Summary

1. The distribution of minute quantities (*ca.* $10^{-12} - 10^{-15}$ g.) of soluble substances between liquid phases is shown in the cases studied to be quantitatively the same as that observed for the same substances in ordinary small concentrations.

2. Distribution ratios of several metallic halides between ether and hydrochloric acid are determined at low concentrations by the use of radioactive substances.

3. It is shown that the technique here employed may be of use in separating and identifying artificially prepared radioactive substances without the use of a non-radioactive carrier.

BERKELEY, CALIFORNIA RECEIVED JULY 19, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERISTY OF ILLINOIS]

Infrared Absorption Studies. VII. Complex Formation Due to Hydrogen Bonding

BY A. M. BUSWELL, W. H. RODEBUSH AND M. F. ROY

In an earlier paper[1] a considerable discussion was given of the conditions under which hydrogen bonding might occur. It was observed that for a hydrogen atom to be capable of forming a "bond" it must be active to a degree (*i. e.*, ionizable in the proper solvents). Furthermore, a generalization due to Venkateswaran[2] was noted. This generalization is that the shift of the fundamental absorption band when hydrogen forms a bond is the greater, and the band itself is the broader, the more active the hydrogen. In order to test the generalizations above it seemed to be desirable to examine compounds containing hydrogen that lay at either extreme of the range of activity. The two which seemed best suited for this purpose are chloroform and hydrogen chloride.

Ether Hydrochloride.—The existence of the ether–hydrogen chloride complex has been known for a long time and it was formerly characterized by organic chemists as an oxonium compound. More recently it has been recognized that it must be in the nature of a hydrogen bonded complex

$$R_2O \longleftarrow HCl$$

Of course by analogy with ammonium compounds, it might be supposed to be ionic in character. Undoubtedly a solution of hydrogen chloride in ether does show some conductance but the amount of ionization cannot be appreciable in a solvent of low dielectric constant for ions of small radius, and no typical salt-like crystal is formed as is the case with ammonium chloride.

Recently a number of spectroscopic studies have tended to confirm the foregoing conclusions. Walkenstein and Syrkin[3] have noted the absence of the Raman lines of hydrogen chloride in ether solutions. West and Edwards[4] have reported the absence of the harmonic at 1.7 μ for hydrogen chloride in ether. Similarly, West and Arthur[5] found no Raman lines for hydrogen chloride in ether solution.

Gordy and Martin[6] have observed the infrared spectrum of hydrogen chloride in ether, dioxane, and ethyl acetate and have found a broad intense band around 4 μ which they attribute to hydrogen bonding between the hydrogen chloride and the solvent.

In the investigation just mentioned the substance to which the hydrogen chloride bonds is used as the solvent. Since the solubility of hydrogen chloride is not large, this procedure has the obvious disadvantage of introducing an excess of solvent and hence a heavy absorption due to C–H in the region of the H–Cl absorption. It is necessary to work with thin layers of solution and as a result it is not possible to make definite observations upon the H–Cl vibration.

In our work we have avoided the above difficulty by using long cells containing a dilute solution of hydrogen chloride and ether in carbon tetrachloride. By changing the concentration of both hydrogen chloride and ether it is possible to produce and observe marked changes in the degree of association between the two substances.

Experimental

An 0.08 molal solution of ether in carbon tetrachloride was saturated with hydrogen chloride under a pressure slightly greater than atmospheric.

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(1) Article No. VI of this series, THIS JOURNAL, **60**, 2444 (1938).

(2) C. S. Venkateswaran, *Proc. Indian Acad.*, **7**, 13 (1938).

(3) M. Walkenstein and J. K. Syrkin, *Nature*, **139**, 288 (1937).

(4) W. West and R. T. Edwards, *J. Chem. Phys.*, **5**, 18 (1937).

(5) W. West and P. Arthur, *ibid.*, **5**, 10 (1937).

(6) W. Gordy and P. C. Martin, *ibid.*, **5**, 1075 (1937).

This solution was then diluted with carbon tetrachloride to the required concentrations and the ratio of the absorption of the solution to the absorption of a solution containing the same amount of ether but no hydrogen chloride was recorded. The hydrogen chloride concentration was determined for each solution by titration of a sample taken at the time the cell was filled. It was not possible in this procedure to maintain absolute constancy for the product of concentration times cell length. Molal absorption coefficients are plotted for the hydrogen chloride in Figs. 1 and 2.

