1030. *Relation between Molecular Structure and Hydrogen Bonding of Aliphatic Alcohols and Aliphatic Esters as Determined by Infrared Spectroscopy.*

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We have studied nine binary combinations of three alcohols (octan-1-ol, isopentyl alcohol, and t-pentyl alcohol) and three esters (n-hexyl hexanoate, n-butyl acetate, and t-pentyl acetate). Using an IBM 7090 computer and a programme designed to treat the " free " and hydrogen-bonded ester-carbonyl bands as Lorentzian curves, we have calculated relative equilibrium constants for these alcohol–ester systems. We have also set up a rating scale whereby one is able to predict the hydrogen-bonding ability of each alcohol and each ester.

In a system containing both hydroxyl and carbonyl groups, an equilibrium exists between hydrogen-bonded carbonyl groups and unbonded groups: $>C{=}O + H{-}O{-} \overset{K}{\rightleftharpoons} >C{=}O \cdots H \cdots O{-}$. In previous papers, the equilibrium constant, K, was determined by measuring the decrease in " free " ester concentration, [E], as a function of alcohol concentration, [A], at one or more temperatures.[1] This was necessary because the low alcohol concentrations used did not give rise to significant quantities of hydrogen-bonded complex, *i.e.*, a separate carbonyl stretching band due to the complex was not observed. In the present work we determined the concentrations of both the unbonded ester (E) and

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[1] Presented at the Pittsburgh Conferences on Analytical Chemistry and Applied Spectroscopy, 1960 and 1961.

the complex (X) directly. This was done by measuring the intensities of the bonded and unbonded carbonyl bands. We believed that this technique would give more accurate data than the previous method which involved the measurement of small differences between relatively large numbers.

In order to make the infrared absorption band due to the ester-carbonyl of the complex clearly distinguishable, its concentration relative to that of the unbonded ester was increased by using high alcohol concentrations. This led us to the problem of resolution of the two absorption bands, for in order to arrive at accurate values for the concentrations [E] and [X], the true intensities of their absorption bands had to be known. Spectroscopically, we were unable to resolve these bands to such an extent that one did not contribute to the intensity of the other. This being the case, a mathematical approach was made.

Ideally, with infinitely narrow slit-widths, an infrared band will be described by the Lorentz function:

$$A_\nu = A_0/[1 + (2/\Delta\nu)^2 (\nu_0 - \nu)^2], \qquad (1)$$

where A_ν is the absorbance at frequency ν, A_0 is the absorbance maximum at the band maximum whose frequency is ν_0, and $\Delta\nu$ is the line-width at half-height of the band.[2] For the case of two overlapping infrared bands, the following should hold:

$$A_\nu = \frac{A_{01}}{1 + (2/\Delta\nu_1)^2(\nu_{01} - \nu)^2} + \frac{A_{02}}{1 + (2/\Delta\nu_2)^2(\nu_{02} - \nu)^2}. \qquad (2)$$

Here the subscripts 1 and 2 refer to the two overlapping bands. An IBM 7090 programme was written (by C. Hassell of Continental Oil Company) to solve this equation. The input data are absorbance values at several frequencies across the two bands. The output of the programme gives the best values for A_{01}, A_{02}, $\Delta\nu_1$, $\Delta\nu_2$, ν_{01}, and ν_{02}.

Nine binary combinations of three alcohols (octan-1-ol, isopentyl alcohol, and t-pentyl alcohol) and three esters (n-hexyl hexanoate, n-butyl acetate, and t-pentyl acetate) were studied in n-tridecane. Solutions of the esters alone were also examined. The values of the absorption intensities for the unbonded ester and the hydrogen-bonded complex were determined for these systems. For a 1 : 1 complex, $[\mathrm{E}]_\mathrm{T} = A_\mathrm{E}/\varepsilon_\mathrm{E}l - A_\mathrm{X}/\varepsilon_\mathrm{X}l$, where $[\mathrm{E}]_\mathrm{T}$ is the total (stoicheiometric) ester concentration, A_E and A_X are absorbances for the ester and complex, ε_E and ε_X are the corresponding molar extinction coefficients, and l is cell thickness. From this equation and the experimental results it was possible to calculate the extinction coefficients for the bonded and unbonded ester in each of the nine systems studied. From these values the concentrations of the two forms of the ester could be calculated.

