6. Three-phase equilibria between homogeneous, anisotropic plastic neat soap, homogeneous, anisotropic middle soap, and homogeneous, isotropic liquid phase A.
7. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and isotropic liquid phase A.
8. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and isotropic liquid phase B.
9. Two-phase equilibria between homogeneous, anisotropic, plastic neat soap, and homogeneous, hydrated potassium laurate crystals, the limiting case of which occurs in the absence of lauric acid.
10. Three-phase equilibria between homogeneous, anisotropic, plastic neat soap, homogeneous, hydrated potassium laurate crystals, and homogeneous isotropic liquid phase B.
11. Two-phase equilibria between homogeneous, hydrated potassium laurate crystals, and homogeneous, isotropic liquid phase B, the limiting case of which occurs in the absence of water when the isotropic liquid phase B is in equilibrium with anhydrous potassium laurate.

Summary

It is attempted for the first time to map out with phase rule diagrams the equilibria existing in an aqueous three-component system of acid soaps. This is done from 100 to 370°, some remarkable and unique equilibria being exhibited.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA

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Solubility. XIII. The Solubility of Iodine in Certain Solvents

BY G. R. NEGISHI, L. H. DONNALLY AND J. H. HILDEBRAND

The solubility of iodine in a variety of solvents is unusually interesting because of the large number of "regular solutions"[1] it forms showing large deviations from Raoult's law. These solutions are particularly striking in the relationship they show between "regularity" and color. The investigations here described were undertaken for the purpose of including certain additional solvents: ethylene bromide, because of its high solvent power, isooctane, to compare with a normal paraffin, and two of the tetrahalides included under a comprehensive investigation now going on under the direction of the senior author,[2] *viz.*, the tetrachlorides of silicon and titanium.

(1) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).
(2) J. H. Hildebrand and J. M. Carter, *ibid.*, **54**, 3592 (1932).

Materials and Purification

The "Reagent Iodine Merck" was dried over phosphorus pentoxide and was used without further treatment.

Eastman ethylene dibromide was washed, several times, with dilute sodium hydroxide and distilled water, shaken with calcium chloride in a sealed flask for two days and fractionally distilled three times. The first and last portions were discarded and the middle portion, boiling at 130.9–131.0° at 755 mm., was collected in a Pyrex flask, which was stoppered with a cork covered with tinfoil. It was kept in the dark.

For the purification of technical titanium tetrachloride, an all-Pyrex apparatus was employed similar to that used by Baxter and Fertig.[3] The apparatus consisted of seven 1500-cc. distilling flasks, each equipped with a fractionating column, an outlet to a vacuum line or to the atmosphere, a water condenser, and a magnetically breakable inner seal. In the fourth flask, a thermometer was hung from a platinum hook inside the projecting fractionating column so as not to touch the wall. The receiving flask was equipped with a number of inner seals and a phosphorus pentoxide tube which could be connected to a vacuum line or to the atmosphere.

The starting material was distinctly reddish-yellow, due to ferric chloride and vanadium chloride. The former is easily removed by distillation, but the latter, imparting a lemon-yellow color,[4a] necessitated refluxing for from four to six hours over dilute sodium amalgam (less than 1%) in the first two flasks. The next flask was dried by evacuating and heating several times. The seal was broken and the material was distilled over at a reduced pressure. The distillate was colorless and clear. The same procedure was followed in the successive operations, except that the boiling point of the material was determined at ordinary pressure. The first and the last portions were discarded and the middle portion obtained was colorless and clear, boiling at 135.7–135.9° at 756 mm. Particular care was taken to prevent the liquid and its vapor from coming in contact with moisture. When the liquid was distilled into the receiving flask, the phosphorus pentoxide tube was sealed off and the liquid was kept in the flask under a reduced pressure.

Technical silicon tetrachloride, which was yellow and slightly turbid, was purified in a similar apparatus. The yellow liquid, which was presumably due to iron and chlorine[4b] was refluxed twice over mercury, and then distilled in an atmosphere of dry nitrogen. The nitrogen from a commercial tank was forced successively through pyrogallol in 12 *N* technical sodium hydroxide, C. P. concentrated sulfuric acid, phosphorus pentoxide tube and a tube of glass wool, into the distilling apparatus. The first and the last portions of each distillation were discarded and the middle portion, boiling sharply at 56.9 at 750 mm., was collected. All precautions were taken to keep out the moisture during the purification.

The isooctane was 2,2,4-trimethylpentane obtained from the Ethyl Gasoline Corporation.

