where x_1 and x_2 are the mole fractions in the liquid phase, and y_1 and y_2 are the mole fractions in the vapor phase, P and P^0 are the vapor pressures (in mm.) over the solution and pure CCl_4, and the subscripts 1 and 2 denote CCl_4 and C_2H_5OH, respectively. The calculations were made by successive approximations, involving the following cycles: beginning with an estimate of f_2 for each of Niini's experimental points, f_1 was obtained for each point by graphical integration via equation 8, assuming $f_1/f_1^0 = x_1$ for the most dilute solution in order to fix the constant of integration. Next y_1 was calculated from equation 6, and finally f_2 from equation 7. The final results are shown in Table IV.

In order to compare these results with ours, the monomer fraction α was obtained from our data, and the Henry's law constant, $f_2/\alpha c$, computed for each of Niini's concentrations. (Here, again, we have made the dilute-solution approximation.) The results are shown in the last column. The variations in $f_2/\alpha c$ are not large and appear to be random. The standard deviation is less than 4% and could be accounted for by an error of only 0.25% in the vapor pressure data.

The assistance of Esther R. Grunwald with the calculations reported in this paper is gratefully acknowledged.

BIRMINGHAM, ALA.
TALLAHASSEE, FLA.

Calculation of Association Constants for Complex Formation from Spectral Data. Infrared Measurements of Hydrogen Bonding between Ethanol and Ethyl Acetate, and Ethanol and Acetic Anhydride

BY ERNEST GRUNWALD AND W. C. COBURN, JR.

A method is reported for the calculation of equilibrium constants for complex formation from quantitative spectral data which is particularly useful when one or both of the ligands are partially self-associated. The method has been applied to infrared data in the OH-stretching region to obtain the following association constants for the formation of 1:1 H-bonded complexes in carbon tetrachloride at 25 ± 2°: ethanol + acetic anhydride, $K = 2.0$; ethanol + ethyl acetate, $K = 1.7$. In these complexes the H-bond is formed to the oxygen atom of the carbonyl group. The unusual stability of hydrogen bonds to carbonyl groups is discussed and empirical equations are given for relating the infrared frequency shift $\Delta\nu$ to the standard free-energy change for complex formation.

Equilibrium Constants for Complex Formation from Quantitative Spectral Data.—In connection with kinetic studies in carbon tetrachloride we have had to measure the association constants for complex formation between ethanol and acetic anhydride, and between ethanol and ethyl acetate. The measurement of these constants was complicated by the self-association of ethanol; a spectroscopic method was devised which made use of absorbancy data in the region of the OH-stretching vibration. This method is of general applicability in the calculation of association constants from spectral data, and is particularly useful when one or both of the ligands are partially self-associated.

Keefer and Andrews[1] have previously described a method for calculating association constants from spectral data for the case where the ligands are not associated themselves. Their method has been widely used because of its simplicity, which is achieved at the expense of somewhat over-weighting the less accurate data at the lower concentra-

(1) R. M. Keefer and L. J. Andrews, THIS JOURNAL, 75, 543 (1953). See also P. A. D. de Maine, J. Chem. Phys., 26, 1036 (1957).

tions. However, when their method is adapted to the case where there are several simultaneous association equilibria, the advantage of simplicity of calculation is lost, yet the disadvantage of over-weighting the data at the lower concentrations remains. Our method has the advantage of weighting the data correctly, and is hardly more laborious.

Description of the Method.—We shall use the laws of the dilute solution; that is, the activity of each species is taken as proportional to the actual molar concentration of the species. To be specific, we shall assume the formation of a 1:1 complex; complex formation of higher order is treated by analogous methods. The ligands are denoted by S and T, and the complex by X. The formal concentrations of the ligands (based on the molecular weights of their monomers) are s and t, and the molar concentration of the complex at equilibrium is x. Since S and T are partially self-associated, their monomer concentrations at equilibrium are written as $\alpha_{s-x}(s-x)$ and $\alpha_{t-x}(t-x)$, respectively. Since we have assumed the laws of the dilute solution, α_{s-x} is the monomer fraction in

a solution containing only S at the formal concentration $(s - x)$, and $\alpha_{t - x}$ is the monomer fraction for T alone at the formal concentration $(t - x)$. These monomer fractions must be measured separately. The association constant is then given by eq. 1.