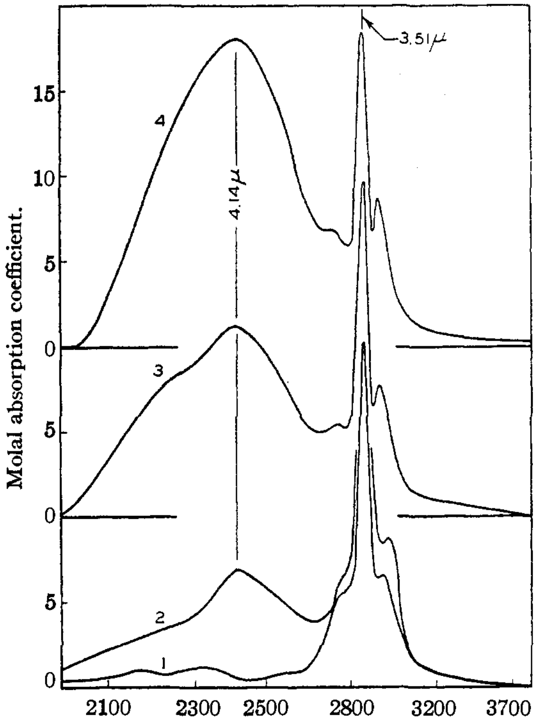

Fig. 1.—(1) 0.129 *M* HCl in CCl_4 *vs.* CCl_4 in 0.158-cm. cell; (2) 0.0264 *M* HCl in 0.02 *M* ether *vs.* 0.02 *M* ether in 0.640-cm. cell; (3) 0.0687 *M* HCl in 0.04 *M* ether *vs.* 0.04 *M* ether in 0.325-cm. cell; (4) 0.154 *M* HCl in 0.08 ether *vs.* 0.08 *M* ether in 0.158-cm. cell.

Discussion of Results

In all of the absorption curves (Fig. 1) for hydrogen chloride in carbon tetrachloride solutions of ether, the hydrogen chloride fundamental is quite evident at 3.51 μ. For the most concentrated solution of both hydrogen chloride and ether (Curve 4), a broad and intense band with a maximum at 4.14 μ is observed. As the concentrations of the hydrogen chloride and ether are decreased simultaneously (Curves 3 and 2), this band decreases in intensity and approaches the absorption for hydrogen chloride itself (Curve 1).

The inference is that hydrogen bonding between the hydrogen chloride and ether molecules causes a shift of the hydrogen chloride fundamental to 4.14 μ. As the concentrations are diminished the amount of H-bonding is decreased and the 4.14 μ band is correspondingly less intense.

The intensity of the hydrogen chloride fundamental decreases slightly as the concentrations increase, but this decrease is not enough to be given any particular significance.

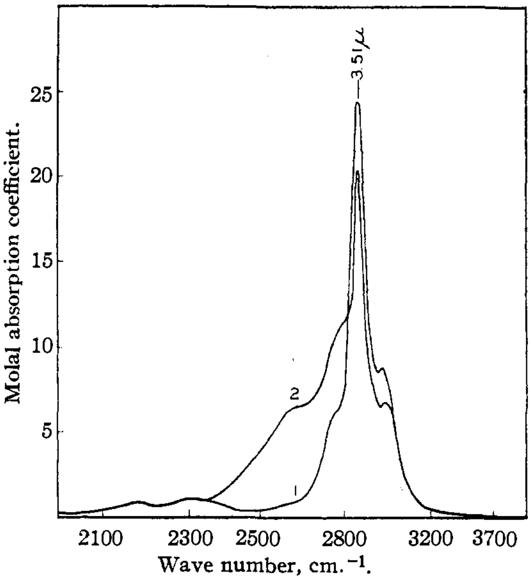

Fig. 2.—(1) 0.129 *M* HCl in CCl_4 *vs.* CCl_4 in 0.158-cm. cell; (2) 0.150 *M* HCl in 0.2 *M* anisole *vs.* 0.2 *M* anisole in 0.158-cm. cell.

The absorption of hydrogen chloride in the carbon tetrachloride solution of anisole is only slightly different from that for hydrogen chloride in carbon tetrachloride (Fig. 2), although the concentrations of both the hydrogen chloride and anisole are greater than the highest ones used in the case of ether. The absorption on the long wave side of the hydrogen chloride fundamental is somewhat increased but there is no intense absorption as there was even at the lower concentrations of ether.

It appears that there is a smaller tendency for the anisole to act as donor in the formation of hydrogen bonds than is the case with ether.

