One other point remains to be mentioned, the variation of solubility with temperature. Both δ_1 and δ_2 decrease with temperature, but ordinarily at different rates, and both are subject to more or less uncertainty. In a calculation of solubility by this theory, since $(\delta_1 - \delta_2)$ appears in the role of an exponent, an error of one unit in $(\delta_1 - \delta_2)$ appears as an error of a factor of ten in the calculated solubility. This exponential form, which gives the equations their wide applicability, also greatly increases the disturbing effects of approximations in the theory and experimental errors in the parameters. As a practical measure for interpolating or extrapolating solubilities, one may employ the procedure used by Hildebrand and Negishi.[10] The values for $\delta_2 - \delta_1$ calculated from solubilities for two or more temperatures were plotted against temperature and a straight or nearly straight line drawn through them, giving points for other temperatures.

Summary

1. The solubility of white phosphorus, P_4, has been measured from 0 to 130° in normal heptane and from 0 to 100° in carbon tetrachloride. Rough measurements of its (small) solubility in acetone are also reported int he range 0 to 40°.

2. These results, together with data from the literature for the solvents carbon disulfide, benzene and ether, are analyzed in terms of present solubility theory for solutions of non-electrolytes. The very different solubilities of phosphorus in carbon disulfide and in carbon tetrachloride are correlated by means of the ordinary equation, with benzene solutions showing only small divergence. Heptane solutions diverge moderately in the same direction as previously found with other solutes, but the correlation is improved by taking into account the entropy of mixing molecules of significantly different size.

BERKELEY 4, CALIFORNIA RECEIVED JUNE 15, 1948

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[10] J. H. Hildebrand, THIS JOURNAL, **59**, 2083 (1937); J. H. Hildebrand and G. R. Negishi, *ibid.*, **59**, 330 (1937).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Phase Studies of Some Group 4a Tetrachloride–Aromatic Ether Systems

BY HARRY H. SISLER, WILBUR J. WILSON, BETTY J. GIBBINS, HARRY H. BATEY, BARBARA PFAHLER AND ROBERT MATTAIR

The results of studies of compound formation by the tetrachlorides of carbon, silicon, germanium and tin with diphenyl ether and with anisole have been reported.[1] The present work was undertaken with the objective of expanding these studies to include various other aromatic ethers with the hope of obtaining information which would serve to answer some of the questions raised by the work on anisole and diphenyl ether. As this work progressed the previously reported data on the anisole systems seemed more and more anomalous. It was decided, therefore, to study the anisole systems again. We regret to report that the previously recorded results on the anisole systems, which were carried out by a co-worker of one of the authors in another laboratory, and published jointly with him, have been shown to be unreliable[1] (ref. 1, pp. 1517–1518). The new results, which have been obtained by four of us, are reported in this paper. In addition, the binary systems of phenetole with each of the group 4a tetrachlorides, methyl *m*-cresyl ether with each of the group 4a tetrachlorides, methyl *o*-cresyl ether with germanium tetrachloride, and *n*-propyl phenyl ether with germanium tetrachloride have been studied and are discussed below.

Experimental

Preparation of Materials.—The carbon tetrachloride was purified by fractionation in a five-foot column packed with glass helices at atmospheric pressure. Silicon tetrachloride from Eimer and Amend, germanium tetrachloride from the Eagle-Picher Lead Co., and tin tetrachloride from Baker and Adamson were similarly purified by fractionation at atmospheric pressure, protected from moisture by drying tubes filled with drierite. In each case a constant boiling middle fraction was taken and its purity checked by taking its freezing point.

Anisole, phenetole, methyl *m*-cresyl ether, methyl *o*-cresyl ether, and *n*-propyl phenyl ether, obtained from the Eastman Kodak Co., were dried by allowing them to stand over sodium wire, and were purified by fractional distillation. In each case a constant boiling middle fraction was retained and its purity checked by taking its freezing point.

