[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PHOSPHATE DIVISION, MONSANTO CHEMICAL COMPANY]

The Solubility of *p*-Terphenyl in *o*- and *m*-Terphenyls and in Biphenyl[1]

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The phase diagrams in the binary systems of *p*-terphenyl with *o*- and *m*-terphenyls and with biphenyl have been determined. The solubilities are very nearly "ideal" in all three cases. Equations are presented for the explicit comparison of the solubility of a solid in two different solvents. The difference in the logarithm of the volume fraction or "site fraction" solubility is employed. This method eliminates the uncertainty as to the "ideal" solubility which is due to the limit of accuracy of the measurement of heat of fusion, and to the uncertainty in extrapolation of the heat capacity of the liquid below the melting point. The theories of Hildebrand, *et al.*, and the "quasi-lattice" theory of Huggins, Guggenheim and others are used. It is shown that Hildebrand's "regular solution" equation is equivalent to Guggenheim's formula for the heat of mixing, provided that the molecules are of the same chain length with no "doubling back on themselves"; that the differences in molar volumes can be neglected; and that $W << 2RT$. The difference between the solubility of *p*-terphenyl in *o*- and in *m*-terphenyl is given very well by the equation

$$RT(\ln x_{ac} - \ln x_{ab}) = V_a[(\delta_a - \delta_b)^2\phi_b^2 - (\delta_a - \delta_c)^2\phi_c^2]$$

The difference between the solubility of *p*-terphenyl in biphenyl and in *o*-terphenyl, and also that between biphenyl and *m*-terphenyl, are best given by the equation

$$RT(\ln \psi_{ac} - \ln \psi_{ab}) = V[(\delta_a - \delta_b)^2\phi_b^2 - (\delta_a - \delta_c)^2\phi_c^2] + T\left\{\left(1 - \frac{m_a}{m_b}\right)\psi_b - \left(1 - \frac{m_a}{m_c}\right)\psi_c + \frac{2}{zq_a}\left[\left(1 - \frac{m_a}{m_b}\right)^2\psi_b^2 - \left(1 - \frac{m_a}{m_c}\right)^2\psi_c^2\right]\right\}$$

The small discrepancy from this equation is attributed to the unequal size of the "segments" of the molecules, which should make a small positive contribution to the excess partial molal entropy of mixing.

Theory.—The theories of the solubility of solids in liquids are customarily tested by calculating the "ideal" solubility of the solid, adding the correction due to the heat and excess entropy of mixing with the particular solvent, and comparing with experiment. This has the disadvantage that the heat of fusion, ΔH^F, and the difference between the heat capacities of the solid and the supercooled liquid, ΔC_p, are necessary parameters for the calculation of the ideal solubility

$$-RT\ln x_a^i = \Delta H^F(1 - T/T_m) - \Delta C_p[(T_m - T) - T\ln(T/T_m)] \quad (1)$$

Here x_a^i is the ideal solubility of substance a, expressed in mole fraction.

There are limits to the accuracy of measurement of ΔH^F, and ΔC_p must in general be obtained by extrapolation of the heat capacity down below the melting point. So the calculation of the ideal solubility becomes quite uncertain at temperatures very far below the melting point.

This uncertainty may be removed by comparing the solubility of the solid in two different solvents. The fundamental equation[2] for the solubility of a solid equates the free energy of fusion at the temperature under consideration, *i.e.*, ΔF^F, to the partial molal free energy of mixing of the pure (supercooled) liquid a and the solvent, *i.e.*, $\overline{\Delta F}_a^M$.

$$\overline{\Delta F}_a^M = -\Delta F^F \quad (2)$$

For non-ideal solutions, we may write

$$\overline{\Delta F}_a^M = RT\ln y_a + \overline{\Delta H}_a^M - T\overline{\Delta S}_a^{M*} \quad (3)$$

Here y is a concentration variable, whose form depends on the particular theory employed for the entropy of mixing. Thus for ideal or regular solutions (in which the volume fraction ϕ is the same as the mole fraction x) $y = x$. When the "free volume" method is used, (equation 8, below), $y = \phi$ When the "quasi-lattice" method is used (equations 11 and 12, below), $y = \psi$, the "site fraction." If molecule a can occupy m_a "lattice sites," and molecule b can occupy m_b "sites," then

$$\psi_a = \frac{m_a x_a}{m_a x_a + m_b x_b}$$

$\overline{\Delta S}_a^{M*}$ is the excess partial molal entropy of mixing of a, defined by

$$\overline{\Delta S}^M = -R\ln y + \overline{\Delta S}^{M*} \quad (4)$$

It is equal to zero if the solution is ideal. $\overline{\Delta H}_a^M$ is the partial molal heat of mixing of a.

If we let b and c refer to the different solvents, we can write

$$\overline{\Delta F}_{ab}^M = RT\ln y_{ab} + \overline{\Delta H}_{ab}^M - T\Delta S_{ab}^{M*} \quad (5)$$

Subtracting the corresponding equation for solvent c

$$RT(\ln y_{ac} - \ln y_{ab}) = \overline{\Delta H}_{ac}^M - \overline{\Delta H}_{ac}^M - T(\overline{\Delta S}_{ab}^{M*} - \overline{\Delta S}_{ac}^{M*}) \quad (6)$$

The theory of the heat and excess entropy of mixing has been treated by Scatchard,[3] Hildebrand and co-workers,[2,4,5] Huggins,[6,7] Flory,[8,9] Orr,[10,11] Guggenheim[12,13,14] and others. Hildebrand has proposed the equations

$$\overline{\Delta H}_{ab}^M = V_a(\delta_a - \delta_b)^2\phi_b^2 \quad (7)$$

$$\overline{\Delta S}_{ab}^M = -R\left[\ln\phi_a - \phi_b\left(1 - \frac{V_a}{V_b}\right)\right] \quad (8)$$

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(1) Presented at the Twelfth International Congress of Pure and Applied Chemistry, September 11, 1951.

