

so long as $K \geq 5 \times 10^{-3}$. It may be remarked parenthetically that this conclusion requires that the curves shown in Fig. 1 must approach the axis of ordinates with infinite slope, for as c approaches zero

$$\frac{d\Lambda_0'}{dc} = \frac{\Lambda_0' - \Lambda_0}{c} = \frac{A \log c - B}{1 - \alpha\sqrt{c}} = -\infty \quad (5)$$

The values of $\Lambda_{0(\text{av.})}$ determined by equation (3) are in excellent agreement with those originally derived from the same data by other methods. The latter are recorded as Λ_0 in the next to the last column of Table I. Λ_0 for potassium chloride¹⁴ and barium chloride¹⁵ were determined analytically by the use of an equation which is more complicated than equation (3), but reduces to it in the limit. Λ_0 for lanthanum chloride⁴ was estimated from a plot of Λ_0' against c . Recent independent measurements of Shedlovsky are reported²⁰ to lead to a slightly higher value, $\Lambda_0 = 145.9$. Λ_0 and K for potassium ferrocyanide are taken from the calculations of Davies²¹ based on the data of Jones and Jelen¹⁷ alone. Because of the use of the Debye-Hückel limiting law in the estimation of the activity coefficients used in Davies' calculations, the discordance of one unit in Λ_0 does not seem excessive. The values of K and Λ_0 for hydrochloric acid in 70% dioxane¹⁹ and zinc sulfate in water⁸ were determined by the methods of Fuoss⁶ and Shedlovsky,⁷ respectively.

Although the suitability of equation (3) as a practical extrapolation function for all valence types seems demonstrated by Fig. 3 and Table I,

(20) Longworth and MacInnes, *THIS JOURNAL*, **60**, 3070 (1938).

(21) Davies, *ibid.*, **59**, 1760 (1937).

its limitations should not be overlooked. In the first place its use is confined to concentrations below 0.01 normal for the strongest electrolytes, and for electrolytes whose apparent ionization constants are as low as 5×10^{-3} it is unreliable above 0.005 normal. In the second place the relatively large values of A observed for the last three electrolytes in the table, and the fact that the effect of the $A \log c$ term, as here employed, is to duplicate that of the introduction of K in better known methods, lead one to suspect that the numerical values of A and B "observed" for these electrolytes are without definite physical significance. This situation would be greatly clarified by a theoretical computation of the constant A , for if this is known it would be a simple matter to use equation (3) and the concept of ion association, a combination that should yield precise values of both Λ_0 and K , and give the numerical value of the latter quantity more definite physical significance than it now enjoys.

Summary

The equation of Onsager and Fuoss is shown to be in formal agreement with the conductivity data for 1-1, 2-1, 3-1, 4-1, and 2-2 valence type strong electrolytes over a limited range in concentrations. It is pointed out that this equation therefore offers a practical means of extrapolating the data for higher valence type strong electrolytes for which accurate activity coefficient data are not available. A simple graphical technique is outlined in some detail.

NEW HAVEN, CONN.

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Infrared Bands and Association of Some Hydroxylic Compounds

BY H. W. THOMPSON¹

The phenomenon of association and the existence of "hydrogen bonds" has been studied in many recent measurements of infrared spectra. The present paper summarizes data relating to a series of molecules which, although in physical properties such as solubility and volatility are not entirely suited to this type of investigation, nevertheless appeared worth examination. These substances were β -hydroxypropionitrile (ethylene cyanhydrin), γ -hydroxybutyronitrile, β -mercap-

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toethanol (β -hydroxyethyl mercaptan), ethanolamine (β -hydroxyethylamine), and acetone cyanhydrin, and the investigation centered primarily on a study of the position and nature of the O-H absorption in the region of the third harmonic 8000-10,000 Å. Work with other similar substances suggested that several phenomena might be noticed. Thus the presence of the O-H group might in itself lead to association such as is found in the alcohols²; second, some of the molecules might be

(2) Badger and Bauer, *J. Chem. Phys.*, **5**, 859 (1937); Fox and Martin, *Proc. Roy. Soc. (London)*, **163**, 419 (1937).