Apparatus and Procedure

For the solubility of iodine in ethylene bromide we used, with but slight modification, the apparatus of Hildebrand and Jenks.[5] After the chamber was dried, iodine was introduced and dibromoethane distilled into it. It was then stoppered with a ground-glass stopper and the bulb was placed in the thermostat in the rocking device. After the equilibrium was reached, the bulb was tilted so that the outlet was almost perpendicular. The stopper was replaced by the pipet and a portion of the solution was

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[3] G. P. Baxter and G. J. Fertig, THIS JOURNAL, **45**, 1229 (1923).

[4a] Gmelin-Kraut's "Handbuch der anorg. Chemie," 1912, Vol. III, 1, p. 61.

[4b] Gmelin-Kraut's "Handbuch der anorg. Chemie," 1912, Vol. III, 1, 1268.

[5] J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **42**, 2184 (1920).

transferred into the pipet by forcing dry air at the temperature of the bath, saturated with dibromoethane through the side tube provided with a stopcock. The construction of the bulb was such that the solid was kept away from the tip of the pipet. The bulb was kept under the surface of water in the thermostat during the filling of the pipet. When approximately 10 cc. of liquid was forced into the bulb of the pipet, it was removed, the liquid adhering to the stem was wiped off with filter paper and, after slipping on a glass tube closely fitting the stem at each end of the pipet, it was weighed, the contents washed into a flask, and titrated with sodium thiosulfate. The weights and the buret used were standardized.

For the determination of the solubility of iodine in titanium chloride an apparatus of Pyrex, as shown in Fig. 1, was used. Four of these were fused onto a Pyrex tube with a water condenser, which in turn was fused onto an inner seal connected to the receiving flask. The system was dried by repeatedly evacuating, heating and introducing dry, pure nitrogen. A steady stream of nitrogen prevented other gases from entering into the system. When the system was filled with nitrogen, each of the large bulbs was cooled with ice and salt, the projecting tube was broken off at C, and iodine was introduced into the bulb. While the stream of nitrogen was passing through, the tube was sealed off by heating about 5 cm. below C. The same procedure was followed until iodine was introduced into each of the large bulbs. The nitrogen was then shut off, the system evacuated, the seal broken and titanium chloride was distilled into each bulb. As each one was filled, it was sealed off at B.

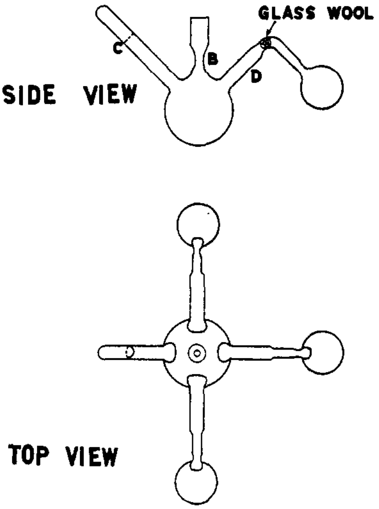

Fig. 1.

The bulb was shaken in the bath in such a way as to rock the contents back and forth along the projecting tube. The length of the tube D was sufficient to eliminate any danger of liquid in the bulb reaching a wad of glass wool in the tube. The equilibrium was approached from above in every case. When equilibrium was reached, portions of the solution were drained into the smaller bulbs by tilting. During the transferring of the solution, the whole apparatus was kept under the surface of the water. When the transfer was complete, the apparatus was taken out of the bath, immersed in ice and salt mixture and each bulb was sealed off. The neck of the smaller bulb was drawn and constricted so that very little heating was required in sealing it off. A very small amount of white substance was formed in the neck where it was heated, but any error due to this was considered negligible.

The method of analysis was similar in manipulation to that of Baxter and Fertig.[3] The small bulb was washed successively in cleaning solution and distilled water. After drying and weighing carefully, it was put in a flask with a ground glass stopper containing 500 to 750 cc. of potassium iodide solution saturated with carbon dioxide gas. After carbon dioxide was bubbled through the solution in the flask for about forty minutes to displace the air, the stopper was replaced, and the bulb was broken by shaking it violently against the thick walls of the flask. After the white cloud had disappeared, the contents was titrated with sodium thiosulfate. A steady stream of carbon dioxide was passed into the flask during the titration. It was essential to prevent all access of oxygen, since, in such a strongly acid solution, it would oxidize iodide ion. The end-point of the titration was quite sharp in spite of the presence of the white titanic acid. The broken glass pieces were collected, boiled in nitric acid to dissolve any precipitate adhering to them, transferred to a weighed Gooch crucible, dried carefully and weighed.