Hydrogen Bonding Involving Chloroform.—The tendency of chloroform to form complexes with a large number of substances such as ethers and ketones has been recognized by many investigators. Recently Huggins[7] has reviewed this evidence and explained it as due to hydrogen bonding. More recently Zellhoefer, Copley and Marvel[8] have studied exhaustively the tendency of chloroform to form complexes by the very simple method of solubility measurements and have adduced an enormous amount of evidence in favor of the activity of the hydrogen in chloroform. Since the hydrogen in chloroform is probably the least active of any hydrogen which is known to form bonds, it may be expected according to the rule of Venkateswaran that the shift in absorption would be so small as to be difficult of observation. Our first experiments showed that this is so, particularly with a molecule such as ether which has a strong C–H absorption. For that reason a considerable amount of our work was done with quinoline in which the absorption due to the aromatic C–H is less and is located at a somewhat different wave length than that for chloroform.

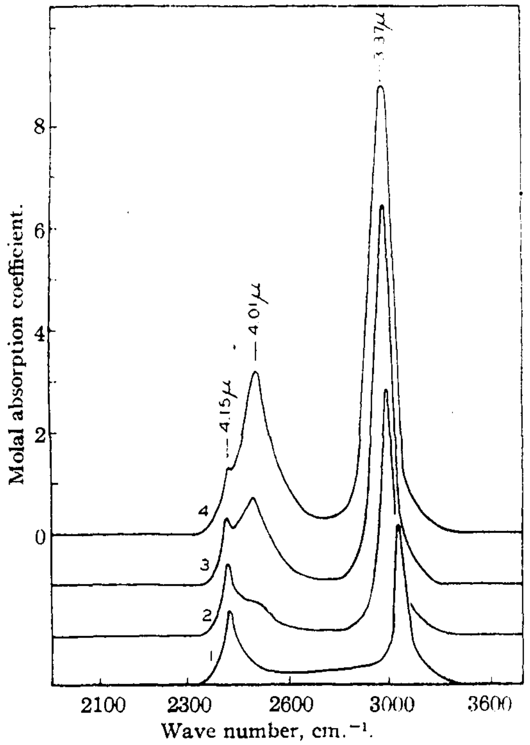

Fig. 3.—Quinoline–$CHCl_3$: (1) 4 *M* $CHCl_3$ in CCl_4 *vs.* CCl_4 in 0.0374-cm. cell; (2) 0.25 *M* $CHCl_3$–0.25 *M* quinoline *vs.* 0.25 *M* quinoline in 0.640-cm. cell; (3) 1 *M* $CHCl_3$–1 *M* quinoline *vs.* 1 *M* quinoline in 0.158-cm. cell; (4) 4 *M* $CHCl_3$–4 *M* quinoline *vs.* 4 *M* quinoline in 0.0374-cm. cell.

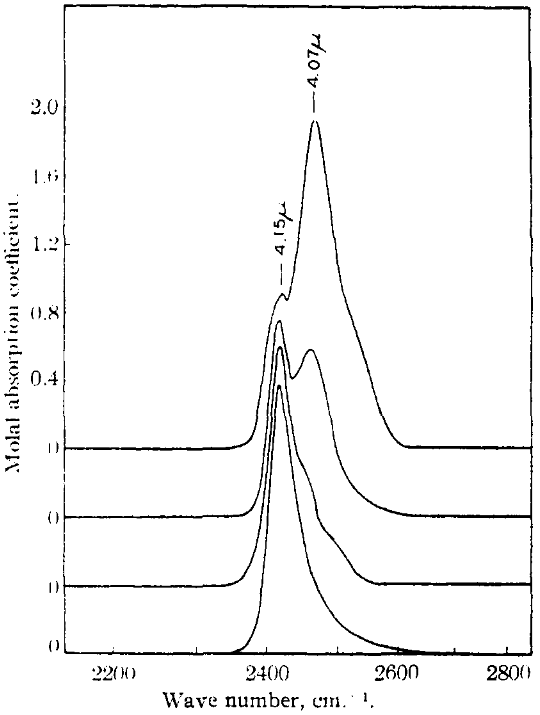

Fig. 4.—Acetone–$CHCl_3$: (1) 4 *M* $CHCl_3$ in CCl_4 *vs.* CCl_4 in 0.0374-cm. cell; (2) 0.25 *M* $CHCl_3$–0.25 *M* acetone *vs.* 0.25 *M* acetone in 0.640-cm. cell; (3) 1 *M* $CHCl_3$–1 *M* acetone *vs.* 1 *M* acetone in 0.158-cm. cell; (4) 4 *M* $CHCl_3$–4 *M* acetone *vs.* 4 *M* acetone in 0.0374-cm. cell.