$$K = \frac{x}{\alpha_{s-x}(s - x)\alpha_{t-x}(t - x)} \quad (1)$$

If the spectral slit width of the measuring instrument is sufficiently small, the absorbancy *per unit cell length* of the complex, A_x, at a given wave number is given in eq. 2 as a function of the absorbancy per unit cell length of the mixture, A_m, of S alone at the formal concentration $(s - x)$, $A_{s - x}$, and of T alone at the formal concentration $(t - x)$, $A_{t - x}$. It is also given by Beer's law in eq. 3, where a_x is the molar absorbancy index (extinction coefficient) of the complex.

$$A_x = A_m - A_{s-x} - A_{t-x} \quad (2)$$

$$A_x = a_x(x) \quad (3)$$

K is obtained by a trial-and-error method as follows. Some reasonable value is assumed for K; using this value, x is computed for each experimental point via eq. 1; on the basis of the computed values of x and experimental data for A_m, $A_{s - x}$ and $A_{t - x}$, A_x is obtained from eq. 2 for each experimental point. The validity of the assumed value for K is then tested by fitting the A_x vs. x data to eq. 3, and computing the standard error of fit. In the common case where the error in A_x is approximately constant, independent of x, then $a_x = \Sigma x A_x / \Sigma x^2$ by the method of least squares.

The calculation is repeated for other values of K, and the standard error of fit of eq. 3 is plotted vs. the assumed value of K. This curve will have a single minimum which indicates the correct value of K. The error of fit at this minimum must be consistent with the known experimental error. If it is significantly greater, the assumed association equilibrium (1:1 complex, 1:2 complex, or whatever) is incorrect.

Application of the Method.—The method has been applied to the association of ethanol with acetic anhydride and of ethanol with ethyl acetate in carbon tetrachloride at 25°. Typical absorbancy data for these systems in the OH-stretching region (3800–3200 kayser) are shown in Fig. 1. There is strong additional absorption around 3550 kayser, which is attributed to complex formation. In processing the data, α-values for the self-association of ethanol were taken from the preceding paper,[2] and the self-association of ethyl acetate and acetic anhydride was neglected. The latter seemed justified because of the "normal" cryoscopic behavior of these and similar solutes in benzene,[3] and because association constants for the formation of dipole–dipole complexes, where measured, have turned out to be one or two orders of magnitude less than those for H-bonded complexes.[4] The complexes were supposed to be of the 1:1 type, as suggested by freezing-point data

(2) W. C. Coburn, Jr., and E. Grunwald, THIS JOURNAL, **80**, 1318 (1958).

(3) G. Scheibe, *Ber.*, **60**, 1406 (1927).

(4) R. L. Denyer, A. Gilchrist, J. A. Pegg, J. Smith, T. E. Tomlinson and L. E. Sutton, *J. Chem. Soc.*, 3889 (1955).
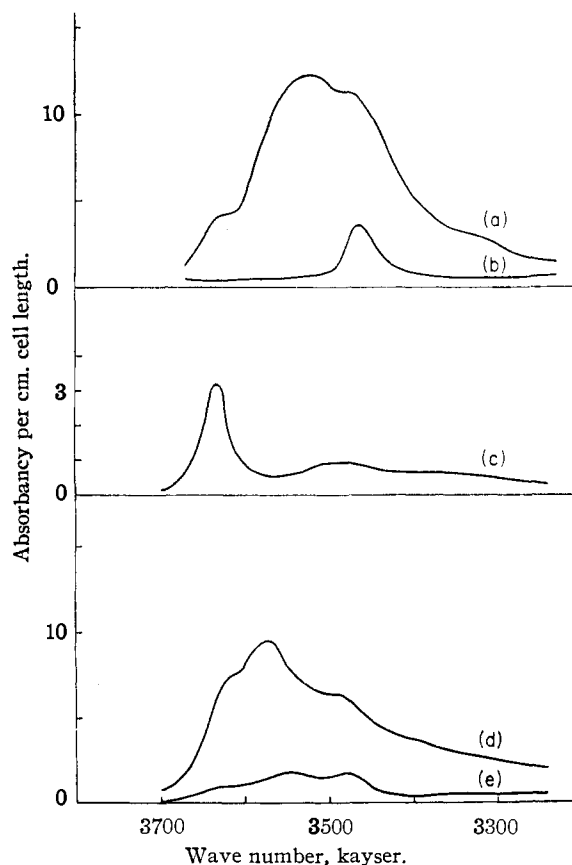

