[Contribution from Southern Research Institute and the Chemistry Department of Florida State University]

Infrared Measurements of the Association of Ethanol in Carbon Tetrachloride

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The association of ethanol in carbon tetrachloride was reinvestigated by infrared absorption in the concentration range 0–1 M because of discrepancies in previous data. The area of the monomer OH-stretching band at 3631 K. was measured at 25 ± 2°. Correction was made for the contribution of the H · · · O–H end groups of linear complexes by supposing that dimers and trimers are largely linear, and tetramers and the next few higher complexes are largely cyclic. The experimental and theoretical basis for this assignment is reviewed. To fit the monomer concentration c_1 (as obtained from the corrected area) as a function of the total concentration c, the equation $c - c_1 = 2K_2c_1^2(1 + 2.25K_2c_1) + 4K_4c_1^4/(1 - 1.25K_4^{1/4}c_1)$ was derived. For c-values up to 0.5 M, the experimental data were fitted to 2%, using these values for the association constants: $K_2 = 0.639\ M^{-1}$ and $K_4 = 14.3\ M^{-3}$.

We report (a) new measurements of the infrared absorption of ethanol in carbon tetrachloride in the region of the OH-stretching vibration, and (b) an evaluation of the monomer fraction as a function of ethanol concentration, using these data, based on recent ideas regarding the structure and O–H vibrations in hydrogen-bonded complexes. This reinvestigation was undertaken because of serious discrepancies between the monomer fractions deduced from Hoffmann's infrared data[1] and those deduced from Niini's vapor pressure data.[2] Our new results are in fairly good agreement with Niini's.

OH-Vibrations in H-Bonded Complexes.—In the measurement of complex formation the infrared method is superior to other methods in which some average property of the solute molecules is measured, such as molar polarization,[3a] viscosity,[3b] or nuclear magnetic resonance,[3c] because the spectrum is more specific.

Smith and Creitz, in their recent comprehensive study of the infrared absorption of alcohols,[4] have shown that one must consider three distinct O–H stretching vibrations in alcohol complexes. Their vibrational assignments for a typical alcohol are given in Fig. 1. The monomer absorbs at *ca.* 2.74 μ (3650 K.). In the complexes, the H · · · O–H terminal groups absorb at *ca.* 2.76 μ (3620 ks.), the O–H · · · O terminal groups at *ca.* 2.86 μ (3500 ks.), and the H · · · O–H · · · O interior groups at *ca.* 2.96 μ (3380 ks.). (There are small variations from these "average" values for individual alcohols.) The band at 2.96 μ is broad and overlaps that at 2.86 μ, so that this region of the spectrum is not very suitable for measuring concentration. The absorption due to the monomer and the H · · · O–H terminal groups forms a single band, well separated from the rest of the spectrum, the doublet structure of which is resolved only for some alcohols, and then only at the higher concentrations.

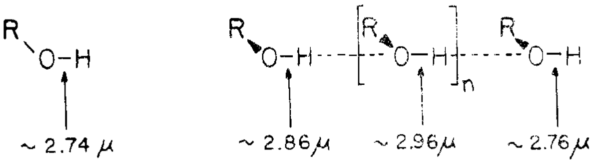

Fig. 1.—Fundamental OH-stretching vibrations of alcohols (after Smith and Creitz[4]).

Our new data for ethanol, samples of which are shown in Fig. 2, fit well into this scheme. The "monomer" band at 3631 ks. is broadened significantly with increasing concentration, presumably due to H · · · O–H absorption at a slightly lower frequency (see column 4, Table II). The bands centered at 3490 ks. (O–H · · · O) and at 3338 ks. (H · · · O–H · · · O) vary with concentration in the expected manner if the first complex is a linear dimer which, at higher concentrations, associates further to linear and/or cyclic complexes of higher order.

