditions between solid and liquid, and the freezing curve for this substance was not satisfactory for determining per cent purity. A fairly satisfactory melting point, however, was obtained. It differed by 0.1° from a recent literature value (*1*). Based on this information and gas chromatograms of the purified material, the purity is estimated to be better than 99.0%.

Apparatus, Temperature Scale, and Accuracy of Measurements. The freezing point apparatus has been described previously (*4*). Temperatures were measured with a platinum resistance thermometer of laboratory designation T-2, the calibration of which has been previously described (*5*). The temperature scale is conservatively estimated to be accurate to within ±0.05° over the temperature range of the measurements. The calibration of the thermometer was checked both at the beginning and the completion of the work, with no significant changes observable.

Time-temperature cooling and warming curves were obtained. Freezing points of solutions were determined by extrapolation across the supercooled region. Agreement between the freezing and melting points was generally within .03°. The accuracy of the freezing points of the solutions and the invariant temperature points where stirring was possible is estimated to be within 0.1° in the CCl_4 and $CFCl_3$ systems. Because of the uncertainty in the purity of $CBrCl_3$, the accuracy may be less for this system. For this reason, freezing points have not been tabulated and only the freezing point curve given since its general shape would be affected very little by the impurity.

RESULTS AND DISCUSSION

Table I summarizes the freezing point data and Figures 1–4 show the resulting phase diagrams for the three binary systems composed of *p*-dioxane with CCl_4, $CFCl_3$, and $CBrCl_3$. Figure 2 shows more detail of the solid solution region of the CCl_4 system.

The invariant temperature line at the far right of all three diagrams is the solid phase transition in *p*-dioxane at 272.80 ± 0.3° K. reported in an earlier paper (*5*).

The existence of a compound with the empirical formula $p\text{-}C_4H_8O_2 \cdot (CCl_4)_2$ and a melting point of 255.71° K. is evident in Figures 1 and 2. Solid solutions form over the range 0–0.480 mole fraction dioxane, and the liquidus and solidus lines merge at the maximum, which occurs at a molecular ratio of one $pC_4H_8O_2$ to two CCl_4. The two eutectics in this system occur at mole fractions dioxane of 0.045 and 0.480, and temperatures of 248.17° K. and 254.72° K., respectively. Liquidus, but not solidus points for this system have been reported previously by Kennard and McCusker (*8*). The liquidus data of the two studies are in general agreement, except at the lower temperatures of the diagrams where the temperatures of the present study are as much as 0.5 to 1° K. higher. Kennard and McCusker (*8*) also did not report the solid phase transition in *p*-dioxane.

Table I. Freezing Points[a]

Mole Fraction Dioxane	Freezing Point, ° K.	Mole Fraction Dioxane	Freezing Point, ° K.	Mole Fraction Dioxane	Freezing Point, ° K.
		p-Dioxane–Carbon Tetrachloride System			
0.0000	250.41[b]	0.3305	255.68	0.7457	271.13
0.0180	249.55	0.3441	255.70	0.7755	272.61
0.0301	248.97	0.3936	255.66	0.8004	274.10
0.0400	248.49	0.4460	255.22	0.8449	276.70
0.0473	248.30	0.4654	254.94	0.8945	279.30
0.0538	248.60	0.4727	254.82	0.9493	282.27
0.0984	250.63	0.4942	256.00	0.9834	284.05
0.1466	252.40	0.5447	259.67	0.9990	284.84
0.1980	253.85	0.5937	262.71	1.0000	284.95[b]
0.2483	254.87	0.6465	265.82		
0.2969	255.46	0.6940	268.40		
		p-Dioxane–Trichlorofluoro Methane System			
0.0000	162.67[b]	0.2196	238.83	0.5012	261.22
0.0060	162.48	0.3312	249.90	0.6707	269.00
0.0140	162.25	0.3495	251.28	0.8109	275.57
0.0346	188.2[c]	0.3733	253.28	0.9193	280.94
0.0712	208.2[c]	0.4068	255.14	1.0000	284.95[b]
0.1461	227.90	0.4500	258.15		

[a] 0° C. = 273.150° K. [b] Corrected to zero per cent impurity. [c] Less accurate values on steep portion of freezing curve.

