where prominent lines are rare in organic compounds. Furthermore, a considerable number of the frequencies correspond to the weaker Raman lines in the spectra of benzene,[14] monosubstituted benzenes,[15] and compounds containing one or more —CH_2— groups. Because of certain remaining inconsistencies and difficulties in the measurement of the weaker lines, only the more prominent frequencies of the various compounds are listed at present.

The use of a low pressure mercury arc, with a consequent diminution in the amount of continuous radiation in the exciting light, and the method of illuminating the comparator are, without doubt, two of the factors contributing to the observance of so many lines. The number obtained is greater for some of the compounds than for others. This is due to the fact that some compounds decompose more readily when illuminated, resulting in the presence of small amounts of fluorescent materials. The consequent increase in the strength of the continuous background makes the measurement of weak lines extremely difficult.

Acknowledgment.—This work was aided in part by a grant from the Virginia Academy of Science from funds allotted it by the American Association for the Advancement of Science.

Summary

1. The principal lines in the Raman spectra of 3-chloro-1-phenylpropyne-1, 4-chloro-1-phenylbutyne-1, 5-chloro-1-phenylpentyne-1, 3-bromo-1-phenylpropyne-1, 3-phenyl-2-propynol-1, 4-phenyl-3-butynol-1, and 3-chloro-1-phenylpropene-1 (cinnamyl chloride) are reported.

2. Many other lines of very low intensity have been observed. Many of these are characteristic of benzene, monosubstituted benzenes, and compounds containing the —CH_2— group.

LYNCHBURG, VIRGINIA RECEIVED AUGUST 26, 1938

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[14] P. Grassmann and J. Weiler, *Z. Physik*, **86**, 321 (1933).

[15] J. W. Murray and D. H. Andrews, *J. Chem. Phys.*, **1**, 406 (1933); L. Kahovec and A. W. Reitz, *Akad. Wiss. Wien, Ber.*, **145**, 1045 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE WILLIAMS OIL-O-MATIC HEATING CORPORATION]

Hydrogen Bonds Involving the C–H Link. IV. The Effect of Solvent Association on Solubility

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

In a series of papers,[1-3] by the authors, solubility data have been reported on a number of gaseous halogenated hydrocarbons (of the types CH_3X, CH_2X_2, CHX_3, CX_4, and C_2X_6) in a variety of solvents containing donor atoms (oxygen, nitrogen, and sulfur). The successive replacement of three of the hydrogen atoms of methane by halogen atoms results in each case in an increase of solubility, and for the type CHX_3 solubilities much in excess of the theoretical have been observed in many solvents; however, replacement of the fourth hydrogen produces an enormous drop in solubility compared to that shown by the haloform type. These results readily are interpreted by assuming that complex formation takes place through the bonding of a hydrogen atom of the halogenated hydrocarbon to an exposed pair of electrons on the nitrogen or oxygen atoms in solvent molecules. The presence of the strongly electron-attracting halogen atoms on the carbon activates the hydrogen atom and makes it available for coördination to the donor atom.

Latimer and Rodebush[4] first suggested the theory that a proton in certain cases is capable of forming a bond between two atoms. Since then numerous investigations have confirmed this theory and shown its great utility. The possibility that the hydrogen atom of a haloform molecule might be capable of forming such a bond to an oxygen or nitrogen atom in a molecule was proposed by Glasstone[5] to account for the dielectric behavior of binary mixtures, containing a haloform and either an ether, an ester, or an amine. The ease with which the large amount of solubility data[2] accumulated by the authors may be

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

[2] G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337 (1938).

[3] G. F. Zellhoefer and M. J. Copley, *ibid.*, **60**, 1343 (1938).

[4] Latimer and Rodebush, *ibid.*, **42**, 1419 (1920).

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

correlated on the basis of this idea affords strong support for it. Rodebush[6] has informed the authors that infrared absorption measurements on solutions in carbon tetrachloride of chloroform with an ether or amine show definite evidence of complex formation.

Although extremely high solubilities were observed for halogenated hydrocarbons of the haloform type in practically all solvents containing an effective donor atom (nitrogen or oxygen), an exception was found in the case of alcohols. These low solubilities in alcohols[2] are related to the intermolecular association through hydrogen bonding which takes place between alcohol molecules.[7,8] It was thought that a more extended study should be made of solvents where association between solvent molecules is known to occur. Such an investigation should furnish data to aid in stating more precisely the factors which are important in producing solubility and should also provide new information about the amount and type of association occurring in these liquids. For this purpose measurements were made of the solubility of monofluorodichloromethane ($CHCl_2F$) in a number of alcohols, ethers, acids, esters, amides, substituted amides, primary and tertiary amines, and oximes. The effect on solubility of each of the two factors (a) unsaturation and (b) chelation was studied also by measuring solubility of this haloform in compounds containing an aliphatic double bond and in compounds where chelation is known to exist.