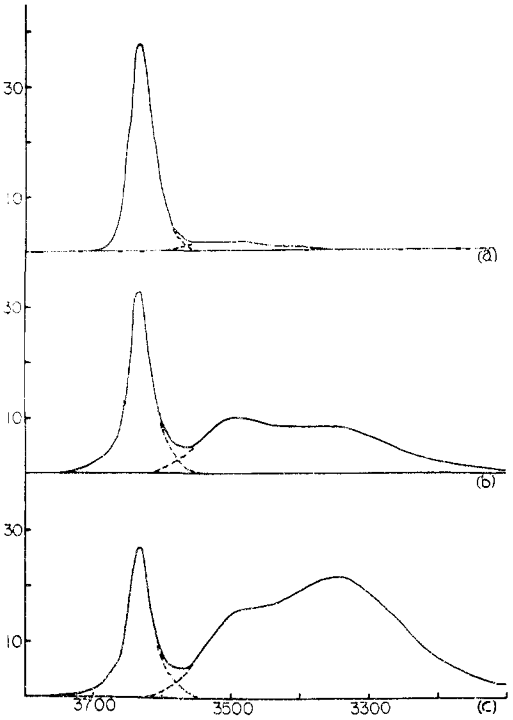

Fig. 2.—Molar absorbancy index for ethanol in carbon tetrachloride at 25 ± 2° in the OH-stretching region: concentration of ethanol, (a) 0.00511 M; (b) 0.102 M; (c) 0.170 M.

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(1) E. G. Hoffmann, *Z. physik. Chem.*, **B53**, 179 (1943).

(2) A. Niini, *Ann. Acad. Sci. Fennicae*, **A55**, No. 8 (1940); *C. A.*, **37**, 1313^2 (1943).

(3) (a) A. H. Bond, D. Cleverdon, G. B. Collins and J. W. Smith, *J. Chem. Soc.*, 3793 (1955); (b) L. A. K. Stavely and P. F. Taylor, *ibid.*, 200 (1956); (c) A. D. Cohen and C. Reid, *J. Chem. Phys.*, **25**, 790 (1956).

(4) F. A. Smith and E. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, 145 (1951).

Following the methods laid out 20 years ago,[5–9] our analysis of the spectral data concentrates on the "monomer" band at 3631 ks. It differs, however, in that it makes use of the area rather than the height, and in that a correction is made for the contribution of the H · · · O–H groups. For this purpose, it is necessary to determine whether the complexes are linear or cyclic.

Structure of H-Bonded Complexes.—Much insight regarding ethanol complexing can be gained from the equation of state of ethanol vapor. Recent careful heat capacity[10] and $P-V-T$[11] data at moderate pressures are best represented by the virial equation

$$PV = RT + BP + DP^3$$

the third virial coefficient C being close to zero. According to Woolley,[12] the virial coefficients are related to the association constants for the formation of dimeric, trimeric, . . ., clusters or complexes from monomer as

$$B = -K_2RT; \quad C = (3K_2^2 - 2K_3)RT;$$
$$D = (-10K_2^3 + 12K_2K_3 - 3K_4)RT$$

Since $C \approx 0$, $K_3 \approx 3/2K_2^2$, and, since D is large and negative, K_4 is large, indicating that the tetramer is unusually stable. This is confirmed further by the heats of association. Values of K_2, K_3, and K_4 were calculated from Kretschmer and Wiebe's[11] empirical equations for B and D at 20 and 80°, and values of ΔH_2, ΔH_3, and ΔH_4 calculated therefrom.[13] The results are shown in Table I. Since $\Delta H_3 \approx 2\Delta H_2$, but $\Delta H_4 \approx 4\Delta H_2$, the data point to a linear structure for the dimer (one H-bond) and trimer (two H-bonds), but a cyclic structure for the tetramer (four H-bonds).

TABLE I

ASSOCIATION OF ETHANOL IN THE GAS PHASE[a]

Reaction	K_p[b] 20°	K_p[b] 80°	ΔH (cal.)	No. of H-bonds
$2EtOH = (EtOH)_2$	0.143	3.24×10^{-2}	− 5,090	1
$3EtOH = (EtOH)_3$	.0306	1.58×10^{-3}	−10,180	2
$4EtOH = (EtOH)_4$	.197	2.73×10^{-4}	−22,560	4

[a] Based on data by Kretschmer and Wiebe.[11] [b] Association constant; partial pressures in atm.