Procedure.—The systems were studied by the freezing point method, the freezing points being determined by means of cooling curves. The cell used in these experiments was similar to that in previously reported studies.[1] The thermocouple well was filled with a mixture of carbon tetrachloride and chloroform to minimize convection effects. The stirrer in the cell consisted of a stainless steel wire coil attached to an iron cylinder coated with nickel; the stirrer was operated by means of an air-cooled solenoid which was wired through a motor driven interrupter, thus allowing continuous stirring. Weighed quantities of the components of the system being studied were introduced from a Lunge pipet, the pipet having a ground-glass surface of the same taper as the opening. While the sample was being introduced, another opening was open to the atmosphere through a drying tube filled with drierite. A copper–constantan thermocouple attached to a Leeds–Northrup Micromax self-recording potentiometer was used to measure the temperatures and record the cooling curves.

The various mixtures were cooled in a solid carbon dioxide–carbon tetrachloride–chloroform-bath, or in liquid air, depending upon the freezing point for the particular mixture. The rate of cooling was modified further by surrounding the cell with one or more test-tubes of larger

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[1] Sisler and Cory, THIS JOURNAL, **69**, 1515 (1947).

diameter. The break in the curve was taken as the freezing point, except in those cases where unavoidable supercooling made extrapolation according to the accepted method necessary. All freezing points reported were determined at least twice. In view of the fact that the freezing points did not vary with rate of cooling (within the range of rates of these experiments) it may be assumed that equilibrium was obtained. In cases where the tendency to supercool was great, the mixtures were cooled until solidification took place, then warmed rapidly to a temperature just above the freezing point, and then cooled in the regular manner. No system was completed from a single batch of material, and, in most systems, the data were obtained using materials from several different batches. Data obtained are believed accurate to ±1.5° unless otherwise noted.

It will be noted that, in certain cases, freezing points for only the lower melting form of germanium tetrachloride were obtained. No explanation can be given for this, and, because of the low temperatures involved and the necessity for working in a closed system, attempts to obtain the higher melting form by such methods as seeding were deemed unfeasible. Attempts to obtain this form by varying the rate of cooling and by cooling far below the freezing point were not successful.

The Anisole Systems.—The data obtained for the anisole systems are illustrated graphically in Fig. 1, curves A, B, C and D.

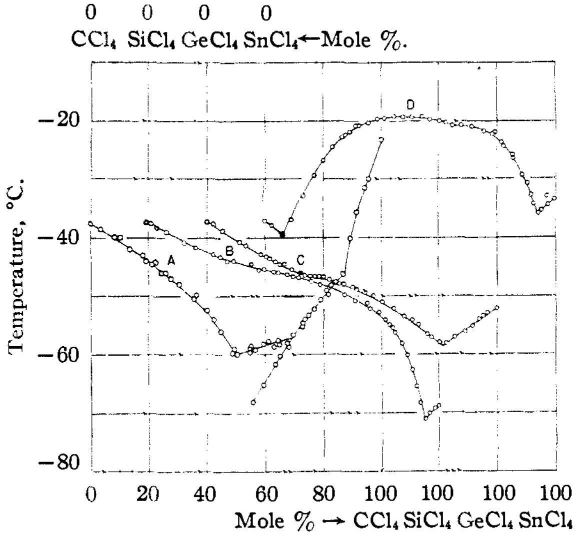

Fig. 1.—Anisole systems.

The strong tendency for mixtures of anisole and carbon tetrachloride to supercool lowered the precision of the determinations in the middle portion of this system (curve A). The following features are apparent, however: the two components of this system form an addition compound, apparently highly dissociated. The course of the curve does not indicate precisely the composition of the compound, but the composition $CH_3OC_6H_5 \cdot 2CCl_4$ is in accord with the data. If this is the correct composition, the melting point of the compound is about −58°. Such compositions as $2CH_3OC_6H_5 \cdot 3CCl_4$ are not eliminated, however, because the maximum in the curve is extremely flat and the points do not clearly indicate where it occurs. An eutectic between solid anisole and the compound occurs at about 50 mole per cent. carbon tetrachloride and −60°. The transition of carbon tetrachloride to a different crystal form at about −48° previously reported in the literature[2] is indicated by a break in the freezing point in the curve.