Solutions containing various concentrations of chloroform and quinoline, chloroform and acetone, and chloroform and ether in carbon tetrachloride were studied. In Figs. 3, 4 and 5 the absorption due to chloroform only is plotted since the control cell in these experiments contained not the pure solvent but a solution containing the same concentration of the substance other than the chloroform of the pair that was being studied. In the solutions of chloroform and quinoline it was possible to observe the C–H absorption of the chloroform with precision. At low concentrations the absorption was of the same wave length and intensity as for solutions of chloroform alone in carbon tetrachloride. As the concentration was increased the absorption shifted toward longer wave lengths and increased in intensity. In a solution 4 molal with respect to chloroform and quinoline, the maximum absorption is at 3.37 μ as compared with 3.28 μ for chloroform alone and the height of the peak has increased nearly three-fold. This would appear to be conclusive evidence for the formation of a hydrogen bond between chloroform and quinoline. Upon inspection of Fig. 3,

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(7) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).

(8) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, This Journal, **60**, 1337 (1938).

one's attention is attracted immediately to the absorption at 4.15 μ. This absorption increases with increasing concentration but is shifted to shorter wave lengths, which is contrary to any previous behavior noted. The positive identification of this relatively weak absorption is necessarily not easy. It is presumably an overtone or combination frequency and, since it is about the same for bromoform, one suspects it to be connected with the hydrogen.

Voge and Rosenthal[9] have assigned the value 1225 cm.$^{-1}$ as the frequency in wave numbers of the perpendicular vibration in chloroform which involves mainly the hydrogen atom; 2400 cm.$^{-1}$ or 4.15 μ would therefore be a reasonable value for the second harmonic. The fact that this frequency is affected by complex formation is confirmatory of the foregoing. It is easy from a rather crude mechanical picture of the hydrogen bond to argue that, while the stretching frequency should be lowered, the bending frequency should be increased, when a hydrogen bond is formed. However, these conclusions must be admittedly tentative until confirmed by further study.

In solutions of acetone and quinoline the same results confirmatory of complex formation are obtained but they are of much smaller magnitude. While the fundamental C–H frequency shows marked increase in height, the shift in wave length is barely observable. Similarly the behavior of the 4.15 μ absorption is less striking. In solutions of ether and chloroform it is impossible because of the strong absorption of the ether to observe the C–H fundamental but the harmonic at 4.15 μ shows quite clearly the same behavior as for chloroform and quinoline.

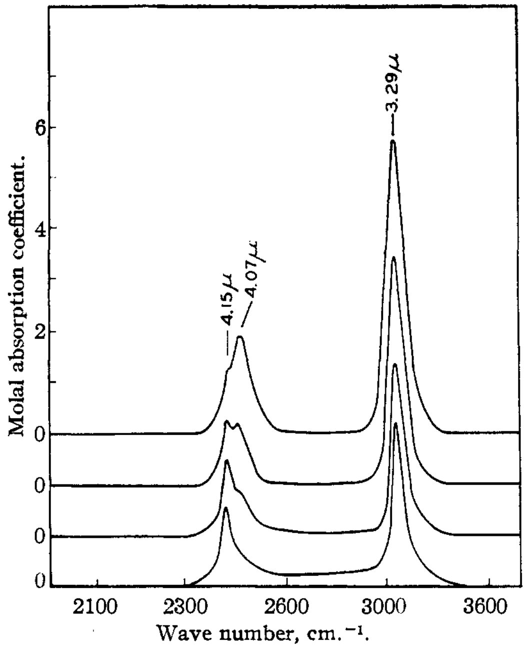

Fig. 5.—Ether–$CHCl_3$: (1) 4 M $CHCl_3$ in CCl_4 *vs.* CCl_4 in 0.0374-cm. cell; (2) 0.25 M $CHCl_3$–0.25 M ether *vs.* 0.25 M ether in 0.640-cm. cell; (3) 1 M $CHCl_3$–1 M ether *vs.* 1 M ether in 0.158-cm. cell; (4) 4 M $CHCl_3$–4 M ether *vs.* 4 M ether in 0.0374-cm. cell.

Summary

The tendency of hydrogen chloride and chloroform toward complex formation with ether and other substances through hydrogen bonding has been investigated. These two compounds stand at opposite extremes in the scale of activity of the hydrogen. The rule of Venkateswaran has been verified for the shift of the fundamental frequency of the hydrogen. An absorption band which shifts to shorter wave lengths upon bond formation has been observed in the case of chloroform and this absorption has been ascribed tentatively to the second harmonic perpendicular vibration of the hydrogen.

URBANA, ILLINOIS RECEIVED JULY 20, 1938

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(9) H. H. Voge and J. E. Rosenthal, *J. Chem. Phys.*, **4**, 137 (1936).