These results are consistent with current theories of the hydrogen bond. The bond is most stable if the covalent O–H donor bond is colinear with the orbital occupied by the acceptor electron pair.[3a,14] Using a model analogous to that developed by Pople for liquid water,[14b] the bonding and non-bonding electrons in ROH occupy approximately tetrahedral orbitals, and the most stable bond directions are as shown in Fig. 3a. Consequently, if the trimer were cyclic, the strain angle θ would have a value of 49°28′ (minimum in a planar structure), but in the tetramer the minimum value would be only 19° 28′ (see Figs. 3b, 3c). Pople[14b] has estimated the force constant for O–H · · · O bending in liquid water and has concluded that, due to thermal excitation, the average value of θ is *ca.* 26° at room temperature. Thus the observation that a cyclic tetramer is formed, but a cyclic trimer is not, appears reasonable. In fact, if the older view is correct, that the covalent bonding electrons and one of the unshared pairs of ROH occupy nearly orthogonal p-orbitals,[15] a cyclic tetramer could be formed with essentially strainless hydrogen bonds.

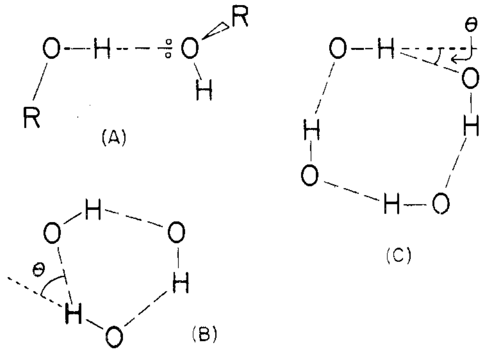

Fig. 3.—Strain angles in cyclic ethanol complexes: (A) preferred linear orientation; (B) planar cyclic trimer, θ = 49°28′; (C) planar cyclic tetramer, θ = 19°28′. The angles H- - -O–H are shown as tetrahedral. In (B) and (C) the R-groups are not shown. The angles H–O–R are nearly tetrahedral, with the R-groups above and/or below the plane of the $(OH\text{- - -})_n$ rings.

From similar arguments one would expect cyclic strain-free structures for the complexes of the fifth and next higher orders, although for very high orders the entropy of ring closure may become unfavorable and linear structures prevail.[16]

Regarding the structure of the complexes in solution, the linear structure for the dimer is by now generally accepted.[3a,4] The evidence regarding the trimer is conflicting. Hoffmann[1] concludes from his infrared data that the trimer is unusually stable (and hence probably cyclic), but he does not consider the matter settled and points out some discrepancies between his data and data from non-spectroscopic sources. For example, for *t*-butyl alcohol in cyclohexane, his data at 21.5° indicate predominance of trimer, but cryoscopic data at 6°

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[5] (a) J. Errera and P. Mollet, *Nature*, **138**, 882 (1936); (b) J. Errera, R. Gaspart and H. Sack, *J. Chem. Phys.*, **8**, 63 (1940).

[6] J. J. Fox and A. S. Martin, *Proc. Roy. Soc.* (*London*), **A162**, 419 (1937).

[7] R. Freymann, *Compt. rend.*, **195**, 39 (1932).

[8] A. M. Buswell, V. Deitz and W. H. Rodebush, *J. Chem. Phys.*, **5**, 501 (1937).

[9] R. Mecke, *Disc. Faraday Soc.*, **9**, 161 (1950).

[10] (a) W. Weltner and K. S. Pitzer, THIS JOURNAL, **73**, 2606 (1951); (b) G. M. Barrow, *J. Chem. Phys.*, **20**, 1739 (1952).

[11] C. B. Kretschmer and R. Wiebe, THIS JOURNAL, **76**, 2579 (1954).

[12] H. W. Woolley, *J. Chem. Phys.*, **21**, 236 (1953).