The apparatus and the method of analysis employed for silicon chloride were the same as above except that silicon tetrachloride was distilled in an atmosphere of nitrogen. When the small bulbs were sealed off, no white deposit was formed. When the bulb was broken in potassium iodide solution in the flask, there was only slight or no cloud formation, and the solution was practically clear.

Since blank tests made for iodine–titanium chloride checked with the theoretical results, it was thought unnecessary to make the blank test runs for the iodine–silicon tetrachloride system.

The temperature of the thermostat at 25° was kept within ±0.01° and that at 40° and above maintained within ±0.03°.

The results of the measurements are summarized in Table I, and represented graphically in Fig. 2 in comparison with published measurements in

TABLE I

SOLUBILITY OF IODINE

Temp., °C.	Wt. per cent.			Average	Mole per cent.
		Solvent, titanium tetrachloride			
0.10	1.152	1.153		1.153	0.8633
25.00	2.856	2.853	2.856	2.855	2.150
40.00	4.626	4.640	4.626	4.631	3.499
49.90	6.499	6.504	6.496	6.500	4.939
		Solvent, silicon tetrachloride			
0.10	0.2569	0.2544	0.2551	0.2555	0.1713
25.00	.7462	.7431	.7417	.7433	.4987
40.00	1.310	1.308	1.311	1.309	.8801
		Solvent, ethylene bromide			
8.00	6.707	6.496	6.467	6.557	4.925
10.00	6.792	6.851	6.886	6.850	5.161
15.00	7.875	7.843		7.859	5.937
20.00	9.139	9.086	9.058	9.091	6.895
24.80	10.38	10.38		10.38	7.895[a]
25.00	10.32	10.30	10.33	10.32	7.815
30.02	11.88			11.88	9.073[a]
34.20	13.10	13.17		13.14	10.07[a]
35.00	13.40	13.42	13.43	13.42	10.28
35.07	13.73	13.59		13.66	10.49[a]
45.00	17.45	17.42	17.43	17.43	13.51
49.60	19.18	19.05		19.12	14.89[a]
60.00	25.55	25.50	25.57	25.54	20.24
70.00	33.33	33.26		33.30	26.97
75.00	37.61	37.56		37.61	30.85
76.50	39.85			39.85	32.90[a]
78.40	42.41	42.38		42.40	35.26[a]
		Solvent, isooctane (2,2,4-trimethylpentane)			
24.92	1.302	1.303		1.303	0.5900[a]
35.00	1.922	1.915	1.917	1.918	.8711[a]

[a] Measurements by L. H. Donnally.

other solvents. Several points may be mentioned in connection with the plot. First, the solutions in titanium and silicon tetrachlorides and in isooctane fit into the family of "regular" curves previously found for all violet colored solutions and obeying rather closely the equation

$$\log N_2^i/N_2 = kN_1^2/4.575\,T \tag{1}$$

The value of N_2^i for iodine can be calculated from the equation

$$\log N_2^i = \frac{-\Delta H}{4.575}\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{2}$$

where ΔH, the heat of fusion per mole, is 4010 cal., and T_m, the melting point, is 387.2°. Substituting Equation 2 with these values in Equation 1 gives

$$-\log N_2 = (kN_1^2 + 876)/T - 2.262 \tag{3}$$

TABLE II

t, °C.	Molal vol. I_2, cc.	V_1	100 N_2	k	A	V_1	100 N_2	k	A
			Solvent $TiCl_4$				Solvent $SiCl_4$		
0.1	57.6	107.8	0.863	308	24.3	111.5	0.171	501	39.7
25.0	59.0	110.5	2.150	309	23.5	115.3	.499	490	37.8
40.0	59.8	112.5	3.499	310	23.0	117.8	.880	485	36.7
49.9	60.4	113.5	4.939	308	22.3	...	...	...	...
			Mean	309	23.8			492	37.1
			Calcd.	Eq. 7	26.7				39.2
			Solvent $C_2H_4Br_2$				Solvent CS_2		
0.0	57.6	...	....	...	...	58.9	2.50	188	14.9
10.0	58.2	85.3	5.161	144	10.9	59.6	3.41	180	14.4
25.0	59.0	86.6	7.815	151	11.0	60.7	5.76	190	14.7
42.0	59.9	...	....	...	...	61.8	9.86	190	14.2
45.0	60.1	88.3	13.51	161	11.2	...	...	...	...
60.0	60.9	89.6	20.24	173	11.3	...	...	...	...
75.0	61.7	91.0	30.85	188	11.3	...	...	...	...
			Mean	163	11.1			187	14.6
			Calcd.	Eq. 7	16.0				15.1

For CCl_4, from 0 to 50°, k varies from 395 to 384; A from solubility 31.2 to 28.5; A from Eq. 7, 28.5. For C_7H_{16}, A from solubility, 40.7; from Eq. 7, 29.6.