In order to calculate the equilibrium constants for complex formation, it was necessary to determine the effective concentration of the alcohol portion for each system. Since it is probable that only the monomeric and possibly terminal hydroxyl groups of open-chain polymeric alcohols enter into ester–alcohol complex formation,[1,3,4] it is the concentration of these hydroxyl groups which must be determined. It did not prove feasible to measure the actual concentrations of free hydroxyl; however, the relative free hydroxyl content of the various alcohol solutions was determined from the relative intensities of the corresponding 3630 cm.$^{-1}$ stretching bands.

For this reaction, we may write $K = [\mathrm{X}]/[\mathrm{A}][\mathrm{E}]$, from which the equilibrium constants for the nine sets of data were calculated. We found that the equilibrium constant, K, could be expressed as a function of the alcohol and ester components, *i.e.*, $K = PQ$, where P is a function of the alcohol and Q is a function of the ester.

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[2] Jones and Sandorfy in "Chemical Applications of Spectroscopy," ed. W. West, Interscience Publ., Inc., New York, 1956.

[3] Smith and Crietz, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 145; Van Thiel, Becker, and Pimentel, *J. Chem. Phys.*, 1957, **27**, 486.

[4] Becker, Liddel, and Shoolery, *J. Mol. Spectroscopy*, 1958, **2**, 1.

EXPERIMENTAL

Materials.—The octan-1-ol, n-hexyl hexanoate, and t-pentyl acetate were synthesised in our laboratories. n-Butyl acetate and t-pentyl alcohol were of Fisher Reagent grade. Isopentyl alcohol used was of Baker's Analysed Reagent grade. "Pure" n-tridecane from Phillips Petroleum Company was used as solvent. All materials had a purity of 98 ± 1%, as determined by gas chromatography.

Technique.—Forty-four solutions of alcohols and esters in n-tridecane were prepared, as listed in Table 1.

TABLE 1.

Solutions prepared.

Ester	Alcohol	[Ester] (M)	[Alcohol] (M)	No. of solns.
n-Hexyl hexanoate	Octan-1-ol	0·01056—0·02548	2·4948—6·2780	6
	Isopentyl	0·01030—0·03143	2·9140—5·4532	5
	t-Pentyl	0·00901—0·02913	2·9421—5·4504	5
n-Butyl acetate	Octan-1-ol	0·01570—0·03860	2·4958—6·3000	6
	Isopentyl	0·01364—0·03743	2·9140—5·4512	5
	t-Pentyl	0·01780—0·03512	2·9421—5·4492	5
t-Pentyl acetate	Octan-1-ol	0·01856—0·02947	2·5305—3·7926	4
	Isopentyl	0·01509—0·02931	2·9140—5·4552	4
	t-Pentyl	0·01911—0·03140	2·9421—5·4484	4

Spectra were determined on a Perkin-Elmer model 221 double-beam infrared spectrophotometer fitted with a prism–grating interchange and a Reeder thermocouple. To maintain constant temperature, an air-bath, capable of holding a desired temperature to ±0·2°, surrounded the sample cell. Spectra were determined at 36·3° ± 0·2°.

The cell used for the carbonyl work had a path-length of 0·499 mm., that for the hydroxyl monomer concentration 0·179 mm.

Carbonyl band spectra were run against a reference solution composed of the same alcohol–tridecane blend as the sample. The spectral range covered was 1800—1700 $cm.^{-1}$. The base-line (I_0 line) was determined by running the reference solution in both beams.

We determined the hydroxyl content of the various solutions from the absorbance of the free hydroxyl stretching band in the 3600 $cm.^{-1}$ region. For this absorbance measurement a base-line was drawn across the shoulders of the band.

Treatment of Results.—For each spectrum, intensity and frequency values for 18—25 points ranging over the two carbonyl bands were given to the IBM 7090 computer for Lorentzian analysis.[4] By using the intensity values from the computer, the extinction coefficients of the ester and the hydrogen-bonded complex were calculated. With these, we calculated the concentrations of these two types of carbonyl groups.

The octan-1-ol solution of lowest concentration (2·50M) was assigned a relative hydroxyl monomer concentration of 1·00. All other hydroxyl values were assigned relative to this.

