acid may be prepared by acetylation, bromination and subsequent hydrolysis. Attempts to prepare 3(α),11-dihydroxycholanic acid from this by the Wolff–Kishner and Clemmensen methods have been unsuccessful.

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Hydrogen Bonds Involving the C–H Link. The Solubility of Haloforms in Donor Solvents

BY G. F. ZELLHOEFER, M. J. COPLEY[1] AND C. S. MARVEL[1]

A recent paper[2] by one of the authors reported the solubilities of a number of low boiling halogenated hydrocarbon refrigerants in a variety of organic solvents. Since the publication of this paper, the measurements have been extended to include other types of halogenated hydrocarbons and new solvents. In this paper the earlier results and the new data are discussed in order to give a comprehensive picture of the factors leading to high solubility.

The halogenated hydrocarbons which have been used in this investigation include the types CH_3X, CH_2X_2, CHX_3, CX_4, C_2H_5X and C_2X_6 where X may be either a chlorine or a fluorine atom. The solvents which were tested include ethers, thioethers, esters, ether-esters, ketones, aldehydes, alcohols, alcohol-ethers, primary and tertiary amines, amides, nitro compounds, hydrocarbons and halogenated hydrocarbons. It has been observed that almost invariably solvents which contain donor atoms (oxygen or nitrogen) dissolve the halogenated hydrocarbons, which have at least one hydrogen atom in the molecule, in excess of the amount predicted from Raoult's law. The generality of this effect which is greatest for the CHX_3 type has led us to suggest that the formation of a hydrogen bond ($C–H \leftarrow O$ or $C–H \leftarrow N$) is the important factor in producing this high solubility.[3]

It has been known for some time that mixtures of halogenated hydrocarbons of the types CHX_3 and C_2HX_5, where X is a halogen atom, with ethers and ketones show large negative deviations[4,5] from Raoult's law. This behavior has been attributed to compound formation[6,7] between the two components. Further evidence indicating the same conclusion has been obtained from measurements of heats of mixing,[8] of viscosities,[9] of dielectric constants,[10] and of freezing points.[11] The bonding forces responsible for complex formation have been assumed to be either chemical and resulting from the formation of a coördinate link, or physical and due to forces between dipoles.

A suggestion as to the type of coördinate link formed was made by Glasstone[10] in 1936. He determined the total polarization of mixtures of ethers, acetone and quinoline with a number of halogenated hydrocarbons ($CHCl_3$, CH_3CCl_3, $CHBr_3$, CHI_3, CCl_4, CBr_4, C_2HCl_5, C_2Cl_6). His results were interpreted by him as indicating considerable complex formation. It is most pronounced in the case of halogenated hydrocarbons of the type CHX_3, and this led him to suggest the existence of a hydrogen bond between the hydrogen of the CHX_3 and the oxygen of the ether and ketone, or the nitrogen of quinoline. One may picture the bond as formed by the donation of an unshared pair of electrons of the oxygen or nitrogen atoms to the hydrogen.[12,13] The presence of the strongly electron-attracting halogen atoms on the carbon loosens the hydrogen and makes it available for coördination to the donor atom. Hence the amount of complex formation should increase as the X in CHX_3 is varied in the order $I < Br < Cl < F$. The complex may be considered as resonating between the two structures

$$[R_2O\ H—CX_3] \quad [R_2\overset{+}{O} \longrightarrow H\ \overset{-}{C}X_3]$$

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[2] G. F. Zellhoefer, *Ind. Chem. Eng.*, **29**, 584 (1937).

[3] As this manuscript was being prepared the paper by Gordy [THIS JOURNAL, **60**, 605 (1938)] giving infrared absorption data which indicate the formation of hydrogen bonds between chloroform and acetone, ethyl acetate and dioxane was published.

[4] Kohnstamm and Dalfsen, *Proc. Akad. Wet.*, **29**, 156 (1901).

[5] Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

[6] Dolezalek, *ibid.*, **64**, 727 (1908).

[7] Dolezalek and Schulze, *ibid.*, **83**, 45 (1913).

[8] McLeod and Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

[9] McLeod, *ibid.*, **30**, 482 (1934).

[10] Glasstone, *ibid.*, **33**, 200 (1937).

