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The Solubility of Biphenyl in Non-Polar Solvents

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The solubilities of biphenyl, between 30° and 60°, in benzene, carbon disulphide, carbon tetrachloride, heptane, dioxane and *p*-dichlorobenzene have been determined. The solubilities, in all cases, are lower than ideal. The freezing point-composition diagram for the system biphenyl-*p*-dichlorobenzene has been determined. These components yield a simple eutectic at 27.7° and at 42.5 mole percent biphenyl. Hildebrand's equation, based upon the simple Baud-Heitler equation for the heat of mixing, yields fairly satisfactory results for solutions of biphenyl in benzene,

carbon disulphide, *p*-dichlorobenzene and dioxane. The results are not very satisfactory when the equation is applied to the solutions of biphenyl in carbon tetrachloride and heptane. Hildebrand's more recent equation, based upon the Menke probability function, yields fairly satisfactory results considering the nature of the assumptions made in its derivation. It is concluded that regular solution behavior should be expected only when the molecules of the constituents, in addition to being non-polar, possess spherical symmetry.

IN recent years, the properties of "regular solutions" have been the subject of a number of experimental and theoretical studies.¹ In regular solutions, due to the absence of special orientations of the molecules of the constituents with respect to each other, the partial molal entropies are assumed to be the same as in an ideal solution of the same composition. Since it has been postulated that orientation results through the operation of dipole and coulomb forces and not from shorter range forces of the van der Waal type, it has been assumed that solutions in which both constituents are non-polar should behave like regular solutions. In this investigation, we have determined the solubility of biphenyl in six non-polar solvents over a range of temperature and have examined our results to see what support they lend to current theories.

MATERIALS AND PURIFICATION

The chemicals used were all Eastman's "Best-Grade." The *n*-heptane and *p*-dichlorobenzene were used without further purification. Benzene (thiophene free) and carbon tetrachloride were dried over calcium chloride and redistilled. Only the middle fractions were used. Carbon disulphide was dried over calcium chloride and twice redistilled over mercury to remove sulphur. Dioxane was dehydrated by refluxing over

metallic sodium and then fractionated over phosphorous pentoxide. Biphenyl, melting point 69.0°, was prepared by recrystallizing three times from alcohol, washing with ether and drying in an oven at 100°.

EXPERIMENTAL METHOD

Preparation of samples

All solubility measurements were made by a sealed tube method. Small pieces of Pyrex tubing (approximately seven-tenths cm in diameter and twelve cm long) were sealed at one end, cleaned, dried and weighed accurately. A small quantity of the solute, biphenyl, was admitted to the tube and by melting allowed to run to the bottom. All solute clinging to the sides of the tube was removed. The tube was then restricted, reweighed and the weight of the biphenyl determined. An appropriate quantity of the solvent was added and the closed end of the tube immersed in ice water to decrease the vapor pressure of the solvent. The tube was partially evacuated, sealed and reweighed to determine the weight of solvent introduced.

Procedure

Samples in the sealed tubes were completely liquified and then rapidly cooled to insure small, uniform crystals of biphenyl. The tubes were then fastened to stirring flippers immersed in a water bath. The flippers were so arranged that they moved through an angle of ninety degrees and vibrated at a rate of about one hundred and eighty per minute. The temperature of the bath was rapidly raised to within five degrees of the

¹ a. Hildebrand, J. Am. Chem. Soc. **51**, 66 (1929); b. Hildebrand and Carter, J. Am. Chem. Soc. **54**, 3592 (1932); c. Negishi, Donnally and Hildebrand, J. Am. Chem. Soc. **55**, 4793 (1933); d. Hildebrand, Phys. Rev. **34**, 984 (1929); e. Hildebrand and Wood, J. Chem. Phys. **1**, 817 (1933); f. Scatchard, Chem. Rev. **8**, 321 (1931).

actual solution temperature and the heating continued from this point at the rate of one-half degree per minute. The tube was shaken for about thirty seconds, stopped just long enough to examine for disappearance of solid and again set in motion. After determining approximately the temperature at which complete liquefaction occurred, the experiment was repeated, the temperature of the bath being raised at a rate of only one-tenth degree per minute. Four determinations, agreeing within 0.2° were made on each sample. The average of these four readings was taken as the actual solution temperature.