Experimental

The method used in making the solubility measurements has been described previously in detail.[1] The solvents tested were all purified carefully and their boiling or melting points checked. The solubility measurements on the monofluorodichloromethane were made over a range of pressures at a temperature of 32.2°. While it is important that complete pressure–composition studies be made on the various mixtures, it is felt that at present it is more important to have partial data on a large number of combinations. The results of these measurements are shown in Figs. 1–3. To compare the solvents tested the mole fraction solubilities at a partial pressure of monofluorodichloromethane corresponding to its vapor pressure at 4.5° are used in the following discussion and given in Table I. The "ideal" or theoretical mole fraction stated at the top of Table I was calculated using Raoult's law, and it is the ratio of the vapor pressure (0.847 atm.) of monofluorodichloromethane at 4.5° to its value (2.221 atm.) at 32.2°. The statement in the table that the solubility is *very low* in the case of acetamide and diphenylamine, is based on the observation that when these solvents, which are solids at 32.2°, were melted, insufficient monofluorodichloromethane dissolved in the liquid in the pressure range used, to lower the melting point appreciably.

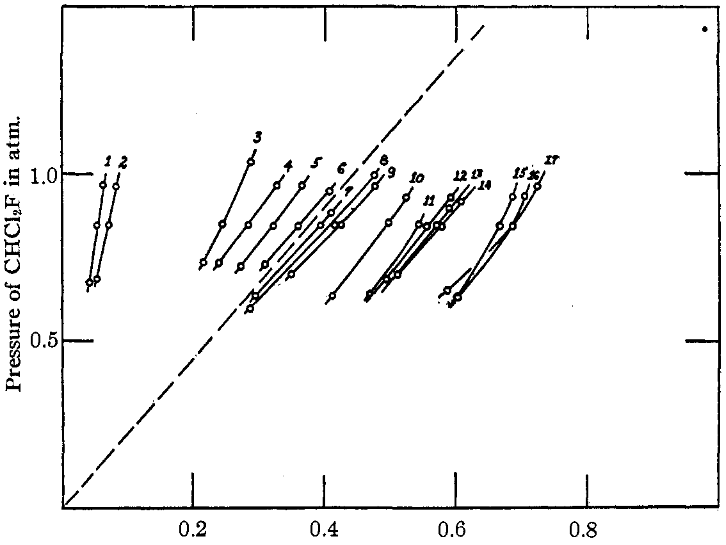

Fig. 1.—The solubility of monofluorodichloromethane as a function of pressure in alcohols, ethers, acids, and esters. The dotted line represents the "ideal" solubility: 1, ethylene glycol; 2, triethylene glycol; 3, phenol; 4, acetic acid; 5, propionic acid; 6, dimethyl sulfate; 7, phenyl vinyl ether; 8, anisole; 9, phenetole; 10, cyclohexylmethyl ether; 11, *n*-butyl butyrate; 12, diethyl oxalate; 13, 1,4-dimethoxycyclohexane; 14, dimethyl ether of ethylene glycol; 15, triethyl phosphate; 16, tributyl phosphate; 17, tri-(β-methoxyethyl) phosphate.

In a few cases a slow reaction was noted between the monofluorodichloromethane and the solvent used. This was particularly true with the amines and the values given for the solubility in these compounds are subject to a possible error of several per cent.

Discussion

Alcohols and Ethers.—In a preceding paper[2] the extremely low mole fraction solubilities of monofluorodichloromethane in ethylene glycol (0.055) and trimethylene glycol (0.073) were reported. In the present paper data are presented on the solubility of monofluorodichloromethane in phenol (0.197) and a similar low solubility compared to the theoretical (0.381) was observed.

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[6] Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2528 (1938); see also Gordy, *ibid.*, **60**, 605 (1938).

