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The Absorption Spectra of Benzoic Acid and Esters

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The absorption spectra of benzoic acid and some of its simple esters have been determined in various concentrations in polar and non-polar solvents. Changes in solvents and concentrations affect the fine structure of the curves more than the wave lengths and intensities of the maxima and the conclusions are therefore based primarily on variations in fine structure. The spectral changes are discussed in terms of dimerization, bonding with the solvent and ionization.

Introduction

A survey of the literature shows three absorption bands for benzoic acid in the range of 200–300 mμ, designated as A, B and C-bands.[2] Only Moser[2] has observed the A-band. All authors agree quite well on the general shape and position of the B and C-bands, but there is some discrepancy in the fine structure of the C-band and there are deviations in the extinction values in non-polar (hydrocarbon) solvents.[3] Similar disagreement is found in aqueous solutions[4] while the values for alkaline and acid solutions agree quite well.[4b–6] Absorption curves for alcoholic solutions vary with respect to fine structure and there is some question as to precisely what effect alcoholic solvents will have on the shape of the curve or the position of the maxima. Esters of benzoic and other aromatic acids are said to be virtually unaffected by solvents.[3a,7]

The present study represents an attempt to clear up disagreements in the literature and to provide a rational explanation for the collective experimental data.

Experimental

Absorption spectra were determined with a Model DU Beckman spectrophotometer operated at constant voltage (116 v.). Photometric sensitivity was sacrificed in order that all measurements could be made with the narrowest slit width possible. The wave length scale of the instrument was calibrated against a mercury arc. It proved to be correct to within 0.1 mμ. The photometric accuracy of the instrument was checked with potassium acid phthalate solutions. It fell within the reported range.[8] Dilutions of all samples were made from stock solutions containing 1-8 × 10^{-3} mole per liter. Each solution was measured in a 1-cm. silica cell against the pure solvent. The point-by-point extinction measurements were made at intervals of 2 mμ or less on all solutions. Molar extinction coefficients were calculated by dividing the observed densities by the molar cell concentrations. All calculations for benzoic acid were based on the molecular weight of 122. Each of the solutions was recorded and plotted separately. It was found that useful information was obtainable in the density range of 0.05–1.5. A greater density range used in previous work from this Laboratory[9] doubtless included some instrumental deviations. All solvents were checked for transmission and were purified when necessary. Only 95% ethyl alcohol required no further purification.

Benzoic Acid and Esters.—Commercial reagent chemicals were used. The benzoic acid melted at 120.5–121°. *n*-Decyl benzoate was prepared from benzoyl chloride and *n*-decyl alcohol.

Results

Absorption spectra have been determined for benzoic acid and esters in cyclohexane, dioxan, methyl, ethyl, isopropyl and *t*-butyl alcohol, chloroform, water and various solvent mixtures as far as the solubilities permitted (Figs. 1–10, Tables I–IV). Concentration dependence of the absorption spectra has been observed only with benzoic acid in water and cyclohexane solutions. It is most marked in aqueous solutions of this compound and is measured in terms of wave lengths and intensities of the B- and C-band maxima (Table I). All other studies are concerned essentially with changes in the fine structure of the C-band maxima.

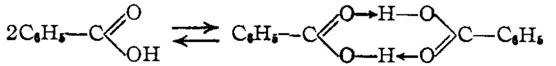
Absorption curves of benzoic acid and esters in water or dilute aqueous alcohols have only a single broad C-band maximum. In less polar solvents fine structure bands are recognizable and in dilute cyclohexane solutions three submaxima can be distinguished.

Alkyl benzoates have identical spectra, independent of concentration, for R = Me to *n*-decyl. Solvents affect only the fine structure but not the wave length of their maxima (Table II). Alkyl benzoate spectra resemble the acid curve in alcoholic solutions and differ from it most in non-polar solvents. Un-ionized benzoic acid (in hydrochloric acid) and aqueous methyl benzoate have identical curves.

Discussion

Non-polar Solvents.—Benzoic acid exists as mixtures of monomers and dimers in solutions of hydrocarbons,[10] chloroform,[10] carbon disulfide[11] and carbon tetrachloride.[12] In the absence of any interaction with the solvent, as in the case of cyclohexane, an infinitely dilute solution should contain only unsolvated monomeric molecules of benzoic acid, a concentrated solution, unsolvated dimers. The molecular weight would increase with concentration and reach the dimer value at around 0.5 molal solution (in benzene).[10]

In the concentration range suitable for spectrophotometric work the equilibrium



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[1] From the master's thesis of R. W. Lamb, 1951.

[2] C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).