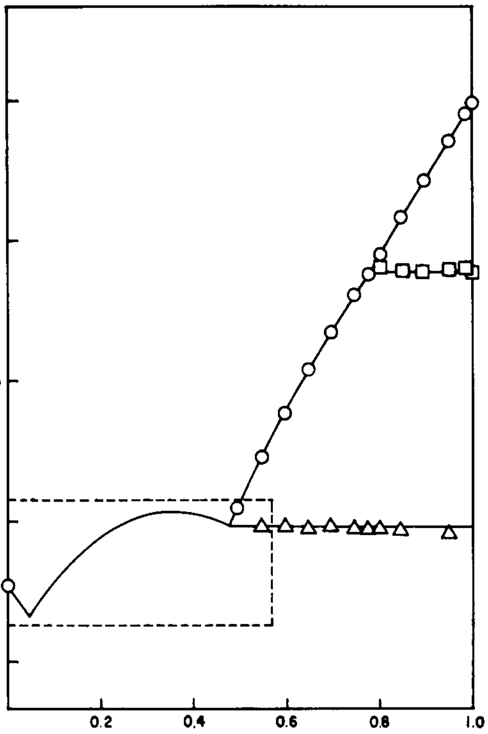

Figure 1. Phase diagram for *p*-dioxane–carbon tetrachloride

Figure 3 shows the existence of the incongruently melting compound $p\text{-}C_4H_8O_2 \cdot (CFCl_3)_2$. Supercooling of the solid compound was exceptionally pronounced in this system, and it was only by cooling to relatively low temperatures followed by several cycles of alternate warming and cooling just above the eutectic that the stable phase below the meritectic could be obtained. The composition of the compound was obtained in the usual way from the maximum in the length of meritectic halt. The length of halt was determined from a warming curve, using a toluene slush bath. The meritectic halt occurs at a temperature of 167.5 ± 1° K. The large uncertainty results because decomposition of this compound was very slow at the metitectic temperature and it was difficult to obtain temperature equilibrium even with the toluene slush bath. The stable eutectic (*p*-dioxane–compound in equilibrium) in this system occurs at a mole fraction dioxane of 0.014 and a temperature of 162.22° K. Unless one goes through the cooling and warming procedure as described above, almost invariably an unstable eutectic with *p*-dioxane and $CFCl_3$ in equilibrium is obtained at 162.08° K. The small difference in temperature between the two eutectics and the supercooling of the solid compound make this system an example of one in which it would be very easy to miss the existence of the solid compound unless special precautions were taken.

The freezing point of 162.67° K. obtained for the pure $CFCl_3$ is the same value obtained by Osborne and coworkers (*10*) in a calorimetric study of this compound.

Figure 4 shows a fairly unusual type of behavior, a solid solution with a maximum melting point. The solidus and liquidus lines do not quite merge at the maximum, peresumably because of the presence of a slight amount