[11] Wyatt, *ibid.*, **25**, 43 (1929).

[12] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[13] M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).

TABLE I

SOLUBILITY OF HALOGENATED HYDROCARBONS

1	2	3	4	5	6	7	8	9	10	11	12	
	V. p. of solute in atm. at		"Ideal solubility" mole fraction	Solvent I Solubility			Solvent II Solubility			Solvent III Solubility		
Solute	4.5°	32.2°		g./g.	mole fr.		g./g.	mole fr.		g./g.	mole fr.	
CH_3Cl	2.90	6.95	0.422	0.333	0.538	1.28	0.325	0.588	1.39	0.382	0.551	1.305
CH_2Cl_2	0.230	0.739	.311	.500	.508	1.63	.575	.600	1.93	,567	.519	1.68
$CHCl_3$	.106	0.355	.283	.800	.542	1.91	.895	.625	2.20	.875	.550	1.94
CH_2Cl_2	.230	0.739	.311	.500	.508	1.63	.575	.600	1.93	,567	.519	1.68
CH_2ClF	1.728	4.35	.398	.538	.581	1.46	.570	.647	1.62	.580	.578	1.45
$CHCl_3$	0.106	0.355	.283	.800	.542	1.91	.895	.625	2.20	.875	.550	1.94
$CHCl_2F$	0.847	2.221	.381	1.020	.635	1.67	1.110	.706	1.85	1.13	.640	1.68
$CHClF_2$	5.63	12.52	.449	1.143	.700	1.56	1.090	.740	1.65	1.127	.678	1.51
C_2H_5Cl	0.735	1.97	.372	0.245	.401	1.08	0.237	.448	1.21	0.306	.434	1.16
CCl_3F	0.478	1.34	.356	.338	.303	0.850	.302	.329	0.923	.495	.370	1.035
CCl_2F_2	3.52	7.78	.453	.267	.280	.619	.215	.282	.622	.458	.380	0.840
$C_2Cl_3F_3$	0.1815	0.550	.330	.330	.248	.750	.275	.212	.642	.465	.288	.872
$C_2Cl_2F_4$	1.032	2.65	.390	.155	.137	.351	.120	.135	.346	.300	.222	.570

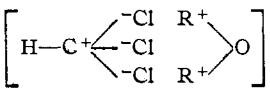
Solvent I: ethyl ether of diethylene glycol acetate; II, dimethyl ether of tetraethylene glycol; III, diethyl ether of diethylene glycol.

Two types of dipole association have been advanced to explain the formation of these complexes. One type is known as "head on" association[14,15] and may be illustrated in the case of the chloroform–ether complex by

$$\left[\overset{+\ \longrightarrow}{R_2O}\quad \overset{+\ \longrightarrow}{HCCl_3}\right]$$

This formulation explains the decreased amount of complex observed by Glasstone[10] in passing from chloroform and bromoform to iodoform, since there is a corresponding decrease in the moment of the C–X linkage. It is evident that this picture of association is structurally similar to the hydrogen bond picture, and differs from it only in that no bonding energy due to resonance is assumed.

The other picture[16,17] of dipole association may be formulated as follows



In this case the attraction is due mainly to the action of the negative chlorine atoms on the polarizable alkyl groups. This explains many of the facts but, as will be shown later, it cannot be used in any simple fashion to explain the remarkable difference in solubilities that we observed for compounds of the types CHX_3 and CX_4.[10] Furthermore, it is not clear why such a type of association should depend on the presence of an oxygen or a nitrogen atom in the solvent as the results in Table II will demonstrate.

Solubility Data

The method of measuring solubilities was described in detail in a previous communication[2] and is not repeated here. In Table I are given the solubilities of a series of halogenated hydrocarbons in three different high boiling solvents (diethyl ether of diethylene glycol, dimethyl ether of tetraethylene glycol and ethyl ether of diethylene glycol acetate). The measurements were made very carefully and are correct to within 1%. The solubilities were determined for a range of pressures, but for comparison the values stated in Table I are the solubilities at 32.2°, with a pressure of halogenated hydrocarbon corresponding to its vapor pressure at 4.5°. Columns 2 and 3 give the vapor pressures in atmospheres of the halogenated hydrocarbons at 4.5 and 32.2°. Column 4 gives the "ideal" mole fraction solubilities calculated from the ratio of the vapor pressures. Columns 7, 10 and 13 give the ratios of the observed mole fraction solubilities to the "ideal" mole fraction solubilities.