(2) Hildebrand and Scott, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1950.

(3) G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).

(4) J. H. Hildebrand, *ibid.*, **44**, 37 (1949).

(5) J. H. Hildebrand, *J. Chem. Phys.*, **15**, 225 (1947).

(6) M. L. Huggins, *ibid.*, **9**, 440 (1941).

(7) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(8) P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941).

(9) P. J. Flory, *ibid.*, **10**, 51 (1942).

(10) W. J. C. Orr, *Trans. Faraday Soc.*, **40**, 320 (1944).

(11) W. J. C. Orr, *ibid.*, **43**, 12 (1947).

(12) E. A. Guggenheim, *Proc. Roy. Soc.* (*London*), **A183**, 203 (1944).

(13) E. A. Guggenheim, *ibid.*, **A183**, 213 (1944).

(14) E. A. Guggenheim, *Trans. Faraday Soc.*, **44**, 1007 (1948.)

where

V = molar volume
$\delta = -(E/V)^{1/2}$
E = energy of vaporization
$\cong \Delta H^{\mathrm{v}} - RT$

Equation 8 is based on the "free volume" treatment, with the assumption that the free volumes are proportional to the molar volumes.

The "quasi-lattice" treatment has been used by Huggins, Flory, Orr and others. Guggenheim has given a derivation based on his "quasi-chemical equilibrium" statistical mechanics. His equation for the heat of mixing may be put in the form

$$\overline{\Delta E_{\mathrm{a}}^{\mathrm{M}}} = zq_{\mathrm{a}}\, W\xi_{\mathrm{b}}^2 \Big/ \left(1 + e^{\frac{-W}{RT}}\right) \qquad (9)$$

$$\xi_{\mathrm{a}} = \frac{x_{\mathrm{a}}q_{\mathrm{a}}}{x_{\mathrm{a}}q_{\mathrm{a}} + x_{\mathrm{b}}q_{\mathrm{b}}} = 1 - \xi_{\mathrm{b}}$$

z is the coördination number in the "lattice," and q is defined by

$$zq = m(z - 2) + 2$$

zq_{a} is the number of "lattice sites" adjacent to the sites occupied by the m segments of molecule a. It can be shown that W is given by

$$W = {}^1/_2\{(f_{\mathrm{a}}(z)\Delta E_{\mathrm{a}}^{\mathrm{v}})^{1/2} - (f_{\mathrm{b}}(z)\Delta E_{\mathrm{b}}^{\mathrm{v}})^{1/2}\}^2$$

$$f_{\mathrm{a}}(z)\Delta E_{\mathrm{a}}^{\mathrm{v}} = W_{\mathrm{aa}} = Nw_{\mathrm{aa}}$$

w_{aa} is the mutual potential energy of a pair of sites each occupied by a segment of a molecule of type a, and N is the Avogadro number. $f(z)$ is characteristic of the molecular geometry. For a "single" molecule, or for a chain molecule which does *not* "double back on itself," $f(z) = 2/zq$; for biphenyl, $f(z) = 1/(z - 1)$; for *m*- or *p*-terphenyl, $f(z) = 2/(3z - 4)$; but for *o*-terphenyl, an examination of Fischer–Hirschfelder molecular models leads to the conclusion that $f(z) = 2/3(z - 2)$. The *o*-terphenyl molecule is "doubled back" so that one of the coördination positions for each end ring must be taken up by the other end ring. This will be discussed further, below.

Since W is in general small compared to $2RT$

$$\overline{\Delta E_{\mathrm{a}}^{\mathrm{M}}} = \frac{zq_{\mathrm{a}}}{2}\,[(f_{\mathrm{a}}(z)\Delta E_{\mathrm{a}}^{\mathrm{V}})^{1/2} - (f_{\mathrm{b}}(z)\Delta E_{\mathrm{b}})^{1/2}]^2\xi_{\mathrm{b}}^2\,\frac{1}{1 - \dfrac{W}{2RT}} \qquad (10)$$

This reduces to equation 7, Hildebrand's formula, under the following conditions: the molecules must have the same chain length and no "doubling back on themselves," the difference in molar volumes can be neglected, and $W_{\mathrm{ab}} \ll 2\,RT$.

Guggenheim's treatment of the entropy of mixing, for zero energy of mixing, yields

$$\overline{\Delta S_{\mathrm{a}}^{\mathrm{M}}} = -R\ln\psi_{\mathrm{a}} - \frac{Rzq_{\mathrm{a}}}{2}\ln\left[1 - \frac{2}{zq_{\mathrm{a}}}\left(1 - \frac{m_{\mathrm{a}}}{m_{\mathrm{b}}}\right)\psi_{\mathrm{b}}\right] \qquad (11)$$

Expansion of the logarithmic term, dropping terms above the second, yields

$$\overline{\Delta S_{\mathrm{a}}^{\mathrm{M}}} = -R\left\{\ln\psi_{\mathrm{a}} + \left(1 - \frac{m_{\mathrm{a}}}{m_{\mathrm{b}}}\right)\psi_{\mathrm{b}} + \frac{2}{zq_{\mathrm{a}}}\left(1 - \frac{m_{\mathrm{a}}}{m_{\mathrm{b}}}\right)^2\psi_{\mathrm{b}}^2\right\} \qquad (12)$$

(The contribution to the entropy of mixing due to non-randomness introduced by the energy of mixing is negligible in the case of the systems studied. See reference 1, pp. 143–148.)

