Table II. Solubility of Naphthalene in Several Surfactant Systems at 21 ± 1 °C[a]

surfactant	solubility[b] in the micelle pseudophase, mol dm^{-3}	molar vol,[c] $dm^3\ mol^{-1}$
CTAB	1.1	0.292
NaLS	0.38	0.227
Brij-35	0.43	0.277[d]
DDAB	0.90	0.454
NaTC	[0.054]	[0.515][e]
NaC	[0.063]	[0.41][e]

[a] Solubility in water is 2.2×10^{-4} M (*9*) and in hexane 0.91 M (*15*). [b] The micelle solubility is calculated from $[[P]_{total} - [P]_{aq}]/([surfactant] - cmc)V$. V is the molar volume of the surfactant. $[P]_{total}$ is the concentration of naphthalene at a particular surfactant concentration above the cmc and $[P]_{aq}$ the concentration of naphthalene in pure water. This equation applies to any micelle solubilized molecule; see ref 10. [c] Molar volumes calculated from hydrocarbon densities are given in ref 12. [d] Molar volume of this polyethylene oxide micelle core is from the data given in ref 14. [e] No literature value for the density of these compounds could be found, so a density of 1 has been used in the calculation.

where *A* and *C* from a linear least-squares analysis take the values given in Table I.

The data given in Figure 2 clearly show that CTAB is by far the best surfactant in solubilizing aromatic compounds. This is further seen in Table II where the solubility of naphthalene in various surfactant micelles is shown.

In the comparison of the solubility of naphthalene in the micelle pseudophase, the volume of which is estimated as the volume of the hydrocarbon tails of the surfactant monomers to that in a hydrocarbon solvent, hexane, it appears that in both CTAB micelles and DDAB vesicles the solubility is the same within the experimental uncertainty, whereas in the other surfactants the solubility is considerably lower. For the solubility to be as high as in a hydrocarbon phase is surprising since, the Laplacian pressure in a micelle core (estimated to be several hundred atmospheres[16]) and the lower microviscosity would both tend to reduce the solubility relative to a bulk hydrocarbon solvent. This relatively high solubility in CTAB and DDAB can be explained if one assumes that there is some specific binding of naphthalene with the quaternary ammonium head group. Such an interaction seems to be the case with pyrene.[10] The bile acid salts form aggregates of about 4 units, which have a microviscosity (measured with 2-methylanthracene as probe)[17] of 675 cP. This can be compared with other micelles: 30 cP for CTAB[18] and DDAB[19] and 15 cP for NaLS.[20] Thus the very much lower solubility in NaC and NaTC micelles is probably due to the comparatively low fluidity in these aggregates.

The data from the solubility in water of these aromatic hydrocarbons coupled with their solubilization in micellar systems can be used to calculate, at least approximately, the maximum amount of compound that will be solubilized by a given amount of surfactant. Some inaccuracy is introduced into the calculation because of the temperature difference of the water solubilities (25 °C) and micelle solubility (21 °C) data. This is, however, only minor, since the solubility in water will only change slightly in the temperature range cited.

For the less solubilized aromatics the aggregation number should not be greatly altered compared to the pure surfactant solution, as has been shown for some compounds, nor will the distribution ratio.[10,19] Consequently the distribution ratio can be used as a guide in nonsaturated solutions to determine the ratio of the concentration of compound solubilized to that in the aqueous phase. This case is particularly useful in interpreting results from photochemical and reaction rate studies of solubilized compounds in micellar systems.

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Liquid–Liquid Equilibrium for the Ternary System $NaOH–H_2O–t$-BuOH

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The ternary diagram for the system $NaOH–H_2O–t$-BuOH was determined by a combination of NMR and potentiometric titration. NaOH is extracted only slightly by *tert*-butyl alcohol from aqueous solution.

Introduction

tert-Butyl alcohol has some unique properties which are of interest in the study of phase equilibrium (*1*). *tert*-Butyl alcohol is the highest molecular weight of the saturated monohydroxy

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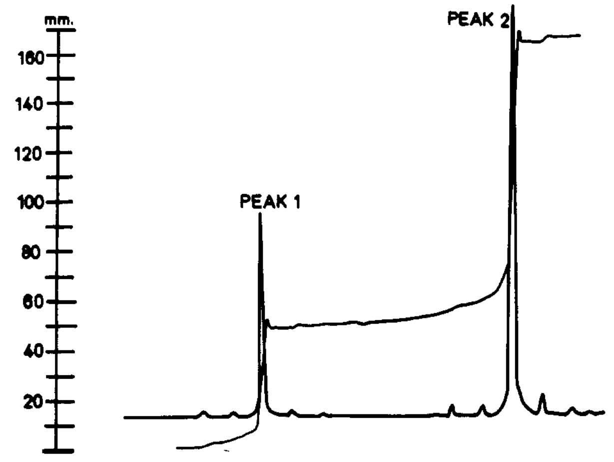

Figure 1. NMR spectra of the *t*-BuOH-rich phase.