In order to illustrate the effect on solubility of different functional groups in the solvent, the solubility of monofluorodichloromethane ($CHCl_2F$) at 32.2°, under a pressure corresponding to its vapor pressure at 4.5°, is recorded in Table II for a large number of solvents. These solvents were chosen primarily on the basis of their high boiling points and chemical stability. The solubilities

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(14) F. H. Müller, *Physik. Z.*, **34**, 688 (1933).

(15) Moelwyn-Hughes and Sherman, *J. Chem. Soc.*, 101 (1936).

(16) R. J. W. Le Fevre, *Trans. Faraday Soc.*, **33**, 207 (1936).

(17) A. R. Martin, *ibid.*, **33**, 208 (1936).

TABLE II

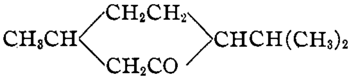
SOLUBILITY OF $CHCl_2F$ IN ORGANIC SOLVENTS

"Ideal" mole fraction 0.381

		Solubility	
Ethers and thioethers	Formula	g./g.	mole fr.
Cyclohexylmethyl ether	$C_6H_{11}OCH_3$	0.90	0.498
Dimethyl ether of ethylene glycol	$CH_3OCH_2CH_2OCH_3$	1.55	.576
Di-β-chloroethyl ether	$ClCH_2CH_2OCH_2CH_2Cl$	0.425	.451
Dimethyl ether of diethylene glycol	$CH_3O(CH_2CH_2O)_2CH_3$	1.20	.611
Diethyl ether of diethylene glycol	$C_2H_5O(CH_2CH_2O)_2C_2H_5$	1.13	.640
Methyl ether of diethylene glycol chloride	$CH_3(OCH_2CH_2)_2Cl$	0.69	.486
Dimethyl ether of triethylene glycol	$CH_3O(CH_2CH_2O)_3CH_3$	1.01	.638
Methyl ether of triethylene glycol chloride	$CH_3(OCH_2CH_2)_3Cl$	0.775	.578
Dimethyl ether of tetraethylene glycol	$CH_3O(CH_2CH_2O)_4CH_3$	1.11	.706
Dimethyl ether of hexaethylene glycol	$CH_3O(CH_2CH_2O)_6CH_3$	0.836	.716
γ,γ'-Dichloro-*n*-propyl ether	$(ClCH_2CH_2CH_2)_2O$	.438	.421
Dichloro-isopropyl ether	$[ClCH_2(CH_3)CH]_2O$	.445	.425
p-Fluoroanisole	*p*-$FC_6H_4OCH_3$	.508	.385
Resorcinol diethyl ether	*m*-$C_6H_4(OC_2H_5)_2$	.52	.456
Dioxane	$C_4H_8O_2$	1.077	.479
Tetrahydrofurfuryl ether of *n*-butyl cellosolve	$(C_4H_7O)CH_2O(CH_2)_2OC_4H_9$	0.791	.608
Ditetrahydrofurfuryl ether of diethylene glycol	$[(C_4H_7O)CH_2OCH_2CH_2]_2O$	.80	.680
Diphenyl sulfide	$C_6H_5SC_6H_5$	.288	.306
Bis-(β-methylthiolethyl) sulfide	$CH_3SCH_2CH_2SCH_2CH_2SCH_3$[a]	.46	.448
Esters			
n-Butyl butyrate	$CH_3(CH_2)_2COO(CH_2)_3CH_3$	0.870	0.546
Ethyl laurate	$CH_3(CH_2)_{10}COOC_2H_5$	.561	.556
Diethyl phthalate	*o*-$C_6H_4(COOC_2H_5)_2$	.561	.543