Equations 7, 8, 10 and 12 may be substituted into equation 6 to give the difference in the solubility of a solid as between two solvents. For molecules of *unequal* size, it is not permissible to use equation 10 except in conjunction with equation 12.

Previous Work.—The system biphenyl–benzene has been studied by Washburn,[15] Warner, *et al.*,[16] Tompa,[17] Penney and Everett,[18] and Baxendale, *et al.*[19] Penney and Everett also studied the systems diphenylmethane–benzene and bibenzyl–benzene. They found that the vapor pressures were in good agreement with theory, but that the heat and entropy of mixing, separately, were not in so good accord with calculations.

Tompa has studied the vapor pressure of benzene over biphenyl, and the heat of mixing. Baxendale, *et al.*, have studied the vapor pressure of benzene, and the solubility of biphenyl. Extensive discussions of the theory as applied to this system are to be found in references 15 to 18. Washburn determined the eutectic temperature.

Warner, *et al.*, measured the solubility of biphenyl in benzene down to 30°. An uncertainty of about 10% in the heat of fusion of biphenyl made Warner's calculation of the ideal solubility doubtful. Also, the value they quoted for the heat of vaporization of biphenyl, 18,870 cal. at 25°, is certainly far too high. This value was derived from vapor pressure measurements of Cork and Wilbur,[20] in the range 81 to 521°. A re-examination of the vapor pressure data leads to a revised extrapolation to 25°, and a heat of vaporization at that temperature of about 15,500 cal. This is in good agreement with the value 15,150 cal., calculated by Scott's equation (ref. 1, p. 427) from the boiling point. The agreement is poorer with the results of Bright,[21] who has recently measured the heat of sublimation of biphenyl. His value together with the data of Parks, *et al.*,[22] gives a heat of vaporization of about 13,000 cal. at 25°. At the boiling point, Cork's data give a heat of vaporization of 12,200 cal., which is in relatively good agreement with the value from Scott's equation, 11,485 cal.

Preliminary data were available in this Laboratory on the solubility of *p*-terphenyl in *o*- and in *m*-terphenyl. These, together with the results of Tompa, Warner and the others, indicated that interesting results could be obtained by a careful measurement of the solubility of *p*-terphenyl in bi-

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(15) E. W. Washburn and J. W. Read, *Proc. Nat. Acad. Sci.*, **1**, 191 (1915).

(16) J. C. Warner, R. C. Scheib and W. J. Svirbely, *J. Chem. Phys.*, **2**, 590 (1934).

(17) H. Tompa, *ibid.*, **16**, 292 (1948).

(18) M. F. Penney and D. H. Everett, presented at the XII International Congress of Pure and Applied Chemistry, New York, September, 1951.

(19) J. H. Baxendale, B. V. Enüstün and J. Stern, *Proc. Roy. Soc.* (*London*), **A243**, 169 (1951).

(20) J. M. Cork and D. A. Wilbur, Department of Physics, University of Michigan. Personal communication to Monsanto Chemical Co. Bulletin, "The Properties of Diphenyl," Monsanto Chemical Co. See also Montillon, Rohrbach and Badger, *Ind. Eng. Chem.*, **23**, 764 (1931).

(21) N. F. H. Bright, *J. Chem. Soc.*, 624 (1951).

(22) M. E. Spaght, S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

phenyl and in *o*- and *m*-terphenyls. The molecules seemed well suited for testing equations 7, 8, 10 and 12 as substituted into equation 6.

Experimental

Materials. Biphenyl.—Commercial biphenyl was recrystallized from alcohol and fractionally distilled under vacuum. The melting point, estimated purity and estimated melting point of the pure substance are given in Table I, for each of the materials.

***o*-Terphenyl.**—A commercial grade of *o*-terphenyl, sold under the name of Santowax O, was recrystallized several times from alcohol and fractionally distilled twice under vacuum.

***p*-Terphenyl.**—Santowax P, a commercial grade of *p*-terphenyl, was recrystallized several times from trichlorobenzene, and distilled at atmospheric pressure with a nitrogen sweep of the distillation flask.

***m*-Terphenyl.**—Santowax M, which is a commercial grade of *m*-terphenyl, was recrystallized repeatedly from alcohol and distilled three times under vacuum through a packed column of at least six theoretical plates. In the last distillation, the first and third cuts had melting points of 87.1°, and were approximately 99.4% pure. The impurity in cut no. 3 was probably *p*-terphenyl. The properties of the second cut are given in Table I. The purities of the samples, and the melting points of the pure substances, were estimated from the freezing ranges, using the method described by Rossini.[23] The melting points agree well with those reported in the literature.[24]

TABLE I

Substance	M.p., °C.	Est. purity, mole %	Est. m.p. of pure substance, °C.
Biphenyl	69.00	99.85	69.10
o-Terphenyl	56.15	99.9	56.25
m-Terphenyl	87.40	99.95	87.45
p-Terphenyl	212.5	99.8	212.7

Apparatus and Procedure.—Temperatures were measured with a 25-ohm Leeds and Northrup laboratory platinum resistance thermometer and a Leeds and Northrup type 8062 Wheatstone bridge. The thermometer was calibrated at the ice-point and against Bureau of Standards thermometers at three points over the range up to 212°, and the data were fitted to a quadratic equation. The accuracy of temperature measurements was estimated to be ±0.1°, and small temperature differences could be measured with an accuracy of ±0.01°.

Cooling curves were determined, using a test-tube in an insulating bath of Santocel, for the pure components. However, this method was found to be unsatisfactory for mixtures except those containing more than 90%, or less than 1% *p*-terphenyl. Some unexpected supercooling effects made it unsatisfactory even for the determination of eutectic temperatures.

