Acid-Catalyzed Reactions of 1 in Water, Methanol, and Acetic Acid. A suspension (water) or a solution (methanol and acetic acid) of the epoxide 1 (0.10 g, 0.53 mmol) in a 0.2 N solution of the acid (H_2SO_4 for the reactions in water and *p*-toluenesulfonic acid monohydrate for the reactions in methanol and acetic acid) in the solvent (10 mL) was stirred at 25 °C for 24 h (reaction in water), 7 h (reaction in methanol), or 1 h (reaction in acetic acid), quenched with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$ (in the case of the reaction in acetic acid the mixture was previously diluted with water), and thoroughly extracted with ether. Evaporation of the washed (H_2O) ether extracts yielded mixtures consisting of diols **12** and **13** (reaction in water), hydroxy ethers **6–8** (reaction in methanol), or monoacetates (reaction in acetic acid) together with different amounts of the rearrangement products **9**, **10**, and **15** which were analyzed by GLC (see Tables I and II), except for the reaction carried out in acetic acid. The crude product obtained from the reaction in acetic acid was analyzed by GLC after saponification of the monoacetates to the corresponding diols **12** and **13** as described later for the reactions of 1 with trichloroacetic acid. The reaction of 1 in methanol and that in acetic acid were also performed in the presence of anhydrous $LiClO_4$ (0.5 M) to give the results reported in Tables I and II.

The solvolysis addition products of these reactions were completely stable under the reaction conditions used.

Reaction of 1 with Methanol in CH_2Cl_2 in the Presence of *p*-Toluenesulfonic Acid. To the epoxide 1 (0.65 g, 3.45 mmol) was added a solution of *p*-toluenesulfonic acid monohydrate and methanol in a molar ratio (epoxide/acid/methanol) of 1:0.1:6 in anhydrous CH_2Cl_2 (65 mL) at 25 °C. The resulting mixture was stirred for 12 h at the same temperature and then treated with solid $NaHCO_3$ and saturated aqueous $NaHCO_3$. Evaporation of the washed (H_2O) organic solvent gave a residue (0.70 g) which was analyzed by GLC (see Table I) and at the same time subjected to preparative TLC (a 9:1 mixture of petroleum ether and ether was used as the eluent; elution was repeated six times). Extraction of the observed bands afforded the following: **15** (R_f 0.27, 0.045 g), **7** (R_f 0.38, 0.078 g), **6** (R_f 0.52, 0.012 g), **10** (R_f 0.65, 0.053 g), **1** (R_f 0.86, 0.045 g). GLC analysis of the crude products obtained by the same reaction of 1, but stopping after different reaction times, showed the same product composition within experimental error.

Reactions of the Epoxide 1 with Trichloroacetic Acid in Several Solvents. The reactions were carried out in anhydrous benzene, cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 in the following way. A solution of 1 (0.10 g, 0.53 mmol) in the solvent (10 mL) at 25 °C was treated with a 1 M solution of trichloroacetic acid in the same solvent (0.58 mL), stirred for 1 h at the same temperature, washed with saturated aqueous $NaHCO_3$ and water, and evaporated to dryness. The residue obtained, consisting of mixtures of monotrichloroacetates and rearrangement products, was hydrolyzed in the following way. The crude product was dissolved in freshly distilled THF (8 mL), treated with 1 M KOH in ethanol (2.5 mL), and then left 5 h at room temperature. Dilution with water, extraction with ether, and evaporation of the washed (H_2O) and dried ether extracts yielded a mixture of **12** and **13** together with **9**, **10**, and **15** which was analyzed by GLC (see Table II). Reaction of 1 in each solvent carried out under the same conditions, but stopping after a longer reaction time of contact with the acid, yielded the same product composition within the experimental error. Experiments showed that the diols **12** and **13** are stable under the saponification conditions and that the method of saponification used does not alter the stereoselectivity of the reactions.

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Registry No. 1, 7583-78-0; **4**, 1944-01-0; **5**, 4714-09-4; **6**, 81523-04-8; **7**, 81523-05-9; **8**, 81523-06-0; **9**, 13694-35-4; **10**, 946-33-8; **11**, 81523-07-1; **12**, 34492-10-9; **13**, 34492-11-0; **14**, 1467-15-8; **15**, 50648-70-9.