Diethyl oxalate	$C_2H_5OCOCOOC_2H_5$	.83	.545
Diethyl malonate	$C_2H_5OCOCH_2COOC_2H_5$	.82	.558
Triacetin	$(CH_3COOCH_2)_2CHOCOCH_3$	.629	.570
Tripropionin	$(CH_3CH_2COOCH_2)_2CHOCOCH_2CH_3$	.617	.609
Tributyrin	$[CH_3(CH_2)_2COOCH_2]_2CHOCO(CH_2)_2CH_3$	.458	.573
Tricaproin	$[CH_3(CH_2)_4COOCH_2]_2CHOCO(CH_2)_4CH_3$	.521	.661
Trimethylene glycol diacetate	$(CH_3COOCH_2)_2CH_2$	.841	.568
α,γ-Glycerol dichlorohydrin acetate	$(ClCH_2)_2CHOCOCH_3$	.440	.397
4-Methyl-2-pentanol acetate	$(CH_3)_2CHCH_2CH(OCOCH_3)CH_3$	.848	.542
Ether-esters			
Cellosolve acetate	$C_2H_5O(CH_2)_2OCOCH_3$	1.04	0.542
Cellosolve succinate	$[C_2H_5O(CH_2)_2OCOCH_2]_2$	0.650	.624
Cellosolve adipate	$[C_2H_5O(CH_2)_2OCO(CH_2)_2]_2$	.717	.662
Benzyl cellosolve acetate	$C_6H_5CH_2O(CH_2)_2OCOCH_3$	.604	.538
Methyl cellosolve phthalate	*o*-$C_6H_4(COOCH_2CH_2OCH_3)_2$	.505	.582
n-Butyl cellosolve phthalate	*o*-$C_6H_4(COOCH_2CH_2OC_4H_9)_2$	.484	.631
Ethylene glycol diethoxy acetate	$(C_2H_5OCH_2COOCH_2)_2$	.670	.602
Diethylene glycol diethoxy acetate	$(C_2H_5OCH_2COOCH_2CH_2)_2O$	.63	.634
Diethylene glycol dimethoxy acetate	$(CH_3OCH_2COOCH_2CH_2)_2O$	.602	.59
Tetrahydrofurfuryl cellosolve acetate	$(C_4H_7O)CH_2OCH_2CH_2OCOCH_3$	.809	.598
Triethylene glycol dimethoxy acetate	$(CH_3OCH_2COOCH_2CH_2OCH_2)_2$	.614	.636
Methoxyacetate of triethylene glycol acetate	$CH_3OCH_2COO(CH_2CH_2O)_3COCH_3$	.843	.681
Triethylene glycol diacetate	$[CH_3COOCH_2CH_2OCH_2]_2$	.759	.631
Carbitol methoxy acetate	$C_2H_5O(CH_2CH_2O)_2COCH_2OCH_3$	.812	.620
n-Butyl carbitol acetate	$C_4H_9O(CH_2CH_2O)_2COCH_3$	.718	.587
Diethylene glycol diacetate	$(CH_3COOCH_2CH_2)_2O$	.792	.599
n-Butyl cellosolve *n*-butyrate	$C_4H_9O(CH_2)_2OCOC_3H_7$	.713	.565
n-Butyl cellosolve acetate	$C_4H_9O(CH_2)_2OCOCH_3$	.804	.562
n-Butyl cellosolve laurate	$C_4H_9O(CH_2)_2OCO(CH_2)_{10}CH_3$	.499	.594
Methyl carbitol acetate	$CH_3O(CH_2CH_2O)_2COCH_3$	.94	.596

[a] This thioether was prepared from sodium methyl mercaptan and di-β-chloroethyl sulfide in yields of 46%: b. p., 107–110° (2 mm.); m. p. 26–27°; n^{20}_D 1.5668; $d^{20°}_{20}$ 1.111. The last two values were determined on the supercooled liquid. *Anal.* Calcd. for $C_6H_{14}S_3$: S, 52.79. Found: S, 53.00.