Most of the melting points were determined by heating in 4-mm. glass tubes, with agitation provided by a piece of Nichrome wire. A 4-liter beaker was used for the heating bath. The temperature of the bath was raised at less than 0.08° per minute, and the temperature at which all solids went into solution were noted. At least three determinations were made, agreeing within 0.2° (in most cases 0.1°) on each sample. The eutectic temperatures were determined with heating at less than 0.005° per minute in the final runs, with agreement to better than 0.05°. The accuracy of the determination of the eutectic compositions is estimated at 0.03%.

Mixtures of *p*-terphenyl with each of the three other components, with compositions giving melting points within a few tenths of a degree of each other, were prepared. In this way the differences in solubility, at constant temperature, were determined to the limit of accuracy of the method (about 0.02%). In the comparison of solubilities, the absolute accuracy of the thermometer calibration does not influence the results.

Molar Volumes.—The densities of liquid *o*- and *m*-terphenyl and also of biphenyl were determined by a hydrometer at 10° intervals from the melting points to 120°. Data are available in the literature on the density of biphenyl.[20,24] This was used to obtain a calibration of the hydrometer, for the densities of *o*- and *m*-terphenyls.

Over the range 70 to 150°, the density of biphenyl fits a linear equation well (although Egloff gives a quadratic equation for the wider range 58 to 230°). Straight lines were also fitted to the density data on *o*- and *m*-terphenyl. Table II gives the constants for the equation

$$D = D_{100} - a(t - 100)$$

For *p*-terphenyl, the density of the supercooled liquid was estimated by assuming that the effect on mole volume relative to that of internal pressure should be the same with the change of structure, on going from *o*- to *m*-terphenyl as on going from *o*- or *m*- to *p*-terphenyl. As a basis for calculation, the equation (see ref. 1, p. 97) was employed.

$$\delta^2 = \left(\frac{\partial E}{\partial V}\right)_T = \frac{a}{V^{n+1}}$$

Here a is the van der Waals constant, and n is close to unity. Differentiation yields

$$2\,\frac{\mathrm{d}\log\delta}{\mathrm{d}\log V} = -(n+1) + \frac{\mathrm{d}\log a}{\mathrm{d}\log V}$$

For *o*- *vs.* *m*-terphenyls, the left member was found to be −5 at 100° and −8 at 25°. Using these results, the density of *p*-terphenyl was estimated from that of *o*- and *m*-terphenyl. (The theoretical curves turned out to be not very sensitive to errors in densities.)

TABLE II

DENSITIES OF LIQUID BIPHENYL AND TERPHENYLS

$D = D_{100} - a\ (t - 100)$

Substance	D_{100}	a
Biphenyl	0.970	0.00082
o-Terphenyl	1.019	.00080
m-Terphenyl	1.037	.00076
p-Terphenyl (est.)	1.044	.00072

The volume fraction in the system *p*-*vs.* *m*-terphenyl was assumed to be the same as the mole fraction. In the systems *p*- *vs.* *o*-terphenyl and *vs.* biphenyl, the volume fractions were calculated assuming the density to be a linear function of molar composition. Tompa[7] states that the apparent molar volume of biphenyl in benzene at 25° "is constant up to a mole fraction of 0.2, and it may be assumed that it remains so up to saturation (mole fraction 0.39)." This report, together with the chemical similarity of the components, makes the above assumption reasonable. The errors that are likely to be introduced by deviations from linearity are small.

Boiling Points.—The normal boiling points of the four substances were required for the calculation of the heats of vaporization by Scott's equation. The boiling point of biphenyl is well known.[23,25] The boiling points of the three terphenyls were determined, using a modified Claisen flask with Vigreux indentations, wrapped with tinfoil and several layers of asbestos rope. The thermometer was an Emil Greiner 200–400° mercury thermometer, which was calibrated at the boiling point of mercury in the same apparatus. It was also checked against a Bureau of Standards thermometer. The temperature readings were found to be constant during the distillation, over a range of up to 30% variation in the heat input. The results are shown in Table V. The values for the terphenyls are generally somewhat higher than those in the literature.

Solubility Results.—The phase diagrams are shown in Fig. 1. There was no evidence for solid solutions in any of the phase diagrams. This was corroborated by X-ray diffraction. (The crystal structures are such that all the diffraction lines occur at low angles. Consequently, small amounts of solid solution would not be detected in the diffraction patterns.) The eutectics are listed in Table III, and Table IV lists the mole fraction solubilities as read off a large-scale plot of log mole fraction *vs.* the inverse of the absolute temperature, Fig. 2.

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(23) F. D. Rossini, "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 454–458.

(24) G. Egloff, "Physical Constants of the Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1946.

(25) D. R. Stull, *Ind. Eng. Chem.*, **39**, 317 (1947).

TABLE III

Eutectic	Temp., °C.	Mole fraction *p*-terphenyl
p- *vs.* *m*-terphenyl	85.50	0.0435
p- *vs.* *o*-terphenyl	55.75	.0155
p-Terphenyl *vs.* biphenyl	67.80	.0290

TABLE IV

Temp., °C.	Mole fraction solubility of *p*-terphenyl In *o*-terphenyl	In *m*-terphenyl	In biphenyl
160	0.3119	0.3228	0.3273
150	.2410	.2523	.2606
140	.1932	.2065	.2138
130	.1415	.1528	.1596
120	.1081	.1169	.1239
110	.0817	.0877	.0948
100	.0605	.0658	.0726
90	.0551	.0494	.0549
80	.0333		.0410
70	.0243		.0309
60	.0175		

Discussion

The energies of vaporization are the principal parameters of equations 7 and 10. It was deemed best to use the heats of vaporization obtained in a consistent manner. Scott's equation, relating heat of vaporization to boiling point, was employed. It was recognized that the very long extrapolation was likely to lead to errors in the absolute values. Still, considering the similarity of molecular type, it is probable that the errors in the *relative* values are much smaller.