In the anisole–silicon tetrachloride system (curve B) there is an inflection in the freezing point curve of anisole but it is by no means certain that compound formation occurs. In any case the tendency toward compound formation is not great. An eutectic occurs at −71.0° and about 95 mole per cent. silicon tetrachloride.

From the curve for the germanium tetrachloride–phenetole system (curve C, Fig. 2) it will be noted that the two forms of germanium tetrachloride reported,[3] namely, those freezing at −49.5 and −52.0°, were obtained, both freezing points having been obtained in numerous cases on a single sample. In this system, however, a freezing point curve was obtained only for the lower melting metastable form. The form of the curve indicates the probable formation of an addition compound of the composition $GeCl_4 \cdot 2CH_3O_6H_5$. An eutectic occurs at −58.5° and about 81 to 82 mole per cent. germanium tetrachloride.

Curve D in Fig. 1 shows that tin tetrachloride and anisole form two solid addition compounds, *viz.*, that of the composition $SnCl_4 \cdot CH_3OC_6H_5$ (m. p. −19.5), and that of the composition $2SnCl_4 \cdot CH_3OC_6H_5$ (m. p. −21.0). As the extremely flat nature of these maxima indicate, these two compounds are highly dissociated at their melting points. Two eutectics, *viz.*, approximately 7 mole per cent. tin tetrachloride and −40.0°, and approximately 94 to 95 mole per cent. tin tetrachloride and −36.5°, occur.

The Phenetole Systems.—The data obtained for the phenetole systems are recorded graphically in Fig. 2, curves A, B and C. As the data in curve A, Fig. 2 indicate, there is no evidence of compound formation in the phenetole–carbon tetrachloride system. A break in the curve at about 7 mole per cent. carbon tetrachloride and about −33° indicates a probable transition temperature for phenetole (particularly since this same break was observed in both the silicon and germanium tetrachloride systems with phenetole). The phase transition at −48° for carbon tetrachloride appears also. The eutectic appears at −62.0° and about 65 mole per cent. of carbon tetrachloride.

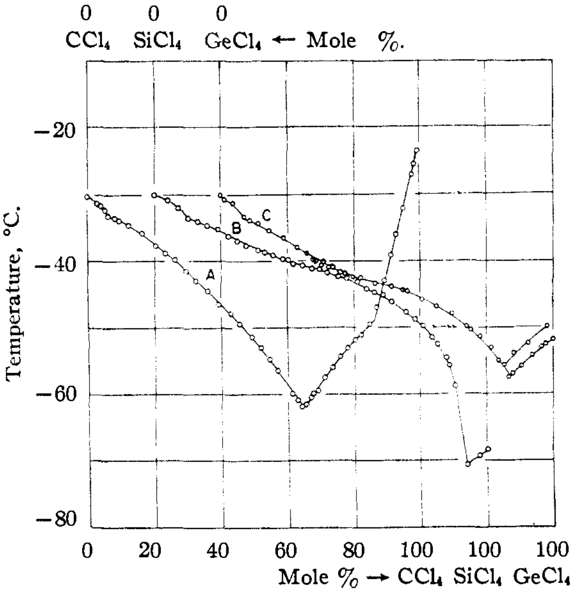

Fig. 2.—Phenetole systems.

The data expressed by curve B, Fig. 2 do not indicate definitely whether or not compound formation occurs in the system silicon tetrachloride–phenetole. There appears to be a slight change in slope at about 41 mole per cent. silicon tetrachloride which may indicate some tendency toward compound formation, but, in any case, such a tendency is not great. The break in the curve indicating a change in form of the phenetole which was observed in the carbon tetrachloride system is observed in this system also. An

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[2] Wyatt, *Trans. Faraday Soc.*, **25** 48 (1929).