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

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

TABLE I

SOLUBILITY OF MONOFLUORODICHLOROMETHANE IN ORGANIC SOLVENTS

Theoretical or "Ideal" mole fraction in saturated solution 0.381

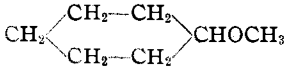
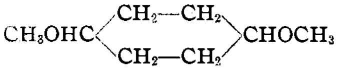
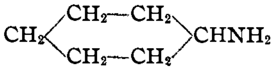
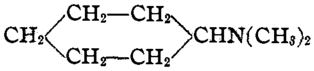
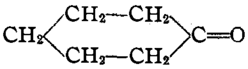
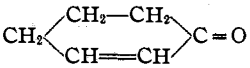
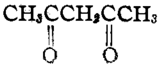
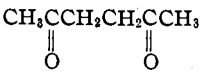
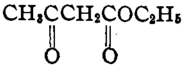
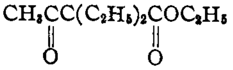
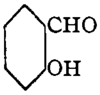
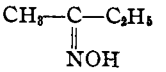
	Formula	Solubility G./g.	Solubility Mole fr.
	Alcohols and Ethers		
Phenol	C_6H_5OH	0.269	0.197
Ethylene glycol	$HOCH_2CH_2OH$	.10	.055
Trimethylene glycol	$HOCH_2CH_2CH_2OH$	.106	.073
Anisole	$C_6H_5OCH_3$	.673	.415
Phenetole	$C_6H_5OC_2H_5$	.625	.425
Phenyl vinyl ether	$C_6H_5OCH{=}CH_2$	.559	.394
Dimethyl ether of ethylene glycol	$CH_3OCH_2CH_2OCH_3$	1.55	.576
Cyclohexyl methyl ether	 $CH_2{<}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}{>}CHOCH_3$	0.900	.500
1,4-Dimethoxycyclohexane	 $CH_3OHC{<}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}{>}CHOCH_3$	0.941	.571
	Acids and Esters		
Acetic acid	CH_3COOH	0.688	0.286
Propionic acid	C_2H_5COOH	.665	.330
n-Butyl butyrate	$CH_3(CH_2)_2COO(CH_2)_3CH_3$	.870	.546
Diethyl oxalate	$C_2H_5OCOCOOC_2H_5$	.561	.556
Dimethyl sulfate	$(CH_3O)_2SO_2$	.463	.361
Triethyl phosphate	$(C_2H_5O)_3PO$	1.132	.666
Tributyl phosphate	$(C_4H_9O)_3PO$	0.842	.685
Tri-(β-methoxyethyl) phosphate	$(CH_3OCH_2CH_2O)_3PO$	.836	.687
	Amines and Substituted Amines		
Cyclohexylamine	 $CH_2{<}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}{>}CHNH_2$	1.070	0.506
Aniline	$C_6H_5NH_2$	0.385	.258
Quinoline	C_9H_7N	.633	.443
Diphenylamine	$(C_6H_5)_2NH$	(Very low)	...
Dimethylcyclohexylamine	 $CH_2{<}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}{>}CHN(CH_3)_2$	0.807	.500
Dimethylaniline	$C_6H_5N(CH_3)_2$	.695	.425
Methyldiphenylamine	$(C_6H_5)_2NCH_3$	.357	.388
	Amides and Substituted Amides		
Formamide	$HCONH_2$	0.075	0.032
Acetamide	CH_3CONH_2	(Very low)	...
Methylformamide	$HCONHCH_3$	0.768	.303
N,N-Dimethylformamide	$HCON(CH_3)_2$	.931	.398
N-Methylacetamide	$CH_3CONH(CH_3)$	.955	.403
N,N-Dimethylacetamide	$CH_3CON(CH_3)_2$	1.87	.614
N-Tetraethyloxamide	$[CON(C_2H_5)_2]_2$	0.965	.651
N,N-Tetramethylsuccinamide	$[CH_2CON(CH_3)_2]_2$	1.180	.663
N-Methyl-N-cyclohexylacetamide	$CH_3CON(CH_3)C_6H_{10}$	1.140	.632
	Aldehydes and Ketones		
Benzaldehyde	C_6H_5CHO	0.750	0.436
Heptaldehyde	$C_6H_{13}CHO$	.979	.519
Paraldehyde	$C_6H_{12}O_3$	.888	.532
Cyclohexanone	 $CH_2{<}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}{>}C{=}O$	1.278	.548
Δ²-Cyclohexenone	 $CH_2{<}\begin{matrix}CH_2-CH_2\\CH{=}CH\end{matrix}{>}C{=}O$	0.903	.457
Acetylacetone	 $CH_3\underset{\underset{O}{\|}}{C}CH_2\underset{\underset{O}{\|}}{C}CH_3$	1.023	.499

TABLE I (*Concluded*)