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Solubilization of Picric Acid by Reversed Micelles of a Double-Chained *N*-Methylpyridinium Chloride Amphiphile

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A spectrophotometric study was made of the binding of picric acid (HP) to reversed micelles of 17-(*N*-methyl-4-pyridinio)tritriacontane chloride (1) in cyclohexane and chloroform. Vapor pressure osmometric (VPO) measurements on solutions of 1 in cyclohexane at 50 °C indicate that the apparent number averaged aggregation number ($\bar{N}_{NA}$) is 16 down to surfactant concentrations of at least 3×10^{-3} *m*. Similar measurements (at 37 °C) on 1 in chloroform indicate a much smaller tendency to aggregate ($\bar{N}_{NA} \leq 2$ up to $[1] = 9 \times 10^{-2}$ *m*). When solutions of 1 in cyclohexane or chloroform were mixed with solutions of HP in the same solvents, a yellow color developed, and the features of the absorption spectrum can be reconciled with the formation of an ion pair. A similar ion pair is formed in solutions of HP in solvents of sufficient polarity and proton-acceptor ability. The spectral behavior of the HP indicator in cyclohexane at varying surfactant concentrations at 37 °C was quantitatively described in terms of simple association equilibria between HP and the surfactant aggregates. The VPO data were incorporated into this analysis. It appears that the results provide a quite realistic picture of the aggregation process, the mean aggregation number increasing with surfactant concentration and gradually reaching a limiting value. A similar treatment of the data for chloroform as the solvent also gave satisfactory results, but at low surfactant concentrations dissociation of the surfactant monomer should be invoked to rationalize the optical absorption measurements.

Many surfactant molecules are known to aggregate in apolar, aprotic solvents.[1-4] These aggregates, called reversed or inverted micelles, are stabilized by dipole–dipole and ion-pair interactions and are capable of solubilizing

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(1) Mittal, K. L., Ed. "Micellization, Solubilization and Microemulsions"; Plenum Press: New York, 1977; Vol. 1, 2.

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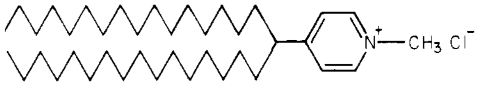
Table I. Spectral Features of Picric Acid in Different Media

solvent	λ_{max}, nm	solvent	λ_{max}, nm
cyclohexane	335[a]	2-*n*-butoxyethanol	358[b,c]
chloroform	335[a]	*n*-decanol	345, 410[d]
acetic acid	332[a]	5 *m* n-Bu_4NBr in H_2O	370[b,c]
1,4-dioxane	333[a]	1 *m* SDS in H_2O	350[f]
tetrahydrofuran	340[a]	0.8 *m* CTAB in H_2O	356, 420[e]
water	355[b]	0.01 *m* n-Bu_4NBr in 1,4-dioxane	373[b,c]
acetonitrile	373[b,c]	0.01 *m* CTAB in 1,4-dioxane	362[b,c]
dimethylformamide	378[b,c]	0.01 *m* imidazole in 1,4-dioxane	352[b,c]
pyridine	383[b,c]	chloroform containing 1	358[f]
2,2,2-trifluoroethanol	345[b,c]	cyclohexane containing 1	358, 425[g]

[a] No absorption in the 400–420 nm region. [b] Shoulder in the 400–420 nm region. [c] Spectrum resembles that in water. [d] Minimum at 385 nm. [e] Minimum at 410 nm. [f] Broad shoulder in the 400–420 region. [g] Minimum at 397 nm. Upon variation of the concentration of 1, an isosbestic point is observed at 295 nm.

considerable quantities of water in their hydrophilic cavities. These water pools provide a unique medium for substrate solubilization and interactions.[5,6] The physicochemical nature of these aggregates has been investigated in a variety of ways and the use of indicator dyes is rather frequent.[7-12] In order to further establish the utility of such indicators, we have studied the behavior of picric acid (HP) in cyclohexane and chloroform solutions of 17-(*N*-methyl-4-pyridinio)tritriacontane chloride (1), a double-chained amphiphile with a positively charged head group.[13]



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Results and Discussion

Vapor pressure osmometric (VPO) measurements on solutions of 1 in cyclohexane at 50 °C indicate the formation of aggregates (reversed micelles) with an apparent number averaged aggregation number ($\bar{N}_{NA}$) of about 16 over a wide concentration range (Figure 1).[14] Comparison with the iodide counterpart of 1 ($\bar{N}_{NA} \approx 13$)[13c,d] indicates that there is a small increase in $\bar{N}_{NA}$ upon replacing the bulky iodide by the smaller chloride counterion. Changing the solvent from cyclohexane to chloroform leads to a dramatic reduction in the size of the aggregates (Figure 1; $\bar{N}_{NA} \leq 2$ at 37 °C). Only very small aggregates are formed, most likely dimers and triple ions. The increase in solvent polarity and hydrogen bonding ability may be invoked to explain this large solvent effect.