[3] W. J. Wilson, thesis, The Ohio State University, 1947.

eutectic occurs at about 94 mole per cent. silicon tetrachloride and at −70.5°.

The data for the germanium tetrachloride–phenetole system as illustrated by curve C, Fig. 2, show that in this case, freezing point curves were obtained for both the stable and metastable forms of the germanium tetrachloride. Probable compound formation between germanium tetrachloride and phenetole is indicated by a change in slope of the freezing point curve at about 40 mole per cent. germanium tetrachloride. The transition of the α to the β forms of phenetole at about −33.0° was observed also. Phenetole forms an eutectic with the stable form of germanium tetrachloride at about 85 mole per cent. of the latter and at −55.8°; it forms an eutectic with the metastable form at about 87 mole per cent. and at −57.5°.

Because of the exceedingly great tendency for mixtures of tin tetrachloride and phenetole, particularly in the range of 35 to 65 mole per cent. of tin tetrachloride, to supercool, a satisfactory thermal analysis of the tin tetrachloride–phenetole system was not obtained. The points which were obtained, however, indicate that there is some sort of compound formation in this system probably in the range of 40 to 60 mole per cent. tin tetrachloride. These points are shown in Fig. 3. What are, from the form of the cooling curves, apparently eutectic freezing points were obtained in this region. Only an occasional freezing point in the region above the apparent eutectics was obtained. The cause of the break in the curve at 80 mole per cent. tin tetrachloride and −42° is not known; no abnormalities could be detected in the region of −42° upon cooling a pure sample of tin tetrachloride in the solid state. Since such equilibria are attained only slowly, however, this does not exclude the possibility of a transition at this point. Because of the incomplete nature of the work on this system and the difficulty attending the obtaining of the data that are given, conclusions based on this part of the work must be considered quite tentative.

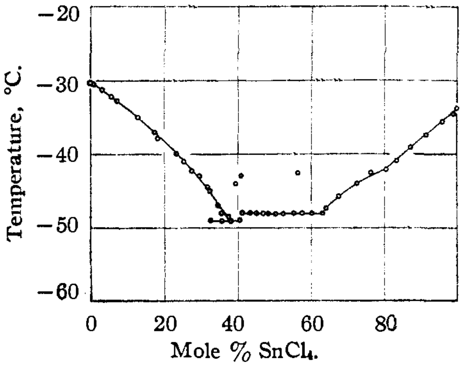

Fig. 3.—Phenetole–$SnCl_4$.

The Methyl *m*-Cresyl Ether Systems.—The data for the methyl *m*-cresyl ether systems are recorded graphically in Fig. 4, curves A, B, C and D. A consideration of Curve A, Fig. 4 leads to some interesting conclusions. The melting point of pure methyl *m*-cresyl ether used in this study was −55.5° in reasonable agreement with the values −55.24°[4] and −55.92°[5] reported in the literature. The results of the thermal analysis of this system show, however, that the form of the ether which melts at this temperature is a metastable form and that there exists a stable form which melts at a higher temperature and undergoes transition to the metastable form at −62.0°. The melting point of the pure stable form could not be obtained, presumably because of a strong tendency to supercool, but extrapolation of its freezing point curve leads to a value in the neighborhood of −47°.

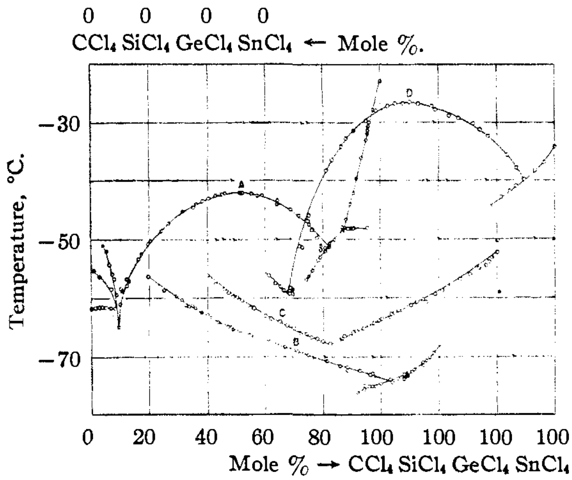

Fig. 4.—Methyl *m*-cresyl ether systems.

