[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WEST VIRGINIA UNIVERSITY]

Solubility Characteristics of Some Binary Liquid Mixtures

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Vapor-liquid equilibrium data for the systems: tin(IV) chloride–octane and tin(IV) chloride–tetrachloromethane, and critical solution temperatures for systems of perfluoroheptane with tin(IV) chloride, tetrachloromethane and octane are reported. The experimental data are interpreted as supporting the generality of the observation that hydrocarbons must be assigned solubility parameters in excess of those calculated as the square root of the quotient of energy of vaporization and molar volume. The calculated parameters are found to be adequate in predicting properties of the tin(IV) chloride mixtures with tetrachloromethane and perfluoroheptane.

Binary liquid mixtures of hydrocarbons with other non-polar substances have been observed to exhibit solubility characteristics not strictly regular[2–5] in the sense of following the Hildebrand equations.[6] The departure from complete regularity has been attributed in part to factors of molecular shape which act to decrease the partial molal entropy of mixing, which for a regular solution should be ideal.

Simons and Dunlap,[2] for example, relate the less than ideal entropy of mixing to the fact that pairs of hydrocarbon molecules interpenetrate, while fluorocarbon–hydrocarbon or fluorocarbon–fluorocarbon pairs do so to a lesser or zero extent, the difference in behavior being ascribed to the difference in atomic radii of covalently bound fluorine and hydrogen, among other factors.

The systems for which data are reported have been chosen for the purpose of further observation of the behavior of a hydrocarbon in a binary mixture with a non-polar substance other than a fluorocarbon, and for examination of the possibility that tin(IV) chloride might exhibit in its solutions the behavior ascribed to interpenetration. Such behavior would not be expected except on the basis of a purely pictorial representation, in which the tin atom of tin(IV) chloride appears to be considerably less shielded than the carbon atom of a fluorocarbon. It is evident, however, that the higher electron density of the chlorine presents a situation far less favorable to interpenetration than that involved with the hydrogen of a hydrocarbon. Simons and Dunlap have pointed out that molecular geometry is not the only or necessarily controlling factor involved in interpenetration.

Experimental

Preparation of Materials.—Perfluoroheptane obtained from the Atomic Energy Commission[7] as represented by the Carbide and Carbon Chemicals Division of Union Carbide and Carbon Corp., was shaken with sulfuric acid and then with water, dried over sodium for 48 hours, and distilled through a column having an efficiency of five theoretical plates. The fraction used had a boiling range of 81.1–81.2° at 743.8 mm. (cor.). Time–resistance cooling curves analyzed by the methods of Rossini and co-workers[8,9] indicated a f.p. of −59.61° and an average purity of about 98 mole %, the impurity being assumed to be fluorocarbon isomers of similar behavior because of the preliminary treatment and the narrowness of distillation range.

Tin(IV) chloride, C.P. Baker Analyzed was distilled four times in an all-glass apparatus, being transferred directly by distillation into the equilibrium still, bulb, or m.p. tube in which it was to be used. The sample studied had a b.p. of 111.0–111.5° at 741.2 mm. (cor.), the temperature being measured by means of a five-junction copper-constantan thermopile calibrated against the resistance thermometer. The f.p. was −33.80°, and the average purity 99.9 mole %.

Successive 40-ml. portions of Eastman White Label octane were each shaken with three 40-ml. portions of concentrated sulfuric acid, the octane samples separated, combined, washed, dried 48 hours over Drierite and distilled through a ten-plate column. The fraction of octane used had a f.p. purity of 98.9 mole %.

Tetrachloromethane, C.P. Baker Analyzed was dried over Drierite for 72 hours, and distilled through a column having an efficiency of 25 theoretical plates, the middle fraction, b.p. 74.6–74.7° at 734.5 mm. (cor.) being used.

Determination of Vapor-Liquid Equilibria.—Vapor-liquid equilibria were determined in a standard Othmer-type still manufactured by the Arthur H. Thomas Co., insulated with asbestos and magnesia pipe lagging. Technique in the use of the still was standardized by repeating the measurements of Campbell and Dulmage[10] for the system tetrachloromethane–benzene. A five-junction copper-constantan thermopile calibrated against the resistance thermometer was used to measure temperature. The tin(IV) chloride was distilled into the Othmer still, and the other materials added through a system provided with drying tubes to prevent access of moisture.