Table II (*Concluded*)

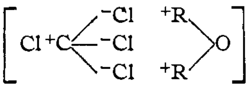
Ether-esters	Formula	Solubility g./g.	Solubility mole fr.
Methyl ether of triethylene glycol acetate	$CH_3O(CH_2CH_2O)_3COCH_3$	.862	.632
Tetrahydrofurfuryl laurate	$(C_4H_7O)CH_2OCO(CH_2)_{10}CH_3$	.935	.610
Furfuryl acetate	$(C_4H_3O)CH_2OCOCH_3$	.575	.438
Ethyl furoate	$(C_4H_3O)COOC_2H_5$	.684	.482
Trimethylene glycol dimethoxy acetate	$[CH_3OCH_2COOCH_2]_2CH_2$	.666	.587
Tetrahydrofurfuryl methoxy acetate	$(C_4H_7O)CH_2OCOCH_2OCH_3$	.839	.586
Tetrahydrofurfuryl benzoate	$(C_4H_7O)CH_2OCOC_6H_5$	.55	.524
Methyl cellosolve carbonate	$[CH_3OCH_2CH_2O]_2CO$	.678	.540
Ketones and aldehydes			
l-Menthone		0.795	0.545
Furfural	$(C_4H_3O)CHO$	.621	.367
Ethyl levulinate	$CH_3COCH_2CH_2COOC_2H_5$	.899	.566
Alcohols and alcohol-ethers			
Ethylene glycol	$HOCH_2CH_2OH$	0.10	0.055
Trimethylene glycol	$HOCH_2CH_2CH_2OH$	.106	.073
Diethylene glycol	$HOCH_2CH_2OCH_2CH_2OH$	.285	.288
Triethylene glycol	$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$	.358	.330
Tetrahydrofurfuryl alcohol	$(C_4H_7O)CH_2OH$	.588	.368
Benzyl cellosolve	$C_6H_5CH_2O(CH_2)_2OH$	.392	.368
Cellosolve glycolate	$C_2H_5OCH_2CH_2OCOCH_2OH$	.509	.423
Amines			
Aniline	$C_6H_5NH_2$	0.385	0.258
Dimethylaniline	$C_6H_5N(CH_3)_2$	.695	.425
p-Aminodimethylaniline	*p*-$(CH_3)_2NC_6H_4NH_2$	.473	.384
Quinoline	C_9H_7N	.633	.443
Amides			
Tetraethyl oxamide	$(C_2H_5)_2NCOCON(C_2H_5)_2$	0.965	0.651
N-Diethylamide of monoethyl malonate	$(C_2H_5)_2NCOCH_2COOC_2H_5$	.950	.633
Acetylpiperidine	$C_5H_{10}NCOCH_3$	1.315	.618
Nitro compound			
Nitrobenzene	$C_6H_5NO_2$	0.471	0.360
Hydrocarbons and their halogen derivatives			
Tetralin	$C_{10}H_{12}$	0.475	0.379
Decalin	$C_{10}H_{18}$	.272	.267
Benzotrifluoride	$C_6H_5CF_3$	.336	.323
α-Monofluoronaphthalene	$C_{10}H_7F$	.327	.317

were measured carefully but the results in some cases are probably not as accurate as those recorded in Table I.

In Fig. 1 the variation in solubility of monofluorodichloromethane as a function of pressure is shown for a number of typical solvents.

Discussion of Results

Table I shows the effect on solubility of (a) the successive replacement of hydrogen atoms in methane by chlorine atoms and (b) the replacement of chlorine atoms by fluorine atoms. Increase in the number of chlorine atoms in the series CH_3Cl, CH_2Cl_2, $CHCl_3$ produces a marked increase in observed solubility over "ideal" solubility. No measurement of the solubility of CCl_4 was made, but the results with CCl_3F and CCl_2F_2 indicate that the replacement of the last hydrogen would produce a large drop in solubility from that observed in the case of $CHCl_3$. This behavior is in accord with the hydrogen bond and "head on" association theories. It is, however, difficult to explain it by the second picture of dipole association, since the uniqueness of the structure H–CCl_3 has little significance in this theory, and the complex



might be expected to approach in stability that formed by the $CHCl_3$.[10]

The replacement of chlorine atoms by fluorine atoms in CH_2Cl_2 and $CHCl_3$ produces an increase in solubility. These results are to be expected from the hydrogen bond theory, since fluorine is a more negative element than chlorine.

The high ratio of observed to "ideal" solubilities in the cases of CH_2Cl_2 and CH_2ClF suggests that even here hydrogen bonding is not negligible.

