[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hydrogen Bonds Involving the C-H Link. X.[1] The Solubility of Donor Solutes in Halogenated Hydrocarbons

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It has been shown[2] that donor solvents such as esters, ethers, nitriles and tertiary amides will dissolve certain hydrogen containing halogenated hydrocarbons in excess of the amount calculated from Raoult's law. This enhanced solubility has been explained by the assumption that hydrogen bonds of the C—H←O and C—H←N type occur in such solutions. When completely halogenated methanes are dissolved in donor solvents hydrogen bonding cannot occur and no enhanced solubility is observed.[3]

These facts have suggested to us that very high solubilities of solid donor solutes should be observed in hydrogen-containing halogenated hydrocarbons. An examination of the literature has shown that while chloroform is almost always a better solvent than carbon tetrachloride for solid organic compounds, the difference is most marked in those cases where hydrogen bonds may form between the solute and chloroform. Some typical cases are reported in Table I. This list is by no means complete but does show the general trend of solubilities in these solvents.

Some of these cases are very interesting. Thus the completely methylated caffeine, which is unassociated and melts lower, is far more soluble in chloroform than is the partially methylated theobromine. The acidic amide hydrogen of theobromine is bonded to oxygen or nitrogen in another molecule of the same type, thus partially preventing combination with the less acid hydrogen in chloroform. The low melting, strongly chelated *o*-nitrophenol, as is to be expected, is highly soluble in both chloroform and carbon tetrachloride and has a low ratio of mole solubilities. The high ratio of solubilities for the associated *p*-nitrophenol is difficult to explain unless it is assumed to associate by the joining together of the OH groups, which form very stable hydrogen bonds, thus leaving the nitro groups free to bond to the active hydrogens of the chloroform molecules. Piperonal seems to be less soluble in chloroform as compared to its solubility in carbon tetrachloride than would be expected. However, some experiments to be reported soon[4] have shown that acetals of formaldehyde may be associated and this would decrease the chances for bonding between the oxygen atoms of piperonal and the hydrogen in chloroform.

In view of the behavior of these monomeric compounds, we decided to examine the solubilities of some polymeric esters, a polymeric ketone and a polymeric halogenated hydrocarbon in the solvents, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and *sym*-tetrachloroethane. From the considerations advanced above it would be expected that polyesters and polyketones would dissolve in chloroform, trichloroethylene and *sym*-tetrachloroethane to a greater extent than they do in carbon tetrachloride and tetrachloroethylene. On the other hand, a polymeric halogenated hydrocarbon would not be expected to show this difference. The data which have been determined are presented in Table II.

The solvents used were commercial samples which were redistilled and collected over a 2° boiling range.

The polymeric materials used as solutes were in general technical samples obtained from various laboratories. The polyvinyl chloride and polyvinyl acetate samples were medium molecular weight polymers which were given to us by Mr. H. B. McClure of Carbide and Carbon Chemicals Corporation. The poly methyl methacrylate used was a sample of commercial granular "Lucite" obtained from the du Pont Company. Superpolyhexamethylene adipate and superpolyethylene adipate were laboratory samples obtained from the du Pont Experimental Station[5] and had viscosities of 400 poises and 1300 poises at 139°, respectively. The cellulose acetate, which contained 62.45% of combined acetic acid, was supplied by the du Pont Company. The ethylene phthalate was prepared from phthalic anhydride and ethylene glycol.[6]

The solubility determinations were made by adding an excess of the polymeric material to the solvent in a glass-stoppered bottle. The stoppered bottle was placed in a rotating device in a thermostat at 30° for forty-eight hours. The saturated solution was removed, weighed, evaporated and the residue weighed. This method worked well in cases where the solubility was low and in duplicate experiments

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[1] For the ninth communication in this series see THIS JOURNAL, **62**, 227 (1940).

[2] (a) Zellhoefer, *Ind. Eng. Chem.*, **29**, 548 (1937); (b) Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938); (c) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666, 2714 (1938).

[3] Copley, Zellhoefer and Marvel, *ibid.*, **61**, 3550 (1939).

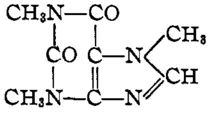
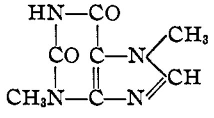
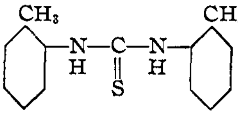
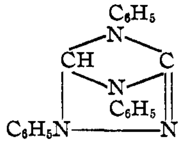
[4] Ph.D. Thesis of Emanuel Ginsberg, University of Illinois, 1940.

