C	mol of H_2O/mol of *tert*-butyl alcohol
M	molecular weight
W	weight percent

Subscripts

1	NaOH
2	water
3	*tert*-butyl alcohol

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Association Studies of 1-Butanol in *n*-Heptane as a Function of Temperature

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The association of 1-butanol in *n*-heptane has been investigated by near-infrared spectrophotometry. Calculation of the average size of 1-butanol polymers shows that no single 1-*n* polymer is the predominant associated species over the complete concentration range. The one parameter infinite series model for alcohol association is shown to be invalid for these alcohol solutions. The simplest model which adequately represents the data in the dilute alcohol solutions is the 1–2–4. The unitary thermodynamic changes are calculated for this model and are as follows: dimer $\Delta G^\circ_{\mathrm{u}}$ (295 K) = −2.3 kcal/dimer, ΔH° = −4.3 kcal/dimer, $\Delta S^\circ_{\mathrm{u}}$ = −6.8 gibbs/dimer; tetramer $\Delta G^\circ_{\mathrm{u}}$ (295 K) = −8.6 kcal/tetramer, ΔH° = −12.9 kcal/tetramer, $\Delta S^\circ_{\mathrm{u}}$ = −14.6 gibbs/tetramer. At this level of aggregation stability increases with degree of aggregation.

There have been many reported studies[1] of self-association between simple alcohol molecules in nonpolar solvents. While it is generally agreed that there exist multiple equilibria among the many possible hydrogen bonded species, considerable controversy has arisen over the specific species present and their relative abundances.

During the course of spectroscopic fluorescence investigations[2] of exciplex formation between indole and substituted indoles with 1-butanol in *n*-heptane, it became necessary to obtain information on the degree of alcohol association in heptane and the concentrations of the lower-order associated species. This information was sought in order to interpret the mechanism of fluorescence emission from the excited indole compounds. A literature search indicated the only available information[3] on the binary alcohol–*n*-heptane system was derived from studies of the fundamental OH vibrations. Data obtained from this region generally give considerable error in the derived results because of experimental complications and data analysis. As well, on the basis of criteria proposed by Smith,[4] it appears that data from the fundamentals cannot yield high accuracy for association parameters at low concentrations. Luck[5] also has pointed out that studies of the effect of concentration or temperature on the degree of association in alcohols are less subject to experimental error if derived from the overtone vibrations. For these reasons, studies were made of solutions of 1-butanol in *n*-heptane by using the infrared absorption of the first overtone of the O–H stretch vibrations of the monomer.

Experimental Section

Solutions of 1-butanol (Fisher Spectranalyzed) in *n*-heptane (Fisher Spectranalyzed) were prepared by weight. Volumes were calculated by assuming zero volume change upon mixing and by using density data as a function of temperature for *n*-heptane and 1-butanol.[6,7] Concentrations ranged from 0.005 to 1.10 mol L^{-1} with the majority of measurements being made in the range of 0–0.30 M. Fresh materials were used without further purification.

Near-infrared spectra were obtained with a Cary Model 14 spectrophotometer over the spectral region 1340–1500 nm. Matched 1-cm Infrasil cells (with tight-fitting Teflon stoppers) were used for the sample and reference, and the cells were always filled so as to minimize any head-space loss problems.[8] The cells were contained in thermostatable cell jackets connected to an external constant-temperature bath (±0.1 °C). Periodic checks of the temperature within the cell with an accurate thermometer showed no heat drift effects. The reference beam always passed through a 1-cm cell filled with *n*-heptane maintained at the same temperature as the sample. Measurements were made at 6.0, 22.0, 31.0, and 44.5 °C so as to provide data as close as possible to the temperature conditions used in the fluorescence studies.[2] As a check on the instrument and techniques, data were obtained independently by two operators at a single temperature, using fresh chemicals from the same supplier and a second spectrophotometer. The agreement between the results was within the errors reported below. By use of a double-beam technique with *n*-heptane in the reference cell, virtually all of any absorbance due to CH_2 groups of the hydrocarbon in the spectral region of interest is cancelled.

Results

In the analysis of the data it is assumed that the absorbance peak at 1405 nm is due solely to the monomer. Pimentel and McClellan[1a] have suggested that the absorbance associated with the monomer cannot be related directly to the concentration of the monomer if linear polymeric species are present (–OH end groups of linear polymers may absorb at or near the wavelength of the monomer). Recent work,[9] however, has shown that the end-OH of linear self-association polymers do not contribute significant absorbance at the monomer peak in the first overtone region so the analysis was carried out assuming the observation to be correct.

