[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Infrared Absorption Spectra of Certain Liquid Mixtures

BY WALTER GORDY[1]

Numerous investigations of liquid mixtures[2] have been made recently by means of the Raman spectra. With few exceptions, however, in all of these studies the spectra obtained were the sum of the spectra of the individual components for the lines which were observed. Infrared studies of alcohol–water mixtures[3] and of acetone–water mixtures[4] have revealed bands not characteristic of either of the components. It was suggested that these were associational bands indicating some type of linkage between the two liquids. Associational bands had been reported previously for aqueous solutions[5] of some inorganic acids, hydroxides and salts, and for alcoholic solutions of some hydroxides.[6] More recently[7] a study of alcohol–acetone mixtures has revealed changes in the spectrum of both components indicating association of the two liquids through dipole interaction.

The present work was undertaken as an attempt to determine whether there is association between aniline and certain other liquids, and, if possible, to determine the nature of the linkage. We may anticipate a linkage of aniline with liquids like acetone through the formation of hydrogen bonds, the hydrogen of the NH aniline group forming a bond between the nitrogen of the NH aniline group and the oxygen of the CO acetone group. The hydrogen bond theory[8] has received considerable attention recently.

Experimental

A Hilger infrared spectrometer with a fluorite prism was used throughout the investigation. Cell windows were of fluorite and were sealed with paraffin. The absorbing layer was maintained at a constant thickness of 0.002 cm. by means of mica washers. The chemicals were Baker certified products.

Results

Studies were made of 50% mixtures of aniline with acetone, ethyl acetate, ethyl formate, methyl cyanide, isopropyl ether and carbon tetrachloride. Figure 1 shows the results obtained in the region 2.5 to 3.1 μ. The band appearing at 2.85 μ in pure aniline arises from changes in the vibrational energy of the NH group. For mixtures of aniline with acetone, ethyl acetate, ethyl formate, isopropyl ether and methyl cyanide, this band is shifted to the shorter wave lengths by about 0.05 μ, and its intensity is definitely increased.

These changes are more apparent when the experimental transmission curves for the mixtures are compared with the theoretical transmission curves for a purely mechanical mixture in which no interaction occurs. The theoretical curves are represented by the broken lines in the figure. Here the transmission of the mechanical mixture for a given frequency is represented by

$$T = e^{-f_1m_1-f_2m_2}$$

where f_1 and f_2 are the fractional parts of aniline and the liquid with which it is mixed, respectively, and where m_1 and m_2 are defined by

$$T_1 = e^{-m_1}, \quad T_2 = e^{-m_2}$$

T_1 being the transmission of pure aniline for the given frequency, and T_2 that of the second liquid. It should be remembered that the cell thickness was the same in all cases.

In contrast to the pronounced shifts and changes in intensity observed in the NH band for other mixtures, no measurable changes were observed in the case of mixtures of aniline with carbon tetrachloride, Fig. 1, F.

Figure 2 shows the effects of aniline on the vibrational band of the CO group of acetone, ethyl acetate and ethyl formate. In each of these mixtures the CO band is shifted to the longer wave lengths by approximately 0.05 μ, and in each mixture the intensity of the band is slightly increased. The experimental curves for the mix-

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(2) S. Parthasarathy, *Phil. Mag.* (Suppl.), **17**, 471 (1934); A. Dadieu and K. W. F. Kohlrausch, *Physik. Z.*, **31**, 514 (1930); Whiting and Martin, *Trans. Roy. Soc. Can.*, **25**, 87 (1931); Crigler, THIS JOURNAL, **54**, 4207 (1932).

(3) D. Williams, R. D. Weatherford and E. K. Plyler, *J. Optical Soc. Am.*, **26**, 149 (1936).

(4) D. Williams and E. K. Plyler, *J. Chem. Phys.*, **4**, 154 (1936).

(5) E. K. Plyler and W. Gordy, *ibid.*, **2**, 470 (1934); W. Gordy, *ibid.*, **2**, 62 (1934); E. K. Plyler and E. S. Barr, *ibid.*, **2**, 306 (1934).

(6) E. K. Plyler and F. D. Williams, *ibid.*, **2**, 565 (1934).

(7) W. Gordy, *Phys. Rev.*, **50**, 1151 (1936).