Glasstone[10] observed a small amount of compound formation between compounds of the type CX_4 and diethyl ether, the amount increasing in the order $CCl_4 < CBr_4 < CI_4$. He suggested the possibility that this might be due to a donation of a pair of electrons by the oxygen to the halogen atom, with the expansion of the outside shell of the halogen atom to hold ten electrons. Owing to the circumstance that the fluorine atom has a maximum covalence of four, that is, a capacity for only eight electrons, the increase in solubility in going from CCl_2F_2 to CCl_3F and from $C_2Cl_2F_4$ to $C_2Cl_3F_3$ is probably to be expected.

In the following paragraphs a discussion will be given of solubilities of $CHCl_2F$ in different types of solvents. The comparison of solubilities is made at an arbitrary pressure and, as the examples given in Fig. 1 show, if some other pressure were chosen, a different order of solubilities would be obtained in certain cases. However, a close inspection of all the curves indicates that the conclusions drawn here would not be materially changed.

Ethers.—An oxygen in an ether group is exceptionally effective in producing high solubility. The highest mole fraction solubilities of $CHCl_2F$ are obtained with the polyethylene glycol ethers. However, as a succeeding paper will show, due to steric hindrance only alternate oxygen atoms are effective.

The comparatively low mole fraction solubility in dioxane in contrast to that in dimethyl ether of ethylene glycol shows that a ring oxygen is not as effective as one in a straight chain compound.

The low mole fraction solubility in resorcinol diethyl ether indicates that the attachment of an oxygen atom by one bond to a benzene nucleus decreases the tendency of the oxygen to share a pair of electrons as would be expected from the opportunity that exists here for the internal neutralization of the basic property of the oxygen. It is significant that in the case of diethyl phthalate where the oxygens are separated from the benzene ring by an intervening carbon atom, high solubility is observed.

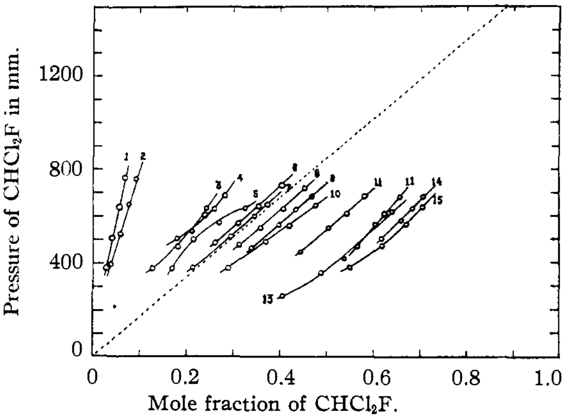


Fig. 1.—The solubility of $CHCl_2F$ as a function of pressure in typical solvents. The dotted line represents the "ideal" solubility. 1, ethylene glycol; 2, trimethylene glycol; 3, decalin; 4, aniline; 5, benzotrifluoride; 6, nitrobenzene; 7, tetralin; 8, bis-β-methylthiolethyl sulfide; 9, dimethylaniline; 10, dioxane; 11, diethyl oxalate; 12, diethyl acetate; 15, dimethyl ether of tetraethylene glycol.

The low solubility in $CH_3SCH_2CH_2SCH_2CH_2SCH_3$ compared to $CH_3OCH_2CH_2OCH_2CH_2OCH_3$ is difficult to explain by the picture of "head on" association since the C–S moment is larger than the C–O moment; also the substitution of a sulfur atom for an oxygen atom should make little difference according to the second picture of dipole association. It is, however, in accord with the fact that there are no stable examples of hydrogen bonds in which the sulfur atom is a member.

The low solubility in di-β-chloroethyl ether (mole fraction 0.451) compared to that of cyclohexyl methyl ether (mole fraction 0.498) is to be expected from the hydrogen bond picture, since the electron-attracting chlorine atoms should decrease the tendency of the oxygen atoms to donate a pair of electrons to the hydrogen atom of the $CHCl_2F$.

Esters.—An examination of the data on esters shows that the ester group, —COOR, is approximately as effective as an ether group, R_2O, in increasing solubility. This is shown clearly by the data in Table I. Solvent I is the ethyl ether of diethylene glycol acetate and differs from Solvent III, the diethyl ether of diethylene glycol, only by the replacement of the ether group —OC_2H_5 with the ester group —$OCOCH_3$. The mole fraction solubilities in the two solvents for all halogenated hydrocarbons containing hydrogen atoms differ by only a few per cent.