Temperatures were measured with 100° thermometers graduated in tenths suspended rigidly with the bulb not more than one centimeter from the path of one end of the sealed tube. All thermometers were compared with one of the same type which had been calibrated by the Bureau of Standards.

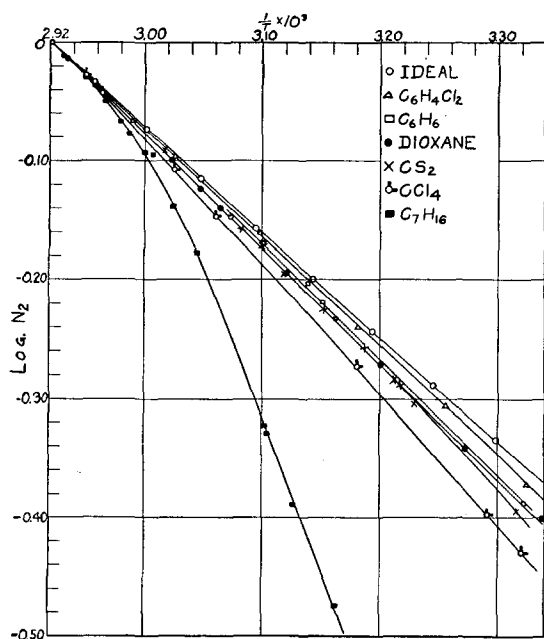
EXPERIMENTAL RESULTS

The results of the measurements are summarized in Table I and represented graphically in Fig. 1 in comparison with the ideal solubility of biphenyl. Because of the rapid change in the slope of the curve with heptane as the solvent

TABLE I. Solubility of biphenyl in non-polar solvents. Summary of calculations.

Mole fract. sol'y of biphenyl	Temp. $^\circ\text{C}$	"k"	$\bar{F}_2^r - \bar{F}_2^i$ cal.	$\bar{E}_2 - E_2^0$ cal.	Mole fract. sol'y of biphenyl	Temp. $^\circ\text{C}$	"k"	$\bar{F}_2^r - \bar{F}_2^i$ cal.	$\bar{E}_2 - E_2^0$ cal.
<i>Solvent-Heptane</i>					<i>Solvent-Carbon disulphide</i>				
0.972	68.1	1090	4		0.810*	58.3	40	7	
.934	66.0	300	6	7	.694	51.3	50	20	14
.892	64.0	235	13		.674*	49.5	32	17	
.857	62.5	220	21		.637*	47.6	46	28	
.836	61.6	212	26	43	.595	44.1	35	26	23
.806	60.5	211	36		.553	40.7	30	28	
.803*	59.5	151	26		.520	38.2	32	34	
.726	57.5	200	68		.514	37.7	32	34	
.665	55.3	192	99		.498	36.6	35	41	28
.475	49.1	186	235	478	.404	28.4	38	62	
.468	49.0	187	243		<i>Solvent-p-Dichlorobenzene</i>				
.409	46.7	186	298		0.923	65.0	66	2	
.335	43.1	184	373		.859*	61.4	64	6	
.2735	39.9	188	456	942	.802	57.4	11	2	
.216	35.2	192	540		.692*	49.8	6	3	
.140	26.5	197	659		.575	41.2	11	10	
<i>Solvent-Carbon tetrachloride</i>					.496	34.1	9	11	
0.939	66.0	140	2		.425	27.7E	11	23	
.906	64.3	140	6	7	<i>Solvent-Dioxane</i>				
.782	57.4	83	18		0.969	67.7	418	2	
.714	53.6	82	31	63	.896*	63.4	50	3	
.534	41.3	57	57		.796	57.7	58	11	
.518	40.0	56	59	170	.752	55.0	52	15	
.401	30.7	58	96		.725	53.1	41	14	
.372	28.1	59	107		.638	47.3	32	23	
<i>Solvent-Benzene</i>					.535	39.3	31	32	
0.713	52.3	40	15		.457	32.4	29	39	
.677	49.4	25	17	55	.398	26.4	28	47	
.626*	45.5	18	17		<i>Ideal Solubility</i>				
.605	44.3	27	19		1.0000	69.0			
.585	43.1	29	24	87	.9266	65.0			
.410	27.9	30	47		.8451	60.0			
					.7679	55.0			
					.6966	50.0			
					.6317	45.0			
					.5708	40.0			
					.5149	35.0			
					.4632	30.0			