(8) L. Pauling, THIS JOURNAL, **57**, 2680 (1935); *ibid.*, **58**, 94 (1936); L. Onsager, *ibid.*, **58**, 1486 (1936); R. H. Gillette and A. Sherman, *ibid.*, **58**, 1135 (1936); R. H. Gillette and F. Daniels, *ibid.*, **58**, 1139 (1936).

tures should be noted especially in comparison with the theoretical curves for the same mixtures.

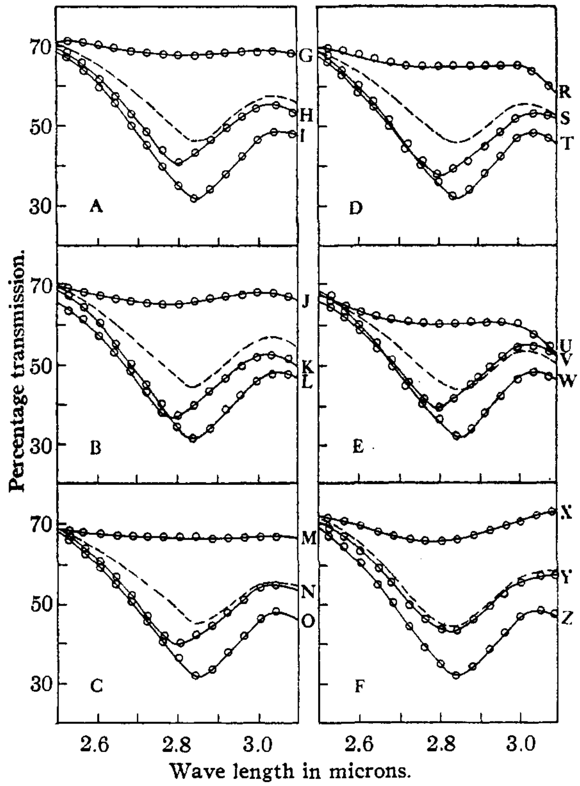

Fig. 1.—Transmission curves in the region 2.5 to 3.1 μ: ----, theoretical for 1:1 mixtures; ——, observed. A, Curve (G) pure isopropyl ether, (H) 1:1 volume mixture with aniline, (I) pure aniline. B, Curve (J) pure acetone, (K) 1:1 volume mixture with aniline, (L) pure aniline. C, Curve (M) pure methyl cyanide, (N) 1:1 volume mixture with aniline, (O) pure aniline. D, Curve (R) pure ethyl formate, (S) 1:1 volume mixture with aniline, (T) pure aniline. E, Curve (U) pure ethyl acetate, (V) 1:1 mixture with aniline, (W) pure aniline. F, Curve (X) pure carbon tetrachloride, (Y) 1:1 mixture with aniline, (Z) pure aniline.

A study was made of aniline bands appearing in the regions of 6.15 μ and 6.65 μ. Transmission curves obtained for these regions are not given. No shifts could be detected in either of the bands for any of the mixtures. Because of overlapping of bands it was not found practicable to study the mixtures in other regions below 8.5 μ.

Discussion

The pronounced changes in the dipole moments of the NH group of aniline and the CO group of acetone, ethyl acetate and ethyl formate, as revealed by changes in the vibrational infrared bands of these groups, in contrast to the approximate constancy of the moments of other groups, indicate association of the liquids through the dipole interaction of these groups. A pos-