	Formula	Solubility G./g.	Solubility Mole fr.
Acetonylacetone	 $CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{C}CH_3$	1.163	0.563
Ethyl acetoacetate	 $CH_3\underset{\underset{O}{\|}}{C}CH_2\underset{\underset{O}{\|}}{C}OC_2H_5$	0.913	.536
Ethyl diethylacetoacetate	 $CH_3\underset{\underset{O}{\|}}{C}C(C_2H_5)_2\underset{\underset{O}{\|}}{C}OC_2H_5$	.880	.614
Salicylaldehyde		.501	.372
	Oximes		
Ethylmethylketoxime	 $CH_3-\underset{\underset{NOH}{\|}}{C}-C_2H_5$	.650	.338

When the hydrogen of the hydroxyl groups of alcohols is replaced by alkyl groups the resulting ethers show a high solvent power in excess of the theoretical as is illustrated by the examples in Table I and the results on a large number of ethers reported in a previous paper.[2] This difference in behavior of alcohols compared to ethers is to be traced to the association that exists in alcohols. Cryoscopic measurements[9] in non-polar solvents and analysis by Zachariasen[10] of X-ray data indicate that alcohols polymerize to form large linear or string polymers. This association takes place as first suggested by Latimer and Rodebush,[4] and later by Huggins,[11] through the bonding of a hydrogen of a hydroxyl group to the oxygen of a neighboring molecule. Recent infra-red absorption measurements[7,8] tend to confirm this picture of association. The low solubility of monofluorodichloromethane in alcohols is then due to the fact that a hydrogen bond formed by a hydrogen atom attached to a carbon atom with an oxygen atom, C–H ← O, is less stable than the O–H–O bonds already present in the alcohols. Hence the monofluorodichloromethane molecules are practically excluded from entering the large complexes present in the alcohol. Intermolecular association is blocked by the replacement of the hydrogen of the hydroxyl by an alkyl group, and then it is possible for C–H ← O bonds to form between the hydrogen of the monofluorodichloromethane and the oxygen atoms of an ether. The formation of this type of complex between the ether and the monofluorodichloromethane is responsible for the enormous solubilities observed for monofluorodichloromethane in ethers.

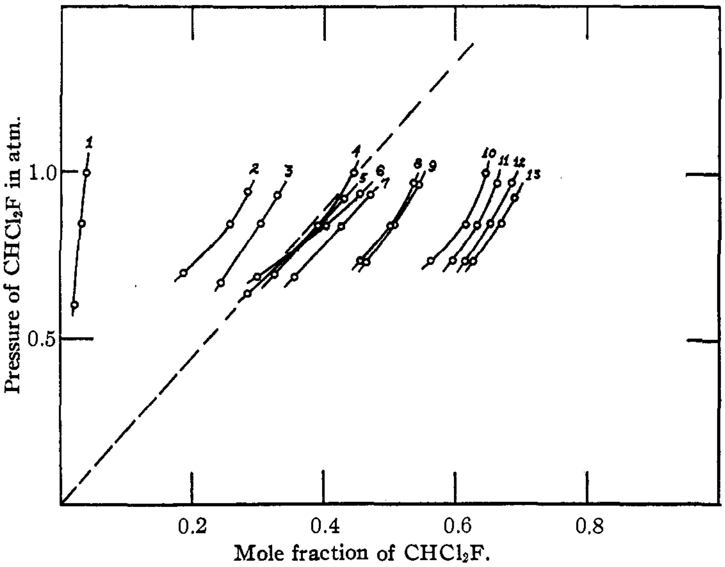


Fig. 2.—The solubility of monofluorodichloromethane as a function of pressure in amines and amides: 1, formamide; 2, aniline; 3, methylformamide; 4, methyldiphenylamine; 5, methylacetamide; 6, dimethylformamide; 7, dimethylaniline; 8, dimethylcyclohexylamine; 9, cyclohexylamine; 10, dimethylacetamide; 11, N-methyl-N-cyclohexylacetamide; 12, tetraethyloxamide; 13, tetramethylsuccinamide.

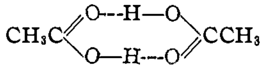
Acids and Esters.—The mole fraction solubility of monofluorodichloromethane is distinctly higher in the fatty acids (0.286 in acetic acid) than in the alcohols although an active hydrogen is present in the carboxyl group of these molecules. This result confirms the viewpoint that a different type of association takes place in the fatty acids than in the alcohols, which previously has been

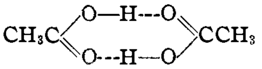
[9] Auwers, *Z. physik. Chem.*, **12**, 689 (1893); *ibid.*, **15**, 33 (1894).

[10] Zachariasen, *J. Chem. Phys.*, **3**, 158 (1935).