The freezing point curve indicates definitely that carbon tetrachloride forms a 1:1 addition compound with methyl *m*-cresyl ether which melts at −42°. The compound dissociates readily, as is indicated by the very flat nature of the maximum in the freezing point curve. The transition of α to β carbon tetrachloride at −48° appears in this system. Eutectics are found at about 10 mole per cent. of carbon tetrachloride and −64.5° and at about 82 mole per cent. and −51.0°.

Curve B in Fig. 4 gives no indication of compound formation between silicon tetrachloride and methyl *m*-cresyl ether. An eutectic is indicated at about 82 mole per cent. silicon tetrachloride and about −74.5°. No curve for the higher melting form of the ether was obtained.

A freezing point curve was obtained for the metastable form only of germanium tetrachloride in the germanium tetrachloride–methyl *m*-cresyl ether system (curve C, Fig. 4). The data for this system give no indication of compound formation. An eutectic at about 42 mole per cent. of the tetrachloride and −67.8° is obtained.

As curve D, Fig. 4 clearly indicates, tin tetrachloride forms a 1:1 addition compound with methyl *m*-cresyl ether. This compound does not crystallize readily and, as is indicated by the flatness of the maximum in the freezing point curve, it dissociates considerably at its melting point. An eutectic is obtained at about 8 mole per cent. of the tetrachloride and −59.5° and another at about 90 mole per cent. and −39.5°.

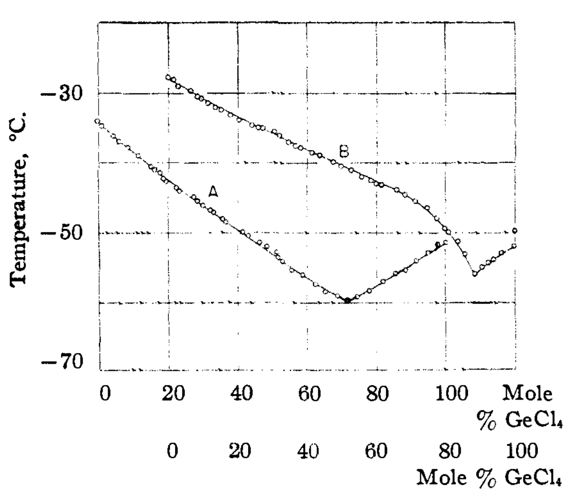

Fig. 5.—The systems $GeCl_4$–*o*-$CH_3C_6H_4OCH_3$ and $GeCl_4$–$C_6H_5OCH_2CH_2CH_3$.

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(4) Ninth Annual Report American Petroleum Institute, The Ohio State University Research Foundation.

(5) Olson, Hipsher, Buess, Goodman, Hart, Lamneck and Gibbons, This Journal, 69, 245 (1947).

The System Germanium Tetrachloride–Methyl *o*-Cresyl Ether.—The data obtained for this system are illustrated graphically in curve A, Fig. 5. Curve A, Fig. 5 gives no indication of compound formation. An eutectic is obtained at about 73 mole per cent. of germanium tetrachloride and about −60°. A freezing point curve for only the metastable form of germanium tetrachloride was obtained.

The System Germanium Tetrachloride–*n*-Propyl Phenyl Ether.—The data for this system are recorded in curve B, Fig. 5. A freezing point curve was obtained for the metastable form only of germanium tetrachloride. Curve B, Fig. 5 gives no indication of compound formation between germanium tetrachloride and *n*-propyl phenyl ether. An eutectic was obtained at about 88.5 mole per cent. of the tetrachloride and −56.0°.