* These solubilities seem least reliable inasmuch as they do not lie on the smooth solubility curves.

FIG. 1. Biphenyl-*p*-dichlorobenzene.

at about 58°, it was considered important to show that the solid phase separating out was the same over the complete temperature range. The solid phase must be either pure biphenyl or a solvate. That no solvate exists at room temperature and that pure biphenyl is the solid phase separating from all the saturated solutions was established by the fact that primary crystals obtained at room temperature melted sharply within 0.05° of the melting point of pure biphenyl. The ideal solubility, expressing the heat of fusion as a function of the temperature, is given by the equation:

$$\log N_2^i = -274/T + 4.38 \log T - 10.2996.$$

ΔH_f at the melting point is taken as 4235 cal. per mole. This is the mean of 4020 cal. per mole reported by Washburn and Read² and 4450 cal. per mole reported by Spaght, Thomas and Parks.³ That the latter value is too high is indicated by the fact that it would require biphenyl to show negative deviations from Raoult's law in some non-polar solvents. C_p for solid biphenyl at the melting point equal to

54.82 cal. per mole was obtained from what appear to be very reliable data by the above authors.³ These authors also give data from which we obtain 63.53 cal. per mole as the molal heat capacity of liquid biphenyl at the melting point. This value seems much more reliable than could be obtained from the previous discordant data.^{4, 5}

The freezing point-composition data for the system biphenyl-*p*-dichlorobenzene are given in Table II and graphically represented in Fig. 2. According to the intersection of the liquidus curves, the eutectic composition is 42.5 mole percent biphenyl and the eutectic temperature is 27.7°. Assuming ideal solution behavior and constant heats of fusion, the calculated eutectic composition is 42.0 mole percent biphenyl and the eutectic temperature is 26.4°. For *p*-dichlorobenzene, we have taken $\Delta H_f = 4120$ cal. per mole.⁶

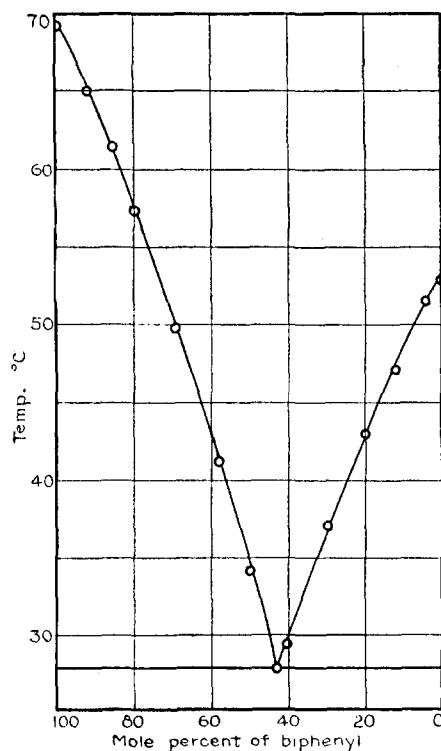


FIG. 2. Solubility of biphenyl in various solvents.

² Washburn and Read, Proc. Nat. Acad. Sci. 1, 191 (1915).

³ Spaght, Thomas and Parks, J. Phys. Chem. 36, 882 (1932).

⁴ Forrest, Brugmann and Cummings, J. Ind. Eng. Chem. 23, 37 (1931).