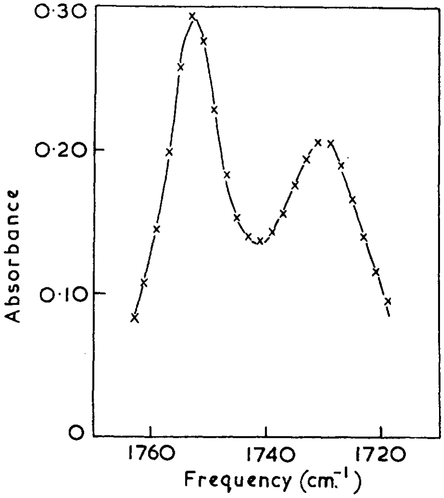
From the ratio of bonded to unbonded ester and the relative concentration of alcohol monomer, the equilibrium constants for each system were calculated. These were again put on a relative scale by assigning the value $K = 1·00$ to the system, hexyl hexanoate + octan-1-ol. In order to fit the data to the equation, $K = PQ$ (see above), octan-1-ol was assigned the value $P = 1·00$ and n-hexyl hexanoate the value $Q = 1·00$. The P and Q values of all other systems were derived relative to these.

RESULTS AND DISCUSSION

Since in this paper we treated the carbonyl bands as overlapping Lorentz curves, we need to examine this point. The Figure shows both a typical experimental curve and the points calculated from the computer output for this spectrum. Good agreement exists between the curve and the calculated points. This indicates that the assumption of Lorentzian band shapes is valid, since the computation is based on this premise.

The extinction coefficients calculated from the intensity results are shown in Table 2. The calculated relative equilibrium constants are in Table 3. The parameters P and Q for the alcohols and esters are shown in Table 4.

Conclusions.—We have shown that the relative equilibrium constants for alcohol–ester hydrogen-bonding may be expressed as a product of two parameters, one sensitive to the nature of the alcohol, the other to that of the ester. It is noteworthy that, within the systems studied, the individual P and Q parameters are independent of the system; for example, the P value for t-pentyl alcohol is 0·705 whether the system contains n-butyl acetate, n-hexyl hexanoate, or t-pentyl acetate. These P and Q values can be used as a



Experimental and calculated carbonyl spectra of carbonyl bands of n-butyl acetate in octan-1-ol–tridecane solution.

TABLE 2.

Extinction coefficients for free and complexed esters.

Ester	Alcohol	Extinction coeff. (l. mole^{-1} mm.$^{-1}$) Free ester	Complexed ester
n-Hexyl hexanoate	Octan-1-ol	68·88 ± 0·36	45·53 ± 0·74
	Isopentyl	68·88 ± 0·36	45·53 ± 0·58
	t-Pentyl	68·88 ± 0·36	49·46 ± 0·28
n-Butyl acetate	Octan-1-ol	65·05 ± 0·46	44·59 ± 1·74
	Isopentyl	65·05 ± 0·46	45·81 ± 1·10
	t-Pentyl	65·05 ± 0·46	48·00 ± 1·14
t-Pentyl acetate..................	Octan-1-ol	76·93 ± 1·42	49·96 ± 0·78
	Isopentyl	76·93 ± 1·42	51·72 ± 1·30
	t-Pentyl	76·93 ± 1·42	58·72 ± 0·60

TABLE 3.

Relative equilibrium constants for various alcohol–ester systems.

Alcohol	Ester	Relative equil. constant	Alcohol	Ester	Relative equil. constant
Octan-1-ol	Hexyl hexanoate	1·000	t-Pentyl	Hexyl hexanoate	0·705
,,	n-Butyl acetate	1·113	,,	n-Butyl acetate	0·817
,,	t-Pentyl acetate	0·968	,,	t-Pentyl acetate	0·615
Isopentyl	Hexyl hexanoate	1·229			
,,	b-Butyl acetate	1·311			
,,	t-Pentyl acetate	1·158			

TABLE 4.

Parameters P and Q.

Alcohol	P	Ester	Q
Octan-1-ol..............................	1·000	n-Hexyl hexanoate	1·000
Isopentyl	1·229	n-Butyl acetate	1·113
t-Pentyl	0·705	t-Pentyl acetate	0·927

quantitative measure of hydrogen-bonding propensity. It may be possible to use P and Q to determine the hydrogen-bonding equilibrium constant for a system not yet measured. For example, using the P value for t-pentyl alcohol and Q for n-butyl acetate, the equilibrium constant calculated is 0·785. The experimental value for K is 0·817, indicating an error of only 3·9%.

Also, Table 4 indicates that the P parameter is more sensitive to the structure of the alcohol than is Q to the structure of the ester. This is not surprising since the carbon chain of the alcohol is closer to the reaction centre than is that of the ester.

We plan to obtain more results on other alcohol–ester systems in order further to test this hypothesis.

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