sodium acetate (pH 4.655). These pH values, without correction for liquid junction potentials, serve to establish a pH scale which may be used to obtain the values of thermodynamic dissociation constants at 38°.

New Haven, Conn. Received July 29, 1938

[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. V. The Solubility of Methylene Chloride in Donor Solvents

By M. J. Copley, G. F. Zellhoefer and C. S. Marvel

Recent publications[1-3] by the authors have shown that hydrogen bonding, involving the C–H link, occurs in solutions of the haloforms in solvents containing the donor atoms, oxygen or nitrogen. In one article[1] data were included on the solubilities of the two dihalogenated methanes, methylene chloride and monofluoromonochloromethane, in three donor solvents (diethylene glycol dimethyl ether, ethyl ether of diethylene glycol acetate and tetraethylene glycol dimethyl ether). Their solubilities were in considerable excess of the values predicted by Raoult's law and almost comparable with the solubilities observed for the haloforms in the same solvents. These results led the authors to suggest that a hydrogen atom of a dihalogenated methane is also capable of forming a hydrogen bond with an oxygen or nitrogen atom having an exposed pair of electrons. Such an activity for hydrogen bonding on the part of the hydrogen atoms, in these very stable compounds, was somewhat unexpected and it seemed important to extend the investigation to include a larger number of types of solvents.

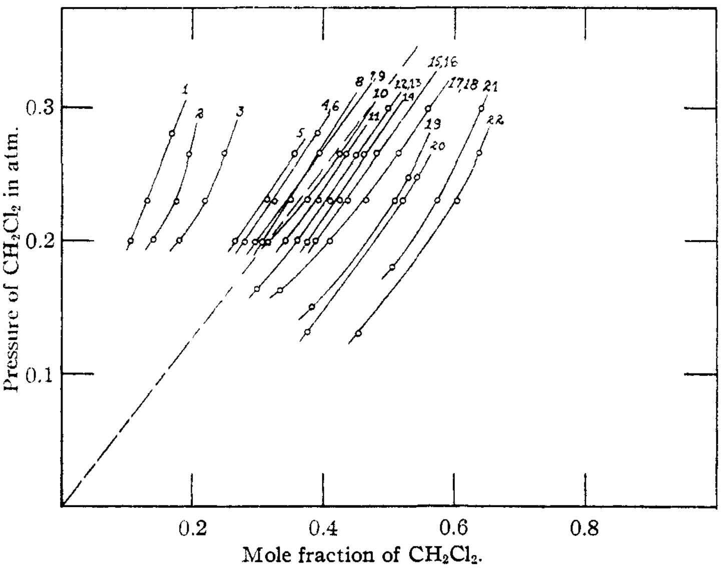

Fig. 1.—The solubility of methylene chloride as a function of pressure in alcohols, ethers, acids, esters, aldehydes, and ketones: 1, phenol; 2, acetic acid; 3, propionic acid; 4, anisole; 5, salicylaldehyde; 6, phenyl vinyl ether; 7, benzaldehyde; 8, Δ^2-cyclohexenone; 9, acetylacetone; 10, paraldehyde; 11, heptaldehyde; 12, ethyl acetoacetate; 13, triphenyl phosphite; 14, cyclohexanone; 15, acetonylacetone; 16, 1,4-dimethoxycyclohexane; 17, ethyl diethylacetoacetate; 18, tri-*o*-cresol phosphate; 19, ethyl ether of diethylene glycol acetate; 20, diethyl ether of diethylene glycol; 21, tri-*n*-butyl phosphate; 22, dimethyl ether of tetraethylene glycol.

The present paper reports the solubilities of methylene chloride in the same group of solvents[3] as was used by the authors in their study of the effect of solvent association on the solubility of haloforms. The remarkable similarity we have observed in the behaviors of dihalogenated methanes and haloforms clearly demonstrates that a hydrogen atom in either type of compound interacts with an unshared pair of electrons on an oxygen or nitrogen atom of a solvent and thus gives rise to the phenomenon called hydrogen bonding.

Experimental

The method[4] used in making the solubility determinations has been described previously in detail. The solvents tested were purified carefully and their boiling or melting points checked. The solubilities were determined over a range of pressure at a temperature of 32.2°. The results of the solubility measurements are plotted in Figs. 1 and 2. To compare the solvents conveniently, the gram per gram and mole fraction solubilities at a partial pressure of methylene chloride corresponding to its vapor pressure at 4.5° are given, re-

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(1) Zellhoefer, Copley and Marvel, This Journal, **60**, 1337 (1938).

(2) Zellhoefer and Copley, *ibid.*, **60**, 1343 (1938).

(3) IV, Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666 (1938).