Table II gives empirical values of k calculated from the equation which show how well the new systems fit this relation. The good agreement for the other violet solutions has been previously pointed out.

The only considerable deviation in the case of a violet solution is for ethylene bromide, shown by the smaller slope in Fig. 2, and by the increase in k from 144 at 10° to 188 at 75°. It is not possible, from the data at hand, to determine whether this is due to failure of the solution to behave "regularly," in the sense of possessing ideal entropy of mixing, or to failure to obey the simple relation of Equation 1. In other words, the change of solubility with temperature is a total differential, since both composition and temperature are changing, and a complete understanding of the system requires a knowledge of the partial differentials of the activity with respect to both variables. This may be formally expressed by writing the mathematical identity

$$\mathrm{d}\ln a_2 = \left(\frac{\partial \ln a_2}{\partial \ln \mathrm{N}_2}\right)_T \mathrm{d}\ln \mathrm{N}_2 + \left(\frac{\partial \ln a_2}{\partial T}\right)_\mathrm{N} \mathrm{d}T$$

We can set a_2 in the left-hand member equal to N_2^i and rearrange, giving

$$\frac{\mathrm{d}\ln \mathrm{N}_2^i}{\mathrm{d}T} = \left(\frac{\partial \ln a_2}{\partial \ln \mathrm{N}_2}\right)_T \frac{\mathrm{d}\ln \mathrm{N}_2}{\mathrm{d}T} + \left(\frac{\partial \ln a_2}{\partial T}\right)_\mathrm{N} \qquad (4)$$

We can measure the total differential by the solubility, but cannot evaluate either partial differential from the same data. We must measure one of them independently.

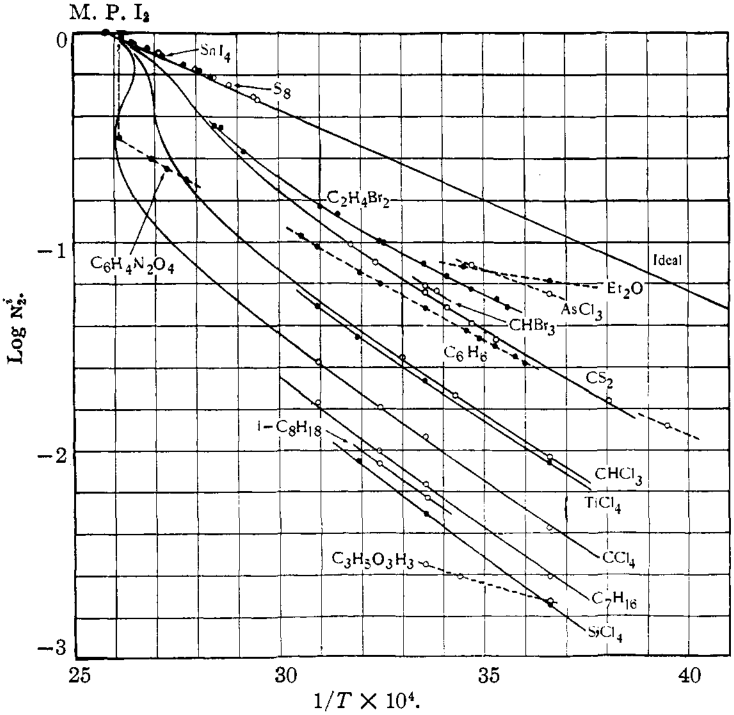

Fig. 2.—Solubilities of iodine.

It is worth noting that a regular solution may depart from Equation 1, requiring some more complex relation, such as

$$\log \frac{\mathrm{N}_2^i}{\mathrm{N}_2} = \frac{1}{4.575\,T}\left(k\mathrm{N}_1^2 + l\mathrm{N}_1^3 + \ldots\right) \qquad (5)$$

and still not diverge from the family of regular curves, provided N_2 is so small that N_1 is practically unity. Divergence in this range must be regarded as evidence of irregular entropy, and hence oriented molecules. However, when N_2 is large, as in the region between 0 and 0.1, different regular (violet?) solutions might fail to show parallel curves because of the higher coefficients of Equation 5, such as might arise from inequality in molecular volumes. It is doubtless significant that whereas carbon disulfide, which obeys the simple Equation 1 with iodine, has almost the same volume; ethylene bromide, whose solutions with iodine deviate from Equation 1, has a much larger molal volume. The tetrachlorides here used and heptane have still larger molal volumes, but the smaller concentration of iodine in their solutions in the range herein studied prevents any difference between Equations 1 and 5 coming to light.