Mixtures containing tin(IV) chloride were analyzed by titrating the hydrochloric acid liberated when the bulb in which the sample had been collected was broken beneath the surface of a large excess of water, followed by quantitative dilution of the resulting solution. Suitability of this method was established by check determinations of known mixtures of tin(IV) chloride and octane, giving results within 3–5 parts per thousand of the known compositions.

The extent to which the tin(IV) chloride might isomerize or chlorinate the octane was examined by refluxing for 18 hours a mixture of equal weights of the chloride and purified octane in a system protected from moisture. Freezing point purities determined for the original sample and that recovered after hydrolysis of the tin(IV) chloride in a large excess of water, separation and drying, showed a decrement of 0.414 mole % in purity. In view of the drastic conditions of the test, and the slight decrement in purity, it was felt that chemical reaction of the octane could be ignored.

Critical Solution Temperature (c.s.t.).—Critical solution temperatures were determined by transferring weighed portions of the substances to sealed bulbs, precautions against the access of moisture being taken. The temperatures of phase separation were determined by slow cooling or heating,

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[1] Based in part on the Ph.D. Dissertation of Donald N. Campbell, West Virginia University, 1952.

[2] J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

[3] J. W. Mausteller, Ph.D. Dissertation, the Pennsylvania State College, State College, Pa., 1951, p. 56.

[4] J. H. Hildebrand, *J. Chem. Phys.*, **18**, 1337 (1950).

[5] J. H. Hildebrand, B. B. Fisher and H. A. Benesi, THIS JOURNAL, **72**, 4348 (1950).

[6] J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, pp. 119–133, 251–269.

[7] The perfluoroheptane used was furnished under special price considerations for research purposes, for which grateful acknowledgement is made.

[8] B. J. Mair, R. D. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

[9] F. D. Rossini and W. J. Taylor, *ibid.*, **32**, 197 (1944).

[10] A. N. Campbell and W. J. Dulmage, THIS JOURNAL, **70**, 1723 (1948).

and each listed value represents the average of at least ten determinations, five approaches being made from each side. The maximum variation in temperature of phase separation for a given sample was 0.4°.

F.p. of Tin(IV) Chloride.—The f.p. and purity values for pure tin(IV) chloride were determined in an all-glass unstirred f.p. tube, the Rossini-type tube used for other determinations allowing too much contamination by water. Copper sponge in contact with the sample served as a heat conductor. A well for the resistance thermometer was sealed into the glass, acetone being used in the well as a heat-transfer medium. Tests of a number of modifications of the f.p. apparatus with known substances and mixtures showed that the dimensions were critical. The form finally developed, 25 cm. in length and 2 cm. in diameter, provided with a 4-cm. diameter air jacket covering the lower 15 cm. of the tube gave f.p. values identical with those obtained in the stirred tube (for non-hygroscopic test samples) ±0.007°.

Experimental Results

Figures 1 and 2 represent the experimental data, and Tables I and II the activity coefficients calculated from the vapor–liquid equilibria for the systems tin(IV) chloride–tetrachloromethane and tin(IV) chloride–octane. Figure 3 represents the temperatures of phase separation as a function of concentration for liquid mixtures of perfluoroheptane with tin(IV) chloride, tetrachloromethane and octane. For these three systems the c.s.t. and mole percentages of perfluoroheptane at the c.s.t are as follows: 97°, 28%; 58°, 25%; 68°, 32%.

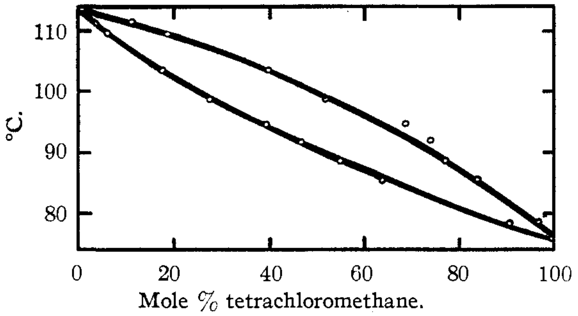

Fig. 1.—Composition of vapor (upper line) in equilibrium with liquid mixtures of tin(IV) chloride and tetrachloromethane.

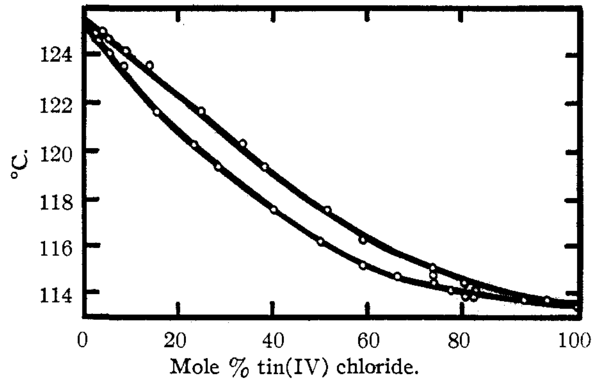

Fig. 2.—Composition of vapor (upper line) in equilibrium with liquid mixtures of tin(IV) chloride and octane.