[3] (a) E. D. Bergmann, Y. Hirschberg and S. Pinchas, *ibid.*, 2351 (1951); (b) H. Mohler and J. Pólya, *Helv. Chim. Acta*, **20**, 96 (1937); (c) V. Henri, "Int. Crit. Tables," Vol. V, p. 359 (1929).

[4] (a) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2716 (1947); (b) W. D. Kumler and L. A. Strait, *ibid.*, **65**, 2349 (1943).

[5] The published values fall on the curves which are reported in the present investigation.

[6] (a) L. A. Flexser, L. P. Hammett and A. Dingwall, THIS JOURNAL, **57**, 2106 (1935); (b) E. A. Fehnel, *ibid.*, **72**, 1404 (1950).

[7] G. Scheibe, *Ber.*, **59**, 2617 (1926); K. L. Wolff and O. Strasser, *Z. physik. Chem.*, **21B**, 389 (1933).

[8] G. W. Ewing and T. Parsons, *Anal. Chem.*, **20**, 423 (1948).

[9] H. E. Ungnade and I. Ortega, THIS JOURNAL, **73**, 1564 (1951); H. E. Ungnade, V. Kerr and E. Youse, *Science*, **113**, 2943 (1951).

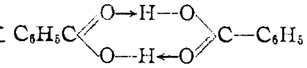
[10] (a) F. T. Wall and P. E. Rouse, THIS JOURNAL, **63**, 3002 (1941); (b) E. N. Lassettre, *Chem. Revs.*, **20**, 259 (1937).

[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 307–327.

[12] (a) M. St. C. Flett, *J. Chem. Soc.*, 962 (1951); (b) M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755 (1938).

TABLE 1

ABSORPTION SPECTRA OF BENZOIC ACID

Solvent	Concn., moles/l. × 10³	B-band λmax, mμ	B-band log ε	λmax, mμ	log ε	C-band λmax, mμ	C-band log ε	λmax, mμ	log ε
	I. $2C_6H_5COOH \rightleftharpoons$ 								
Cyclohexane	1.77	...	..	..	..	274	3.04	282	2.96
	0.375	...	..	..	..	274	3.03	282	2.96
	0.0805	232	4.10	268	2.91	274	3.02	282	2.96
Chloroform	1.282	...	..	..	..	274	3.02	282	2.95
	0.256	...	..	..	..	274	3.02	282	2.95
	0.051	...	..	..	..	274	3.03	282	2.96
	II. C_6H_5COOH hydrate + $H_2O \rightleftharpoons C_6H_5COO^-$ hydrate + H_3O^+								
0.01 *N* HCl	0.078	230	4.05	..	..	274	3.01	..	..
Water	1.748	...	..	..	..	272	2.97	..	..
	0.349	...	..	..	..	272	2.94	..	..
	.0715	228	3.97	..	..	272	2.89	..	..
0.01 *N* NaOH	.327	224	3.91	262	2.70	268	2.69	..	..
	III. C_6H_5COOH solvates								
MeOH	0.0482	226	3.97	..	..	272	2.92	280[a]	2.81
EtOH	.0716	228	4.04	268[a]	2.89	272	2.95	280	2.84
i-PrOH	.0472	228	4.08	268[a]	2.88	272	2.92	280	2.84
t-BuOH	.0354	...	..	268[a]	2.87	272	2.97	280	2.88
Dioxane	.0658	228	4.06	268	2.91	272	2.98	280	2.92

[a] Shoulder.

would undoubtedly be shifted toward the monomer, although some dimer remains.[13]

The absorption spectrum of benzoic acid in cyclohexane (Fig. 1) is somewhat concentration-dependent since the resolution of the fine structure bands is sharpened on dilution. The absorption curve in chloroform resembles that in concentrated cyclohexane solution (Fig. 1). Both lack the sharp and narrow bands which are observed in cyclohexane solution of the esters, both are shifted slightly to the red and show higher extinction values than any of the other solutions of benzoic acid or its esters.[14] These absorption characteristics are attributed to the presence of dimer.