[13] The interpretation of virial coefficients in terms of molecular, particularly H-bonded, complexes is of course an oversimplification, but one which can be justified in the present case. According to a method proposed by Lambert, Roberts, Rowlinson and Wilkinson, *Proc. Roy. Soc.* (*London*), **A196**, 113 (1949), the contribution to the second virial coefficient of interactions which become negligible at the critical temperature is given by

$$(B - 9RT_c[1 - 6T_c^2/T^2]/128P_c)$$

For ethanol at 20°, this contribution amounts to 76% of B. According to the method of Scatchard and Ticknor,[27] the fraction of B which is due to "non-polar" interactions at 20° is estimated as 10%.

[14] (a) J. R. Hulett, J. A. Pegg and L. E. Sutton, *J. Chem. Soc.*, 3901 (1955); (b) J. A. Pople, *Proc. Roy. Soc.* (*London*), **A205**, 163 (1951).

[15] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 78.

[16] J. N. Wilson, *Chem. Revs.*, **25**, 400 (1939).

point to the predominance of tetramer.[17] Likewise, for ethanol in carbon tetrachloride, his results are not consistent with the vapor pressure data of Niini.[2]

It is our view that both theory and the balance of the experimental evidence indicate strongly that the dimer and trimer are predominantly linear, and that the tetramer and the next few higher complexes are predominantly cyclic. The analysis of our experimental data is based on this premise.

Experimental

Materials.—U. S. I. reagent grade absolute *ethyl alcohol* was treated by the method of Lund and Bjerrum,[18] and was then fractionated through a 30-inch column at a reflux ratio of 20:1. The middle half, n^{25}D 1.3598, was collected. Karl Fisher analysis for water showed less than 0.01%.

Merck spectroscopic grade *carbon tetrachloride* was used without further purification. Its infrared spectrum in a 5-mm. cell showed negligible water absorption.

Infrared Measurements.—A Perkin-Elmer Model 21 double-beam spectrophotometer with sodium chloride prism was used. Instrumental conditions were as follows: resolution, 960; gain, 5.1; response, 1:1; speed, 230 kaysers/minute; suppression, 0. The spectral slit width at 3631 ks. was about 25 ks. The instrument was calibrated using atmospheric absorption bands and polystyrene film, and the accuracy is estimated as ±10 ks. in the O–H stretching region. The instrument was operated with the sample cell in the sample beam and nothing in the reference beam. Cells were calibrated by comparison of the absorbancy of a standard material to its absorbancy in a 0.106 mm. cell which had been calibrated by the interference fringe method. Solutions were made up volumetrically. Room temperature was 25 ± 2°.

Treatment of Results.—Absorbancies were measured in the standard way, correcting for any background absorption. Curves of linear absorbancy against frequency in kaysers were plotted from the data, and areas were measured with a planimeter. A correction for the tail of the dimer band was made by extrapolation, as shown in Fig. 2. Like any graphical procedure, this procedure is somewhat subjective. However, duplication of the curve plotting and area measurement in several cases showed that areas were reproducible to 2% or better. At the lower concentrations the monomer band shape (after correction) was symmetrical about the maximum, except for a very small shoulder at about 3710 ks., which probably was due to a combination frequency.

The absolute accuracy of the area measurements is undoubtedly less than their reproducibility. "Wing" corrections of the type described by Ramsay[19] are estimated as amounting to about 6% of the measured band area. Corrections for finite slit width are probably much smaller. (For 0.17 *M* ethanol, 8.4-fold change in cell length resulted in less than 2% change in measured area.)[19] No corrections were made for the shoulder at 3710 ks., which amounted to perhaps 4% of the measured area. Additional error was introduced in correcting for the tail of the dimer band; its magnitude is difficult to estimate, but a systematic procedure was used. The measured areas, which are listed in Table II, were not corrected for any of these effects. In the treatment of the data only *ratios* of areas were used, and it was expected that the errors would largely cancel out.