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Table I. Values of the Molar Absorptivity, ϵ_1, for the Alcohol Monomer as a Function of Temperature

temp, °C	ϵ_1, cm^2 mol^{-1}	σ^a	N^b
6.0 ± 0.1	2.10	0.048	9
22.0 ± 0.1	2.06	0.018	8
31.0 ± 0.1	2.09	0.043	11
44.5 ± 0.1	1.99	0.019	10

[a] Standard deviation. [b] Number of low concentration points used in extrapolation.

The monomer overtone band of the alcohol showed structure, a weaker absorbance peak occurring at 1410 nm. The relative ratio of the absorbances of the two peaks in the monomer band remained constant with increasing alcohol concentration. These results appear to be similar to those observed[10] for alcohols in CCl_4 where the band structure has been shown to correspond to different conformations based on carbon-hydrogen substitution at the C atom adjacent to the OH group. However, at high degrees of aggregation packing should restrict conformational freedom and may be manifested in the intensity of this band.

Absolute absorbances were measured relative to the absorbance baseline obtained with *n*-heptane in both sample and reference cells at each temperature. The latter were routinely determined before, during, and after each series of alcohol measurements at each temperature.

The absorbance at 1405 nm, A, is assumed to measure the monomer at concentration C_1 (vide supra) where the formal alcohol concentration is C_0. The molar absorptivity, ϵ_1, was calculated for the alcohol monomer by using two procedures. In the first method, from the relationship $\epsilon_c C_0 = A$, a plot of A/C_0 vs. C_0 gives a constant value ϵ_1, as $C \rightarrow 0$. A more accurate value can be obtained from a plot of ϵ_c vs. $\epsilon_c^2 C_0$ since it allows a more exact extrapolation of ϵ_1.[5] A typical plot for the latter is shown in Figure 1. While there is reasonable agreement between the values derived from both methods, only values obtained from the more exact graphical method are shown in Table I. These were obtained by fitting a first-order regression line to the data by use of a computerized least-squares fitting program with weighting factors dependent upon the experimental errors in absorbance.

The variation of ϵ_1 with temperature is well within the error limits at all but the highest temperature. Even at that temperature it is not clear whether or not the observed decrease is significant and, if so, whether real or an artifact of the experimental method and data used to derive concentration values.

Using the values of ϵ_1 reported in Table I, we can calculate the monomer concentration C_1 in any sample from the relationship $C_1 = A/\epsilon_1$. The total associated species are given by $(C_0 - C_1)$ in formal concentration. The fraction of monomer α can be calculated from the expression $\alpha = C_1/C_0$. These values were fit to a power series (eq 1) in formal concentration

$$\alpha = b_1 + b_2 C_0 + b_3 C_0^2 + \cdots + b_n C_0^{n-1} \qquad (1)$$

using a least-squares program with weighting factors dependent on the errors in the experimentally determined absorbance and derived value of ϵ_1; the coefficients are reported in Table II. Note that the monomer is the only species determinable with confidence from spectrophotometric data. Anharmonicity effects, intensity shifts in the fundamentals due to rehybridization and other specific details of the aggregates make the relationship between spectra and their concentrations highly uncertain.