Conclusions

The results reported in this paper may be summarized as follows: (a) Carbon tetrachloride forms addition compounds with some aromatic ethers but not with others. In general these addition compounds are highly dissociated and difficult to crystallize. (b) Silicon and germanium tetrachlorides exhibit no more than a very slight tendency to form addition compounds with the aromatic ethers studied. (c) Tin tetrachloride forms addition compounds with all the aromatic ethers with which it was studied. These also do not appear to be very stable.

Since there are so many different factors involved in the formation of solid addition compounds, the formation of such compounds cannot be taken as evidence of any particular mechanism. However, the failure of silicon and germanium tetrachlorides to exhibit more than a slight tendency to form addition compounds with aromatic ethers does indicate that the oxygen atoms in these ethers probably do not readily share electron pairs with the silicon and germanium atoms in the respective tetrachlorides. It may, of course, be stated that in those cases where carbon tetrachloride forms such addition compounds, some mechanism other than the acceptance of an electron pair from the oxygen by the carbon atom must be involved, for the valence shell of the carbon does not have an orbital available for accepting such an electron pair. Our results, with respect to silicon tetrachloride, are in accord with results obtained with this substance and dioxane.[6,7,8]

The failure of oxygen atoms in aromatic ethers to share electron pairs with silicon and germanium in their respective tetrachlorides may result from one or more of the following factors: the electron withdrawing effect of the benzene ring reducing the electron density about the oxygen, the steric interference by the aromatic group, the steric interference of the halogen atoms on the silicon or germanium atom, or too high an electron density about the silicon and germanium atoms. The latter possibility can be eliminated in terms of known reactions of the tetrachlorides. The relative importance of the other three factors cannot be evaluated from the present data.

Summary

Freezing point curves for the binary systems of a variety of aromatic ethers with the tetrachlorides of the elements of group 4a have been constructed. Compound formation occurs in some of the carbon tetrachloride systems and in all the tin tetrachloride systems. Silicon and germanium tetrachloride exhibit little tendency to form addition compounds with aromatic ethers.

(6) Lane, McCusker and Curran, THIS JOURNAL, **64**, 2076 (1942).

(7) Kelley and McCusker, *ibid.*, **65**, 1307 (1943).

(8) Kennard and McCusker, *ibid.*, **70**, 1039 (1948).

COLUMBUS 10, OHIO RECEIVED JUNE 24, 1948

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Phase Studies of Some Group 4a Tetrachloride–Aliphatic Ether Systems

BY HARRY H. SISLER, HARRY H. BATEY, BARBARA PFAHLER AND ROBERT MATTAIR

In the last publication[1] in this series it was shown that silicon and germanium tetrachlorides exhibit little tendency to form addition compounds with various aromatic ethers and, therefore, it was concluded that there is probably little tendency for the oxygen atom of the aromatic ether to share electrons with the silicon or germanium atoms in the respective tetrachloride. Tetrahydrofuran has been shown to have a strong tendency to form addition compounds with certain electron acceptor molecules.[2] It was considered desirable, therefore, to carry out phase studies of the systems of the four group 4a tetrachlorides with tetrahydrofuran. Since it was expected that tetrahydropyran would be similar to tetrahydrofuran in its ability to form addition compounds, it was decided that the germanium tetrachloride–tetrahydropyran and tin tetrachloride–tetrahydropyran systems should be studied.

It has long been known that tin tetrachloride forms stable addition compounds of the formula $SnCl_4 \cdot 2R_2O$, which are solid at room temperature, with a number of aliphatic ethers including diethyl ether.[3] It has also been shown that carbon tetrachloride forms the addition compound $CCl_4 \cdot 2Et_2O$[4] which is, however, much less stable and of much lower melting point than the tin compounds. It was decided to complete the diethyl ether series by investigating the systems silicon tetrachloride–

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(1) Sisler, Wilson, Gibbins, Batey, Pfahler and Mattair, THIS JOURNAL, **70**, 3818 (1948).

(2) Brown, unpublished.

(3) Pfeiffer and Halperin, *Z. anorg. Chem.*, **87**, 335 (1914).

(4) Wyatt, *Trans. Faraday Soc.*, **25**, 43 (1929).