The data in Table II on the mole fraction solubility of $CHCl_2F$ in the dimethyl ether of diethylene glycol compared with the methyl ether of diethylene glycol acetate and the dimethyl ether of triethylene glycol compared with the methyl ether of triethylene glycol acetate lead to the same conclusion.

Ketones.—The one simple ketone tested (*l*-menthone) showed a high mole fraction solubility of $CHCl_2F$, considering the fact that there is only one oxygen present. This is in accord with the large negative deviations[4] from Raoult's law shown by acetone–chloroform mixtures and the results of Glasstone[10] on the amount of complex formation in acetone-chloroform mixtures.

Alcohols.—The solubilities were extremely low in ethylene glycol and trimethylene glycol. This low solubility is undoubtedly connected with the fact that alcohols are highly associated liquids.[18-20] This association takes place by means of hydrogen bonding (O–H–O). There is considerable evidence[21] to indicate that the tendency of hydrogen to act as an acceptor increases in the order

$$H—C < H—N < H—O < H—F$$

consequently it is not to be expected that the addition of the $CHCl_2F$ would disrupt the O–H–O bonds to form a less stable C–H–O bond.

Amines.—The nitrogen in a tertiary amine is effective in increasing solubility as shown by the solubility in N,N-dimethylaniline and quinoline. The smaller solubilities in aniline and *p*-aminodimethylaniline may be due to intermolecular association of the molecules of these liquids through the formation of N–H–N bonds. Thus, there is a striking parallelism between the behavior of alcohols and primary amines and between that of ethers and tertiary amines.

No solubility data were obtained with aliphatic amines, so that it is not possible to make a direct comparison between the effectiveness of an amine nitrogen and an ether oxygen. The higher solubility in dimethylaniline, compared to *p*-fluoroanisole, is probably without significance. It should be interesting to determine the solubility of $CHCl_2F$ in the polyethylene amines.

Amides.—The fact that higher solubilities are observed in tetraethyl oxamide and N,N-diethyl amide of monoethyl malonate than in diethyl oxalate and diethyl malonate indicates that an amide nitrogen is superior to the singly linked oxygen of an ester group.

Nitro Compounds.—The solubility in nitrobenzene has almost the "ideal" value. On first thought one might expect hydrogen bonding to occur here; however, the low solubility of nitrobenzene in water indicates that the oxygens of a nitro group have poor donor properties. The stability of the chelate ring formed by *o*-nitrophenol[20,22] may be due largely, as suggested by Wulf, *et al.*, to resonance between the different possible ring structures.

Hydrocarbons.—The solubilities observed in hydrocarbons and halogenated hydrocarbons in general, do not deviate much from the "ideal" solubilities. This is to be expected, as there is no opportunity for hydrogen bonding. The low solubility in benzotrifluoride and α-monofluoronaphthalene suggests that a fluorine atom attached to a carbon atom is not available for hydrogen bonding.

The evidence presented here shows that for the series of solutes, CH_3X, CH_2X_2, CHX_3, CX_4, the solubilities in solvents containing the donor atoms, oxygen or nitrogen, increase to a maximum with CHX_3 and drop markedly on passing to the CX_4 type. The solubility of the CHX_3 type is enormously greater than that predicted from Raoult's law. The theory of hydrogen bonding offers the most consistent explanation of these observations. This theory not only accounts for the cases of high solubility but also affords an explanation of the apparent exceptions, such as low solubilities in alcohols and primary amines. Hildebrand[23] previously has shown the utility of the concept of O–H–O, O–H–N and N–H–N types of hydrogen bonding in accounting for the solubility of various organic liquids in water. He pointed out that the relative values of the dipole moments were inadequate to explain the observed order of solubilities. Sidgwick[24] has also discussed the influence of hydrogen bonding on solubility. The success of the concept of C–H←O and C–H←N bonds in explaining the observed solubilities of gaseous halogenated hydrocarbons in solvents, in-

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[18] K. L. Wolf, *Trans. Faraday Soc.*, **33**, 179 (1937).

[19] Errera and Mollet, *Nature*, **138**, 882 (1936).