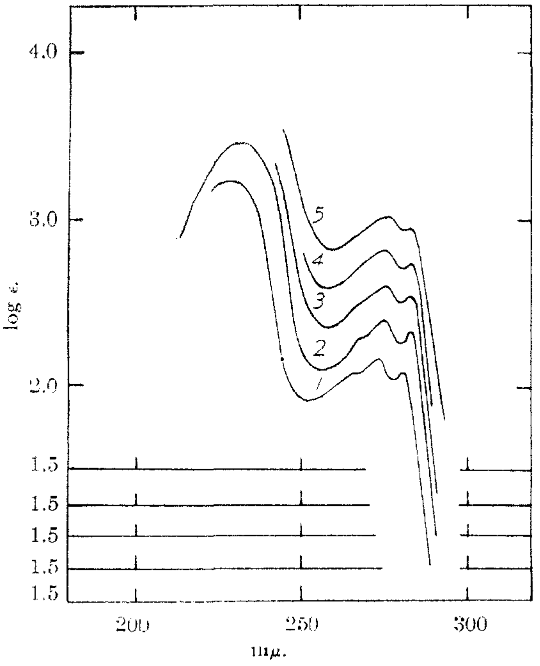


Fig. 1.—Benzoic acid in: 1, dioxane (6.58×10^{-5} mole/l.); 2, cyclohexane (8.05×10^{-5} mole/l.); 3, cyclohexane (3.75×10^{-4} mole/l.); 4, cyclohexane (1.77×10^{-3} mole/l.); 5, chloroform (2.56×10^{-4} mole/l.).

TABLE II

ABSORPTION SPECTRA OF METHYL BENZOATE

Solvent	Concn., mole/l. × 10³	B-band λmax, mμ	B-band log ε	λmax, mμ	C-band log ε	C-band λmax, mμ	log ε
Cyclohexane	0.0777	228	4.09	273	2.97	280	2.92
Dioxane	.104	228	4.06	273	2.94	280	2.86
t-BuOH	.317	...	..	273	2.95	280	2.89
EtOH	.0480	228	4.04	273	2.92	280	2.84
MeOH	.0694	228	4.09	273	2.95	280	2.88
Chloroform	.539	...	..	273	2.97	281	2.88
Water	.0471	230	4.05	273	3.00	...	..

Alkyl benzoates are monomeric in hydrocarbons.[10] They cannot dimerize and are not expected to solvate with paraffin solvents. Their absorption spectra in cyclohexane (Fig. 2) therefore represent the monomeric molecules.

Dioxane.—Methyl benzoate has far less fine structure in dioxane than in cyclohexane (Fig. 3) and its curve in this solvent is very similar to the corresponding curve for benzoic acid. It may be concluded, therefore, that a similar solvate occurs in both compounds.

Electron-donor solvents, such as ethers and dioxane tend to stabilize benzoic acid as monomer.[11] In order to compete successfully with dimerization, such solvents must form a fairly stable hydrogen bond with benzoic acid, probably as

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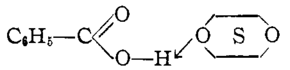
[13] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D Van Nostrand Co., Inc., New York, N. Y., 1946, p. 680.

[14] At a concentration of 1.027×10^{-2} mole per liter and 0.110-cm. cell length the c-band maxima are at 276 mμ (log ε 3.05) and 284 mμ (log ε 2.99).



Such a bond will not appreciably affect the spectrum and obviously cannot account for the solvent effect in methyl benzoate. It is necessary to assume an additional bonding, perhaps with the carboxyl carbon or the nucleus in order to explain the latter effect. The dielectric constants of cyclohexane and dioxane are almost identical and therefore would not account for the difference in fine structure in the two solvents.

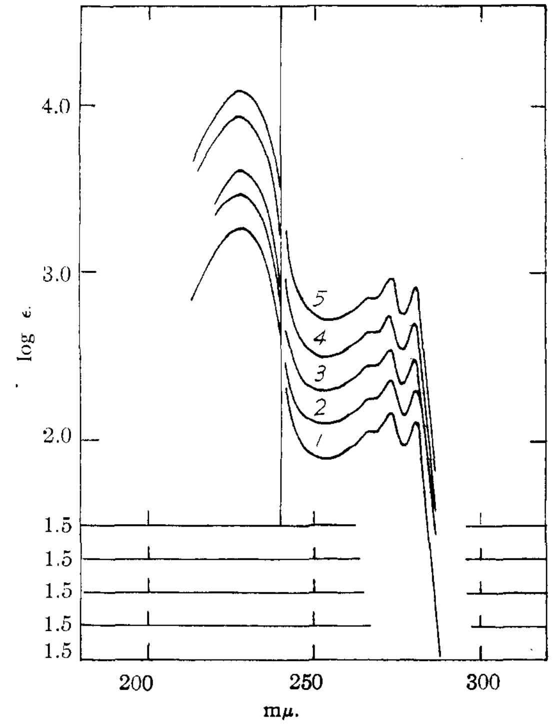
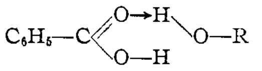
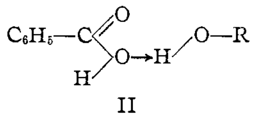


Fig. 2.—Alkyl benzoates in cyclohexane: 1, Me; 2, Et; 3, *i*-amyl; 4, *n*-hexyl; 5, *n*-decyl; B-maxima at 5 × 10⁻⁵ mole/l.; C-maxima at 5 × 10⁻⁴ mole/l.