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

shown by the fact that the polymerization in acetic acid stops at the dimer stage. The existence of the dimers of acids is shown by numerous cryoscopic and distribution measurements. Recent vapor density,[12,13] and electron diffraction measurements[14] show the presence of these dimers in the vapor whereas there is no appreciable association in the vapor phase of alcohols. The association presumably takes place through hydrogen bonding and results in an eight-membered ring. The stability of the ring as suggested by Pauling and Brockway[14] probably is due to a resonance between the two structures (I and II) of equal energy.


I


II

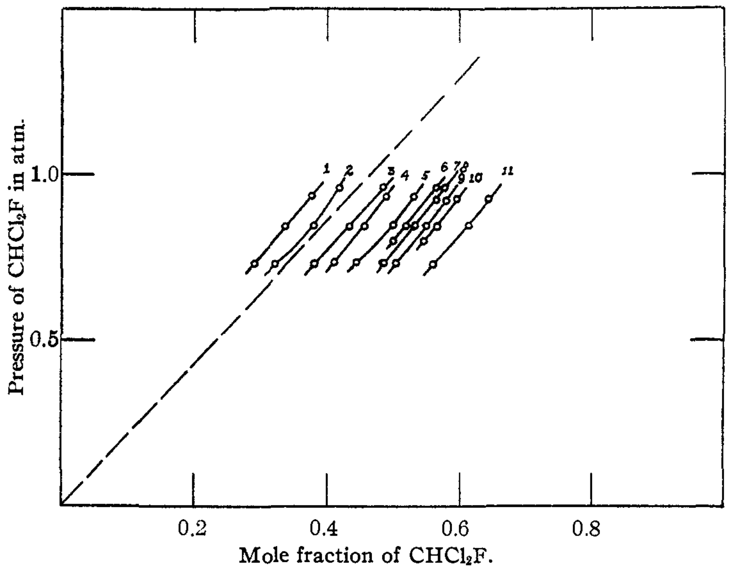


Fig. 3.—The solubility of monofluorodichloromethane as a function of pressure in aldehydes, ketones, and oximes: 1, ethylmethylketoxime; 2, salicylaldehyde; 3, benzaldehyde; 4, cyclohexenone; 5, acetylacetone; 6, heptaldehyde; 7, paraldehyde; 8, ethyl acetoacetate; 9, cyclohexanone; 10, acetonylacetone; 11, ethyl diethylacetoacetate.

When the mole fraction solubility of acetic acid is calculated using the molecular weight of the dimer instead of that of the monomer, its value (0.445) does not exceed the theoretical (0.381) to any marked extent. This result indicates that when an oxygen atom has shared one of its two exposed electron pairs its basic or donor properties are strongly reduced. Further evidence of this decrease in donor property of an oxygen atom after sharing one of its electron pairs will be given in the section on chelated compounds.

As in the case of alcohols the replacement of the active hydrogen of an acid by an alkyl group blocks association and extremely high solubility is observed for monofluorodichloromethane in esters. In general the solubility in an ester is of about the same magnitude as in an ether of similar structure although the ether has only one oxygen. Apparently this is due, as was shown in a previous paper,[3] to steric hindrance. The close proximity of the two oxygens prevents the simultaneous attachment of two monofluorodichloromethane molecules to the two oxygen atoms of the ester group.

Some measurements of solubility were also made using esters of phosphoric and sulfuric acids. The esters of phosphoric acid are extremely effective as solvents for monofluorodichloromethane but the one ester of sulfuric acid tested showed rather poor solvent power.

Amines and Substituted Amines.—Very high solubilities in excess of the theoretical were observed in cyclohexylamine (0.506) and dimethylcyclohexylamine (0.499). The almost equal solubilities of monofluorodichloromethane in these two compounds suggests that aliphatic amines are unassociated and that an aliphatic amine hydrogen is not sufficiently active to form hydrogen bonds. The failure to form bonds certainly cannot be due to any lack of donor properties on the part of the nitrogen atom since the high solubility of monofluorodichloromethane indicates ready sharing of the electron pair of the nitrogen to form C–H ← N bonds. This conclusion of lack of association in liquid amines from our solubility measurements is in accord with their cryoscopic[15] behavior in non-polar solvents. Also the substitution of a methyl group for the hydroxyl hydrogen of an alcohol causes a lowering of the boiling point, whereas the replacement of one or both hydrogens on the nitrogen of a primary amine raises the boiling point.

The considerably lower solubility of monofluorodichloromethane in aniline (0.258) than in dimethylaniline (0.425) suggests that in aromatic

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(12) Fenton and Garner, *J. Chem. Soc.*, 674 (1930).

