296. *The Infra-red Spectra of Mixtures of Aldehydes and Alcohols.*

By A. Ashdown and T. A. Kletz.

The infra-red spectra of mixtures of various alcohols and aldehydes have been recorded. Bands were observed which are not due to either component, and it is considered that these are due to the formation of a hemi-acetal.

In 1928 Adkins and Broderick (*J. Amer. Chem. Soc.*, 1928, **50**, 499) measured the refractive indices of mixtures of various aldehydes and alcohols, and obtained results indicative of compound formation; they therefore postulated the formation of an unstable hemi-acetal:

$$\mathrm{R{\cdot}CHO + R'{\cdot}OH \rightleftharpoons R{\cdot}CH(OH){\cdot}OR'}$$

This is supported by some chemical evidence such as the formation of a certain amount of ester when alcohols are oxidised with dichromate (Karrer, " Text Book of Organic Chemistry ", 1938, p. 142):

$$\mathrm{R{\cdot}CH_2{\cdot}OH \xrightarrow{O} R{\cdot}CHO \xrightarrow{R{\cdot}CH_2{\cdot}OH} R{\cdot}CH(OH){\cdot}O{\cdot}CH_2R \xrightarrow{O} R{\cdot}CO{\cdot}O{\cdot}CH_2R}$$

Ratovski and Zabrodine (*J. Appl. Chem. Russia*, 1938, **11**, 302) isolated the compounds formed from certain higher alcohols and aldehydes as unstable crystalline solids. Gauditz (*Z. physikal. Chem.*, 1941, *B*, **48**, 228) examined the ultra-violet absorption spectra of mixtures of propaldehyde with various alcohols and showed that the strength of the band due to the carbonyl group was weaker than the concentration of propaldehyde warranted, thus supporting the theory of hemi-acetal formation. Sutherland and Phillpotts (*Trans. Faraday Soc.*, 1945, **41**, 206), in the course of work on the determination of small amounts of ethyl alcohol in acetaldehyde by infra-red spectroscopy, observed bands which could not be attributed to either component and suggested that these might be due to the formation of a hemi-acetal.

We have recently examined the infra-red spectra of mixtures of various aldehydes and alcohols and obtained results which provide considerable support for the hemi-acetal theory.

The spectrometer used was a Hilger D.209, fitted with a rock-salt prism and used as a single-beam instrument. Two 10 μ-thick absorption cells were placed in series before the slit of the spectrometer; the aldehyde was placed in one and the alcohol in the other so that the spectrum recorded was the sum of the spectra of these two substances. A 1 : 1 mixture of the alcohol and the aldehyde was then placed in the two cells and the spectrum again recorded. Considerable differences were observed between the two spectra, a typical pair obtained for mixtures of *iso*valeraldehyde and *n*-octyl alcohol being shown in the diagram. Altogether eight mixtures were examined involving three aldehydes (*iso*valeraldehyde, *iso*butaldehyde, and *n*-butaldehyde) and six alcohols (*n*-octyl, *sec.*-octyl, *iso*amyl, *iso*butyl, *n*-butyl, and *iso*propyl), and in all cases similar differences were observed though they were less marked in the case of the two secondary alcohols.

The chief differences observed between the two spectra are:

(i) The aldehyde band at about 1730 cm.$^{-1}$ due to the valence vibration of the carbonyl group is decreased in strength on mixing.

(ii) The aldehyde band at about 2720 cm.$^{-1}$ due to the valence vibration of the C–H bond of the –CHO group is decreased in strength on mixing.

(iii) The alcohol band at about 3300 cm.$^{-1}$ due to the valence vibration of the O–H bond is unchanged in strength though it sometimes shows slight changes in shape.

(iv) A new strong band appears at about 1020 cm.$^{-1}$.

(v) A new strong band appears at about 1110 cm.$^{-1}$.

(vi) A new weak band appears at about 1275 cm.$^{-1}$.

(vii) A new weak band appears at about 850 cm.$^{-1}$.

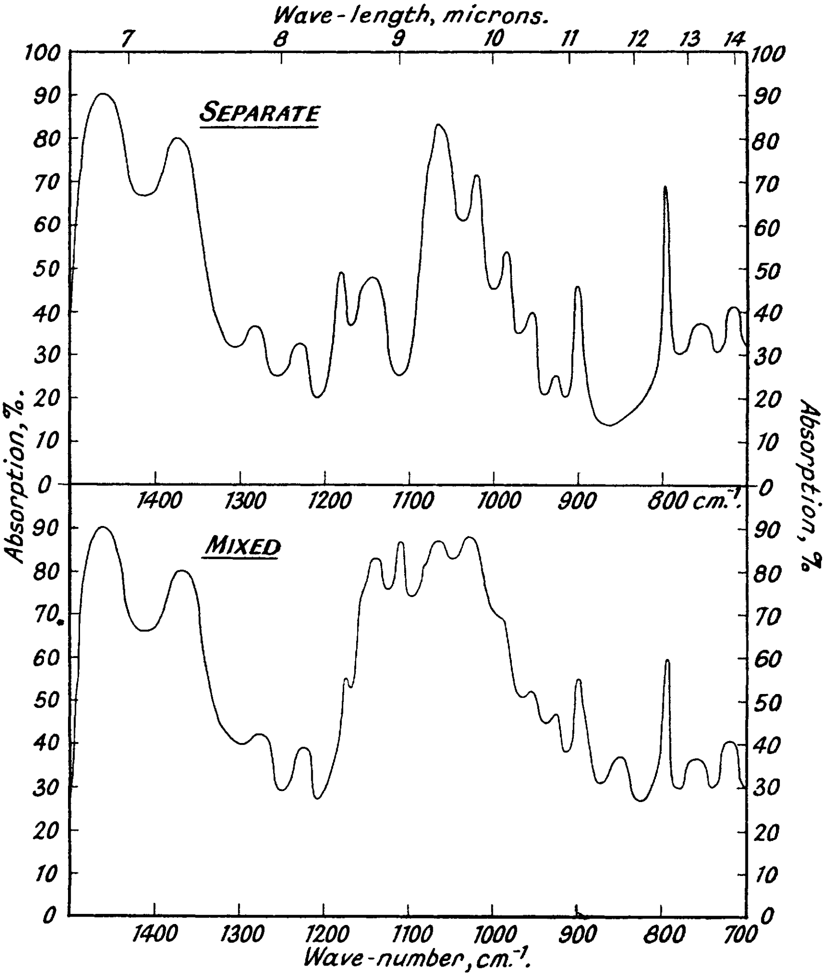
(viii) An aldehyde band near 900 cm.$^{-1}$ is weakened.