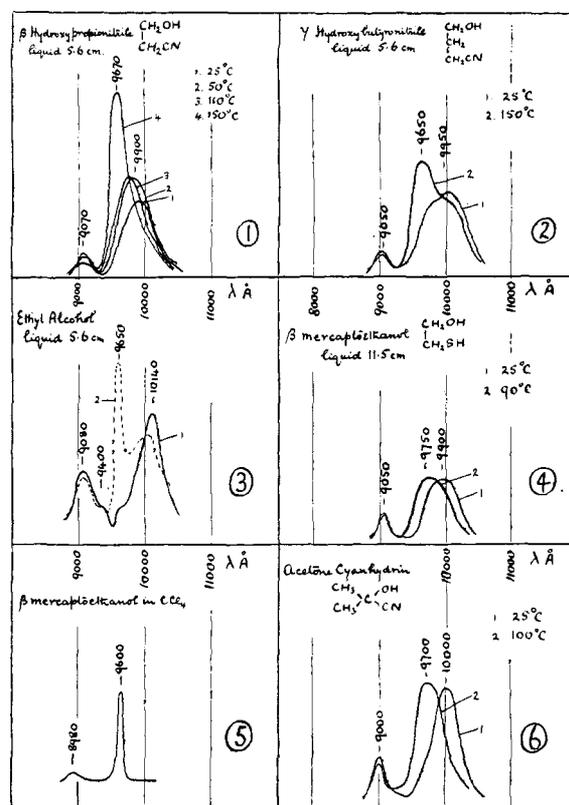
expected to reveal a hydrogen bond formation in which nitrogen is involved,³ third, the occurrence of displaced components of the O-H bands might arise in some of the cases, such as has been detected in the spectra of the halogen substituted alcohol vapors.⁴ Moreover, the exact conditions essential for, and favorable to, the formation of hydrogen bonds are by no means yet established, so that a study of as many more simple molecules as possible is desirable.

The acetone cyanhydrin was a specimen kindly supplied by Dr. J. Koepfli. All the other substances were Eastman Kodak Co. products of the highest purity obtainable. In investigating absorption of the liquids two cells were used, 5.6 and 11.5 cm. in length, respectively, each about 10 mm. in diameter. These were wired and could be heated electrically to any desired temperature; the latter could only be measured within about 10°, but since only qualitative results have so far been attempted, this was not a serious difficulty. In investigating the vapors a Pyrex tube 20 feet (6 meters) in length was used which could be raised to the desired temperature. The liquid under examination was contained in a side arm fitted with auxiliary heater. A tungsten filament lamp was the continuous source and the spectrograph used was a glass Littrow instrument giving 70 Å. per mm. at 9000 Å. Arc lines of the alkalis and alkaline earths were used as wave length standards. All the wave lengths given below are approximate since for the most part diffuse bands are involved. Eastman 1 Z plates were used, hypersensitized in dilute ammonia before use.

Results and Discussion

(1) **β -Hydroxypropionitrile.**—This substance is too insoluble in carbon tetrachloride or carbon disulfide to make a study of the absorption by solutions possible, since the path lengths of solution required would be very large. Figure 1 depicts the absorption by 5.6 cm. of the liquid at a series of temperatures. In this and subsequent diagrams an attempt has been made to correct for the change in plate sensitivity with wave length. It is seen that at room temperatures there is a narrow band at 9070 Å. and a much broader and more intense one with maximum at 9900 Å. With increasing temperature the broad band is gradually displaced toward shorter wave lengths

so that at about 150° there is a marked peak at 9670 Å. The feebler absorption makes it difficult to say exactly how the 9070 Å. band is affected by temperature, but there may be a very slight displacement to longer wave lengths as the temperature increases, with a concurrent slight diminution of intensity. Measurements on the vapor of this substance were unsuccessful since at the highest temperatures which could be conveniently used without decomposition the vapor pressure was too low to give sufficient absorption.



Figs. 1-6.

(2) **γ -Hydroxybutyronitrile.**—The results here are similar to those with the previous compound. Figure 2 shows the data for 5.6 cm. of the liquid at two temperatures. The broad band at 9950 Å. at room temperature lies at rather longer wave length than the corresponding band of β -hydroxypropionitrile, and has an inflection at one side which suggests that it is really composite. At higher temperatures this broad band moves to shorter wave length and shows a peak at 9650 Å. There is again a much weaker band at 9050 Å. which is not much affected by temperature.