(13) MacDougall, This Journal, **58**, 2585 (1936).

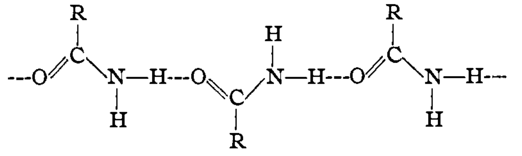
(14) Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(15) E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

amines some association, probably of the linear polymer type, takes place.

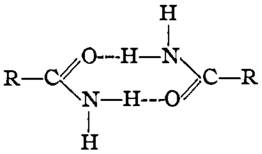
The almost equal solubilities observed in methylcyclohexyl ether (0.500), cyclohexylamine, and dimethylcyclohexylamine indicate that the donor properties of an aliphatic ether oxygen and an aliphatic amine nitrogen are almost equivalent.

Amides and Substituted Amides.—Extremely low solubilities were observed for monofluorodichloromethane in formamide (0.0318) and acetamide (*very low*). These much lower solubilities than those observed in the fatty acids suggest that dimers are not formed in amides but instead polymers of indefinite size. Cryoscopic measurements[15] on amides also indicate the formation of large polymers in non-polar solvents. A possible reason for the polymerization failing to stop at the dimer stage might be the formation of linear polymers as shown in structure III

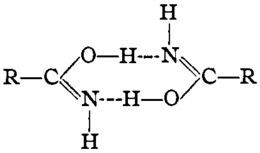


III

since the two resonating structures of the dimer illustrated in IV and V would be of unequal energy.

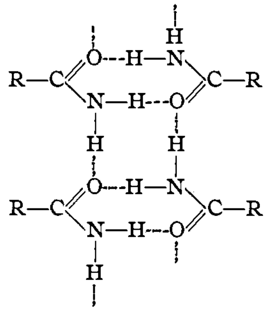


IV



V

On the other hand, the formation of linear polymers in alcohols does not lead to excessively high melting points, while amides melt much higher than alcohols containing the same number of carbon atoms. A different type of association is also indicated by the ease with which amides crystallize compared to alcohols which tend to form glasses. A type of association which might account for these differences in behavior of amides and alcohols is shown in structure VI where the association takes place through the fusing of dimers. It is true that the formation of such a polymer requires the sharing of the second pair of electrons on the oxygens; however, the behavior of acetic acid and chelated compounds indicates that this tendency while small is not negligible; also the numerous possible resonating structures in such a polymer would contribute to its stabilization. An association through the fusing of dimers would explain the intermediate solvent power for monofluorodichloromethane of a monosubstituted amide between that of the amide and the disubstituted amide (where no association exists) as is illustrated by the data in Table I. The substitution of an alkyl group for one of the hydrogens on the nitrogen would block the fusing of the dimers and should lead to a solubility comparable to that observed in the fatty acids. Chaplin and Hunter[16] have made some cryoscopic measurements on solutions of monomethyl and monoethyl acetamide in benzene which indicate that these compounds are associated, but the measurements are not complete enough to establish whether large polymers or only dimers are formed. Jenkins and Taylor[17] have investigated solutions of α-piperidone in benzene and find no evidence for polymerization proceeding past the dimer stage. It is recognized that the high dielectric constants of the amides and of the monosubstituted amides[18] appear to offer an objection to this latter picture of association, since the formation of such a symmetrical structure would apparently involve a neutralization of dipole moments of the amide molecules. However, it is possible that there are present in the liquid a sufficient number of the monomers to account for the observed dielectric constants.



VI

The solubility in N,N-dimethylacetamide (0.614) is extremely high and a similar high solubility has been observed in all completely substituted amides with the exception of N,N-dimethylformamide (0.398). This difference in behavior of dimethylformamide as a solvent may be caused by the existence of some polymerization involving the hydrogen on the carbon of the formic acid residue. The strong negative groups attached to

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[16] Chaplin and Hunter, *J. Chem. Soc.*, 1114 (1937).

[17] Jenkins and Taylor, *ibid.*, 495 (1937).

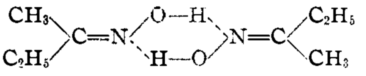
[18] Kumler, THIS JOURNAL, **57**, 600 (1935).

this carbon might be expected to cause its activation. If this is correct, a similar activity on the part of the hydrogen in formic acid would be expected, and indeed has already been suggested by Huggins[11] to account for the high dielectric constant of formic acid[18] compared to that of the other fatty acids.