Fig. 1.—Infrared absorption spectra in the OH-stretching region at $25 \pm 2°$ for the following solutions in CCl_4: (a) 1.00 M ethyl acetate plus 0.200 M ethanol; (b) 1.00 M ethyl acetate; (c) 0.0952 M ethanol; (d) 0.791 M acetic anhydride plus 0.204 M ethanol; (e) 0.682 M acetic anhydride.

for the system ethanol–acetic anhydride,[5] and by somewhat less relevant refractive-index data.[6] The concentrations of ethanol were 0.1 or 0.2 M (this placed $(s - x)$ in the range where the α-values were thought to be quite accurate), and those of ethyl acetate and acetic anhydride ranged from 0.05 to 1.0 M. For each assumed value of K, A_x was computed for each solution at 5 separate wave numbers near the maximum, the average value being used in fitting the data to eq. 3. The required values of $A_{s - x}$ and $A_{t - x}$ were obtained by interpolation on large-scale plots of data for the respective single solutes.

The standard errors of fit are shown as a function of the assumed values of K in Fig. 2. The positions of the minima indicate that $K = 1.7$ for the formation of EtOH·AcOEt, and $K = 2.0$ for the formation of EtOH·Ac$_2$O. Actual results for these K-values are shown in Table I.

The error of fit is seen to amount to about 2% of A_m for both sets. This is of the order of the actual experimental error, indicating that the assumption of an 1:1 complex is consistent with the data.

(5) K. Tarama, S. Teranishi and T. Kubota, *J. Chem. Soc. (Japan), Pure Chem. Sect.*, **75**, 192 (1954); *C. A.*, **49**, 8793f (1955).

(6) F. M. Arshid, C. H. Giles, S. K. Jain and A. S. A. Hassan, *J. Chem. Soc.*, 559 (1956).
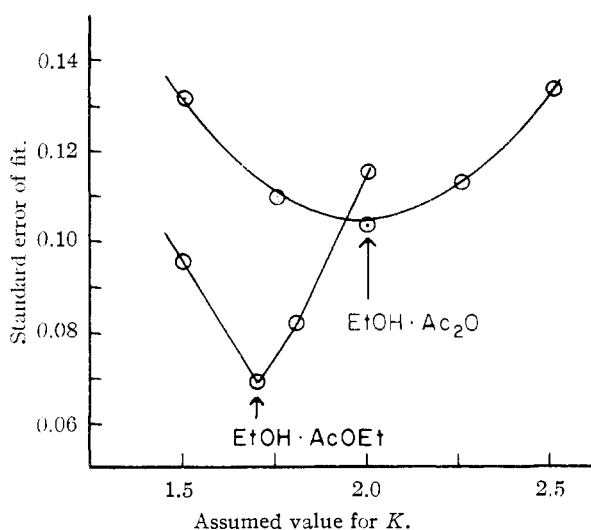
Fig. 2.—Standard error of fit of A_x to eq. 3 for various assumed values of K.

Accuracy of K-Values.—The minima in Fig. 2 are fairly shallow, indicating that K is of only moderate accuracy; an estimate of $\pm 20\%$ for the standard error seems reasonable. In addition to

TABLE I

RESULTS FOR OPTIMUM K-VALUES AT 25°

EtOH (s)	t	x	$A_m{}^a$	A_x	A_z (calcd.)
Ethanol + ethyl acetate; $K = 1.7^b$					
0.200	0.0500	0.0094	2.94	0.95	0.88
.200	.100	.0182	3.70	1.85	1.71
.200	.200	.0347	4.93	3.28	3.26
.200	.500	.0740	8.20	6.91	6.96
.200	1.00	.1140	11.78	10.73	10.72
Ethanol + acetic anhydride; $K = 2.0^c$					
0.204	0.106	0.0220	2.94	1.48	1.44
.204	.264	.0502	4.79	3.29	3.27
.204	.791	.1088	9.00	7.04	7.11
.102	.264	.0302	2.76	1.85	1.97
.102	.791	.0585	5.72	4.00	3.83

^{a} Mean of values obtained at 5 separate wave numbers. ^{b} Measurements made at 3520, 3530, 3540, 3550 and 3560 ks. Cell length 0.0360 cm., $a_x = 94.1$. ^{c} Measurements made at 3550, 3560, 3570, 3580 and 3590 kayser. Cell length 0.0892 cm., $a_x = 65.4$.