Alcohols.—In aliphatic alcohols, water and in phenol, benzoic acid is monomeric[10b] and the monomers are stabilized by hydrogen bonds stronger than those in benzoic acid dimer. In the absence of literature data, it has been ascertained that this is also true for *t*-butyl alcohol. A stabilization of this sort could be depicted as in I and II

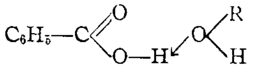


I

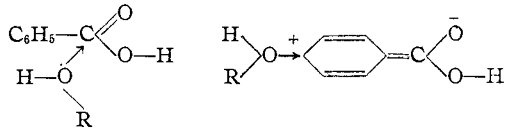


II

Since alcohols can also serve as electron donors, another type of bonding can occur, as in III and IV.[15,16]

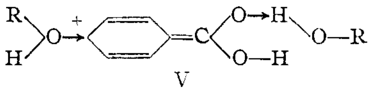


III



IV

Each type of solvate bond will exert an electronic effect upon the resonating system in benzoic acid. Since these effects are in the same direction for types I, II and IV, any combination of these solvates will lead to an increased electronic and spectral effect. Structure V illustrates a combination of types I and IV.



V

Solvent effects of this sort should be similar to substituent effects but weaker and may therefore consist in increased absorbance, a red shift of the bands and a decrease in fine structure (which accompanies a dampening of the benzenoid resonance).[17]

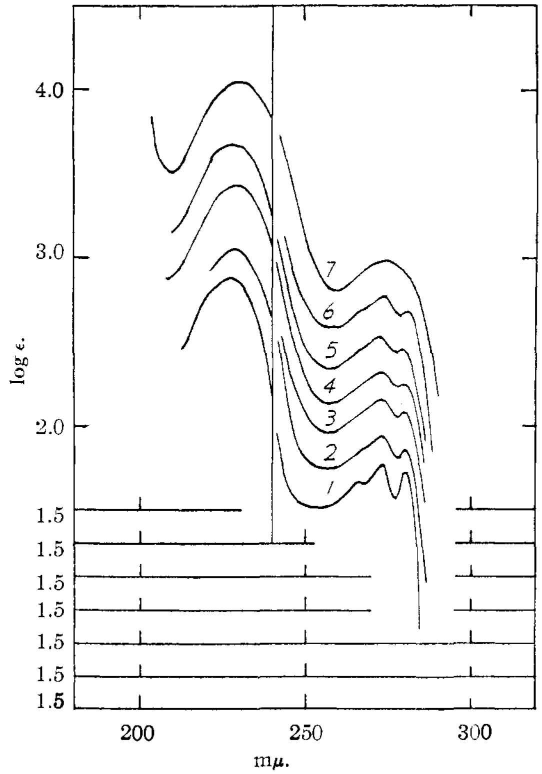


Fig. 3.—Methyl benzoate in seven solvents: 1, cyclohexane; 2, dioxane; 3, *t*-BuOH; 4, EtOH; 5, MeOH; 6, chloroform; 7, water; B-maxima at 4–10 × 10⁻⁵ mole/l.; C-maxima at 2–6 × 10⁻⁴ mole/l.

It has been determined experimentally (Fig. 4) that the absorption curves of benzoic acid in hydroxylic solvents gain fine structure in the order

H_2O < MeOH < EtOH < *i*-PrOH < *t*-BuOH

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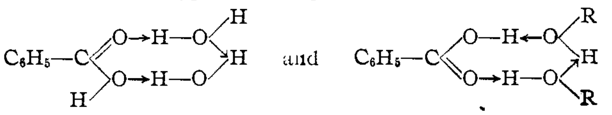
[15] Evidence for bonding with aromatic nuclei has been presented by L. H. Jones and R. M. Badger (THIS JOURNAL, **73**, 3132 (1951)).

[16] Solvate molecules of this sort may be further stabilized by ring formation as proposed by M. L. Huggins (*J. Org. Chem.*, **1**, 429 (1936)). They may involve hydrogen bonds of types I–III and structures in which the solvent oxygen donates a pair of electrons, such as



[17] W. R. Brode, "Chemical Spectroscopy," John Wiley and Sons Inc., New York, N. Y., 2nd ed., 1943, p. 231.