δ, the square root of the internal pressure, was calculated as a function of temperature, assuming the heats of vaporization to vary linearly with temperature. This assumption makes δ very nearly a linear function of temperature, over the range 25 to 150°. Table V shows the result of this calculation, at two temperatures. For comparison, the values from Cork's vapor pressure data are also shown.

TABLE V

Substance	Boiling point, °C.	Value of δ From b.p. equation 25°	 100°	From v.p. data 25°	 100°
Biphenyl	254.9	9.84	9.11	9.92	9.24
o-Terphenyl	337.5	9.28	8.84		
m-Terphenyl	379	9.85	9.24		
p-Terphenyl	389	9.98	9.39		

It is of interest, and also important for the discussion later, to consider the source of the differences in the δ's. The value for *o*-terphenyl is significantly lower than the values for the other three compounds. There are two possible explanations for this fact: either that the intermolecular forces per benzene ring are significantly lower for *o*-terphenyl; or else the "doubled back" configuration of the molecule makes each of the end rings a "nearest neighbor" of the other. Molecular models make the latter suggestion appear extremely reasonable.

To consider the second suggestion first, let us assume the intermolecular forces per benzene ring are "nearly independent of the state of combination."[17] Then, by the quasi-lattice treatment, the energies of vaporization will be in the ratio $(3z - 4)/(3z - 6)$. Since $T_b = \Delta H^v/\Delta S^v$, and since the entropies of vaporization should be nearly the same (following the Trouton–Hildebrand rule), we can calculate the boiling point of *o*-terphenyl from that of *m*-terphenyl. The result for $z = 9$ is 335, *vs.* 337.5° observed; and other reasonable values of z give boiling points not too far removed.[26]

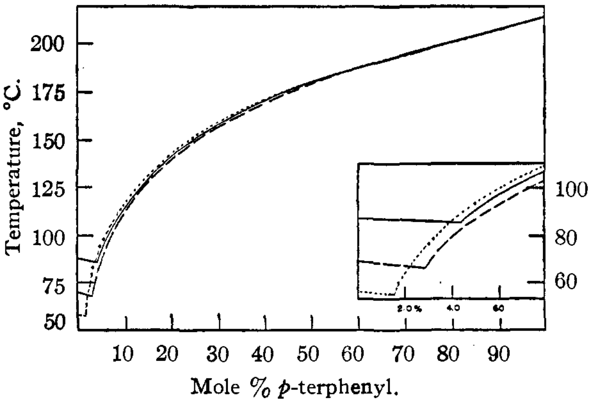

Fig. 1.—Solubility of *p*-terphenyl in: ——·——, biphenyl; ——, *m*-terphenyl; - - - - - - -, *o*-terphenyl.

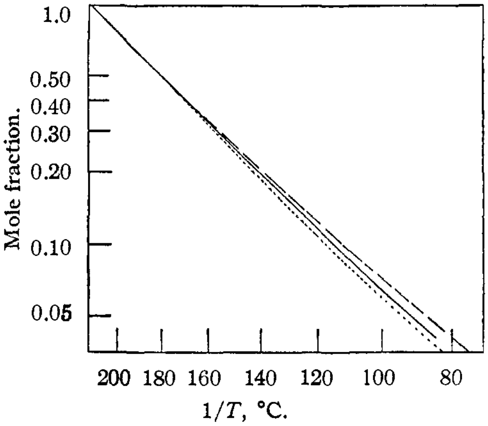

Fig. 2.—Solubility of *p*-terphenyl in: — —, biphenyl; ——, *m*-terphenyl; - - - - - -, *o*-terphenyl.

On the other hand, the two end phenyls of *o*-terphenyl could be assumed *not* to act as "nearest neighbors." This would correspond to a considerable degree of stretching out of the molecule, or to a very low coördination number. (X-Ray data on the solid would cast light on this question.) The calculated energy of vaporization per benzene ring would then be about 11% less for *o*- than for *m*-terphenyl.

Qualitatively, this difference is quite reasonable. The complete hindering of coplanarity in *o*-terphenyl should completely prevent inter-ring resonance. Consequently the polarizability per benzene ring (and hence also the dispersion forces), should be very nearly that of benzene. At 25°, δ for benzene is 9.15 (see reference 1), which is close to the value 9.28 for *o*-terphenyl in Table V. For biphenyl, *m*- and *p*-terphenyl, the order of size of the δ's also agrees with this hypothesis. The reso-

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[26] M. K. Phibbs, *J. Chem. Phys.*, **19**, 1420 (1951), has noticed qualitative evidence that the "differences among the boiling points of the isomeric pentanes are probably determined largely by the possible area of contact between adjacent molecules." This corresponds to the above calculation of the difference in boiling points of *o*- and *m*-terphenyls. Compare reference 1, p. 436, where the δ's of three pentanes may be seen to show the same trend.

nance, and hence polarizability, of *p*-terphenyl should be the greatest, because of crossed conjugation in *m*-terphenyl, and because there are only 2 rings in biphenyl. It is not at all unreasonable that the δ's should be nearly the same for biphenyl and *m*-terphenyl.

It will be seen, below, that the solubility data are in poor accord with the "doubled up" model for *o*-terphenyl, but agree very well with model in which *o*-terphenyl is "stretched out," and has a lower polarizability per ring.