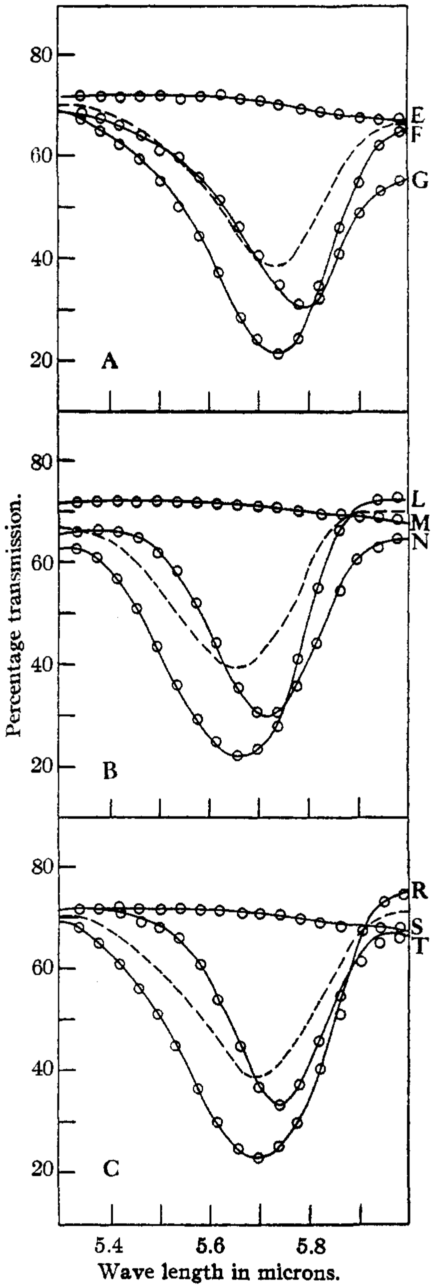

Fig. 2.—Transmission curves in the region 5.3 to 6.0 μ: ----, theoretical for 1:1 mixtures; ——, observed. A, Curve (E) pure aniline, (F) pure acetone, (G) 1:1 volume mixture. B, Curve (L) pure ethyl acetate, (M) pure aniline, (N) 1:1 volume mixture. C, Curve (R) pure ethyl formate, (S) pure aniline, (T) 1:1 volume mixture.

sible explanation of this interaction would be the formation of hydrogen bonds, the hydrogen of the NH aniline group forming a bond between the nitrogen of this group and the oxygen of the CO group. Likewise, the pronounced changes in the NH aniline band in the aniline–isopropyl ether mixtures and the aniline–methyl cyanide mixtures suggest the association of these liquids through the formation of hydrogen bonds. There seems to be no interaction between the NH aniline group and carbon tetrachloride.

The apparent changes in the polarization of molecules in liquid mixtures as determined by dielectric constant measurements are no doubt in many cases due to changes in the electric moments of certain groups resulting from association of the liquids through the interaction of the dipoles of these groups. It should be possible through infra-red absorption measurements to ascertain in many of these mixtures which dipoles undergo pronounced changes and thereby to determine something of the nature of the linkage. The work is being continued on other mixtures in which the formation of hydrogen bonds may be anticipated. Preliminary results,[9] similar to those given above for aniline mixtures, indicate that water and also alcohols associate with certain other liquids through the formation of hydrogen bonds.

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Summary

In mixtures of aniline with acetone, ethyl acetate, ethyl formate, methyl cyanide and isopropyl ether, the NH vibrational band of aniline is shifted to shorter wave lengths and its intensity is increased. In mixtures of aniline with carbon tetrachloride this band appears to remain constant. Other aniline bands remain approximately constant for all the mixtures. The CO band of acetone, ethyl acetate and ethyl formate is shifted to longer wave lengths, and its intensity increased in mixtures of these liquids with aniline.

It is suggested that the observed changes in the spectrum indicate association of the liquids through dipole interaction. The formation of hydrogen bonds is proposed as a possible interpretation of the results.

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[9] Unpublished data obtained by the author.

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Kinetics of Condensation Polymerization; the Reaction of Ethylene Glycol with Succinic Acid

BY PAUL J. FLORY

Bifunctional condensation polymerizations, such as the formation of polyesters either from hydroxy acids or from glycols and dibasic acids,[1] proceed through the intermolecular reaction of the functional groups attached to bifunctional reactants. The reaction involved is fundamentally no different than the reaction between monofunctional reactants bearing the same functional groups; *e. g.*, in polyester formation the reaction is simply esterification, as Kienle and Hovey[2,3] have shown. Unless the reaction of one functional group of a bifunctional reactant changes the reactivity of the other group, all functional groups may be assumed to be equally reactive. When this is true, the reaction should be of the same kinetic character as the analogous monofunctional reaction. Unpublished experiments carried out in this Laboratory verify this deduction.

Recently Dostal and Raff[4,5] have examined the course of the reaction of ethylene glycol with succinic acid. They combined equimolar quantities either in dioxane solution or in the absence of solvent, and in two sets of experiments the succinic acid was dissolved in a large excess of glycol. The progress of the reaction was followed by titration of the unreacted acid in samples heated for various lengths of time at constant temperatures.

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[1] Carothers, *Chem. Rev.*, **8**, 359 (1931).

[2] Kienle and Hovey, THIS JOURNAL, **52**, 3636 (1930).

[3] Kienle and Hovey, *ibid.*, **51**, 509 (1929).

[4] Dostal and Raff, *Monatsh.*, **68**, 188 (1936).

[5] Dostal and Raff, *ibid.*, **68**, 117 (1936).