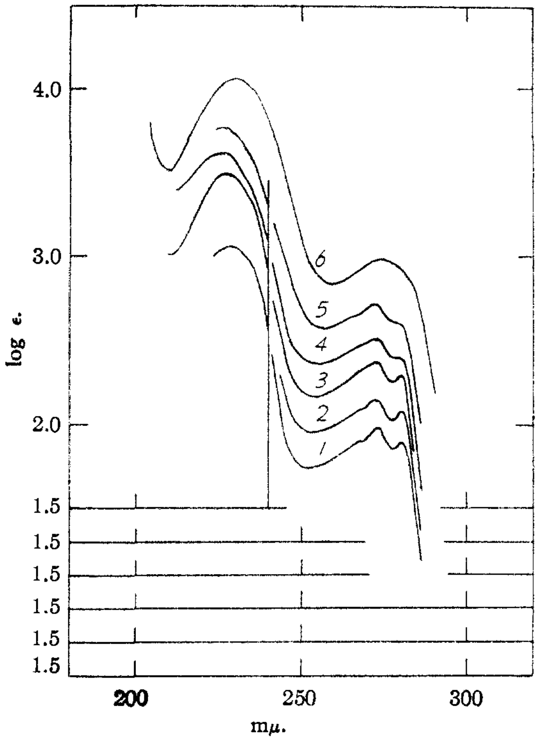


Fig. 4.—Benzoic acid in six solvents: 1, dioxane; 2, *t*-BuOH; 3, *i*-PrOH; 4, EtOH; 5, MeOH; 6, 0.01 *N* HCl; B-maxima at 4–8 × 10^{-5} mole/l.; C-maxima at 1–4 × 10^{-4} mole/l.

The un-ionized hydrate has the highest extinction values among these solvates and its bands are shifted furthest toward the visible. It is therefore reasonable to assume that all the above solvate bonds occur in water and that some types are suppressed with an increase in the size of the alcoholic alkyl group. While solvates such as V may contribute to the structure of benzoic acid hydrate, the actual molecule is probably far more complex.[16] An attempt to duplicate a solvate of type V by use of a mixture of *t*-butyl alcohol and dioxane failed to give an increased solvent effect (Fig. 5).

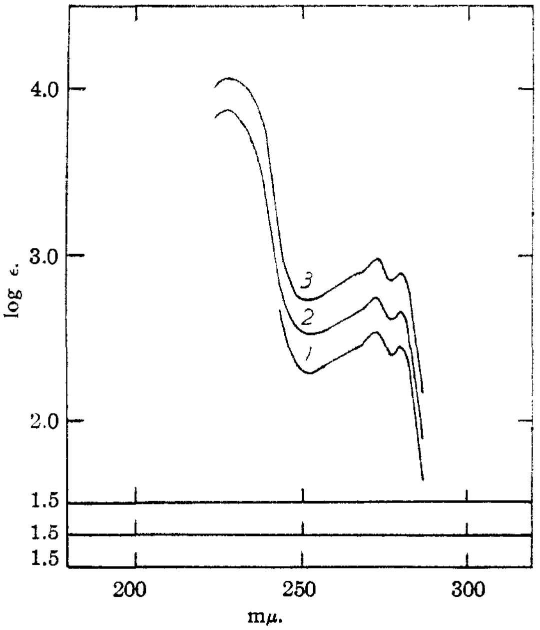


Fig. 5.—Benzoic acid in: 1, *t*-buyl alcohol (1.77 × 10^{-4} mole/l.); 2, 1:1 (by wt.) *t*-butyl alcohol and dioxane (6.82 × 10^{-5} mole/l.); 3, dioxane (6.58 × 10^{-5} mole/l.).

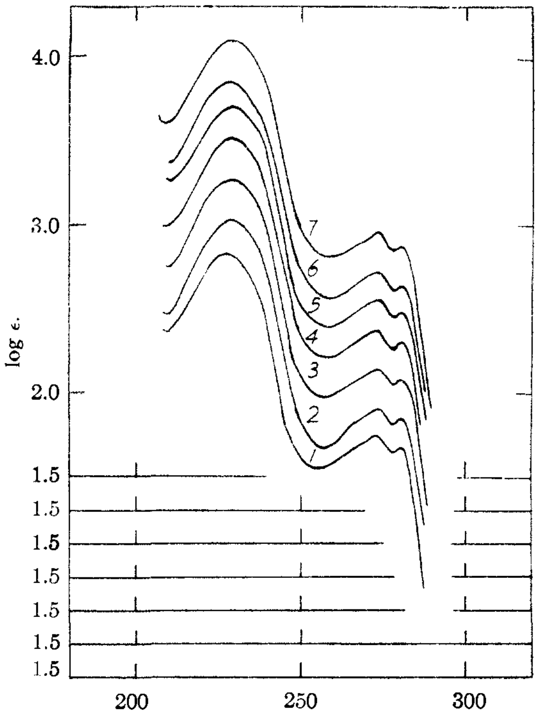


Fig. 6.—Benzoates C_6H_5COOR in 95% ethanol: R = 1, H; 2, Me; 3, Et; 4, *i*-Pr; 5, *i*-Am; 6, *n*-hexyl; 7, decyl; concentrations, 3–10 × 10^{-5} mole/l.