Test of "Regular Solution" Equations.—Figure 3a shows the difference between the log mole fraction solubility of *p*-terphenyl in *o*- and in *m*-terphenyl, as read off a large scale plot of Fig. 2. Figure 3b shows the corresponding data for biphenyl *vs.* *m*-terphenyl, and 3c is for biphenyl *vs.* *o*-terphenyl as solvent for *p*-terphenyl. The solid curves were calculated for "regular" solutions, by substitution of equation 7 into equation 6, assuming the entropy of mixing to be ideal.

$$RT\,(\ln x_{ac} - \ln x_{ab}) = V_a\,[\phi_b^2\,(\delta_b - \delta_a)^2 - \phi_c^2(\delta_c - \delta_a)^2] \quad (13)$$

The observed volume fractions were used, on the right side of this equation.

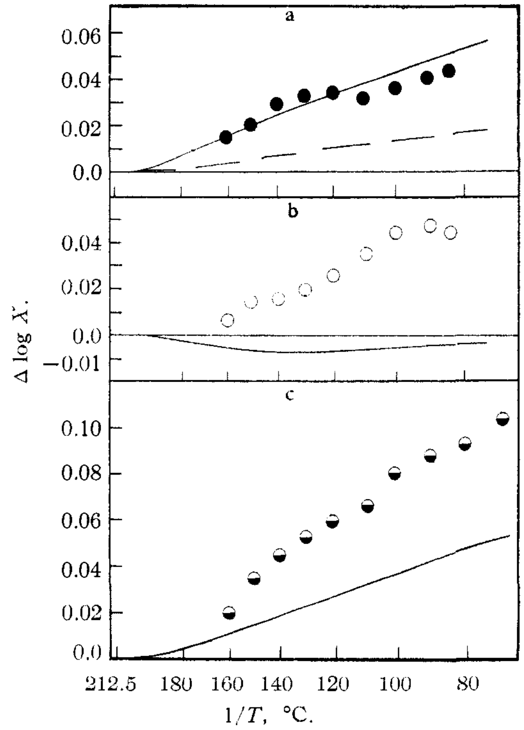

Fig. 3.—Differences in log mole fraction solubilities: circles, observed values; ——, calculated by equation 13; — —, calculated by equation 14; curve a, *o*- *vs.* *m*-terphenyl as solvent; curve b, biphenyl *vs.* *m*-terphenyl as solvent; curve c, biphenyl *vs.* *o*-terphenyl as solvent.

It may be seen that the agreement between the observed solubilities and the "regular solution" theory is excellent for *o*- *vs.* *m*-terphenyl as solvent. By contrast, the disagreement for biphenyl *vs.* *m*-terphenyl is far beyond the experimental error and the uncertainty of the assumptions. The discrepancy for biphenyl *vs.* *o*-terphenyl is just as great. (There is no improvement in Fig. 3b from using equation 14, below. In Fig. 3c, the discrepancy is just as bad or worse. This was to be expected—as was noted at the close of the "Theory" section, above.)

The experimental error is probably about 0.005 in log x. The probable errors of the theoretical treatment are harder to evaluate. In particular, the assumptions used in estimating the density of supercooled liquid *p*-terphenyl are difficult to verify. But it was calculated that an error of 1% in any one density would be necessary to give an error of 0.005 unit in Δ log x. Similarly, an error of 5° in any *one* boiling point would yield an error of 0.005 in Δ log x. Systematic errors would lead to compensating errors in the other densities or boiling points, reducing the error in the calculated Δ log x. This is illustrated by the fact that when calculations were made using the boiling points of Bachmann and Clarke,[27] namely, *o*-terphenyl 332°, *m*-terphenyl 365°, *p*-terphenyl 376°, theoretical curves not very different from those in Fig. 3 were obtained. Thus at 100°, for *o*- *vs.* *m*-terphenyl, the observed value was 0.036, *vs.* 0.032 calculated from Bachmann's boiling points and 0.042 from the new boiling points. The uncertainty in extrapolating Scott's curves for heat of vaporization *vs.* boiling point has already been mentioned. However, the most likely type of errors is systematic errors, which would cancel in this treatment.

Two calculations were made by the lattice treatment, corresponding to the two models of *o*-terphenyl mentioned above. Equation 10, when substituted into equation 6, gives equation 14

$$RT\,(\ln x_{ac} - \ln x_{ab}) = {}^1/_2\, zq_a \{ [(f_a(z)\Delta E_a^V)^{1/2} - (f_b(z)\Delta E_b^V)^{1/2}]^2\,\xi^2 - [(f_a(z)\Delta E_a^V)^{1/2} - (f_c(z)\Delta E_c^V)^{1/2}]^2\,\xi^2 \} \quad (14)$$

It turned out that $W/2RT$ could be neglected in every case. The "stretched-out" model gave a theoretical curve so close to that calculated by equation 13 that it has not been included in Fig. 3. At 100°, the two curves differed by only 0.001, which is negligible.

The dashed line in Fig. 3a was obtained using equation 14 and the "doubled-up" model of *o*-terphenyl. z was taken as 12. The agreement is very much poorer. Choice of a different value of z does not improve the agreement, since the calculated difference in solubility is zero for z between 6 and 7. To fit the experiment, very large values of z would be required (and anything over 12 is physically unreasonable) or else $z = 3$, which is equally unreasonable.

We cannot at present decide between the two models for *o*-terphenyl; independent physical data will be required to settle the question. As between equations 7 and 10, the uncertainty about the *o*-terphenyl model prevents our reaching a conclusion from the present data. On theoretical grounds, the derivation of equation 10, from the "lattice" hypothesis, seems rather more rigorous than the derivation of equation 7. But we pay for mathematical rigor, first because the assumption of a rigid

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(27) W. E. Bachmann and H. T. Clarke, This Journal, **49**, 2089 (1927).

lattice prevents allowance for differences in volumes of the units occupying the "lattice sites" (see below). Second, two additional parameters have appeared: z, and the configuration-dependent term f(z). There is at present no satisfactory way of evaluating z in the general case, although X-ray data indicate values in the range 6 to 12 in the cases that have been studied. Hence the strong temptation exists to treat z as an adjustable constant within that range. When the question of the molecule's "doubling back on itself" is not otherwise settled, f(z) also becomes an adjustable constant.