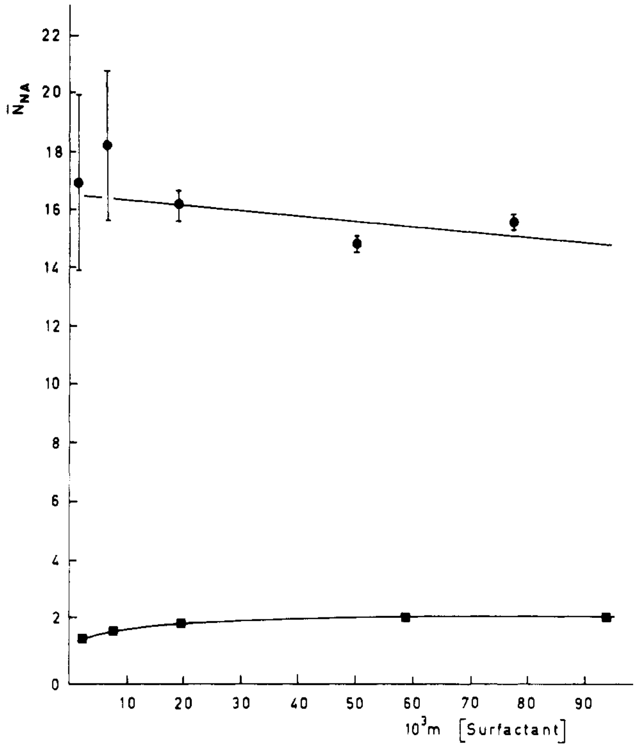

Figure 1. Apparent number-averaged aggregation number (N_{NA}) as a function of the concentration of 1: ●, in cyclohexane at 50 °C; ■, in chloroform at 37 °C.

A 0.1 *m* (*m* = molal) solution of 1 in cyclohexane was found to solubilize ca. 10 μL of water/mL of solution. The near-infrared spectrum of this solution exhibited two distinct peaks at 5190 and 5115 cm^{-1} and a small shoulder at ca. 5270 cm^{-1}. These absorptions should be assigned to ν_2 (scissoring) and ν_3 (asymmetric stretching) combination modes.[15-17] The shoulder can be attributed to free water dispersed in the organic solvent.[15] The two peaks are attributable to hydrogen-bonded water in the water pool.[15-17] The peak at 5190 cm^{-1} is close to that found in pure water (5211 cm^{-1}),[15] and the other one at 5115 cm^{-1} is appreciably shifted and should be assigned to water molecules interacting strongly with the ionic head groups of the surfactant.

Solutions of 1 in cyclohexane and chloroform are colorless, as are solutions of picric acid (HP) in these solvents. When the solution of 1 is mixed with that of HP, a yellow

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(3) Eicke, E. F. *Top. Curr. Chem.* **1980**, *87*, 85.

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(5) Menger, F. M.; Donohue, J. A.; Williams, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 286.

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(8) Nome, F.; Chang, S. A.; Fendler, J. H. *J. Chem. Soc., Faraday Trans. 1*, **1976**, *72*, 296.

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(10) Tamura, K.; Schelly, Z. A. *J. Am. Chem. Soc.* **1979**, *101*, 7643.

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(12) Tamura, K.; Schelly, Z. A. *J. Am. Chem. Soc.* **1981**, *103*, 1013, 1018 (1981).

(13) The aggregation behavior of the corresponding iodide has already been examined in water as well as in apolar organic solvents: (a) Sudhölter, E. J. R.; Engberts, J. B. F. N.; Hoekstra, D. *J. Am. Chem. Soc.* **1980**, *102*, 2467. (b) Sudhölter, E. J. R.; de Grip, W. J.; Engberts, J. B. F. N. *Ibid.* **1982**, *104*, 1069. (c) Sudholter, E. J. R.; Engberts, J. B. F. N. *J. Phys. Chem.* **1982**, *86*, 263; (d) Sudhölter, E. J. R. Ph. D. Thesis, University of Groningen, 1981.

(14) There is a slight decrease of $\bar{N}_{NA}$ at high concentrations, possibly as a result of intermolecular repulsive interactions. The measurements were performed at 50 °C to prevent solubility problems.

(15) Sunamoto, J.; Hamada, T.; Seto, T.; Yamamoto, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 583.

(16) Seno, M.; Araki, K.; Shiraishi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 899.

(17) Bonner, O. D.; Choi, Y. S. *J. Phys. Chem.* **1974**, *78*, 1723, 1727.