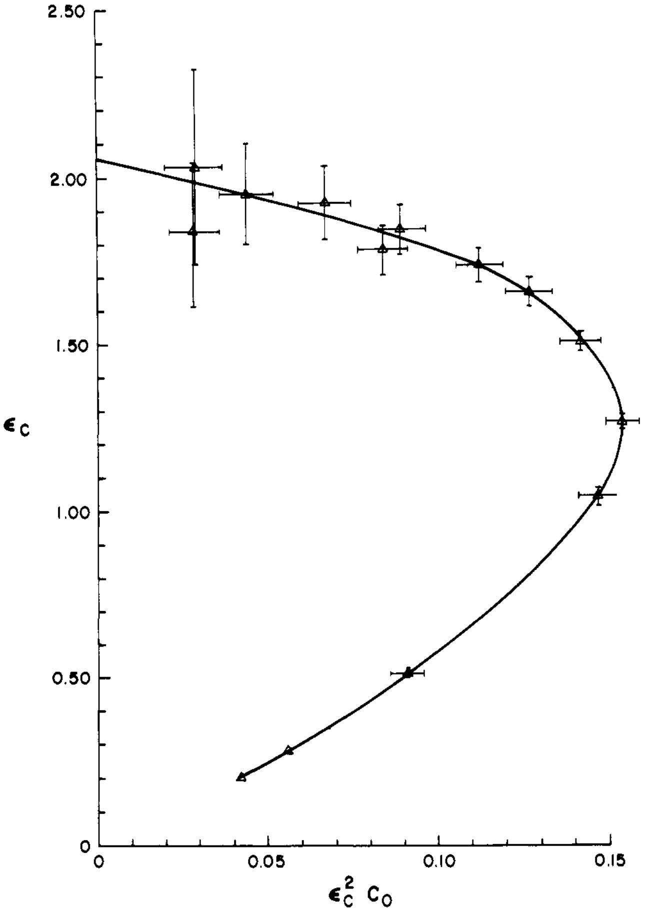

Figure 1. Determination of ϵ_1 with $\epsilon_c = f(\epsilon_c^2 C_0)$ at low concentrations.

Analysis of Data

To gain some estimate of the degree of aggregation over the complete concentration range, we carried out the following analysis. It has been previously shown by Hoffmann[11] that molecular weight data for alcohol solutions can be obtained by numerical integration of an appropriate function involving only monomer and formal concentrations. In general the following relationship exists between the formal alcohol concentration C_0 and apparent alcohol concentration C_A, i.e.

$$dC_A = (C_0/C_1)\, dC_1 \qquad (2)$$

The apparent alcohol concentration C_A can be obtained from the integrated form of eq 2 without reference to any particular association model by numerically integrating the curve C_0/C_1 vs. C_1.

$$C_A = \int_0^{C_1} (C_0/C_1)\, dC_1 \qquad (3)$$

Values of C_A were obtained by using a simple trapezoidal method for the integration. The average size of alcohol polymer can be defined[1d] as

$$n = (C_0 - C_1)/(C_A - C_1) \qquad (4)$$

Table II. Coefficients of the Regression Equation $\alpha = b_1 + b_2 C_0 + b_3 C_0^2 + \ldots + b_5 C_0^4$

temp, °C	b_1	b_2	b_3	b_4	b_5	σ^a
6.0	0.999 818	−7.726 97	25.466 2	−33.823 3	15.062 6	1.343 72
22.0	1.000 07	−5.097 65	12.721 8	−14.313 2	5.748 65	0.381 295
31.0	1.000 40	−4.401 04	10.687 2	−13.843 1	8.943 98	0.900 430
44.5	1.000 04	−2.488 62	1.506 13	1.959 75	−1.719 26	0.499 272

[a] Average relative standard deviation.

Table III. Root-Mean-Square Deviations and Equilibrium Constants for Various Fits of 1-Butanol-*n*-Heptane Near-Infrared Data

model	T, °C	rmsd,[a] M × 10^4	K_{12}, M^{-1}	K_{13}, M^{-2}	K_{14}, M^{-3}	K_∞, M^{-1}	comments
1-2-∞	6	1306	3.92 ± 0.07			9.98 ± 0.12	analysis of concn range 0-1.0 M
	22	2550	2.56 ± 0.06			5.88 ± 0.10	
	31	1754	2.19 ± 0.06			4.85 ± 0.14	
	44.5	1862	1.24 ± 0.04			3.27 ± 0.09	
1-2-∞	6	251	3.92 ± 0.06			9.63 ± 0.10	analysis of concn range 0-0.15 M
	22	56.9	2.56 ± 0.06			5.44 ± 0.07	
	31	25.9	2.19 ± 0.05			4.54 ± 0.12	
	44.5	8.8	1.24 ± 0.05			3.05 ± 0.11	
1-2-3	6	333	3.87 ± 0.3	38.1 ± 3.2			analysis of concn range 0-0.15 M
	22	117	2.52 ± 0.03	38.1 ± 0.4			
	31	68.1	2.16 ± 0.03	10.3 ± 1.6			
	44.5	17.3	1.23 ± 0.002	4.67 ± 0.13			
1-2-4	6	250	4.10 ± 0.03		1350 ± 100		analysis of concn range 0-0.15 M
	22	26.0	2.65 ± 0.03		376 ± 18		
	31	5.5	2.25 ± 0.03		210 ± 18		
	44.5	1.4	1.29 ± 0.01		59 ± 5		

[a] rmsd is the square root of the summed squares of deviations between C_0(exptl) and C_0(calcd) divided by the degrees of freedom (i.e., number of data points minus number of parameters) in the system.