The data on which observations (iv)—(viii) are based are summarised in the Table. Owing to the overlapping of the bands their positions cannot be determined very accurately and the frequencies given are consequently only approximate.

In addition to the eight differences tabulated above other differences also occur which are typical of the particular mixture; thus alcohol and aldehyde bands may be weakened and other new bands may appear.

The diagram shows part of the spectra obtained using *iso*valeraldehyde and *n*-octyl alcohol. It is seen that strong new bands appear in the " mixed " spectra at about 1030 and 1110 cm.$^{-1}$ overlapping with existing bands, and that weak new bands appear at about 850 and 1300 cm.$^{-1}$, the latter being unresolved from the adjacent bands. The alcohol band at 790 cm.$^{-1}$ is weakened, and if allowance is made for the overlapping strong absorption centred near 1030 cm.$^{-1}$ it is seen that the 900 cm.$^{-1}$ band is slightly weakened. This band is due to both the alcohol and the aldehyde.

The infra-red spectra of isovaleraldehyde *and* n-*octyl alcohol.*



New Bands in the Infra-red Spectra of Mixtures of Aldehydes and Alcohols.

Constituents.		Weakened aldehyde band.	New bands (cm.$^{-1}$).			
Aldehyde.	Alcohol.					
*iso*Valeraldehyde	*iso*Propyl	900	1010	1035	1140	1250—1300
*iso*Valeraldehyde	*n*-Butyl	900	845	1015	1140	1250—1300
*iso*Valeraldehyde	*iso*Butyl	900	850	1010	1105	1250—1300
*iso*Valeraldehyde	*iso*Amyl	900	850	1010	1075	1250—1300
*iso*Valeraldehyde	*n*-Octyl	900	845	1030	1110	1250—1300
*iso*Valeraldehyde	*sec.*-Octyl	—	—	1075	1110	1250—1300
n-Butaldehyde	*n*-Butyl	780	900	1000, 1060	1105	1250—1300
*iso*Butaldehyde	*iso*Butyl	795 (and 905)	950 (and 930)	1015	1080	—

Observation (i) shows that the concentration of $>C=O$ groups decreases on mixing the aldehyde with the alcohol, while observation (ii) shows that the concentration of ^{-}CHO groups decreases, though it does not indicate unambiguously whether this is due to the removal of the H atom or to change of the double bond to a single bond. Observation (iii) shows that the concentration of hydroxyl groups remains unchanged. Taken together these three facts give considerable support to the theory that hemi-acetals are formed, as this involves change of a carbonyl bond to an ether bond, the number of hydroxyl groups remaining the same :

$$\mathrm{R{\cdot}CHO + R'{\cdot}OH \rightleftharpoons R{\cdot}CH(OH){\cdot}OR'}$$

Although the valence vibration of the hydroxyl group in the hemi-acetal will in general give rise to an absorption band at a slightly different frequency from that in the alcohol, the broad nature of these bands will make their resolution impossible, and a slight change in the shape of the hydroxyl band is the only change that is to be expected.

If it is assumed that hemi-acetal formation takes place then many of the other changes in the spectrum are readily explained. Thus one of the two new strong bands which appear at 1020 and 1110 cm.$^{-1}$ will be due to the ether link (which usually gives rise to a strong band in this region) and the other to the hydroxyl group. Lecomte has shown that hydroxyl groups give rise to a strong band in this region, the frequency depending principally on whether the alcohol is primary, secondary, or tertiary; it is thus to be expected that in the case of this band the hemi-acetal will absorb at a different frequency from the original alcohol.

The appearance of a new band at about 1250—1300 cm.$^{-1}$ was observed in most cases and may be typical of the $\mathrm{{-}CH(OH){\cdot}O{-}}$ group. The *iso*valeraldehyde band at 900 cm.$^{-1}$ may be due to the deformation vibration of the C–H bond of the $\mathrm{{-}CHO}$ group, and this would account for the reduction in its strength indicated in the Table. The new band which appears near 850 cm.$^{-1}$ may be due to the corresponding vibration for this C–H bond in the hemi-acetal. These last two changes were not observed in the case of *iso*valeraldehyde and *sec.*-octyl alcohol, but this may be due to the changes being insufficiently intense to show up; all the observed changes were very much weaker than in the other cases.

Mixtures of di*iso*propyl ketone with *iso*propyl alcohol and *n*-butyl alcohol and of diethyl ketone with *n*-butyl alcohol were also examined in the same way. In all cases only very slight differences between the " separate " and " mixed " spectra were observed, thus indicating that these ketones do not interact with alcohols to any appreciable extent; this is in accordance with expectation since ketones do not form acetals directly.

It is concluded that the infra-red spectra of mixtures of alcohols and aldehydes are consistent with and provide considerable support for the theory of hemi-acetal formation.

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RESEARCH DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES LTD.,
BILLINGHAM DIVISION.

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