Results and Calculations.—The relevant experimental data for the monomer band are shown in Table II: c is the molar concentration of ethanol, l the cell length, $\nu_{\max}$ the frequency (in kaysers) of the band maximum, $\Delta\nu_{1/4}$ the band width (in kaysers) at one quarter of maximum height, a_M the molar absorbancy index (extinction coefficient) for the band maximum, $S = 2.303 \int a d\nu$, the molar absorption area for the band, and α_a and α_s the apparent monomer fractions deduced from a_M and S, respectively. As usual, $a_M = A/lc$, where A is the measured absorbancy (optical density). Values of $\Delta\nu_{1/4}$ are included to show the broadening with increasing concentration. It will be noted that α_s is generally slightly greater than α_a. This is as expected on the basis of Fig. 1. If there is a contribution to the monomer band by the H · · · O–H end groups for which $\nu_{\max}$ is slightly smaller than for the free OH groups of the monomer, S would be increased relatively more than a_M.

TABLE II

RESULTS FOR THE MONOMER BAND OF ETHANOL IN CCl_4, 25 ± 2°

c	l (cm.)	$\nu_{\max}$	$\Delta\nu_{1/4}$	a_M	S	α_a[a]	α_s[b]
0.00511	0.439	3629	60	37.6	420_0	0.99_5	1.00_3
.0102	.439	3632	60	37.6	413_0	$.99_5$	0.98_6
.0511	.0892	3631	62	36.2	410_0	$.95_8$	$.97_8$
.0852	.0892	3634	65	33.9	400_0	$.89_7$	$.95_3$
.102	.0892	3631	62	32.6	367_0	$.86_2$	$.87_6$
.170	.0892	3631	67	27.2	328_0	(Mean)	(Mean)
.170	.0106	3631	68	27.2	334_0	$.72_0$	$.79_0$
.511	.0106	3634	76	15.5_5	200_6	$.41_1$	$.47_9$
1.02	.00403	3631	78	9.1_0	117_2	$.24_1$	$.28_0$

[a] $a_M/37.8$. [b] $S/419_0$. The limiting values of a_M and S were obtained by linear extrapolation of the data at the lowest concentrations.

In deriving equations 1–5, we shall assume the laws of the dilute solution; that is, the activity of each species is proportional to the actual molar concentration of that species. On this basis, the general expression for the concentration, c_C, of the complexes (based on the molecular weight of the monomer) as a function of monomer concentration, c, is shown in equation 1

$$c_C = 2K_2c_1^2 + 3K_3c_1^3 + 4K_4c_1^4 + 5K_5c_1^5 + \ldots \quad (1)$$

In treating our data, we felt that our accuracy warranted the use of no more than two adjustable parameters. One of the parameters we chose was K_2, since some idea of its magnitude already was available.[4] In analogy with the data for gaseous ethanol, K_3 was set equal to $3/2\ K_2^2$. The second parameter was K_4. Assuming a cyclic structure for the tetramer, K_4 may be written as $(K_4^{1/4})^4$, where $K_4^{1/4}$ is the contribution per hydrogen bond. By analogy, the association constants for the formation of cyclic pentamer, hexamer, . . ., may be approximated by $K_5 = K_4^{5/4}$, $K_6 = K_4^{6/4}$, ... Equation 1 was then written as

$$c_C = 2K_2c_1^2(1 + 2.25K_2c_1) + 4K_4c_1^4(1 + 1.25K_4^{1/4}c_1 + 1.5K_4^{2/4}c_1^2 + \ldots) \quad (2)$$

Equation 2 was reduced to closed form by making the further approximation that $(1 + 1.25K_4^{1/4}c_1 + 1.5K_4^{2/4}c_1^2 + \ldots) \approx (1 - 1.25K_4^{1/4}c_1)^{-1}$. The final equation was

$$c_C = 2K_2c_1^2(1 + 2.25K_2c_1) + 4K_4c_1^4/(1 - 1.25K_4^{1/4}c_1) \quad (3)$$

Of the approximations made, the one regarding K_5, K_6 . . . was thought to be the least satisfactory, but the error arising from this source is small at the lower concentrations.

The monomer concentration was evaluated from the area of the monomer band by supposing (a) that only the dimers and trimers have H · · · O–H end groups, and (b) that the molar absorption area for the H · · · O–H end groups is equal to that for

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(17) K. L. Wolf, H. Dunken and K. Merkel, *Z. physik. Chem.*, **B46**, 287 (1940); H. Dunken, *ibid.*, **B45**, 201 (1940).