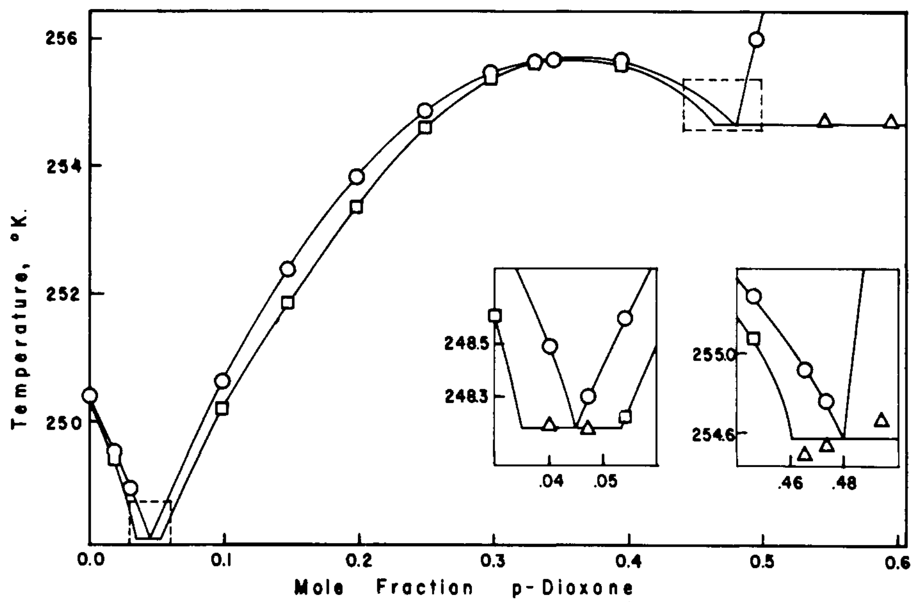

Figure 2. Solid solution region in the *p*-dioxane–carbon tetrachloride system

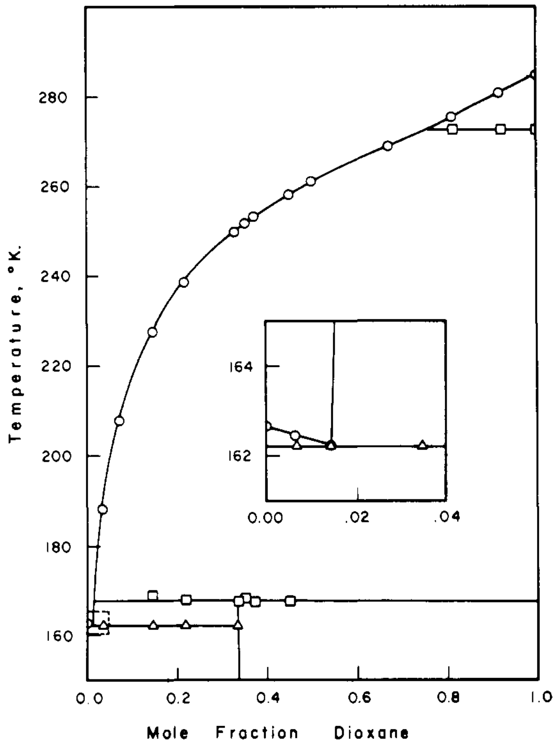

Figure 3. Phase diagram for *p*-dioxane–trichlorofluoromethane

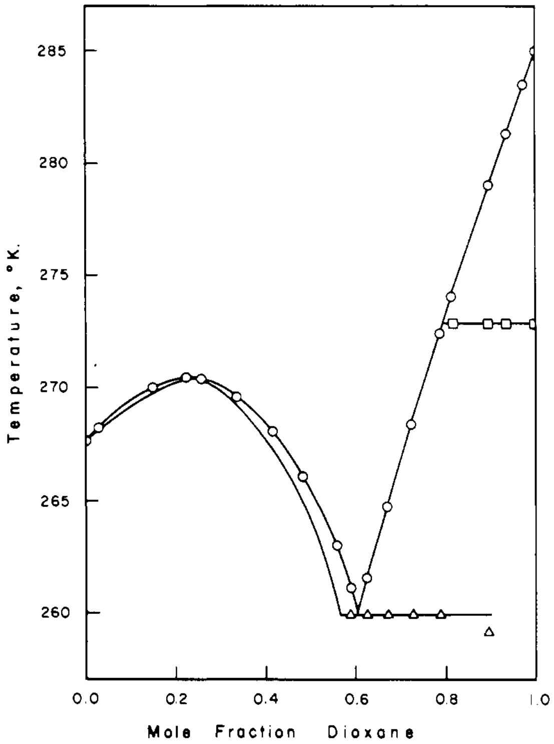

Figure 4. Phase diagram for *p*-dioxane–trichlorobromomethane

of impurity. The existence of but one eutectic, occurrence of the maximum at a composition other than some simple molecular ratio (0.227 mole fraction dioxane), and the appearance of a solid state transition in $CBrCl_3$ over the whole range of composition are good, although not conclusive against the existence of a compound in this system.