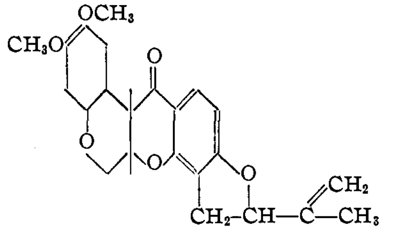
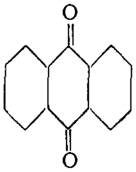
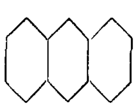
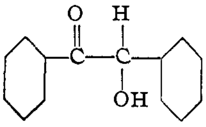
[5] U. S. Patent 2,071,250.

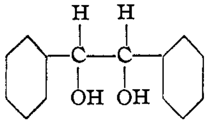
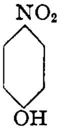
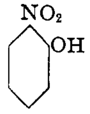
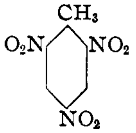
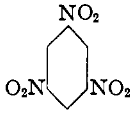
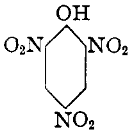
[6] Kienle and Hovey, THIS JOURNAL, **52**, 3636 (1930).

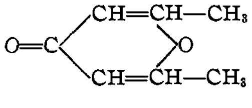
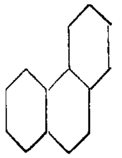
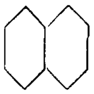
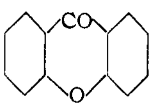
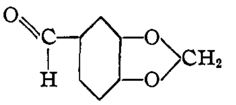
Table I

Solubilities of Some Organic Compounds in Chloroform and Carbon Tetrachloride

Compound		Caffeine	Theobromine	*o*-Ditolylthiourea	Nitron
Formula					
Temp., °C.		18	15.5	20	20
Soly., g. per 100 g.	$CHCl_3$	11.8	0.060	9.54	2.55
	CCl_4	0.089	.020	0.10	0.03
Approx. ratio[a]		103	2.3	74	66
Reference		7	8	9	9

Compound		Rotenone	Anthraquinone	Anthracene	Benzoin
Formula					
Temp., °C.		20	20	20	20
Soly., g. per 100 g.	$CHCl_3$	49.3	0.54	1.74	4.01
	CCl_4	0.4	.043	0.47	0.20
Approx. ratio		95	9.7	3.0	15.5
Reference		10	9	9	9

Compound		Hydrobenzoin	*p*-Nitrophenol	*o*-Nitrophenol	2,4,6-Trinitrotoluene	1,3,5-Trinitrobenzene	Picric acid
Formula							
Temp., °C.		20	14	15.5	20	15	20
Soly., g. per 100 g.	$CHCl_3$	1.60	2.99	99.7	19.0	6.24	1.86
	CCl_4	0.105	0.050	40.4	0.65	0.237	0.07
Approx. ratio		12	46.4	2	22.7	20.5	20.6
Reference		9	11	11	12	13	9

Compound		Dimethylpyrone	Phenanthrene	Naphthalene	Xanthone	Piperonal
Formula						
Temp., °C.		20	25	20	20	20
Soly., g. per 100 g.	$CHCl_3$	34.4	54.6	46.6	11.24	200.8
	CCl_4	1.04	22.5	25	0.96	69.5
Approx. ratio		26	2	1.4	9	2.2
Reference		9	14	15, 16	9	9

[a] Approximate ratio: (Moles of solute per mole of $CHCl_3$)/(Moles of solute per mole of CCl_4).

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(7) H. Göckel, *Forsch.-Ber. üb. Lebensm. u. ihre Bez. z. Hyg. etc.*, **4**, 173–177 (1897); *Chem. Zentr.*, **68**, II, 401 (1897).

(8) R. V. Wadsworth, *Analyst*, **45**, 133 (1920).

(9) B. Pawlewski, *Chem. Polski*, **14**, 245–246 (1914), "Tables Annuelles de Constantes et Donneés Numeriques," Vol. V, Gauthier-Villars et Cie., Paris, 1926, p. 947.

(10) H. A. Jones and C. M. Smith, This Journal, **52**, 2554 (1930).

(11) L. Desvergnes, *Rev. chim. ind.*, **36**, 194 and 224 (1927).

(12) C. A. Taylor and W. Rinkenbach, This Journal, **45**, 44 (1923).