Equations for Molecules of Unequal Size.—Figures 4 and 5 show the results for biphenyl *vs.* m-terphenyl and *vs.* o-terphenyl as solvent for p-terphenyl. In each case, the solid curve was calculated using equation 12 in combination with equation 7, substituted into equation 6

$$RT \ln \frac{\psi_{ac}}{\psi_{ab}} = V_a\,[\phi_b^2(\delta_b - \delta_a)^2 - \phi_c^2(\delta_c - \delta_a)^2] + T\left\{\psi_b\left(1 - \frac{m_a}{m_b}\right) - \psi_c\left(1 - \frac{m_a}{m_c}\right) + \frac{2}{zq_a}\left[\psi_b^2\left(1 - \frac{m_a}{m_b}\right)^2 - \psi_c^2\left(1 - \frac{m_a}{m_c}\right)^2\right]\right\} \quad (15)$$

The coördination number, z, was taken as 12. This makes the last term quite small; its contribution is only -0.0055 at 100°. (For $z = 8$, the contribution is -0.0088.) The dashed curve in Figs. 4 and 5 employs equation 8 instead of equation 12

$$RT \ln \frac{\phi_{ac}}{\phi_{ab}} = V_a\,[\phi_b^2(\delta_b - \delta_a)^2 - \phi_c^2(\delta_c - \delta_a)^2] + T\left[\phi_b\left(1 - \frac{V_a}{V_b}\right) - \phi_c\left(1 - \frac{V_a}{V_b}\right)\right] \quad (16)$$

It is clear from Fig. 4 that for biphenyl *vs.* m-terphenyl as solvent, equations 15 and 16 both give a far better fit to the experimental points than does the "regular solution" treatment. Both fit the higher-temperature points very well, and fall a little below the lower-temperature points. Quantitatively, the discrepancies at 100° are: from Fig. 3b, (equation 13) 0.050; from Fig. 4, (equation 15 or 16,) 0.018.

Figure 5 shows that equation 15 gives a good fit to the data, for the case of biphenyl *vs.* o-terphenyl as solvent. Again, the curve tends to be a little low at the lower temperatures. The agreement is very much poorer for equation 16. Indeed, the fit is about as bad as when the "regular solution" equations are used. It is not clear why equation 16 should fit the data so much more poorly in Fig. 5 than in Fig. 4.

The discrepancies in Figs. 4 and 5 from the curves of equation 15 are not serious. The experimental error increases on going toward lower temperatures, since the curve of solubility *vs.* temperature becomes steeper. This might account for the divergence with decreasing temperature. Alternatively, there is a suggestion of Huggins[7]: "The effect on the entropy of mixing . . . of a difference in volume between a type 1 (sub-) molecule and a type 2 submolecule is difficult to determine. A satisfactory treatment . . . even for spherical solvent and solute molecules, has not yet been published." The ratio of the molar volumes of p-terphenyl and biphenyl is about 1.39, which indicates an appreciable difference in space requirements of the "submolecules." Hence there might be some difficulty in fitting both types into the same "lattice," a difficulty which should increase with dilution. This would lead to a decrease in disorder, which corresponds to a positive contribution to $\overline{\Delta S}^{M}$. This is just what is needed to bring the low temperature end of the curve into agreement with the data.

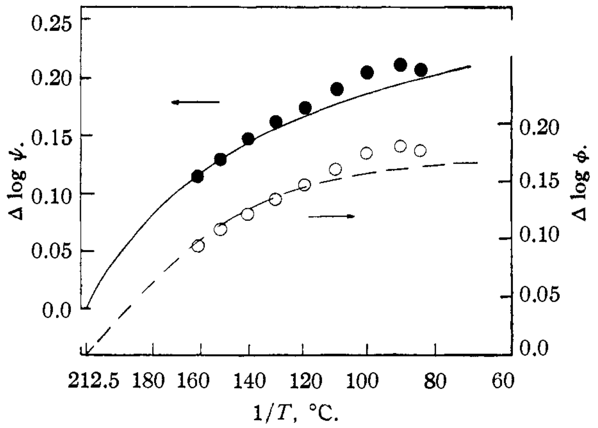

Fig. 4.—Biphenyl *vs.* o-terphenyl as solvent: ●, observed Δ log ψ; ——, calculated Δ log ψ (scale on left); O, observed Δ log φ; — —, calculated Δ log φ (scale on right).

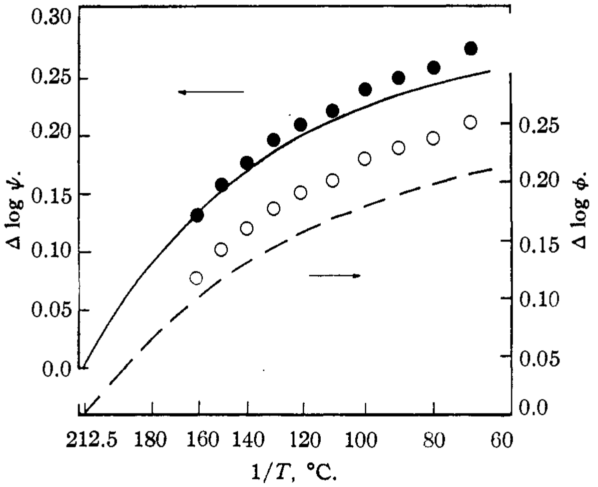

Fig. 5.—Biphenyl *vs.* m-terphenyl as solvent: ●, observed Δ log Z; ——, calculated Δ log ψ (scale on left); O, observed Δ log φ; — —, calculated Δ log φ (scale on right).