this statistical error, there is instrumental error resulting from the finite spectral slit width of the measuring instrument.[7] This error becomes considerable when the slit width is of the order of the half-width of the absorption bands,[7] and neither eq. 2 nor eq. 3 is perfectly accurate. In our measurements, the spectral slit width, about 25 ks., was not insignificant compared to $\nu_{1/2}$ (see Table II). It was not practical to obviate this difficulty by using integrated intensities because of the pronounced overlapping of the absorption bands over much of the region of interest. Our compromise solution was to measure A_m, A_{s-x} and A_{t-x} under identical instrumental conditions at 5 separate wave lengths at 10 ks. intervals near the absorption maximum of the complex, to compute the apparent A_x via eq. 2, and to use the average

(7) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

of the A_x values in the calculation of K. This procedure is tantamount to integration over a spectral range of the order of two slit widths. It is plausible that slit width errors are thus greatly reduced, but it is difficult to demonstrate that they have become less than the statistical error of the measurements.

Discussion

Plots of a_x vs. ν for the ethanol complexes, as deduced from our data, are shown in Fig. 3. In spite of the need to make large corrections for the
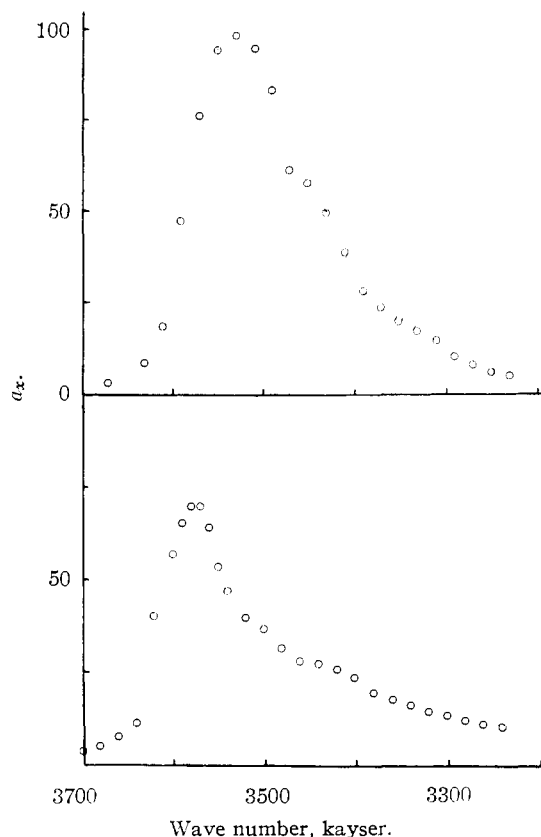

Fig. 3.—Molar absorbancy indexes of ethanol complexes, calculated via eq. 2 and 3. Top, ethanol–ethyl acetate complex, $K = 1.7$; bottom, ethanol–acetic anhydride complex, $K = 2.0$.

absorbancy of the uncomplexed ligands, the points fall on smooth curves, indicating that the K-values are substantially correct. The curves are not quite symmetrical, but at least part of the excess absorption at the lower frequencies may be wing absorption from the strong C–H stretching mode at ~3000 kayser. Table II summarizes the data for the frequencies ν_{max} of the absorption maxima, for the frequency shifts $\Delta\nu$, and for the band widths $\nu_{1/2}$ at one-half of maximum height. In agreement with the correlations of Huggins and Pimentel,[8] $\Delta\nu$ varies approximately linearly with $\nu_{1/2}$, the average slope being 0.91.

The relatively large values of the association

(8) C. M. Huggins and G. C. Pimentel, J. Phys. Chem., **60**, 1615 (1956).

TABLE II
DATA FOR COMPLEX FORMATION IN CARBON TETRACHLORIDE, 25°

Solute	ν_{max}, kayser	$\Delta\nu$, kayser	$\nu_{1/2}$, kayser	K (obsd.)	K^a (cor.)	ΔF^0 (kcal.)	ΔF^0 (calcd.)
EtOH	3631	0	40	...	...	...	...
EtOH·Ac₂O	3575	56	94	2.0	1.0	0.00	−0.08[b]
EtOH·AcOEt	3531	100	153	1.7	1.7	−0.31	−0.30[b]
(ROH)₂[d,11]	...	127	...	0.68	0.34	0.64	0.71[c]
C₆H₅OH·C₆H₅OH[8,12]	...	130	...	0.57[e]	0.28	0.74	0.70[c]
EtOH·EtOH[2]	3840	141	...	0.64	0.32	0.68	0.65[c]
C₆H₅OH·(CH₃)₂CO[13]	...	266	...	8.5	8.5	−1.27	−1.13[b]
EtOH·Et₃N[9]	...	~400	...	2.9	2.9	−0.63	−0.65[c]
(AcOH)₂[8−10]	...	~500	...	~1800	~1800	−2.22[f]	−2.30[b]