(13) L. Desvergnes, *Mon. sci.*, **15**, 149–158 (1925).

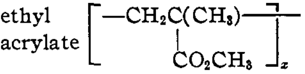
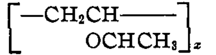
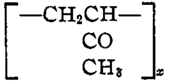
(14) H. Henstock, *J. Chem. Soc.*, **121**, 2125 (1922).

(15) M. A. Étard, *Bull. soc. chim.*, (3) **9**, 82 (1893).

(16) I. Schröder, *Z. physik. Chem.*, **11**, 449–465 (1893).

TABLE II

SOLUBILITY OF POLYMERS IN CHLORINATED SOLVENTS

Solute	Grams solute in 100 g. solvent				
	$CHCl_3$	CCl_4	$CHCl{=}CCl_2$	$Cl_2C{=}CCl_2$	$CHCl_2CHCl_2$
Ethylene phthalate $[-CH_2CH_2-O-COC_6H_4CO-O-]_x$	>100	0.021	1.0	0.007	33
Superpolyhexamethylene adipate $[-(CH_2)_6-O-CO-(CH_2)_4-CO-O-]_x$	> 87	10.0	55.0	.06	77
Superpolyethylene adipate $[-(CH_2)_2-O-CO(CH_2)_4CO-O-]_x$	>100	0.114	>85	.078	>100
Poly methyl methacrylate  $\left[\begin{matrix}-CH_2C(CH_3)- \\ \vert \\ CO_2CH_3\end{matrix}\right]_x$	77	.116	96	.047	>100
Cellulose acetate	5.2	.002	0.002	.001	5.8
Polyvinyl chloride $[-CH_2CHCl-]_x$	0.078	.004	.014	.003	0.054
Polyvinyl acetate  $\left[\begin{matrix}-CH_2CH- \\ OCHCH_3\end{matrix}\right]_x$	>100	9.3	64	.003	>100
Poly methyl vinyl ketone  $\left[\begin{matrix}-CH_2CH- \\ CO \\ CH_3\end{matrix}\right]_x$	>100	0.002	78	.001	70

the amount of polymer dissolved usually checked within about 10%. With solvents and solutes where hydrogen bonding was possible this method could not be used as the concentrated solutions became thick, viscous, and impossible to filter. In these cases to a weighed sample of polymer was added a weighed amount of solvent. The mixture was shaken and allowed to stand at 25 ± 1° for forty-eight hours to see whether it became homogeneous. It was impossible to make accurate measurements even by this procedure as absorption of the solvent and swelling by the polymer made it difficult to decide whether the solution was homogeneous. Hence, the values given in Table II for these high solubilities are to be regarded as minimum values.

Discussion of Results

Inspection of the data in Table II shows that all of the polyesters and polyketones are far more soluble in chloroform and *sym*-tetrachloroethane than they are in carbon tetrachloride and tetrachloroethylene. On the other hand, the solubility of polyvinyl chloride is of the same order in all five chlorinated solvents. The very low solubilities which are reported in Table II may possibly be due to slight traces of foreign bodies in the polymers which were used. These values should therefore be considered as the higher limits of solubility in the cases studied.

It may be noted that polyvinyl chloride has hydrogen atoms which may be of sufficient activity, due to the adjacent chlorine atoms, to form hydrogen bonds. This view would account for the fact that it is very soluble in dioxane, a donor solvent. Polyethylene, a hydrocarbon, is reported[17] as being negligibly soluble in trichloroethylene, chloroform and carbon tetrachloride as well as in donor solvents such as amyl acetate and acetone.

The solubility of cellulose acetate is much lower in the hydrogen-containing halogenated solvents than was expected and the solubility in trichloroethylene shows that essentially no effect of the hydrogen of the solute is being exerted. In general, the hydrogen atom in trichloroethylene seems to have less effect in promoting solubility of donor solutes than do the hydrogen atoms in chloroform and *sym*-tetrachloroethane. The solubilities of polyvinyl acetate and superpolyhexamethylene adipate in carbon tetrachloride are considerably higher than were anticipated. It is thus obvious that while hydrogen bonding is an important factor in determining solubility other factors are also involved.

Summary

Organic compounds containing donor centers generally are much more soluble in hydrogen-containing halogenated hydrocarbons than in completely halogenated hydrocarbons. These higher solubilities are attributed to solute–solvent association by means of CH←O or CH←N bonds.

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[17] U. S. Patent 2,153,553.