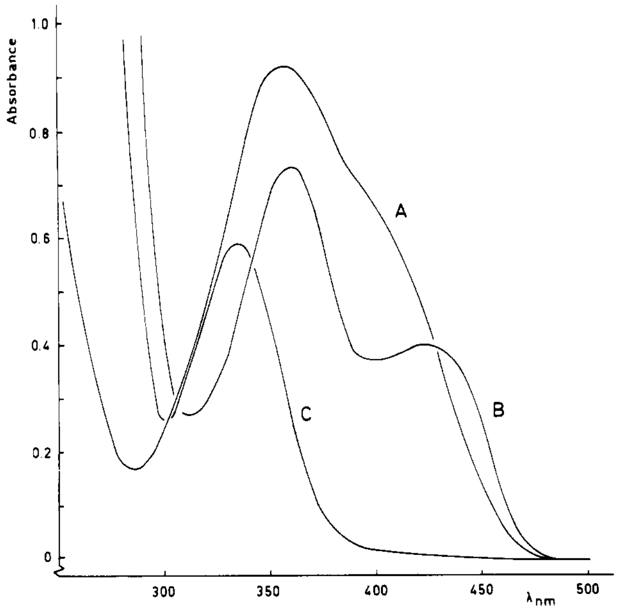

Figure 2. Optical absorption spectra of picric acid in water (A), in cyclohexane in the presence of 1 (B), and in cyclohexane (C).

coloration was observed, indicative for dissociation of HP in the presence of the surfactant. In order to understand the nature of the dissociative state of HP in these solutions, we studied the spectral properties of HP in the UV-visible region in a variety of media (Table I).[18] In polar solvents like water, DMF, and pyridine, HP shows an intense peak in the region λ_{max} = 355–385 nm and a shoulder at longer wavelengths (spectrum A, Figure 2). It appears that HP is completely dissociated into free ions in these solvents. In apolar solvents like benzene,[12] 1,4-dioxane, and cyclohexane, HP is colorless and exhibits a peak of moderate intensity around 335 nm (spectrum C, Figure 2). These solutions turn yellow upon addition of 1 or other surfactants like cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) and/or small quantities of water. Now an intense peak is observed around 358 nm as well as a broad shoulder in the 400–435-nm region, and in some cases even a distinct absorption maximum can be distinguished between 410 and 420 nm (spectrum B, Figure 2). A similar spectrum is also observed in *n*-decanol and in aqueous solutions of CTAB (0.8 *m*) and SDS (1 *m*). We suggest that HP forms ion pairs in these media. Spectral measurements in 1,4-dioxane–H_2O as a function of water concentration support this conclusion. In anhydrous dioxane, HP shows a peak at 335 nm and does not absorb above 390 nm (spectrum C, Figure 2). Upon gradual addition of water the solution turns yellow, and an absorption band in the 400–430-nm region appears. Up to about 90% (w/w) dioxane–H_2O this spectrum resembles spectrum B shown in Figure 2. Upon further addition of water, the spectral features become similar to spectrum A (Figure 2). The gradual changes of the spectrum from C to B to A and the plot of $\bar{\epsilon}_{420}$ against the mole fraction of water (n_{H_2O}) as shown in Figure 3 are consistent with the dissociation of HP into, ultimately, free ions through the various stages of ion-pair formation.[19] We can only speculate on the exact identity of the ion pair formed from HP in cyclohexane or chloroform in the presence of 1. Probably the proton is bound to one or more water molecules near the