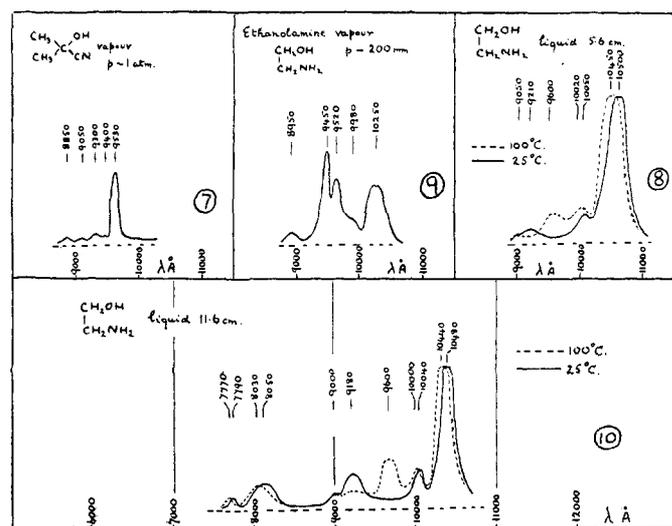
(3) Hendricks, Wulf, Hilbert and Liddel, *THIS JOURNAL*, **58**, 1991 (1936).

(4) Zunwalt and Badger, *J. Chem. Phys.*, **7**, 87 (1939).

(3) **β -Mercaptoethanol.**—Figure 4 shows the absorption curve for 11.5 cm. of the liquid. As with the above substances there is a weak band at 9050 Å. and a broader and more intense one at longer wave length. The position of the latter shifts to shorter wave lengths with increasing temperature. With this substance the shift and development of the peak at shorter wave length is less marked than with the previous two substances.

The solubility of β -mercaptoethanol in carbon tetrachloride was just sufficient to make measurements possible. Figure 5 shows the absorption of 32 cm. of a saturated solution (about 10% by volume). It is seen that a relatively sharp and intense band appears at 9600 Å. and a weaker one at 8980 Å.

Measurements with the vapor were again unsatisfactory for the reasons given above.



Figs. 7-10.

It is convenient to discuss the above substances together since the relationships with all of them seem to be similar. For the purpose of comparison Fig. 3 shows the absorption curve for 5.6 cm. of liquid ethyl alcohol; the dotted curve relates to a dilute solution of ethyl alcohol in carbon tetrachloride as found by Badger and Bauer.⁵ The relationships with alcohol itself are seen to be paralleled by the above derivatives. The broad band at longer wave lengths can be attributed to a modified O-H band consequent upon molecular association, extra-molecular in type. Increase of temperature or solution in carbon

(5) Badger and Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

tetrachloride leads to a dissociation of the polymer and the normal O-H band at 9650 Å. increases in intensity. In this connection it may be worth mentioning that both β -hydroxypropionitrile and γ -hydroxybutyronitrile are highly viscous at room temperatures and lose their viscosity as the temperature is raised. The bands at *c.* 9050 Å. are presumably predominantly due to the $4\nu_{\text{CH}}$ vibrations, although the small alterations with temperature suggest the presence in this region of some other superposed band connected with the association phenomenon.

With the cyano compounds there is the possibility of a cyclic hydrogen bond formation of the type $\begin{matrix} \text{CH}_2\text{O}-\text{H} \\ | \\ \text{CH}_2\text{CN} \end{matrix}$, which might be more pronounced with ethylene cyanhydrin where the ring would be smaller. The data do not preclude such a possibility, but their close similarity with those of alcohol may suggest that it occurs less readily than an extra-molecular association.

(4) **Acetone Cyanhydrin.**—The absorption of 5.6 cm. of liquid is shown in Fig. 6. Here again there is a band at 9000 Å. and a broader and more intense one at longer wave length. The latter band is displaced toward shorter wave lengths with increasing temperature. The interpretation of this appears to be the same as that given above, namely, that the broad band is an association band, gradually giving way, as the associate is decomposed, to the normal O-H band at 9600 Å.

The results for absorption by the vapor are shown in Fig. 7. Complications arose here due to decomposition and formation of hydrogen cyanide and acetone vapors, both of which absorb in this region. The main

feature is a narrow band at 9530 Å. At lower wave lengths occur weaker bands, the precise significance of which is uncertain. The band at 9530 Å. corresponds to the band of isopropyl alcohol vapor at 9560 Å.⁶

(5) **Ethanolamine.**—A new feature is noticed with this substance. The absorption by 5.6 cm. of liquid is shown in Fig. 8. At 25° there are feeble bands at 9000 Å. and 9180 Å., a stronger one at 10,040 Å., and a very intense one at 10,480 Å. The very intense band is broad and there is a slight suggestion of doublet structure at the center. At 100° the feebler bands at 9000 and

(6) Badger and Bauer, *ibid.*, **4**, 711 (1936).