It is possible that, in spite of the violet color, there is some approach to solvation in ethylene bromide which would be revealed by a study of the absorption spectrum over a range of temperature, as in the case of carbon disulfide.[6] Or it may be that the discrepancy is due to the polarity of the ethylene bromide. Its dipole moment is 1.4×10^{-18} e. s. u.

The relative positions of the curves for violet solutions in Fig. 2 correspond well, on the whole, with the relative values of the intermolecular forces indicated by the values[7] of $\Delta E/V$ and of $(\partial E/\partial V)_T$ shown in Table III. E denotes energy, ΔE the energy of vaporization and V the molal volume. The position of the solubility curve for a new "violet" solvent could therefore be predicted with reasonable accuracy. The minor discrepancy in the position of the curve for silicon tetrachloride with respect to the two paraffins may be connected with the differences in molal volumes. The significance of the reversed S-shape of the upper portion of the curve for carbon tetrachloride has been discussed in an earlier paper.[1]

TABLE III

RELATION OF INTERNAL PRESSURE TO NON-IDEALITY OF IODINE SOLUTIONS

Solvent	k	$(\partial E/\partial V)_T$, atm.	$\frac{\Delta E}{V}$, atm.	Solvent	k	$(\partial E/\partial V)_T$, atm.	$\frac{\Delta E}{V}$, atm.
$SiCl_4$	492	2554	2390	CS_2	190	3670	4120
i-C_8H_{18}	466	...	2040	$CHBr_2$	168	4450	...
C_7H_{16}	450	2510	2310	$C_2H_4Br_2$	151	4420	4040
CCl_4	389	3310	3015	S_8	0	...	...
$TiCl_4$	309	3430	3140	SnI_4	0	...	4220
$CHCl_3$	300	...	3520	I_2	0	...	...

An interesting quantitative treatment of this problem has been given by Scatchard,[8] who has derived the equation

$$RT \log \frac{N_2^i}{N_2} = AV_2 \left(\frac{N_1V_1}{N_1V_1 + N_2V_2}\right)^2 \qquad (6)$$

This reduces to Equation 1 when $V_1 = V_2$, giving $AV = 4.575\ k$

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(6) P. Waentig, *Z. physik. Chem.*, **68**, 513 (1909).

(7) J. H. Hildebrand, *Phys. Rev.*, **34**, 984 (1929).

(8) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

The constant, A, is calculated from the "cohesive energy densities," $\Delta E/V = a$ of the pure components, by the relation

$$A = (\sqrt{a_1} - \sqrt{a_2})^2 \qquad (7)$$

The following values of a, as cal. per cc., at 25°, were used for the substances here concerned: $TiCl_4$, 76.0; CCl_4, 73.0; $C_2H_4Br_2$, 97.5; CS_2, 100.0; $SiCl_4$, 58.0; I_2, 192. These values were taken, in part, from a paper by the senior author;[7] the others were calculated from the vapor pressure curves and the molal volumes.

It can be seen from Table II that the values of A calculated from the solubility data vary with temperature more than the values of k, except in the case of dibromoethane. This variation would probably be largely avoided by treating A, not as a constant, as implied in Scatchard's treatment, but as a variable, since $\Delta E/V$ decreases with temperature. Since $V \Delta E = a$, the van der Waals constant, with sufficient accuracy for this purpose, it would be preferable to substitute for Equation 7 the expression

$$A = \left(\frac{\sqrt{a_1}}{V_1} - \frac{\sqrt{a_2}}{V_2}\right)^2 \qquad (8)$$

In Fig. 2 are included several solubility curves in addition to those previously published. Stannic iodide, as has been pointed out in our paper on its solubilities, gives ideal solutions with iodine. Solutions of iodine in *p*-dinitrobenzene are interesting as illustrating, first, limited solubility in the liquid state, second, the irregular temperature coefficient of a brown solution. The dotted curves in Fig. 2 indicate brown solutions, and it is very evident that they do not belong to the family of violet solutions. In the case of carbon disulfide, the dotted line is drawn in the direction of some rather inaccurate values at much lower temperatures. The color does not change very much as the temperature is lowered, but the absorption band undergoes a great change.

Summary

The solubility of iodine in ethylene bromide and in silicon and titanium tetrachlorides has been measured over a wide range of temperature. The "regularity" of iodine solutions is discussed, together with the relation between solubility and internal pressure and the applicability of an equation derived by Scatchard.

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