[20] Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 84, 501 (1937).

[21] Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, p. 165.

[22] Wulf, Liddell and Hendricks, This Journal, **58**, 2287 (1936).

[23] J. H. Hildebrand, *Science*, **83**, 21 (1936).

[24] Sidgwick, "Electronic Theory of Valence," Oxford University Press, London, 1927, p. 139.

dicates that the same idea will prove useful in predicting solvents for liquid and solid organic compounds.

Summary

The solubilities of a series of halogenated methane and ethane derivatives in many types of organic solvents have been measured.

The existence of a C–H←O or C–H←N type of hydrogen bond has been postulated to correlate the observed solubilities.

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[CONTRIBUTION FROM THE WILLIAMS OIL-O-MATIC HEATING CORPORATION]

The Heats of Mixing of Haloforms and Polyethylene Glycol Ethers

BY G. F. ZELLHOEFER AND M. J. COPLEY[1]

Intermolecular association[2] has been suggested as an explanation for the extreme variation in solubilities observed among the halogenated methanes in solvents containing donor atoms. It has been assumed that a C–H ← O or a C–H ← N bond is formed between a hydrogen of the halogenated hydrocarbon molecule and an oxygen or a nitrogen atom present in the solvent. It is desirable to supplement the solubility data by other physical measurements in order to throw more light on the nature and the amount of this association. For this reason the heats of mixing of chloroform and monofluorodichloromethane with two members of the polyethylene glycol series of ethers have been determined. McLeod and Wilson[3] have measured the heat of mixing of the similar system, diethyl ether–chloroform. They found the maximum in the heat of mixing curve to occur at a mole fraction of 0.5 and interpreted this as indicating the existence of an equimolar complex. Assuming that all the heat liberated was due to complex formation, they calculated degrees of association in mixtures of different compositions and found that they were approximately in accord with the mass law, if the heat of formation per mole of complex was taken in the range 5000–10,000 cal. In order to give a more definite value to the heat of formation they calculated the equilibrium constant at three different temperatures from the viscosity–composition–temperature data of Thorpe and Rodgers[4] using the formula of McLeod.[5] The change of the equilibrium constant with temperature led to a heat of formation of 6070 cal. Huggins,[6] following the proposal of Glasstone[7] that hydrogen bonding exists in this case, has pointed out that these results establish a value for the strength of the C–H ← O bond.

Apparatus and Procedure

The measurements were carried out in a calorimeter similar in design to the one employed by McLeod and Wilson.[3] It is shown in Fig. 1 and consisted of a well-evacuated and silvered Dewar flask of about 500-cc. capacity. It contained approximately 200 cc. of diethyl phthalate, which was agitated by the motor-driven stirrer E. The mixing chamber A was made from a thin copper tube and had a capacity of 50 cc.; it was suspended by a glass rod (not shown) and contained a stirrer C. One of the liquids was placed in A and the other in a pipet B, which was bent in such a manner that its tip passed through a hole in the rubber stopper used to close the mixing chamber.

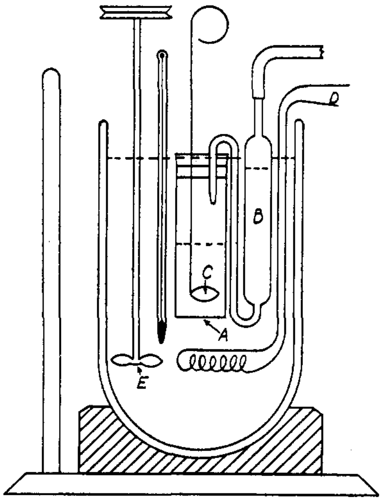

Fig. 1.—Diagram of the calorimeter.

The contents of the calorimeter were cooled to the neighborhood of 0°, and while warming slowly to 3° had time to establish thermal equilibrium. The liquid in the pipet

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[1] Chemistry Department, University of Illinois.

[2] Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).

[3] McLeod and Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

[4] Thorpe and Rodgers, *J. Chem. Soc.*, **109**, 11 (1916).

[5] McLeod, *Trans. Faraday Soc.*, **30**, 482 (1934).

[6] Huggins, *J. Org. Chem.*, **1**, 407 (1936).

[7] Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).