A comparison of our solubility data in amines and amides shows that the tendency for hydrogen bonding is directly connected with the activity of the hydrogens on the nitrogen. However, the basicity of their solutions in water apparently is not related to the donor properties of the nitrogen in forming hydrogen bonds.

Ketones and Aldehydes.—The high solubilities observed for monofluorodichloromethane in aldehydes and ketones are in agreement with the well-known fact that these liquids are unassociated and suggest that the oxygen present in a carbonyl group is an excellent electron donor so that C–H ← O bonds readily form.

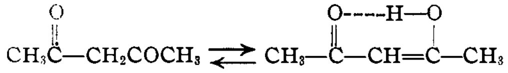
Oximes.—One oxime, methylethylketoxime, was tested. The almost normal solubility (0.338) of monofluorodichloromethane in this compound suggests that oximes form dimers similar in type to those formed by fatty acids and N-monosubstituted amides. A probable structure for this dimer is shown in formula VII.



VII

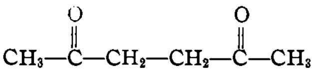
Cryoscopic measurements[15] on acetoxime and *d*-camphoroxime indicate that these compounds form either dimers or relatively small polymers in non-polar solvents.

Effect of Chelation.—The almost normal solubility observed in acetic acid dimers suggests, as was pointed out earlier, that when one pair of electrons on an oxygen is shared, its donor properties decrease. A study of the solubility of monofluorodichloromethane in compounds containing a chelate ring and a comparison of these solubilities with solubilities in compounds containing a similar structure but without chelation, gave further evidence on this point. Two pairs of compounds were tested. One of each pair is known to be chelated and in the other there is no opportunity for chelation. These compounds are shown in the four formulas below with the mole fraction solubility of monofluorodichloromethane in each.



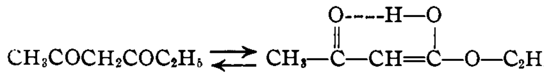
$$CH_3\overset{\overset{O}{\|}}{C}-CH_2COCH_3 \rightleftarrows CH_3-\overset{\overset{O\text{----}H}{\|}}{C}-CH=\overset{\overset{O}{|}}{C}-CH_3$$

Acetylacetone
(0.499)



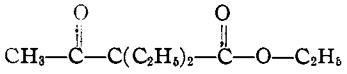
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetonylacetone
(0.563)



$$CH_3COCH_2COC_2H_5 \rightleftarrows CH_3-\overset{\overset{O\text{----}H}{\|}}{C}-CH=\overset{\overset{O}{|}}{C}-O-C_2H_5$$

Ethyl acetoacetate
(0.536)



$$CH_3-\overset{\overset{O}{\|}}{C}-C(C_2H_5)_2-\overset{\overset{O}{\|}}{C}-O-C_2H_5$$

Ethyl diethylacetoacetate
(0.617)

The results indicate an appreciable decrease in the formation of C–H ← O bonds by the compounds in which chelation occurs. A similar conclusion is obtained by comparing the solubility of monofluorodichloromethane in benzaldehyde (0.436) with that in strongly chelated salicylaldehyde (0.372).

Effect of Unsaturation.—A few compounds were examined to test the effect on solubility of an aliphatic double bond in the donor molecule. The solubility in phenyl vinyl ether (0.394) is so near that in anisole (0.415) and phenetole (0.425), as to indicate only a small effect. However, the effect is much more pronounced for Δ^2-cyclohexenone (0.457) when compared to cyclohexanone (0.548).

A phenyl group attached to an oxygen or a nitrogen atom markedly decreases its donor properties. This is clearly shown by the lower solubilities given in Table I for aromatic ethers and amines compared to aliphatic ethers and amines. On the other hand, the hydrogens of an aromatic amine are more active (leads to association) and hence the higher solubility of monofluorodichloromethane in dimethylaniline (0.425) compared to aniline (0.258).

Conclusion

The simple assumption of complexes formed through the medium of C–H ← O bonds in a remarkable manner correlates the large amount of solubility data that has been obtained. Furthermore, as stated earlier in this paper, recent infrared absorption measurements[6] on mixtures of chloroform with ethers, esters, ketones, and amines lead to the same conclusion. The strength of the C–H ← O or C–H ← N bond in the case of halogenated hydrocarbons of the CHX_3 type is less than that of N–H–O and O–H–O bonds, hence the addition of chloroform and monofluorodichloromethane does not cause dissociation in compounds associated by means of hydrogen bonding between two oxygen atoms, or a nitrogen atom and an oxygen atom. In this connection it should be recalled that it has been known for a long time that the haloforms behave essentially as non-polar solvents similar to benzene and hexane in cryoscopic measurements on alcohols, acids, and amides.