(18) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath Co., New York, N. Y., 1941, p. 359.

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

the free O–H groups.[20b] This second assumption seemed reasonable since the values of $\nu_{\max}$ for the free OH groups and the H · · · O–H end groups are nearly equal,[20] and seems to find ample support in the work of Wulf, Liddel and Hendricks[21] on intramolecular H-bond formation where the variation in S upon complex formation seldom exceeds 20%.[22] Thus the true monomer fraction α is related to α_s by the equation

$$\alpha = \alpha_s/(1 + K_2c_1 + 1.5K_2^2c_1^2) \qquad (4)$$

K_2 and K_4 were obtained from the data in Table II by successive approximations. An initial estimate of K_2 permitted the calculation of α *via* equation 4 (where $c_1 = \alpha c$). This led to values for c_0 (equal to $c - c_1$) and, upon fitting the data to equation 3, to new estimates for K_2 and K_4. In each approximation the parameters were calculated by the method of averages. The calculations converged rapidly, the final values being: $K_2 = 0.639$; $K_4 = 0.639$; $K_4 = 14.3$. The data for the 1.02 M solution were not used in these calculations.

The fit of the data to equation 3 is shown in Table III. The values in column 2 are quite insensitive to K_2 and are therefore regarded as experimental values; the values in column 3 are calculated values. At concentrations up to 0.5 M the fit is acceptable: the standard deviation between the two sets is 1.9%, which is in good agreement with the standard experimental precision of 2%. At 1 M ethanol the approximations made in equation 3 are less satisfactory and the discrepancy is about 6%.

TABLE III

VALUES OF α FOR ETHANOL IN CARBON TETRACHLORIDE, 25 ± 2°

c	From α_s and eq. 4[a]	From eq. 3[a,b]	From α_a and eq. 5[a,c]
0.0102	0.980	0.987	0.993
.0511	.948	.932	.949
.0852	.906	.890	.883
.102	.826	.853	.847
.170	.725	.740	.701
.511	.412	.412	.392
1.02	.236	.251	.231

[a] $K_2 = 0.639$. [b] $K_4 = 14.3$. [c] $g = 0.3$.

Further evidence that this method of fitting the data is essentially correct is provided by the reasonable magnitude of the parameters. The parametric value, $K_2 = 0.639$, is very close to the value, 0.68, observed[4] for the dimerization of 2,4-dimethyl-3-ethyl-3-pentanol which, due to steric hindrance, does not associate further. The latter value is quite accurate since the dimer concentrations can be obtained directly from the band at 2.86 μ. The ratio K_4/K_2^3, which is a measure of the extra stability of the cyclic over the linear tetramer, is calculated as 55 from our parameters, as compared to 66 for gaseous ethanol at 20° from Table I.

In most of the previous studies it was assumed that $\alpha = \alpha_a$. Comparison of the relevant data in Tables II and III shows that the error arising from this assumption is relatively small. Assuming the validity of Beer's law, α is related to α_a by the equation

$$\alpha = \alpha_a/(1 + gK_2c_1 + 1.5gK_2^2c_1^2) \qquad (5)$$

where g is the ratio of the molar absorbancy index for the H · · · O–H end groups at $\nu_{\max}$ to that for the monomer at $\nu_{\max}$. Since the absorption maxima for monomer and H · · · O–H end groups do not coincide, g is expected to be less than unity. As a matter of fact, the value $g = 0.3$ fits satisfactorily at the lower concentrations (Table III, column 4).

Comparison with Previous Studies.—The most recent infrared studies are those of Hoffmann[1] and of Ens and Murray,[23] both of which involved harmonics of the OH-stretching vibration. Hoffmann's results, corrected to 25° by the method of Mecke and Nückel,[24] are quite different from ours. The discrepancy in α_a is 9% at 0.1 M, 15% at 0.2 M, and 27% at 0.5 M. We first noted that we could not repeat his values during a preliminary study in 1953 which was entirely independent of the present one.[25] Although less accurate, the preliminary results agree with those we are now reporting.

