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.

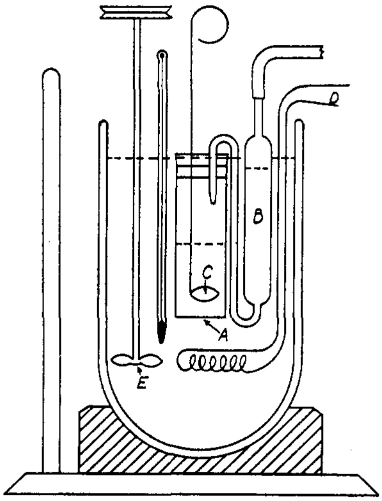

Fig. 1.—Diagram of the calorimeter.

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).

was then blown into the mixing chamber and the rise in temperature was observed. Temperatures were measured by means of a Beckmann thermometer and were estimated to 0.001°. The contents of the calorimeter were again cooled to 0°, and when the temperature warmed up to 3°, electrical energy was added by means of the heating coil D, until approximately the same temperature rise took place. From the amount of electrical energy added and the increments of temperature, the heat liberated on mixing the liquids was calculated.

The materials used were purified by distillation and were stored in tightly stoppered flasks. It was observed that if the ethers were exposed to the air, lower heats of mixing were obtained.

Discussion of Results

The heats of mixing of the combinations chloroform–dimethyl ether of ethylene glycol and monofluorodichloromethane–dimethyl ether of ethylene glycol ($CH_3OCH_2CH_2OCH_3$) are shown, respectively, in Figs. 2 and 3. These curves were constructed from the experimental results by plotting the heats of mixing per mole of solution versus the mole fraction of the halogenated hydrocarbon. A mole of solution is defined as equal to $N_AM_A + N_BM_B$, where N_A and N_B are the mole fractions, and M_A and M_B the molecular weights of constituents. The heights of the maxima of the two curves differ by less than the experimental error, which is about 3%. The location of each maximum is at approximately a mole fraction of 0.5 and this suggests that equimolar complexes are formed between the halogenated hydrocarbons and the ether. The presence of two oxygen atoms in the ether might lead one to expect that combination would occur in the proportion of two molecules of halogenated hydrocarbon to one of the ether. Failure to combine in these proportions is probably due to one or both of the following reasons: (a) the sharing of a pair of electrons by one oxygen decreases the donor properties of the other oxygen; (b) the close proximity of the two oxygen atoms prevents the simultaneous attachment of two halogenated hydrocarbon molecules to an ether molecule.

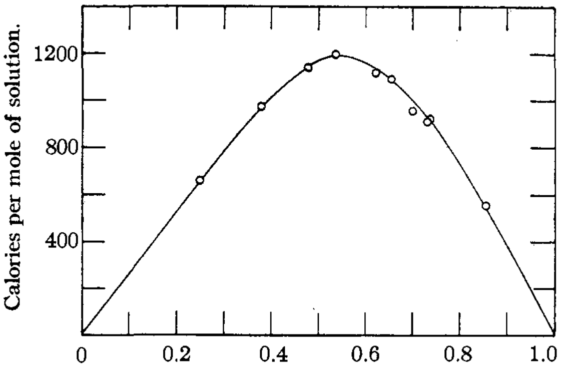

Fig. 2.—Heat of mixing of chloroform and dimethyl ether of ethylene glycol at 3°.

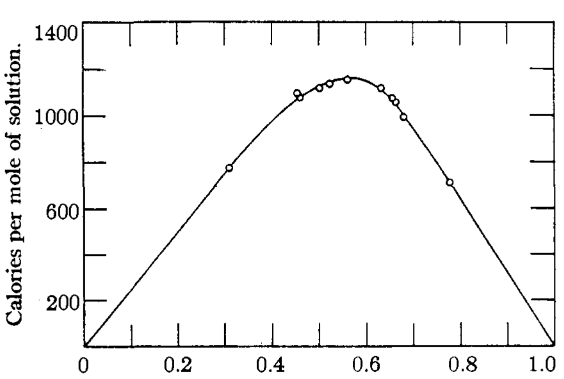

Fig. 3.—Heat of mixing of monofluorodichloromethane and dimethyl ether of ethylene glycol at 3°.

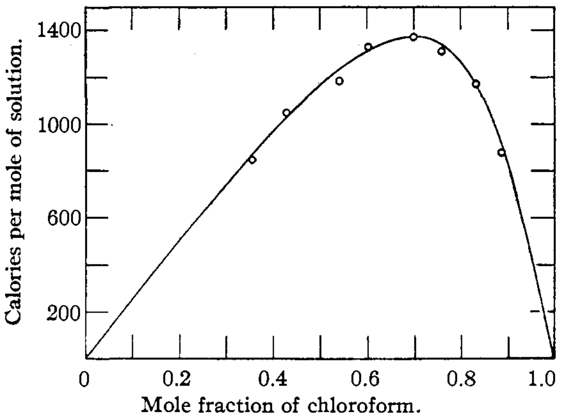

Fig. 4.—Heat of mixing of chloroform and dimethyl ether of tetraethylene glycol at 3°.