9180 Å. remain, the latter with lower intensity, but the other two bands are each displaced to higher frequencies by about 50 cm.^{-1} . More noticeable, however, at the higher temperatures is the appearance of a new band at 9600 Å. A consideration of these facts made it desirable to measure the absorption of a longer path of the liquid, so as to bring out the feebler bands more strongly. Figure 10 shows the absorption by 11.6 cm. of liquid at 25 and 100°. The previous results are reproduced, but in addition at the lower temperature two bands appear at 7790 and 8050 Å., and these are each displaced slightly to lower wave length as the temperature increases, like the bands at 10,040 and 10,480 Å. The most striking feature, however, is the broad nature of the band at 9180 Å., which tends to mask the band at 9000 Å., and the fact that the broad band diminishes in breadth and intensity at the higher temperature when the new band at 9600 Å. appears.

It was also possible to measure the absorption by the vapor of ethanolamine and the results are shown in Fig. 9. The bands at 9980 and 10,250 Å. almost certainly correspond to the liquid bands at 10,040 and 10,480 Å., and that at 8950 Å. to the liquid band at 9000 Å. A new double band appears in the vapor at 9450–9520 Å. This band is overlapped by water vapor absorption so that the relative intensities of the doublet components could not be determined with great accuracy.

The data with ethanolamine need closer study than those given for the previous substances. The results with the vapor agree with what might be expected. There is little doubt that the bands at 10,250, 9980 Å. are the two NH_2 group third harmonic oscillations such as have been found in the amines or amides⁷; and, further, the band at 8950 Å. will be the $4\nu_{\text{CH}}$ band. The doublet band at *c.* 9500 Å. corresponds to the $3\nu_{\text{OH}}$ band of ethyl alcohol. We may therefore regard the molecules of the vapor as "normal."

The liquid bands are less easily interpreted. In the absorption at room temperatures the bands at 10,040 and 10,480 Å. are similarly the two vibrations of the NH_2 group (probably $3\nu_a$ and $(\nu_a + 2\nu_s)$ or $3\nu_s$) and that of 9000 Å. corresponds to $4\nu_{\text{CH}}$. The bands at 7790, 8050 Å. are the next higher harmonics of the bands at 10,040 and 10,420 Å. (*i. e.*, probably $4\nu_a$ and $\nu_a + 3\nu_s$ or

$4\nu_s$). The broad band at 9180 Å. cannot be clearly assigned. As the temperature increases the NH_2 group frequencies are affected, and increase somewhat, indicating a slight strengthening of the N-H bonds; at the same time the band at 9600 Å. appears suggesting absorption of $3\nu_{\text{OH}}$ of a normal O-H linkage, this moreover concurrently with a diminution of intensity in the broad band at 9180 Å. The appearance at higher temperatures of the normal O-H band suggests that deassociation has occurred. On the other hand, there is no indication of a broad association band at longer wave lengths such as usually found. The integral intensity of the band at 9180 Å. lost at the higher temperature seems to be roughly balanced by the gain in intensity of the 9600 Å. band, but the broad band is at higher frequencies than the "normal" and would not therefore be interpreted as a conventional perturbed O-H band. Such a broad band on the high frequency side of the "normal" O-H 9600 Å. band has been noticed, though perhaps to a less extent, in other cases. It appears to be prominent in the alcohols, even in solution, leading to abnormalities in the apparent position of the C-H fourth harmonic band and no very satisfactory explanation has been given for it. On the other hand, in the case of the alcohols there is the broad association band at longer wave lengths, and this is not apparent in the case of ethanolamine. It is possible that the intense absorption due to the NH_2 group in the region 1000–10,500 Å. overlies and masks such a band, but a careful study of the plates reveals no sign of it, and if this were the case, the shift from 9600 Å. would be much greater than usual. Another possibility, though a very improbable one, is that the broad band at 9180 Å. is really the 8050 Å. band of the NH_2 group perturbed by the association and appearing at lower frequencies. In this case the frequency shift would have to be about 1500 cm.^{-1} , which is hardly plausible. At present, therefore, no satisfactory complete interpretation of the data can be given, although it is clear that the nitrogen atom gives rise in some way to peculiarities and that hydrogen bridge formation of some kind exists in the liquid at room temperatures. This may well be of the type $-\text{O}-\text{H} \cdots \text{N}-$. The slight shift in the NH_2 bands with increasing temperature is significant in this connection.