Ens and Murray's work[23] was published after this work had been completed. The agreement of their data with ours is somewhat better. While Hoffmann's α_a values are smaller than ours, theirs are larger, the discrepancy being 8% at 0.1 M and 15% at 0.5 M. They treated their data on the assumption that the average molecular weight of the ethanol complexes is independent of the monomer concentration, an assumption which we regard as unjustified.

It is also of interest to compare our results with Niini's vapor pressure data for the system ethanol–carbon tetrachloride at 20°, which were obtained by the static method.[2,26] In calculating fugacities from these data, the following values were used for the second virial coefficients at 20°: CCl_4, −1,470 ml.,[27] C_2H_5OH, −3,440 ml.[11] The virial coefficient for the interaction of C_2H_5OH and CCl_4 was estimated, by a method analogous to that used by Scatchard and Ticknor for CH_3OH and CCl_4,[27] as −730 ml. The calculation of the fugacities f_1 of CCl_4 and f_2 of C_2H_5OH therefore involved the equations

$$\frac{f_1}{f_1^0} = \frac{y_1P}{P^0} \exp\left\{\left(\frac{P_0 - P}{1000}\right)(0.0804) + y_2^2\left(\frac{0.1887P}{1000}\right)\right\} \qquad (6)$$

$$f_2 = y_2P \exp\left\{\frac{P}{1000}\,[0.1887y_1^2 - 0.1882]\right\} \qquad (7)$$

$$\mathrm{d}\ln f_1 = -\frac{x_2}{x_1}\,\mathrm{d}\ln f_2 \qquad (8)$$

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[20] (a) H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956); (b) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956); (c) we do not expect, however, that data for bonds of the type H · · · OH will necessarily fall on the same line as data for bonds of the type O–H · · · X.

[21] (a) O. R. Wulf and U. Liddel, THIS JOURNAL, **57**, 1464 (1935); (b) O. R. Wulf, U. Liddel and S. B. Hendricks, *ibid.*, **58**, 2287 (1936).

[22] In a recent seminar at Florida State University, Dr. Wilbur Kaye of Beckman Instruments has suggested that the spectra of *ortho*-substituted phenols may be interpreted on the basis of dipole–dipole interactions between the OH-group and the *ortho*-group.

[23] A. Ens and F. E. Murray, *Can. J. Chem.*, **35**, 170 (1957).

[24] R. Mecke and H. Nückel, *Naturwiss.*, **31**, 248 (1943).

[25] W. C. Coburn, Jr., Ph.D. Thesis, Fla. State University, Tallahassee, Fla., 1954.

[26] The more recent data of J. A. Barker, I. Brown and F. Smith, *Disc. Faraday Soc.*, **15**, 141 (1953), unfortunately do not extend to sufficiently low concentrations to be of interest here.

[27] G. Scatchard and L. B. Ticknor, THIS JOURNAL, **74**, 3724 (1952).

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.

TABLE IV

COMPARISON WITH NIINI'S VAPOR PRESSURE DATA[2] AT 20°

c (M)	P (mm.)	f_2 (mm.)	y_2	f_1/f_1^0	α^a (this work)	$f_2/\alpha c^b$
0.00000	90.81	0.00	0.00000	1.00000	1.000	...
.01297	92.044	1.34	.01455	.99875	0.983	106
.02595	93.259	2.65	.02849	.99753	.964	106
.05194	95.65	5.25	.05495	.99509	.924	109
.1041	100.02	10.05	.10079	.99040	.832	116
.2090	105.33	15.82	.15105	.98400	.650	116
.4214	109.45	20.55	.18909	.97662	.437	112
					Av.	111 ± 4^c

[a] Calculated *via* equation 3. At 20°, $K_2 = 0.690$, $K_4 = 20.0$; based on values at 25° and $\Delta H_2 = -2{,}660$ cal., $\Delta H_4 = -11{,}770$ cal. [b] (mm.) M^{-1}. [c] The variation in $f_2/\alpha c$ is not very sensitive to correction for gas imperfection. Niini[2] has treated the gas phase as an ideal mixture. On this basis, the mean deviation in $f_2/\alpha c$ was 3.5% over the same concentration range.

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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

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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 concentrations. 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

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[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).