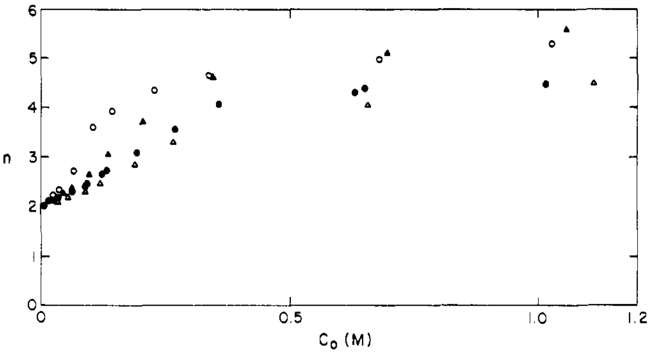

Figure 2. Average size of 1-butanol polymers as a function of 1-butanol molarity in *n*-heptane at four temperatures: (○) 6 °C; (▲) 22 °C; (●) 31 °C; (△) 44.5 °C. *Note*: not all of the low concentration data are shown.

Figure 2 shows values of *n* obtained from the data as a function of formal butanol concentration. The magnitude of *n* should be invariant as a function of concentration within experimental error if only a single polymer of order *n* is formed. It is clear from this figure that no 1-*n* model is a valid approximation for treating 1-butanol association in *n*-heptane. This is in agreement with previous results[1d] obtained for the ethanol-*n*-hexadecane system. The polymer size is close to 2 at very low 1-butanol concentrations and increases to values of $n \geq 4$ at the highest formal alcohol concentrations. There is scatter at higher concentrations and this suggests that the data are not as accurate as in the lower region. Further corroboration of the above observations was obtained in the following manner. If the presence of only one polymer of order *n* is assumed, then one can write

$$C_0 = C_1 + nK_{1n}C_1^{\,n} \tag{5}$$

and

$$\log (C_0 - C_1) = \log (nK_{1n}) + n \log C_1 \tag{6}$$

From eq 6 it can be seen that a plot of log $(C_0 - C_1)$ vs. log C_1 should give a slope of *n* if only one associated species is present. The plots obtained are nonlinear at all temperatures, with slopes of 2.1 ± 0.1 and 4.3 ± 0.4 in the low and high concentration regions, respectively. This is good evidence that at least two associated species are present.

The data do not justify testing a wide variety of models. Several were used to test if a sequential indefinite self-association would describe the observed association over a wide concentration range. In such a model simultaneous equations of the type

$$2C_1 \rightleftarrows C_2 \qquad C_1 + C_2 \rightleftarrows C_3 \tag{7}$$

are considered. In order to handle this model one is forced to make some simplifying assumptions. Kempter and Mecke[12] assumed a single equilibrium association constant, K_∞, for addition of a monomer unit to any alcohol species. This gives the following expression for the formal alcohol concentration

$$C_0 = C_1/(1 - K_\infty C_1)^2 \tag{8}$$

Equation 8 can be rearranged to

$$(C_0 - C_1)/C_0C_1 = 2K_\infty - K_\infty^{\,2}C_1 \tag{9}$$

and a plot of the left-hand side of eq 9 vs. C_1 should give a straight line with slope $K_\infty^{\,2}$ and intercept $2K_\infty$. Such a graph of our data does not give a straight line. Furthermore the slope is positive which predicts a physically impossible negative value of $K_\infty^{\,2}$. Clearly this model is not suitable and supports previously reported results on other alcohol-*n*-alkane systems.

Another variant of the indefinite self-association model assumes all associating species are present but that the molar equilibrium association constant for dimer, K_{12}, is different from all the other molar equilibrium constants; i.e., $K_{12} \neq K_{23} = K_{34} = \ldots = K_\infty$. It has been shown[1d] that the expression for C_0 is given by

$$C_0 = C_1 + \frac{K_{12}C_1^{\,2}(2 - K_\infty C_1)}{(1 - K_\infty C_1)^2} \tag{10}$$

To evaluate K_∞ from this equation one must first evaluate K_{12}. It has been shown[13] that K_{12} may be obtained by plotting $2\alpha^2C_0/(1 - \alpha)$ vs. C_0 and extrapolating to zero concentration. Values of the constants K_{12} and K_∞ are shown in Table III. This model is better than the 1-∞ model but gives a rather poor representation of calculated C_0 values as judged by the magnitude of the root-mean-square deviation (rmsd) Table III.

Since this work was carried out specifically to provide information necessary for interpreting photochemical processes at lower alcohol concentrations, fewer experimental results obtained in the high concentration range have undoubtedly contributed to a greater uncertainty in the association data in this region. Because of this fact, it was felt preferable to restrict the analysis to the concentration range 0-0.15 M.