TABLE I

ACTIVITY COEFFICIENTS, SYSTEM: TIN(IV) CHLORIDE–TETRACHLOROMETHANE

Temp., °C.	Mole fraction CCl_4 Liquid	Mole fraction CCl_4 Vapor	γ_{CCl_4}	γ_{SnCl_4}
80	0.837	0.945	1.02	0.94
90	.505	.750	1.03	1.02
100	.256	.505	1.03	0.96
110	.060	.168	1.14	0.97

TABLE II

ACTIVITY COEFFICIENTS, SYSTEM: TIN(IV) CHLORIDE–OCTANE

Temp., °C.	Mole fraction $SnCl_4$ Liquid	Mole fraction $SnCl_4$ Vapor	γ_{SnCl_4}	$\gamma_{C_8H_{18}}$
114	0.757	0.815	1.04	1.04
118	.362	.456	1.09	1.04
120	.242	.332	1.14	1.01
124	.050	.079	1.17	1.01

Discussion

Within the accuracy of the measurements employed in this work, the system tin(IV) chloride (δ = solubility parameter, $(\Delta H_v/v)^{1/2}$ = 8.7)–tetrachloromethane (δ = 8.6) follows Raoult's law, as would be expected from the equation

$$RT \ln \gamma_1 = \Phi_2^2 v_1(\delta_1 - \delta_2)^2$$

(in which Φ_2 is the volume fraction of component two, as defined by Hildebrand, ref. (6), p. 4) and the fact that the solubility parameters differ by but 0.1 unit. This affords some evidence that departure from regularity of the type ascribed to interpenetration does not exist in a binary mixture of

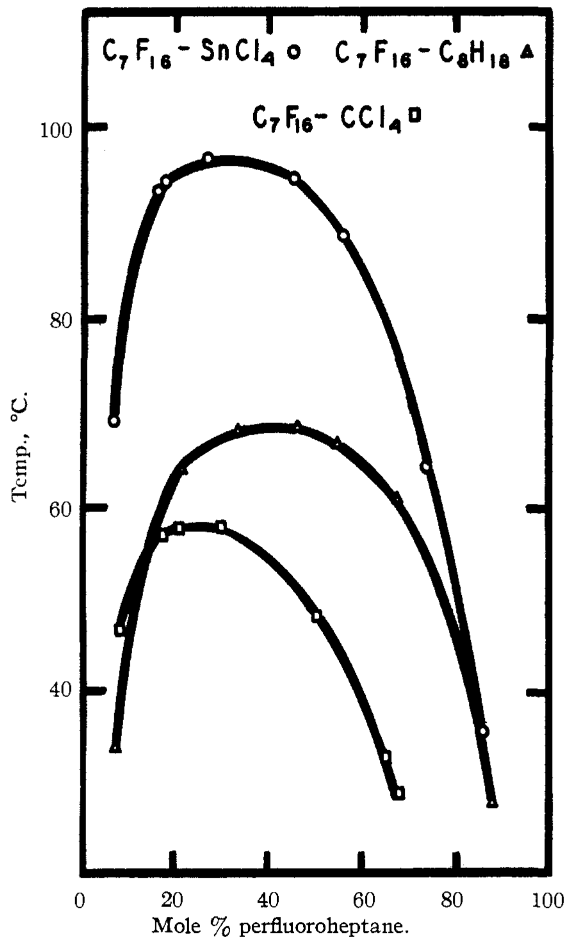

Fig. 3.—Temperature of phase separation for liquid mixtures of perfluoroheptane.

tetrachlorides containing, respectively, a large and a small central atom. The test is insensitive, however, since the solubility characteristics of binary mixtures, according to the Hildebrand equations, depend upon the square of the difference of solubility parameters, and even if, for example, the tin(IV) chloride had an effective solubility parameter considerably different from the theoretical value, the effect on the behavior of the solution would be small.