(4) G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).

spectively, in columns 3 and 4 of Table I. The "ideal" or theoretical mole fraction stated at the top of Table I is calculated using Raoult's law, and it is the ratio of the vapor pressure (0.230 atm.) of methylene chloride at 4.5° to its value (0.739 atm.) at 32.2°. The statement in Table I that the solubility of methylene chloride in each of the two compounds, acetamide and diphenylamine, is *very low* is based on the observation that when these compounds were melted (they are solids at 32.2°) and brought in contact with the vapor of the solute only a minute amount of it dissolved.

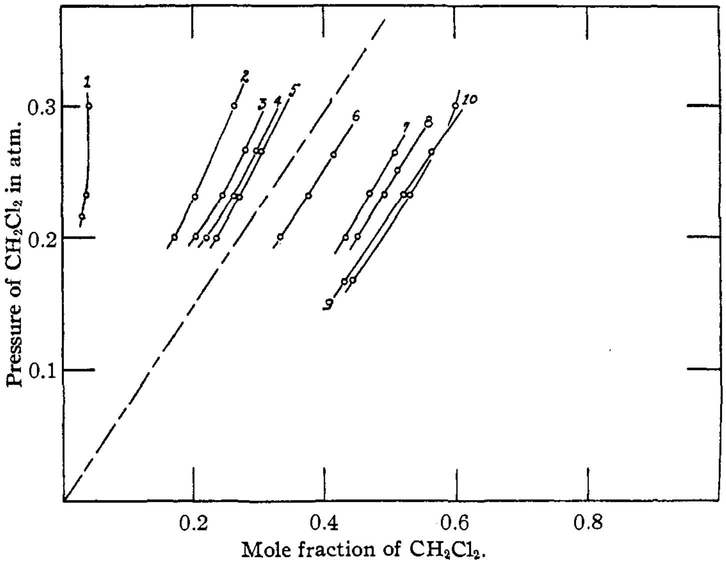

Fig. 2.—The solubility of methylene chloride as a function of pressure in amines, amides, and oximes: 1, formamide; 2, methylformamide; 3, ethyl methyl ketoxime; 4, dimethylformamide; 5, N-methylacetamide; 6, cyclohexylamine; 7, dimethylacetamide; 8, N-methyl-N-cyclohexyl-*n*-butanesulfonamide; 9, N-methyl-N-cyclohexylacetamide; 10, N-ethyl-N-cyclohexylacetamide.

Discussion

A comparison of the solubilities which we have observed for methylene chloride with those reported in a previous communication[3] for monofluorodichloromethane, in the same group of solvents, shows that these two compounds correspond almost exactly in the manner in which their solubilities vary in different types of solvents. In unassociated solvents (ethers, esters, amines and N-disubstituted amides) they both show uniformly high solubilities compared to the values predicted for them by Raoult's law. In solvents which are associated into large polymers (alcohols and amides), by means of the more stable O–H–O and N–H–O bonds, they both show extremely low solubilities compared to the solubilities calculated for them by Raoult's law. In fatty acids, N-monosubstituted amides, and oximes, where the association of the solvent stops at the dimer stage, they have intermediate or almost normal solubilities. It also should be noted that the influence of each of the factors, unsaturation and chelation, is to produce a lowering of solubility in the case of each compound in solvents where these factors are present.

The similar solubilities of methylene chloride and monofluorodichloromethane in widely differ-

TABLE I

SOLUBILITY OF METHYLENE CHLORIDE IN ORGANIC SOLVENTS

(Theoretical or "Ideal" Mole Fraction in Saturated Solution 0.311)

	Formula	Solubility G./g.	Solubility Mole fr.
	Alcohols and Ethers		
Phenol	C_6H_5OH	0.210	0.130
Anisole	$C_6H_5OCH_3$	.385	.328
1,4-Dimethoxycyclohexane	$C_6H_{10}(OCH_3)_2$	.460	.442
Diethyl ether of diethylene glycol	$C_2H_5O(CH_2CH_2O)_2C_2H_5$	.568	.520
Dimethyl ether of tetraethylene glycol	$CH_3O(CH_2CH_2O)_4CH_3$	.580	.602
	Acids and Esters		
Acetic acid	CH_3COOH	0.280	0.174
Propionic acid	C_2H_5COOH	.320	.218
Triethyl phosphate	$(C_2H_5)_3PO_4$	.55	.541
Tri-*n*-propyl phosphate	$(C_3H_7)_3PO_4$	.50	.567
Tri-*n*-butyl phosphate	$(C_4H_9)_3PO_4$	.435	.574
Triphenyl phosphite	$(C_6H_5)_3PO_3$	.192	.412
Tri-*o*-cresol phosphate	$(C_6H_4OCH_3)_3PO_4$	.213	.470
Ethyl ether of diethylene glycol acetate	$C_2H_5O(CH_2CH_2O)_2COCH_3$	.500	.509
Ethyl acetoacetate	$CH_3COCH_2COOC_2H_5$	.454	.410
Ethyl diethylacetoacetate	$CH_3COC(C_2H_5)_2COOC_2H_5$	.403	.468