The arguments against the 1-∞ and 1-*n* models presented earlier still hold for these conditions. However, when one considers the 1-2-∞ model, it can be seen that the fit, as judged by the magnitude of the rmsd value Table III, is considerably

Table IV. $\Delta H°$/Bond Values for 1-2-4 Model

	$-\Delta H$/bond,[a] kcal mol^{-1}	
	$\Delta H°_{12}$	$\Delta H°_{14}$
linear	4.40 ± 0.3	4.30 ± 0.4
cyclic	2.20 ± 0.2	3.20 ± 0.3

[a] Total $\Delta H°$ divided by n for cyclic n-mer and n-1 for linear n-mer.

improved. Other association models such as 1-2-3 and 1-2-4 were also used to fit the data and as may be expected from the preliminary analysis of the data, the 1-2-4 model appeared to give the best fit over the lower concentration region (Table III). In all cases the calculated K's show expected temperature dependence.

The following points are worth noting concerning the derived results for the 1-2-4 model. Calculated values of K_{12} are approximately twice as large as that found[14,15] for alcohol dimer formation in other systems. However, as previously pointed out,[1d] when higher polymers are readily formed it is difficult to determine the value of K_{12} within ±100%. As well, traces of nucleophilic contaminants introduce errors at the lowest alcohol concentration by overemphasizing the amount of aggregated materials, C_0–C_1. On the other hand, in agreement with other results,[16] our results indicate that the dimer concentration in alcohol solutions is not small compared to slightly larger polymer species. The values of the constant K_{14} are of a similar magnitude to those reported by Tucker et al.[1d] for ethanol–n-hexadecane using several models.

The equilibrium constants from the 1-2-4 model were used to determine $\Delta H°$/bond. The slope of the van't Hoff plot gives $-\Delta H°/R$ and the values of $\Delta H°$ association for both linear and cyclic polymers are shown in Table IV. The values are, however, ~50% smaller in magnitude than those previously reported[3] for this system.

The method of analysis does not allow a distinction to be made between cyclic and linear polymer species. If one assumes the associated species are strictly linear then from Table IV it appears that there is no change in $\Delta H°$ per hydrogen bond with increasing number of hydrogen bonds. This is somewhat unusual as one would normally expect from water aggregation an enhanced stability with increasing number of hydrogen bonds. If, on the other hand, one were to assume that the polymers were all of a cyclic nature, then the hydrogen bonds show increasing stability with addition of *n-mer*. Resolution of the relative proportions of cyclic and linear polymer species requires other experimental data. For example, correlation of average polymer size with heat of dilution data[15] would at least provide limiting descriptions and independent estimates of the average hydrogen bond energy as a function of concentration.

We would expect the aggregates to become more stable per mole of monomer as the aggregate site increases. In addition to the improvement in enthalpy of H-bond formation, the statistical factor based on the fact that there are two acceptor sites and only one donor H-bond site per hydroxyl group should increase with aggregate size. These factors are to some extent reflected in the list of unitary[17] changes (that part of the entropy and free energy change that is independent of the composition of the solution) given in Table V. Furthermore there are no factors which would tend toward condensation other than the rearrangements of H bonds possible in cyclic species and that is much limited by packing problems. Hence we suspect the unitary standard free energies to decrease by 2 to 3 kcal/mol of monomer up to somewhat higher degrees of aggregation. The equilibrium constants for higher aggregates can be estimated in a strictly phenomenological way by using the data of Table V. This procedure should be sufficient for most photochemical uses since alcohol concentrations are usually low. However, this approach obviously will not give much detail about the "inverted micelles" (large aggregates indicated as existing at high alcohol concentrations). With better data a cluster approach should provide extremely useful data comparing the self-association of alcohols (a deficiency in H-donor sites), hydrazine or hydrogen peroxide (deficiency in H-acceptor sites), and water (equal numbers of donor and acceptor sites).

Table V. Thermodynamic Changes on Association

1-2-4 Analysis

$\Delta G°_{12}$ (295 K) = -0.57[a]
$\Delta H°_{12} = -4.40$[a]
$\Delta S°_{12} = -13.0$[b]

$\Delta G°_{14}$ (295 K) = -3.48[c]
$\Delta H°_{14} = -12.9$[c]
$\Delta S°_{14} = -32.0$[d]

Unitary Changes

	dimer	tetramer
$\Delta G°_u$ (295 K), kcal	−2.3	−8.6
$\Delta H°$, kcal	−4.3	−12.9
$\Delta S°_u$, gibbs	−6.8	−14.6

[a] kcal/mol of dimer. [b] gibbs/mol of dimer. [c] kcal/mol of tetramer. [d] gibbs/mol of tetramer.

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