The considerations outlined above also should be applicable to the solution of solid organic compounds in monofluorodichloromethane, or other halogenated hydrocarbons of the type CHX_3, C_2HX_5, etc. (and to a lesser extent to the type CH_2X_2), and should allow the qualitative prediction of solubility in such cases.

Summary

The concept of C–H ← O bonds between a hydrogen of a halogenated hydrocarbon and donor atoms in solvents has been shown readily to correlate solubility data on solutions of halogenated hydrocarbons in a large number of solvents of different types.

The most important factors governing the solubility of the types of compounds investigated are: (1) the donor properties of atoms in the solvent for forming C–H ← O or C–H ← N bonds; (2) the presence or absence of intermolecular association through hydrogen bonding in the solvent.

It has been shown that it is possible to predict the type of association occurring in a liquid by means of a solubility measurement. The presence of large linear polymers in the solvent inhibits the solution of monofluorodichloromethane but if the polymerization stops at the dimer stage nearly normal solubility is observed.

URBANA AND BLOOMINGTON, ILLINOIS
RECEIVED AUGUST 29, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

The Reaction of Esters with Aluminum Isopropoxide

BY ROBERT H. BAKER

Aluminum alkoxides react with alcohols[1,2] and catalyze the alcoholysis of esters,[3] but their reaction with esters alone has been studied very little.[1,4]

For the simple esters the reaction is one of exchange of groups and possibly may be of use in the preparation of alkoxides whose alcohols themselves are either unstable or which fail to react with amalgamated aluminum. The reaction also may be used in the preparation of esters.

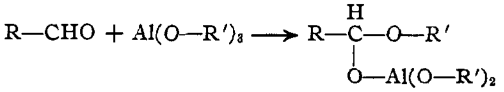
In this work the equilibrium

$$3R{-}COOR' + Al(O{-}i\text{-}Pr)_3 \longleftrightarrow 3R{-}COO{-}i\text{-}Pr + Al(O{-}R')_3$$

has been shifted as far to the right as possible by carrying out the reaction under a fractionating column which permits the removal of only the isopropyl ester. *t*-Butyl acetate failed to react completely, the reaction stopping when two of the isopropyl (or isopropoxide) groups had been replaced. This is in accord with the observations of Tischtschenko,[1] who found that the tertiary alkoxides reacted best with the alcohols.

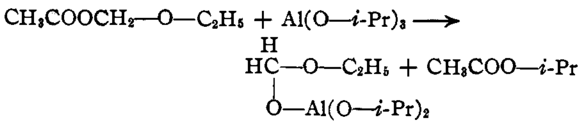
The isopropoxide, which is easily made and purified and which gives rise to low boiling esters, has been used exclusively in this work.

Only one ester, ethoxymethyl acetate, gave rise to reduction products similar to those which the simple esters give with sodium alkoxides.[5] This ester was used in an attempt to prepare an alkoxide of the type which Verley[6] postulated as an intermediate in both the Tischtschenko reaction[4] and in the reduction of aldehydes. This aluminate of a hemiacetal, which Verley claims is formed thus



$$R{-}CHO + Al(O{-}R')_3 \longrightarrow R{-}\underset{\substack{|\\ O{-}Al(O{-}R')_2}}{\overset{H}{C}}{-}O{-}R'$$

was expected to be formed as follows



$$CH_3COOCH_2{-}O{-}C_2H_5 + Al(O{-}i\text{-}Pr)_3 \longrightarrow \underset{\substack{|\\ O{-}Al(O{-}i\text{-}Pr)_2}}{\overset{H}{HC}}{-}O{-}C_2H_5 + CH_3COO{-}i\text{-}Pr$$

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[1] Tischtschenko, *J. Russ. Phys.-Chem. Soc.*, **31**, 694, 784 (1899); *Chem. Zentr.*, **71**, I, 10, 585 (1900).

[2] Adkins and Cox, THIS JOURNAL, **60**, 1151 (1938).

[3] Fehlandt and Adkins, *ibid.*, **57**, 193 (1935); Hatch and Adkins, *ibid.*, **59**, 1694 (1937).

[4] Tischtschenko, *J. Russ. Phys.-Chem. Soc.*, **38**, 355, 482 (1906); *Chem. Zentr.*, **77**, II, 1309, 1552 (1906).

[5] Magnani and McElvain, THIS JOURNAL, **60**, 813 (1938).

[6] Verley, *Bull. soc. chim.*, **37**, 537, 871 (1925).