Alkyl benzoate (R = Me to *n*-decyl) curves (Fig. 6) are nearly identical in the same alcohol and similar to the absorption curve for benzoic acid in the same solvent (Table III). The absorbing system is therefore very similar in the acid and in the ester and is unaffected by the size of the alkyl group. Spectral anomalies in lauryl benzoate, which have been attributed to a steric effect of the alkyl group,[3b] probably are due to other causes.

TABLE III

ABSORPTION SPECTRA OF ALKYL BENZOATES C_6H_5COOR[a]

R	Concn. moles/l. × 10^1	B-band λmax, mμ	log ε	λmax, mμ	log ε	C-band[b] λmax, mμ	log ε
H	0.0716	228	4.04	272	2.95	280	2.84
Me	.0480	228	4.04	273	2.92	280	2.84
Et	.0875	228	4.08	273	2.94	280	2.86
i-Pr	.112	228	4.01	273	2.89	280	2.80
i-Am	.0365	228	4.09	273	2.96	280	2.88
n-Hexyl	.044	228	4.05	273	2.94	280	2.85
n-Decyl	.056	228	4.10	273	2.96	280	2.87

[a] Solvent, 95% ethanol. [b] The results in the C-band were obtained with a concentration five times greater than that given for the B-band.

A hydrogen bond of type III is postulated in aqueous solutions of acids.[16] It cannot exist in esters. Since benzoic acid and its esters have identical alcoholate and hydrate curves, hydrogen bonds of this type have evidently little effect on the absorption curve of the acid.

Water.—It has been assumed that benzoic acid will be un-ionized in 0.1 N sulfuric acid.[6a] The curve is identical with the absorption curve obtained in 0.01 N hydrochloric acid at a concentration of 7 × 10^{-5} mole per liter. Since it also agrees with the hydrate curves observed in aqueous alcohols, one may conclude that it represents hydrated un-ionized benzoic acid. The absorption curve for benzoate ion has been determined in 0.01 N sodium hydroxide,[4b] 0.1 N sodium hydroxide[6a] and 0.1 N sodium ethoxide.[6b] All benzoate ion curves agree perfectly with each other and with the present data although previous workers have paid less attention to fine structure. It appears that the benzoate ion is far less affected by solvents than the acid. Hydrolysis is negligible in these solutions and the light absorption is not concentration dependent.

In water solution benzoic acid is partially ionized and the concentration of benzoate ion increases with dilution. It is actually observed that both B and C maxima in the aqueous solutions vary with concentration within the limits described by the curves for un-ionized acid and benzoate ion (Fig. 7). If it may be assumed that the spectral variations are roughly linear with respect to ionization, it becomes possible to calculate % ionization in a given solution. Such calculations show reasonable agreement with % ionization obtained from the established value for K_a 25°, 6.86 × 10^{-5} (Table IV).

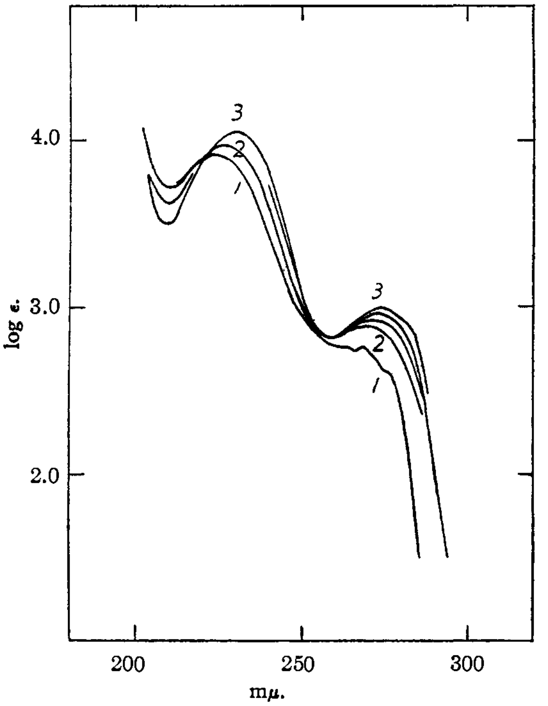


Fig. 7.—Benzoic acid in: 1, 0.01 N sodium hydroxide (6.55 × 10^{-5} mole/l.); 2, water, lower curve, 7.15 × 10^{-5} mole/l., middle curve 3.50 × 10^{-4} mole/l., upper curve, 1.75 × 10^{-3} mole/l.; 3, 0.01 N hydrochloric acid (7.8 × 10^{-5} mole/l.).