⁵ Newton, Kaura and DeVries, J. Ind. Eng. Chem. 23, 35 (1931).

⁶ Int. Crit. Tables 5, p. 133.

TABLE II. The binary system biphenyl-*p*-dichlorobenzene.

Mole percent biphenyl	Initial cryst. temp. °C
100.0	69.0
92.3	65.0
85.9	61.4
80.2	57.4
69.2	49.8
57.5	41.2
49.6	34.1
42.5	27.7 E
40.2	29.3
29.1	37.0
20.0	42.8
18.55	43.4
11.85	47.1
3.8	51.5
0.0	52.9

DISCUSSION

In order to estimate the relative values of intermolecular forces between solute and solvent, certain physical constants such as heats of vaporization and molal volumes must be obtained at various definite temperatures for the constituents in the liquid phase. Since we are interested in the solubility of biphenyl below its melting point, it is necessary to use the values of ΔH_v and V_m for the supercooled liquid. The density⁷ of liquid biphenyl is a linear function of the temperature from 70° to 130°. The heat of vaporization⁸ of liquid biphenyl is also a linear function of the temperature from 69° to 105°. In each case, the curves were extrapolated to give densities and ΔH_v 's of the supercooled liquid. Molal volumes of benzene, carbon tetrachloride, heptane and carbon disulphide were obtained from the densities reported in the I. C. T.⁹ The heats of vaporization of benzene, carbon tetrachloride and heptane were calculated by use of the specific heat equations.¹⁰ The heats of vaporization of carbon disulphide¹¹ were taken from the I. C. T. These constants are summarized in Table III.

In any saturated solution

$$\bar{F}_2^r - \bar{F}_2^i = RT \ln a_2/N_2 = RT \ln N_2^i/N_2. \quad (1)$$

\bar{F}_2^r and \bar{F}_2^i represent the partial molal free energies of solute in a regular and in an ideal solution. Since $\Delta F = \Delta H - T\Delta S$, one may say that for regular solutions

$$\bar{F}_2^r - \bar{F}_2^i = \bar{H}_2^r - H_2^0 = \bar{L}_2,$$

inasmuch as it is assumed that $\Delta S = 0$. Starting with the Baud-Heitler¹² equation for the heat of formation of a mole of solution

$$\bar{L}_2 N_2 + \bar{L}_1 N_1 = \Delta H = b N_1 N_2, \quad (2)$$

Hildebrand^{1a} obtained the equations $\bar{L}_1 = b N_2^2$,

$$\bar{L}_2 = b N_1^2$$

$$\log N_2^i/N_2 = b N_1^2 / 2.303 RT = K N_1^2 / T. \quad (3)$$

His method cannot be justified on rigorous mathematical grounds but only because equations of the correct general form for regular solutions are obtained, namely, $L_1 \rightarrow 0$ as $N_2 \rightarrow 0$, $L_2 \rightarrow 0$ as $N_1 \rightarrow 0$ and $L_2 = L_1$ when $N_2 = N_1$. For regular solutions b , and hence k , is assumed to

TABLE III. Physical constants of biphenyl and the non-polar solvents.

Temp. °C	Molal vol. cc	Heat of vap. cal.
<i>Biphenyl</i>		
25	149.4	18,870
35	150.6	18,310
45	151.8	17,730
55	153.0	17,160
65	154.3	16,570
<i>Benzene</i>		
35	90.5	7,860
45	91.7	7,780
55	92.8	7,660
65	93.9	7,550
<i>Carbon disulphide</i>		
35	61.2	6,520
45	61.9	6,410
55	62.8	6,310
65	63.6	6,200
<i>Carbon tetrachloride</i>		
35	97.8	7,790
45	98.9	7,680
55	99.8	7,560
65	101.0	7,410
<i>Heptane</i>		
35	148.2	8,547
45	149.8	8,400
55	151.3	8,260
65	152.6	8,110

⁷ Private communication from Professor W. L. McCabe, University of Michigan.