The solid state conversion in $CBrCl_3$ referred to above was plainly evident, but because the conversion was slow, our time-temperature apparatus was not suited to make an accurate measurement. We have therefore not reported a temperature for this transition.

Figure 5 shows some representative temperature-time cooling curves over the composition range in which solid solutions occur for both the CCl_4-dioxane (lower set of curves) and the $CBrCl_3$–dioxane (upper set of curves) systems. These curves show the maximum in the freezing point curves at 0.333 and 0.227 mole fraction dioxane in the CCl_4 and $CBrCl_3$ systems, respectively. They also show the definite breaks at the liquidus and solidus points and the lack of supercooling at the liquidus points in these systems.

On the basis of electronegativity of the halogens, $CBrCl_3$ would be predicted to be a poorer electron acceptor than CCl_4 and $CFCl_3$. The fact that *p*-dioxane forms a solid compound with CCl_4 and $CFCl_3$, but apparently not with $CBrCl_3$ is in qualitative agreement with the concept that the halogen compound acts as an electron acceptor in the formation of the intermolecular compounds with *p*-dioxane.

Exploratory measurements were made on mixtures of CH_3CCl_3 and $(CH_3)_3CCl$ with *p*-dioxane. The procedure

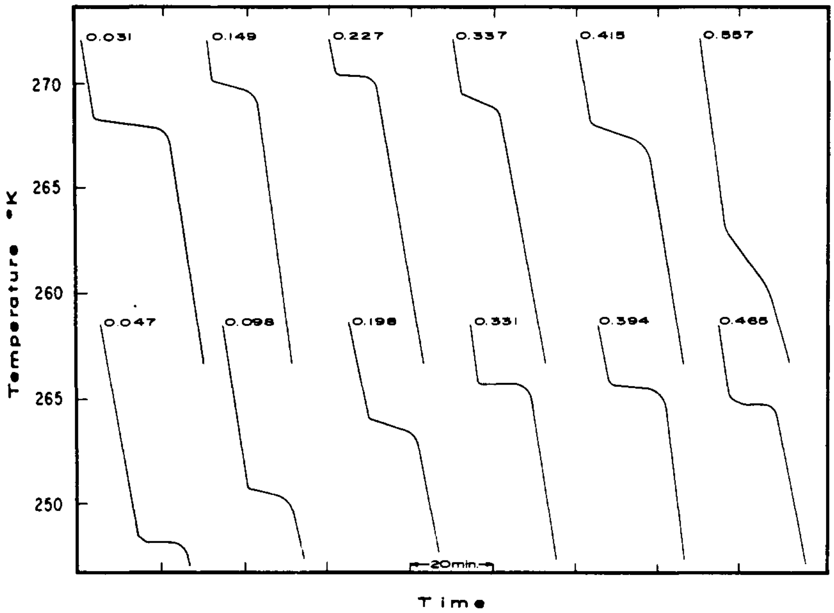

Figure 5. Representative temperature-time cooling curves showing solid solution formation in the systems $CBrCl_3$–*p*-dioxane (upper set of curves) and CCl_4–*p*-dioxane (lower set of curves). The concentrations are in mole fraction *p*-dioxane

consisted of obtaining time-temperature cooling curves in each system on three solutions with the approximate compositions of 0.67, 0.50, and 0.33 mole fraction dioxane. In each system the same eutectic was obtained for all three solutions and no other invariant points were observed. From this, it is concluded that no solid compound exists between *p*-dioxane and CH_3CCl_3 or $(CH_3)_3CCl$.

These results also support the explanation for the bonding given above since the chlorine in each of these compounds should be less electronegative than in CCl_4 or $CFCl_3$.

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