TABLE IV

% IONIZATION IN AQUEOUS BENZOIC ACID

Concn., mole/l.	B-band, %	C-band,[d,f] %	Calcd.,[e] %
1.748 × 10^{-3}	...[a]	15.86	17.90
3.498 × 10^{-4}	29.42[b]	29.92	35.53
7.154 × 10^{-5}	57.32[c]	51.73	61.24

[a] Too concentrated to measure. [b] Determined at 240 mμ, [c] Average of seven values between 228 and 240 mμ. [d] Average of six values between 274 and 284 mμ. [e] $[A^-] = -\frac{K_a}{2} + \sqrt{\frac{K_a^2}{4} + K_a c}$. [f] The accuracy of the method suffers in the C-band because the benzoate ion curve possesses considerable fine structure. This is not true for the B-band and the values are therefore more reliable.

Solvent Mixtures.—According to Mellon[18] mixtures of polar and non-polar solvents will give the same absorption curve as the polar solvent, even where only as little as a few % of the polar solvent are present.

Mixtures of two polar solvents such as alcohol and water permit a study of competitive hydrogen bonding. Pure ethanol gives a curve for benzoic acid with fine structure in the C-band which is independent of the acid concentration. On dilution with water the fine structure disappears and solutions with more than 50 wt. % of water give essentially the hydrate curve (Fig. 8). Dependence upon the acid concentration is observed only below 25 wt. % of alcohol and is attributed to ionization. Solutions of benzoic acid in 25% alcohol show virtu-

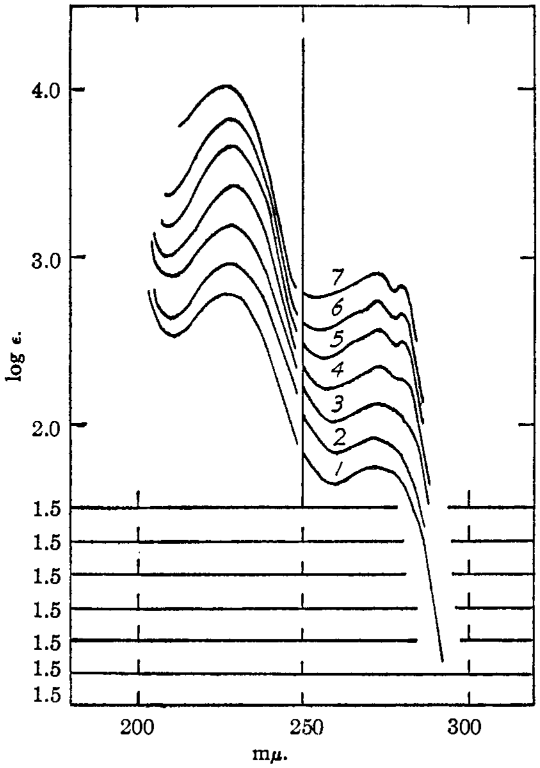


Fig. 8.—Benzoic acid in water–ethanol mixtures, ethanol content: 1, 0%; 2, 10%; 3, 25%; 4, 50%; 5, 80%; 6, 95%; 7, 100%; B-maxima at 6–9 × 10^{-5} mole/l.; C-maxima at 3–4 × 10^{-4} mole/l.

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[18] M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 316.

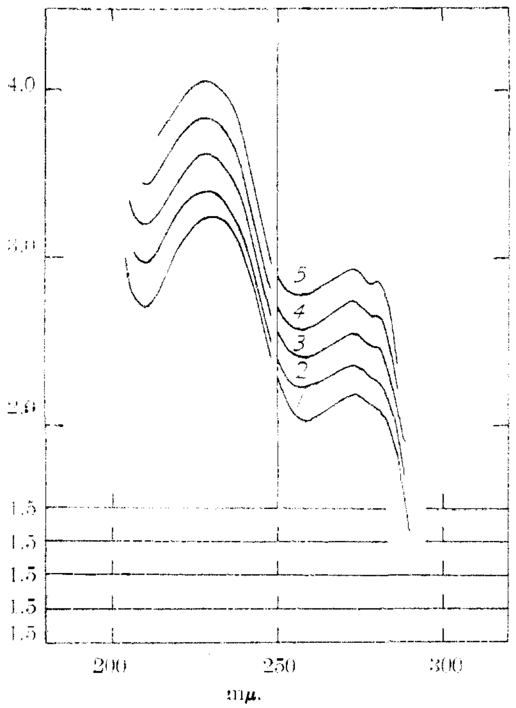

Fig. 9.—1, Benzoic acid in 0.01 *N* hydrochloric acid. Benzoic acid in 50 wt. % aqueous alcohols: 2, MeOH; 3, EtOH; 4, *i*-PrOH; 5, *t*-BuOH. B-maxima at 6–8 $\times$ 10^{-5} mole/l., C-maxima at 1–2 $\times$ 10^{-3} mole/l.