[a] K-values for reactions in which complexing can occur at either of two equivalent oxygen atoms have been multiplied by a statistical factor of $1/2$. [b] Equation 4. [c] Equation 5. [d] R = 2,4-dimethyl-3-ethylpentyl. [e] Measured in benzene. [f] Per H-bond in the cyclic dimer.

constants support previous indications[14] that most of the ethanol is complexed to the carbonyl oxygen
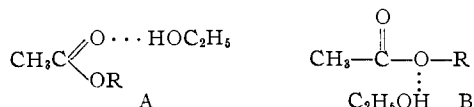
(A) rather than to the ethoxyl or anyhdride oxygen (B). Association constants for the formation of (B) should be smaller than for ethanol dimerization due to the lower basicity of the ethoxyl or anhydride oxygen, and hence should be less than 0.3 (see data in Table II). The putative structure (A) can also accommodate the relatively large value of K for the anhydride since there are two carbonyl groups in the anhydride molecule. After multiplying by the statistical factor $1/2$, the K-values for anhydride and ester lie in the correct sequence as expected from relative base strengths, which is also the sequence of the observed $\Delta\nu$ values.

In addition to the new data, we have collected values of $\Delta\nu$ and K for complex formation in related systems in Table II. In order to make all results comparable, K-values have been corrected by a statistical factor of $1/2$ in those cases where complexing can occur at either of two equivalent oxygen atoms, and values of $\Delta F^0 = -RT \ln K$ have been computed from the corrected data. It is seen that the sequence of the ΔF^0-values does not follow that of $\Delta\nu$. Complexes in which a hydrogen bond is formed to a carbonyl oxygen appear to be more stable than one might have expected from the $\Delta\nu$-values.

Although the data are too scanty to warrant any sweeping generalizations, we would like to record some preliminary observations. According to the Bauer–Badger rule,[14] $\Delta\nu$ is proportional to, or at least monotonic with, ΔH^0, although possible exceptions have been noted.[15] Moreover, in given series of organic reactions involving similar reac-

tants and electronic mechanisms, monotonic relationships between ΔH^0 and ΔF^0 appear to be the rule rather than the exception, and thermodynamic data for H-bond formation for a series of substituted phenols follow the monotonic pattern.[4] One is therefore inclined to look for monotonic relationships between $\Delta\nu$ and ΔF^0, at least for those reactions in which the union of H-bond donor and acceptor enjoys some common electronic feature. As a matter of fact, the data for H-bond formation to a carbonyl group are represented quite satisfactorily by eq. 4, as shown in Table II. In the remaining cases the common electronic feature is

$$\Delta F^0 = 0.20 - 0.005\Delta\nu \qquad (4)$$

that the acceptor electrons occupy orbitals which, on the basis of the angles between the covalent bonding orbitals, are best described as tetrahedral. Here the data are represented satisfactorily by eq. 5, as shown in Table II.

$$\Delta F^0 = 1.35 - 0.005\Delta\nu \qquad (5)$$

Both sets of data are fitted with the same slope This suggests either that the Bauer–Badger rule in its simple form, in which ΔH^0 is proportional to $\Delta\nu$, applies to both sets, the greater stability of the carbonyl complexes resulting from their greater entropy. Or else, that ΔH^0 is a linear function of $\Delta\nu$, rather than proportional to it, the value of the intercept being characteristic of the type of H-bond being formed.

Experimental

Materials.—The purification of ethanol, acetic anhydride, ethyl acetate and carbon tetrachloride are described elsewhere.[16] In addition some of the solutions were made up in Merck spectroscopic grade carbon tetrachloride which was used without further purification. Its infrared spectrum in a long-path (5 mm.) cell showed negligible water absorption.

Apparatus and Method.—The instrument used and the technique of the infrared measurements were made the same as described in the preceding paper.[2] The spectra were run immediately after preparing the solutions. The reaction of acetic anhydride with ethanol is slow at the temperature used in this work (25 ± 2°), so that no error was encountered from this source.

We acknowledge gratefully the assistance of Esther R. Grunwald with the calculations reported in this paper.

TALLAHASSEE, FLORIDA
BIRMINGHAM, ALA.

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