It seems probable that experimental conditions

(7) Buswell, Rodebush and Roy, *THIS JOURNAL*, **60**, 2444 (1938).

will on the whole be more favorable for these studies in the region of the lower harmonics and it is hoped shortly to carry out such measurements.

The above was part of a program of work carried out during the tenure of a Leverhulme Research Fellowship, for which I am grateful to the Leverhulme Trustees. I should also like to thank Professor L. Pauling for many kindnesses, and Professor R. M. Badger for allowing me the facilities of his laboratory and for many helpful discussions.

Summary

The absorption bands in the region 8000–11,000 Å. of a series of simple hydroxylic compounds have been measured. The nature of the bands in some cases and the effect of temperature upon them reveals the existence of molecular association in the liquid state. In some cases, such as that of ethanolamine, unusual effects are noticed which cannot be satisfactorily explained.

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The Thermal Decomposition of Petroleum Hydrocarbons into Free Radicals¹

BY B. L. EVERING

The free radical chain mechanism proposed by Rice² has been successful in explaining the products obtained in the thermal decomposition of hydrocarbons despite the fact that little is known regarding the concentration of these chain carriers during the reaction. Rice and co-workers² have observed that the Paneth effect of mirror removal by free radicals from hydrocarbons is readily exhibited at 1–2 mm. but not at 20–40 mm. pressure. Patat³ has measured the free radical concentration at higher pressures by the para hydrogen method. He arrived at extremely low values for the free radical concentration.

In the present work the free radical concentrations from petroleum hydrocarbon cuts were investigated in the pressure range where the Paneth effect of mirror removal is exhibited. The radical concentration was followed by combination with a surface of lead freshly formed by condensation of the vapor, and analysis of the product for lead. A rapid decrease of free radical concentration with pressure was found but the complexity of the petroleum hydrocarbon used as a source of free radicals did not permit any exact study of the mechanism. It is hoped that this may stimulate some similar work on the pure hydrocarbons in order to learn more concerning the kinetics of free radical formation and recombination.

Experimental

Materials.—Most of the experiments were carried out using close cuts of petroleum hydrocarbons as a source of

free radicals, while a few were made using butane. The petroleum "octane" had a boiling range 121–130.5°, d^{20}_4 0.7519 and n^{20}_D 1.4173. It had approximately the following composition: paraffins 50%, naphthenes 35%, and aromatics 15%. The petroleum "hexane" used contained 48% C₅ hydrocarbons, 48% C₆ hydrocarbons, the remainder being light and heavy ends. It had the following physical properties: d^{20}_4 0.6653, n^{20}_D 1.3742. The "pentane" used in one experiment was obtained by fractionating petroleum "hexane" in an eight theoretical plate column and taking the cut boiling in the range 34–43°. All of the above cuts were from Mid-Continent crude. The butane and propane were commercial products. They showed no unsaturation and were used without further purification.

The lead used throughout was Baker analyzed, antimony-free. It is important that the lead be antimony-free since free radicals readily react with this metal. This would give low results as the free radical concentration was determined on the basis of the lead alkyls in the product.

Apparatus.—The apparatus shown in Fig. 1 was essentially the same as described by Rice, Johnston, and Evering⁴ with the substitution of lead for mercury, and with certain added refinements to enable quantitative measurements to be made. The hydrocarbon used as a source of free radicals was contained in flask A. The vapor pressure of the hydrocarbon, which was controlled by regulating the temperature of the bath surrounding flask A, was determined by the absolute manometer B. The rate of flow of the hydrocarbon vapor was controlled by the needle valve D which consists of a slender, tapered needle fitted into a concentric tube and both carefully ground. The glass needle was sealed to a glass bulb which floated on a pool of mercury maintained at manometric height so that it could be raised or lowered by adjustment of the attached leveling bulb. In this manner the rate of flow was controlled and kept constant once it had been roughly adjusted by stopcock C.

The rate of flow was measured by the flowmeter E which is of the conventional type. Dibutyl phthalate

(1) Presented before the Division of Petroleum Chemistry at the Milwaukee meeting of the American Chemical Society, Sept. 5, 1938.

(2) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, 1935.

(3) F. Patat, *Z. physik. Chem.*, **32B**, 294 (1936).

(4) Rice, Johnston, and Evering, *THIS JOURNAL*, **54**, 3529 (1932).