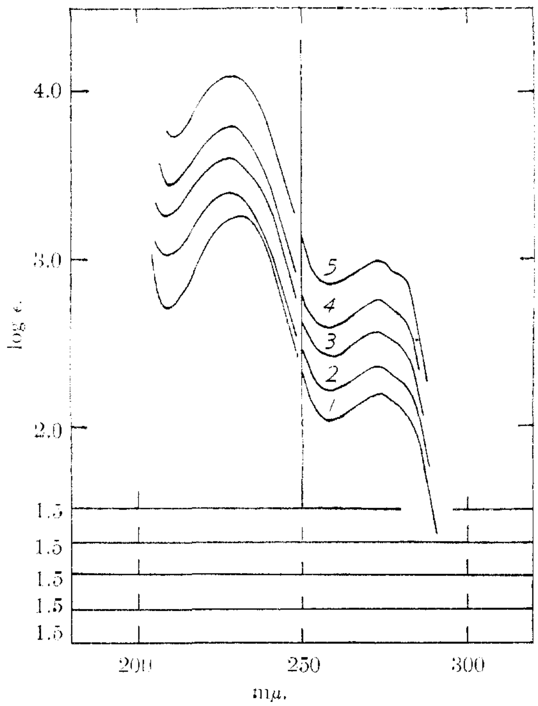

Fig. 10.—1, Benzoic acid in 0.01 *N* hydrochloric acid. Benzoic acid in 25% (by weight) of aqueous alcohols: 2, MeOH; 3, EtOH; 4, *i*-PrOH; 5, *t*-BuOH; B-maxima at 6–8 $\times$ 10^{-5} mole/l.; C-maxima at 1–4 $\times$ 10^{-3} mole/l.

ally no concentration effect and the maxima agree with those of undissociated benzoic acid hydrate in wave length and extinction values. The degree of ionization is therefore too small to be detected by this method.

In 10% aqueous ethanol the C-band maximum is shifted toward shorter wave lengths and the extinction is decreased similarly as in aqueous solution. It may be concluded that the amount of ionization approaches that in aqueous solutions of equivalent concentration. A comparison of the absorption spectra in 50% (Fig. 9) and 25% (by weight) aqueous alcohols (Fig. 10) shows more retention of fine structure in *t*-butyl alcohol than in the other alcohols. While it is true that benzoic acid shows more fine structure in pure *t*-butyl alcohol than in pure methanol (Fig. 4), the difference is small and will be counterbalanced by the smaller mole fraction involved. Thus, 50 wt. % solutions of aqueous alcohols contain 19.55 mole % of *t*-butyl alcohol but 35.98 mole % of methanol. The persistence of fine structure is attributed to retention of alcohol solvate in competition with water and therefore stronger bonding between alcohol and acid. If such conclusions are justified, the relative tendency for ROH to form solvates with benzoic acid is: R = *t*-Bu > *i*-Pr > Et > Me > H.

It is assumed in the present work that fine structure effects attributed to solvation would be absent in molecules which are not normally considered to be solvated. Yet similar effects have been observed in polar solutions of aromatic hydrocarbons.[19] Effects of this sort can hardly be explained of the basis of the dielectric constant of the solvent. In the case of solutions of alcohols in aromatic hydrocarbons, it has been established that the shift of the second overtone of the O–H band is larger than can be accounted for on the basis of the Kirkwood relation.[15] As an explanation, Jones and Badger propose a weak hydrogen bond between the alcohol and the aromatic hydrocarbon (*e.g.*, benzene).

Since the nucleus in benzoic acid will be a better electron acceptor and the carboxyl group a better electron donor than benzene, it is reasonable to conclude that consequently stronger bonds can be formed with solvents which can accept or donate electrons. Such bonding will be accompanied by a shift of the π-electrons in the conjugated system which in turn affects the light absorption. Since shifts in the position of the maxima (upon solvation) affect B and C maxima about equally, both of these maxima may be considered as being due to the whole resonating molecule.[2]

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[19] N. D. Coggeshall and E. M. Lang, THIS JOURNAL, **70**, 3290 (1949).