TABLE I (*Concluded*)

	Formula	Solubility G./g.	Solubility Mole fr.
	Amines, Amides and Oximes		
Cyclohexylamine	$C_6H_{11}NH_2$	0.520	0.377
Diphenylamine	$(C_6H_5)_2NH$	Very low	...
Formamide	$HCONH_2$	0.062	.038
Methylformamide	$HCONHCH_3$	.365	.202
Dimethylformamide	$HCON(CH_3)_2$	.410	.261
Acetamide	CH_3CONH_2	Very low	...
N-Methylacetamide	$CH_3CONHCH_3$	0.427	.269
N,N-Dimethylacetamide	$CH_3CON(CH_3)_2$	.808	.452
N-Methyl-N-cyclohexyl-*n*-butanesulfonamide	$C_4H_9SO_2N(CH_3)C_6H_{11}$	.351	.490
N-Methyl-N-cyclohexylacetamide	$C_6H_{11}N(COCH_3)CH_3$	.600	.521
N-Ethyl-N-cyclohexylacetamide	$C_6H_{11}N(COCH_3)C_2H_5$	.565	.530
Ethyl methyl ketoxime	$C_2H_5(CH_3)C{=}NOH$	.315	.244
	Aldehydes and Ketones		
Benzaldehyde	C_6H_5CHO	0.430	0.349
Salicylaldehyde	*o*-$C_6H_4(OH)CHO$	.320	.315
Heptaldehyde	$CH_3(CH_2)_5CHO$	.473	.388
Paraldehyde	$C_6H_{12}O_3$	.385	.374
Cyclohexanone	$C_6H_{10}O$	.630	.421
Δ^2-Cyclohexenone	C_6H_8O	.473	.349
Acetylacetone	$CH_3COCH_2COCH_3$	.455	.394
Acetonylacetone	$CH_3COCH_2CH_2COCH_3$	.572	.434

ent types of solvents show that the same influence, *viz.*, complex formation by means of hydrogen bonding, is operative in the solutions of each compound.

Summary

The solubilities of methylene chloride have been determined over a range of pressure in several types of organic solvents.

The solubilities are high in esters, ethers, amines and N-disubstituted amides; roughly normal in acids, N-monosubstituted amides and oximes; extremely low in alcohols, and amides.

The remarkable similarity between methylene chloride and monofluorodichloromethane with respect to the way in which their solubilities vary in different types of solvents shows that hydrogen bonding is also present in solutions of methylene chloride in donor solvents.

URBANA AND BLOOMINGTON, ILLINOIS

RECEIVED SEPTEMBER 9, 1938

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. I. The Parachors of a Series of Isomeric Esters[1]

BY OSBORNE R. QUAYLE, KATHERINE OWEN AND REIDUS R. ESTES[2]

Of the many attempts to relate physical properties and structure the parachor[3] has been one of the most successful. It has been of value in the determination of semi-polar bonds,[4] chelation,[5] singlet linkages[6] and degree of aromaticity and unsaturation.[7] From his first observations Sugden[3] concluded that the assigned constants held for all series, that the parachor was not influenced by temperature and that the parachors of isomers were identical. The differences between calculated and observed parachors and the differences between isomers were ascribed to experimental error. However, the parachors of branched heptanes[8] and octanes[9] were found to be

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[1] The authors wish to express their appreciation to Prof. E. Emmet Reid for his kindness in supplying the esters measured and for his valuable practical suggestions on the problem.

[2] Abstracted from a thesis by Reidus R. Estes presented to the Graduate Faculty of Emory University in partial fulfilment of the requirements for the degree of Master of Science, June, 1938.

[3] S. Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

[4] S. Sugden, J. B. Reed and H. J. Wilkins, *ibid.*, **127**, 1525 (1925).

[5] S. Sugden, *ibid.*, **318** (1929).

[6] S. Sugden, *ibid.*, 1173 (1927).

[7] S. Sugden, "The Parachor and Valency," Alfred A. Knopf, New York, N. Y., 1930, pp. 38–40.

[8] G. Edgar and G. Calingaert, THIS JOURNAL, **51**, 1540 (1929).

[9] T. W. Richards, C. L. Speyers and E. K. Carver, *ibid.*, **46**, 1196 (1924).