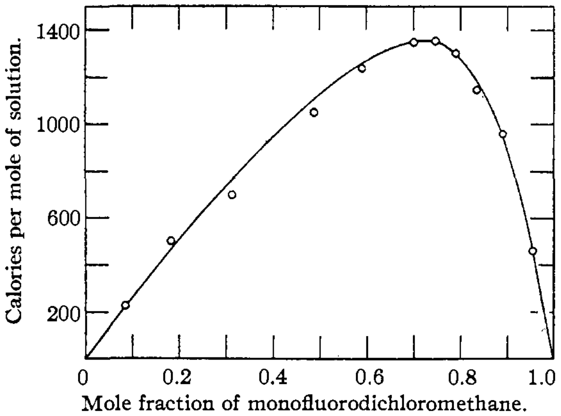

Fig. 5.—Heat of mixing of monofluorodichloromethane and dimethyl ether of tetraethylene glycol at 3°.

Figures 4 and 5 show the results obtained from the measurements on chloroform and monofluorodichloromethane with dimethyl ether of tetraethylene glycol [$CH_3O(CH_2CH_2O)_4CH_3$]. The maxima again do not differ in height by more than the experimental error, and the fact that they come at approximately 0.75 mole fraction of halogenated hydrocarbon indicates that combination occurs between three molecules of halogenated hydrocarbon and one ether molecule. Since the ether contains five oxygen atoms, only alternate ones are available for combination. This result is in accord with the suggestion (b) above and implies that steric hindrance is the most important factor.

The degree of association existing in these mixtures may be estimated roughly by using the value for the strength of the C–H ← O bond found by McLeod and Wilson.[3] From the curves of Figs. 2 and 3 it is calculated that approximately 2300 cal. of heat are liberated when one mole either of chloroform or of monofluorodichloromethane is mixed with one mole of dimethyl ether of ethylene glycol; assuming that all the heat evolved is due to reaction, this corresponds to 38% association. From the maxima of the curves of Figs. 4 and 5, one calculates that 5400 cal. are liberated when three moles of halogenated hydrocarbon are mixed with one mole of the ether. If combination between halogenated hydrocarbon molecules and alternate oxygens of the ether occurs to the same extent, 30% association is indicated.

Conclusion

The large heat of mixing of the CHX_3 type of halogenated hydrocarbon with the polyethylene glycol ethers is explained as due to complex formation. This association is caused by the tendency of the hydrogen of the halogenated hydrocarbon to form a C–H ← O bond with the oxygen of the ether. The locations of the maxima of the heat of mixing curves indicate that, due to steric hindrance, only the alternate oxygen atoms of the polyethylene glycol ether molecules are available for bonding. Complex formation occurs to the extent of from 30–40%.

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[COMMUNICATION NO. 655 FROM THE KODAK RESEARCH LABORATORIES]

Acidity Measurements with the Hydrogen Electrode in Mixtures of Acetic Acid and Acetic Anhydride

BY J. RUSSELL AND A. E. CAMERON

The introduction of the chloranil electrode by Hall and Conant[1] made possible the study of acid and base behavior in glacial acetic acid solutions.[2] The hydrogen electrode has been used in glacial acetic acid by Isgarischew and Pletenew[3] and for the determination of activity coefficients of sulfuric acid in anhydrous acetic acid by Hutchison and Chandlee.[4] The present writers have used the hydrogen electrode for the titration of gelatin and amino acids in glacial acetic acid solutions.[5]

The acetylation of hydroxy compounds, such as cellulose, by acetic anhydride in glacial acetic acid solution is catalyzed by addition of strong acids, such as sulfuric and perchloric acids. Conant and Bramann[6] have investigated the effect of hydrogen-ion activity upon the rate of acetylation of β-naphthol by acetic anhydride and found the rate to vary nearly a millionfold and to depend upon the acidity or basicity of the medium. In their measurements, they apparently assumed that the addition of the acetic anhydride to the buffer of known *p*H(HAc) had no effect upon the hydrogen-ion activity. The chloranil electrode could not be employed in the presence of acetic anhydride because of acetylation of the indicator substances. The hydrogen electrode, however, appeared to offer a means of measuring the hydrogen-ion activity in the presence of anhydride and the measurements described here are the outcome.

Experimental

The customary platinum black electrode catalysts did not prove satisfactory for these measurements. Investiga-

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