⁸ Bulletin, Swann Chemical Co., Birmingham, Ala.

⁹ Int. Crit. Tables, 3, pp. 28, 29.

¹⁰ Int. Crit. Tables, 5, pp. 115, 107, 81; Parks and Huffman, *Free Energies of Some Carbon Compounds*, pp. 68-93; Parks, Huffman and Thomas, J. Am. Chem. Soc. 52, 1032 (1930).

¹¹ Int. Crit. Tables, 5, p. 138.

¹² Baud, Bull. Soc. Chim. (4) 17, 324 (1915); Heitler, Ann. d. Physik (4) 80, 630 (1926).

be independent of composition and essentially independent of the temperature. Values of k calculated from our solubility data are listed in Table I. Reasonably constant values of k are obtained in all cases when the mole fractions of solute are less than 0.65. With higher mole fractions of biphenyl there is a drift toward increased values of k . This drift may not be very significant in the carbon disulphide, dioxane, *p*-dichlorobenzene and benzene solutions since the departure from Raoult's law is slight in each of these solvents. Furthermore, values of k are fairly sensitive to small errors in solubility when the mole fraction of solute is high. With carbon tetrachloride and especially with heptane as solvents the drift in k can hardly be attributed to experimental error. The drift is equally evident when k is calculated from the smoothed curves representing our solubility data (Fig. 1). We must conclude therefore, that Eq. (3) does not apply well to our data; particularly to the solutions of biphenyl in heptane and carbon tetrachloride.

That Eq. (3) should not apply to many solutions even when both constituents are non-polar is indicated by the fact that the Baud-Heitler equation, as shown by Coleman and Germann,¹³ is not adequate for expressing the heat of mixing as a function of the composition. These investigators have developed the following empirical equation from an analysis of the dependence of ΔH on N .

$$\Delta H = N_1 N_2 (\alpha + \beta e^{\gamma N_1}). \quad (4)$$

α , β and γ are constants or functions of the temperature. This equation becomes identical with Eq. (3) when either β or γ is zero. However, an examination of the data compiled by Coleman and Germann shows that neither β nor γ is zero for a variety of solutions in which both compo-

nents are non-polar and it seems likely that neither β nor γ would be zero in some of our solutions.

In a recent investigation, Hildebrand and Wood,¹⁶ by making use of the probability function of Menke¹⁴ as a basis for a statistical treatment of intermolecular potentials in solution, has arrived at the equation

$$\bar{E}_2 - E_2^0 = \left[\frac{n_1 V_1}{n_1 V_1 + n_2 V_2} \right]^2 V_2 \left[\left(\frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} - \left(\frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} \right]^2. \quad (5)$$

\bar{E}_2 represents the partial molal total energy and E_2^0 the molal total energy of the solute. The V 's and ΔE 's represent the molal volumes and the energies of vaporization. It is assumed that for regular solutions

$$\bar{E}_2 - E_2^0 = \bar{F}_2^r - \bar{F}_2^i = RT \ln N_2^i / N_2.$$

We possess sufficient data for the calculation of $\bar{E}_2 - E_2^0$ by Eq. (5) only for the solutions of biphenyl in carbon disulphide, carbon tetrachloride, benzene and heptane. For these four systems, $\bar{E}_2 - E_2^0$ is compared with $\bar{F}_2^r - \bar{F}_2^i$ in Table I. The agreement is as good as could reasonably be expected considering the nature of the assumptions made in the derivation of Eq. (5). The probability function is certainly not the same function of distance in all radial directions from the central molecule for non-spherical molecules. Moreover, the potential function must be dependent upon the shape of molecules and upon the presence or absence of polar bonds in the molecule even when the molecule as a whole possesses a zero moment. It seems likely that the conditions of Hildebrand's original definition of the regular solution can be met only when the molecules of the constituents, in addition to being non-polar, possess spherical symmetry.

¹³ Coleman and Germann, *J. Chem. Phys.* **1**, 847 (1933).

¹⁴ Menke, *Phys. Zeits.* **33**, 593 (1932).