A much better test for possible deviation from regular solution behavior is provided by the c.s.t. data for the system perfluoroheptane ($\delta = 5.7$)–tin(IV) chloride. The predicted (ref. (6), p. 253, equation (3)) c.s.t. of 115° and the observed value of 97° are felt to be in excellent agreement. Since the solubility parameters of the two compounds differ by 3 units, even a small deviation of the effective difference in solubility parameters from that calculated would result in considerable departure of the solution from predicted behavior. The fact that this is not observed is evidence for non-interpenetration in tin(IV) chloride.

The vapor–liquid equilibrium data for the system tin(IV) chloride–octane ($\delta = 7.6$) indicate a system slightly more nearly ideal than predicted by the Hildebrand equations. This is in accord with Hildebrand's and Simons and Dunlap's observation of an effective solubility parameter in excess of the calculated value for the hydrocarbon (making the difference in parameters less than calculated, and hence the behavior more nearly ideal) although the sensitivity is low because of the small difference in the two parameters.

The c.s.t. value for the system perfluoroheptane–tetrachloromethane (84° calculated, 58° found) is in fair agreement with the Hildebrand equation, and is consistent with the fact that the binary mixtures of each of the components of this system with tin(IV) chloride were essentially regular.

A difference of more than 170° between calculated (−106°) and found (68°) c.s.t. for the system: perfluoroheptane–octane corresponds to a solubility parameter for the hydrocarbon greater than that calculated as the square root of the quotient of energy of vaporization and molar volume, the behavior being less ideal than predicted since the fluorocarbon has a parameter lower than that of the hydrocarbon.

Within the accuracy of this work, no evidence has been found for assumption of interpenetration in tin(IV) chloride; this is entirely in accord with the warning of Simons and Dunlap against consideration of interpenetration wholly on the basis of a geometric model. The data obtained correspond with the viewpoint that the unmodified regular solution theory is not applicable to binary mixtures containing a hydrocarbon, regardless of the nature of the second (non-hydrocarbon) component.

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Molecular Addition Compounds of Titanium Tetrachloride with Several Ethers[1]

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The compounds $TiCl_4 \cdot O(CH_2CH_2)_2O$, $TiCl_4 \cdot C_5H_{10}O$, $TiCl_4 \cdot 2C_5H_{10}O$, $TiCl_4 \cdot C_4H_8O$, $TiCl_4 \cdot 2C_4H_8O$ and $TiCl_4 \cdot CH_3OC_6H_5$ have been prepared by the direct combination of titanium tetrachloride with the corresponding ether in carbon tetrachloride solution. These are yellow crystalline solids at room temperature. With diisopropyl ether the compound $TiCl_3(OCH(CH_3)_2)$ is obtained. Titanium tetrachloride splits trioxane to yield formaldehyde and perhaps polymethylene oxide polymers. Molecular weight determinations showed that the molecular formula of $TiCl_4 \cdot 2C_5H_{10}O$ is the same as the empirical formula.

During the past few years several papers have been published from this Laboratory[2–4] dealing with the reactions of carbon, silicon, germanium and tin tetrachlorides and tin tetrabromides and iodides with various ethers. The work reported in these papers indicates that the tetrachlorides of silicon and germanium are sterically incapable of accepting pairs of electrons from oxygen bases. This is apparently due to the small size of the silicon and germanium atoms relative to the size of the chlorine atom. Tin tetrachloride does not appear to be so sterically hindered, but when the chlorine atoms are replaced by the larger bromine atoms, or by the still larger iodine atoms, an increasing amount of steric interference is obtained.[4]

Titanium tetrachloride, in many ways, has properties similar to the tetrachlorides of the carbon–silicon–germanium family. It differs from these, however, in the fact that it has an electronic configuration of the "transitional" type. Furthermore, the atomic and ionic radii of titanium are intermediate between the corresponding values for germanium and tin. We were, therefore, interested in studying the reaction of titanium tetrachloride with a variety of ethers. Numerous addition compounds of titanium tetrachloride with organic nitrogen and sulfur bases, and with oxygen compounds such as alcohols, ketones and esters have been reported. However, the only ether addition compounds with titanium tetrachloride

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(1) Presented at the Atlantic City meeting of the American Chemical Society, September, 1952. Based upon the theses submitted by P. M. Hamilton, and R. McBeth for the M.S. and B.S. degrees, respectively.

(2) H. H. Sisler, W. Wilson, B. Gibbins, H. H. Batey, B. Pfahler and R. Mattair, THIS JOURNAL, **70**, 3818 (1948).

(3) H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, *ibid.*, **70**, 3821 (1948).

(4) H. H. Sisler, E. E. Schilling and W. O. Groves, *ibid.*, **73**, 426 (1951).