Conclusions

We may conclude, first that p-terphenyl forms regular solutions with both o- and m-terphenyl. Second, we can generalize that the *difference* in solubility of a given substance in two solvents may be accounted for by the difference in internal pressures, together with the effect of the difference in molar volumes or in "number of lattice sites" on the entropy of mixing. The present results favor the "lattice" theory.

We can suggest for future work the measurement of differences in solubilities of a given solid in a number of other related solvents, *e.g.*, p-terphenyl in the isomeric quaterphenyls which have different degrees of branching. Also, studies of differences of solubility in the isomeric pentanes having different degrees of branching[26] would cast much light on the concepts discussed above.

The theoretical treatment has been verified in a case where the differences in internal pressures and in molar volumes are relatively small. It will be of interest to see how far from conditions of ideal solubility these equations hold. It seems as if this method, with its explicit elimination of objectionable assumptions about ΔC_p, should be of considerable value in the development of a consistent set of δ parameters.

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The Behavior of Iodine Species in Pyridine and Quinoline

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Spectrophotometric studies have been made of the behavior in pyridine and quinoline of the iodine species elementary iodine, triiodide ion and unipositive iodine ion in the absence of light. It has been shown that iodine reacts slowly with pyridine, giving rise to triiodide ion, which is relatively stable in this medium. On the other hand, iodine reacts rapidly with quinoline, forming triiodide ion, which then reacts further, but at a slower rate. No products could be isolated from solutions of iodine in quinoline. However, unequivocal evidence is offered for substitution of iodine in the quinoline nucleus. Complexes containing unipositive iodine coördinated with quinoline undergo a series of reactions with quinoline to form products apparently of polymeric nature.

In a continuation of previous work[3] on the nature of solutions of iodine in pyridine, the absorption peak in the region of 320 mμ, reported for pyridine solutions of both iodine and compounds containing the unipositive iodine–pyridine complex, could not be reproduced. Instead, it was observed that there occurs in this region a marked increase in absorption, suggesting the existence at a still shorter wave length of a peak which cannot be located because of the strong absorption of pyridine itself. This has led us to an extension of our studies to include a spectrophotometric investigation of iodine, triiodide ion and unipositive iodine complexes both in pyridine and in the stronger base quinoline. In order to eliminate the possibility of complicating photochemical reactions, all solutions were prepared under subdued light and stored in the dark except during the brief period of spectral measurements.

Experimental

Absorption Spectra.—All absorption spectra were measured with a Beckman quartz spectrophotometer, model DU, which was calibrated against the hydrogen-alpha (656.3 mμ) line. Matched silica cells, 0.5 cm. for pyridine and 1 cm. for quinoline, were used. In each case, the pure solvent was employed as a blank. Measurements at wave lengths less than 305 mμ for pyridine and 341 mμ for quinoline could not be obtained because of the strong absorption of the solvent in this region.

Materials.—Eastman Kodak Co. white label pyridine was dried for one week and distilled over barium oxide, the fraction boiling at 103.5–105.4° (574.2 mm.) being collected. It was stored in a dark bottle with moisture and carbon dioxide carefully excluded. Eastman white label quinoline was dried over potassium hydroxide pellets for two weeks, then distilled under reduced pressure. The fraction boiling at 124° (20 mm.) was collected and stored in dark bottles. Iodine (Baker C.P. analyzed) was stored in a desiccator over magnesium perchlorate and used without further purification. Eastman white label tetra-*n*-butylammonium iodide was used without further purification. The positive iodine complex compounds were prepared by the general method previously described[4] and their purity was checked by analysis.

Tetra-*n*-butylammonium triiodide was prepared in pyridine solution by addition of pyridine to a solid mixture of iodine and a 5% molar excess of tetra-*n*-butylammonium iodide. Because of the observed rapidity of reaction between iodine and quinoline, tetra-*n*-butylammonium triiodide for use in this solvent was obtained in the solid state as follows: 95% ethanolic solutions of iodine and tetra-*n*-butylammonium iodide (in slight molar excess) were mixed and the resulting black precipitate was removed by filtration, washed with 95% ethanol and dried; m.p. 67–70°, uncor.

Attempted Isolation of Reaction Products from Solutions of Iodine in Quinoline.—All attempts to isolate the products of reaction between iodine and quinoline proved unsuccessful. When sodium thiosulfate was used to remove the unreacted iodine from solutions of iodine in the amine (approximately 20 g. of iodine in 200 ml. of quinoline), a yellow crystalline product was obtained. Although this solid originally contaminated with large amounts of free sulfur, could not be completely separated from an iodine-containing impurity, and, although analyses for the product obtained from different runs varied beyond experimental limits, nevertheless each analysis showed a 1:1 sulfur:nitrogen ratio and corresponded closely to that for the formula $C_9H_7NSO_3$.

When ether was added to solutions of iodine in quinoline that had stood in the dark for a few days, dark solids, showing qualitative tests for nitrogen and ionic iodine and forming picrate derivatives containing no iodine and having the same melting point as the picrate of quinoline, were precipitated.

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[2] Taken in part from the Master's thesis of Ervin Colton, University of Kansas, June, 1952.

[3] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **73**, 88 (1951).

[4] R. A. Zingaro, J. Goodrich, C. A. VanderWerf and J. Kleinberg, *ibid.*, **71**, 575 (1949).