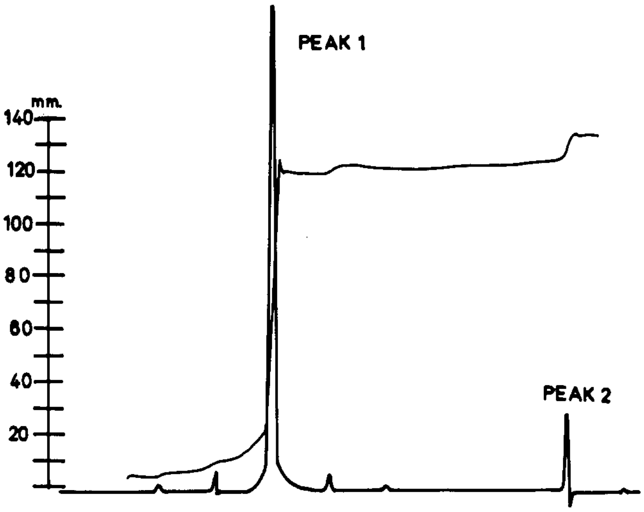

Figure 2. NMR spectra of the water-rich phase.

alcohols that is completely miscible with water at 25 °C. Besides being entirely soluble in water at 25 °C, *tert*-butyl alcohol is also miscible with alcohols, aromatic and aliphatic hydrocarbons, esters, ethers, and a variety of organic solvents. *n*-Butyl alcohol has been reported as a suitable solvent for extracting NaOH from aqueous electrolytic solutions containing NaCl (*2*). Information on the phase equilibrium of *t*-BuOH–NaOH–H_2O system is essential to evaluate *tert*-butyl alcohol as a solvent. In order to determine some points of the binodal curve, we used the turbidity method (*3*). To establish tie lines, we analyzed both phases by a combination of NMR and potentiometric titration.

Reagents

Baker reagent grade *tert*-butyl alcohol was distilled in the presence of metallic sodium; a purity of 99.9% was established by gas chromatography. Merck Reagent grade NaOH with a minimum purity of 99% was used. Water was distilled from a potassium permanganate solution.

Experimental Procedure

A jacketed equilibrium cell with a magnetic stirrer was allowed to reach equilibrium in less than 2 h, but samples were taken after 3 h. Temperature was maintained at 25 ± 0.2 °C.

The protonic contribution in the NMR spectra is due fundamentally to two types of protons: those due to OH groups (alcohols, water, and hydroxide) and those from the methyl group. In Figure 1 and 2 are illustrated the NMR spectra corresponding to the *tert*-butyl alcohol-rich phase and to the water-rich phase.

Table I. Experimental Data for Two-Phase Equilibrium at 25 °C

t-BuOH-rich phase wt %			water-rich phase wt %		
NaOH	H_2O	*t*-BuOH	NaOH	H_2O	*t*-BuOH
0.9	25.87	74.04	7.09	84.02	8.89
0.02	6.34	93.64	16.97	83.03	0.00
0.01	6.18	93.81	25.72	74.28	0.00
0.00	3.86	96.14	33.35	66.65	0.00
0.00	0.94	99.06	64.33	35.67	0.00

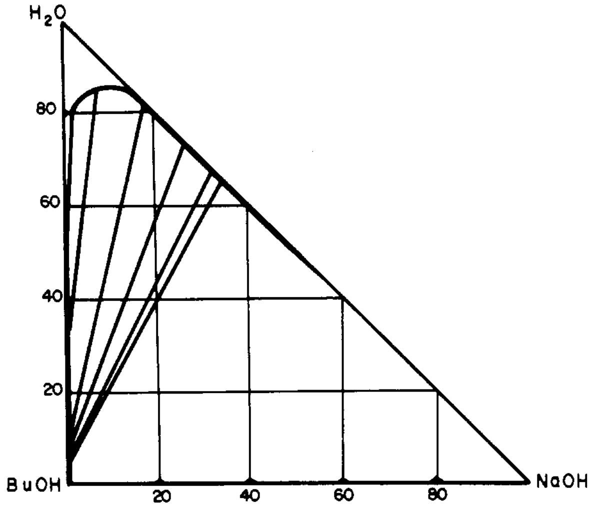

Figure 3. Ternary equilibrium diagram of *t*-BuOH–NaOH–H_2O at 25 °C.

The weight percent composition in a phase is related to the area under the NMR peaks, by the following equations

$$W_1 = \frac{100BM_1}{BM_1 + CM_2 + M_3} \tag{1}$$

$$W_2 = \frac{100CM_2}{BM_1 + CM_2 + M_3} \tag{2}$$

$$W_3 = \frac{100M_3}{BM_1 + CM_2 + M_3} \tag{3}$$

where the constants B and C correspond to

$$B = \frac{F(2M_3 - M_2) + 9M_2X}{((1/G - 1)2M_1 + M_2)F} \tag{4}$$

$$C = \frac{9X - F(1 + B)}{2F} \tag{5}$$

Experimental Results

The experimental results of the conjugated system are shown in Table I. The ternary equilibrium diagram is represented in Figure 3 and it can be inferred that NaOH is extracted only slightly by *tert*-butyl alcohol from aqueous solutions. Each point reported in Table I is the mean value of a minimum of four determinations; the maximum standard deviation found is 0.047.

Acknowledgment

We wish to thank the assistance given by Mrs. Ernestina Cervera Flores with the NMR spectra.

Glossary

G	NaOH concentration (NaOH grams/gram of solution)
X	area under the peak 1
F	area under the peak 2
B	mol of NaOH/mol of *tert*-butyl alcohol

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 ΔG°_u (295 K) = −2.3 kcal/dimer, ΔH° = −4.3 kcal/dimer, ΔS°_u = −6.8 gibbs/dimer; tetramer ΔG°_u (295 K) = −8.6 kcal/tetramer, ΔH° = −12.9 kcal/tetramer, ΔS°_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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