and we hope to give a complete answer to this particular question in the near future.

The experiments described above were performed during the spring of the academic year 1934–35. We wish to thank Prof. The Svedberg and his associates for their interest and assistance with the work.

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## Some Infra-Red Bands in the 3μ Region

IN view of recent communications[1,2,3] on the infra-red band arising from the O—H vibration in certain compounds, it is of interest to direct attention to certain analytical data obtained by us with comparatively high dispersion in the region 3μ, working with solutions about 0·1 mol/lit. in carbon tetrachloride.

In phenol, benzyl alcohol, diphenyl carbinol and triphenyl carbinol, we find that an intense O—H band is obtained in each case, the wave-length being highest for phenol (2·770 μ) and lowest for benzyl alcohol (2·764 μ). The association band[1] is found at 2·87–2·97 μ, the wave-length increasing with the intensity of the band; its shape as shown in Fig. 1 for benzyl alcohol is similar to that for ethyl alcohol in carbon tetrachloride[1]. The intensity of the association band was about the same for phenol and benzyl alcohol, was less for diphenyl carbinol, and with triphenyl carbinol was visible as a small 'hump' on the general absorption at 2·87 μ. These results suggest that the replacement of hydrogen by phenyl groups in benzyl alcohol suppresses intermolecular association.

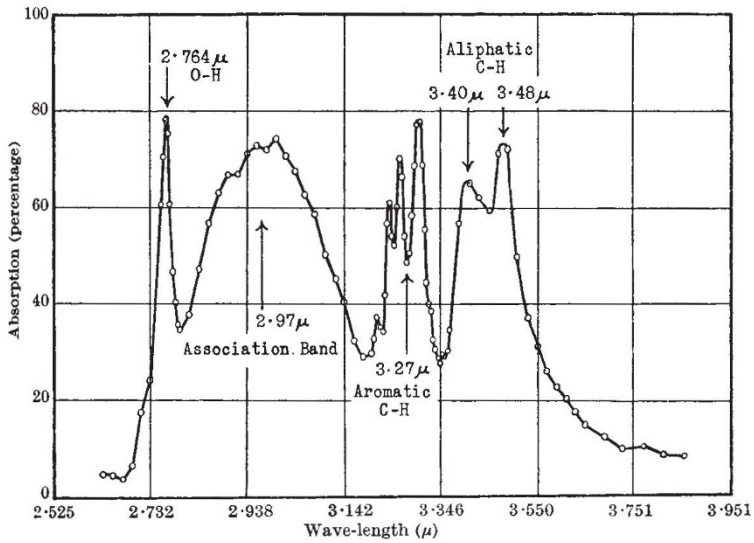


Fig. 1.

ABSORPTION OF A 1·3 MM. LAYER OF BENZYL ALCOHOL IN CARBON TETRACHLORIDE (0·169 MOL/LIT.) AT 18° C.

Dilution was found to reduce the intensity of the association band in the case of phenol much more rapidly than the O—H band (cf. Errera[2]). The former band dropped from 80 per cent absorption in 0·174 mol./lit. (O—H band 94 per cent) to 5½ per cent at 0·0145 mol./lit. (O—H band 58 per cent). The triphenyl carbinol showed 12·5 per cent for the association band at 0·066 mol./lit. as compared with 29 per cent for phenol at the same concentration.

Fig. 1 shows bands due to OH and association, the aromatic C—H bands around 3·27 μ and the aliphatic C—H bands at 3·40 and 3·48 μ.

A full account of the bands of these and other organic compounds will be described elsewhere.

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## A Possible Acid-Dissociation of Metal-Ammonia Ions, and its Bearing on Certain Reactions

RECENT observations[1] on exchange reactions between heavy water and cobaltammines suggest a possible mechanism for certain reactions of the latter.

It would seem that the ammonia molecules in these complexes must, by co-ordination, have lost the ability to form ammonium ions, and therefore if we assume that the exchange reactions take place through the $D^+$ ion, we must conclude that these co-ordinated ammonia groups can dissociate as acids:

$$(Co.6NH_3)^{3+} \rightleftarrows (Co.5NH_3.NH_2)^{2+} + H^+ \quad (1).$$

This seems plausible, since the co-ordination of the analogous water molecule enables it, as is well known, to dissociate as an acid:

$$(Co.5NH_3.H_2O)^{3+} \rightleftarrows (Co.5NH_3.OH)^{2+} + H^+; \quad k = 2 \times 10^{-6} \quad (2).$$

The corresponding dissociation constant for the co-ordinated ammonia molecule would presumably be much smaller, but might still be appreciable.

On this basis it would be possible to account for the rapid replacement of acido-groups by hydroxyl ions:

$$(Co.5NH_3.Br)^{2+} + OH^- \rightarrow (Co.5NH_3.OH)^{2+} + Br^- \quad (3).$$

This reaction is unique, in that such replacements by other anions only take place much more slowly if at all. Alternatively, it may be regarded as catalysis by hydroxyl ion of an aquotization reaction,

$$(Co.5NH_3.Br)^{2+} + H_2O \rightarrow (Co.5NH_3.OH_2)^{3+} + Br^-,$$

followed by instantaneous establishment of the hydroxo-aquo equilibrium.

Now the kinetics of the aquotization of acido-aquo complexes have led to the conclusion[4] that the hydroxo-acido ion undergoes this change much more rapidly than the aquo-acido ion with which it is in equilibrium, presumably in virtue of its smaller positive charge—a conclusion which harmonizes with

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