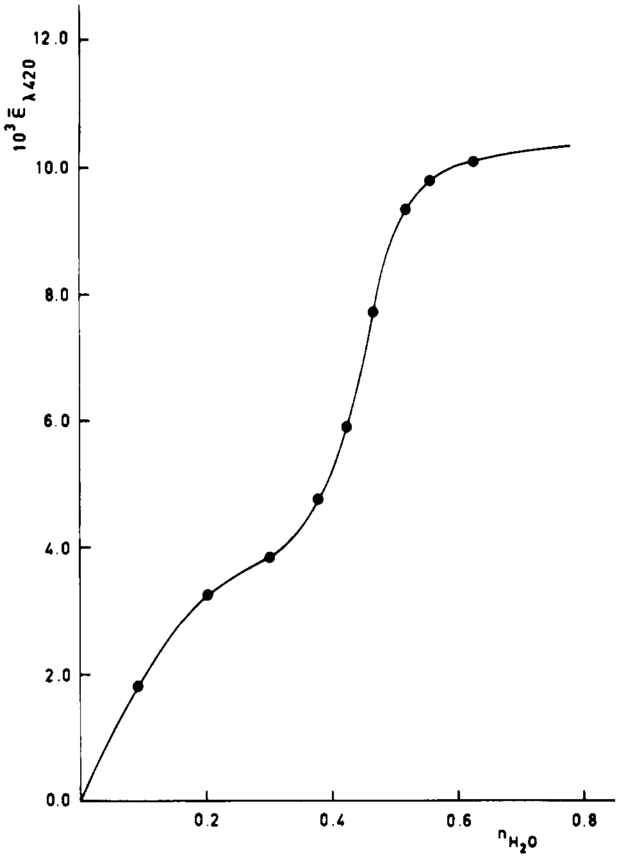

Figure 3. Picric acid in 1,4-dioxane–H_2O at 37 °C. Plot of $\bar{\epsilon}_{420}$ vs. the mole fraction of water.

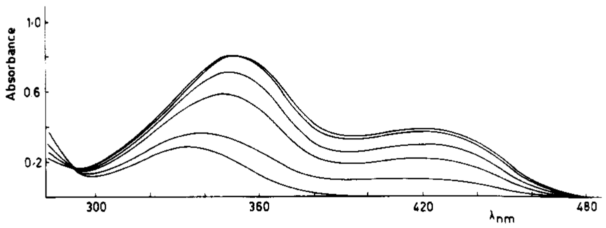

Figure 4. Optical absorption spectra of picric acid (7 × 10^{-5} *m*) in cyclohexane at varying concentrations of 1 (37 °C).

ionic head group of 1. The structure may then be formulated as $S(H_2O)_xH^+P^-$ (S = surfactant), which will be abbreviated to SH^+P^- in the following discussion. Stabilization of the ion pair may be achieved by pyridinium cation–picrate anion interactions (decreasing the basicity of P^-)[20] and hydrogen bonding between SH^+ and chloride ions.[21]

Unfortunately, we were unable to observe a relaxation process by stopped-flow techniques upon mixing a solution of HP with a solution of 1. We suggest that HP is solubilized at the interface where the anion P^- interacts with the pyridinium head group and hence does not move into the water pool.

The spectral behavior of HP in cyclohexane containing 1 was studied as a function of surfactant concentration at 37 °C. At a fixed concentration of HP (7 × 10^{-5} *m*) the absorptions at 358 and 420 nm increase simultaneously and finally attain a limiting value. An isosbestic point is observed at 290 nm (Figure 4). Plots of $\bar{\epsilon}_{app}$ at 358 and 420

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[18] Our results are largely consistent with and extend those performed previously by Schelly et al.[12]

[19] Robinson, B. H. In "Proton Transfer Reactions"; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London; 1975, p 121.

[20] The yellow color of the solution does not disappear after addition of a tenfold excess of hydrochloric acid.

[21] Compare: (a) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 1233. (b) Taylor, R. P.; Kuntz, I. D., Jr. *Ibid.* **1972**, *94*, 7963.

Table II. Optical Absorption Behavior of Picric Acid[a] in Solutions of 1 in Cyclohexane at 37 °C

10^4[1], m	$10^{-3}\bar{\epsilon}_{app}$(420 nm), m^{-1} cm^{-1}	$10^{-4}K_{calcd}$,[b] m^{-1}	n_{calcd}[c]	n_{calcd}[d]
0.143	1.39	20.8	0.94	0.89
0.413	3.14	8.75	1.17	1.08
0.810	4.29	4.16	1.63	1.46
1.236	4.84	2.96	2.13	1.88
1.401	5.08	2.92	2.26	1.97
2.437	5.65	2.16	3.33	2.78
2.834	5.72	1.91	3.76	3.12
3.285	5.91	1.93	4.10	3.31
4.081	6.02	1.69	4.90	3.87
7.844	6.17	0.98	8.60	6.75
19.670	6.17	0.37	21.7	17.0
112.60	7.05			

[a] [HP] = 7.2×10^{-5} m. [b] Calculated from eq 2 by using eq 3-5 and $\epsilon_\infty = 7.05 \times 10^3$ m^{-1} cm^{-1}. [c] Calculated from eq 7 by using $K = 2.55 \times 10^5$ m^{-1} obtained by extrapolating the plot of K_{calcd} vs. [S$_0$] to [S$_0$] = 0. [d] Calculated from eq 7 by using [S$_0$] values and $K = 1.33 \times 10^5$ m^{-1} (from VPO: $\bar{N}_{NA} = 17$, [S$_0$] = 1.97×10^{-3} m).

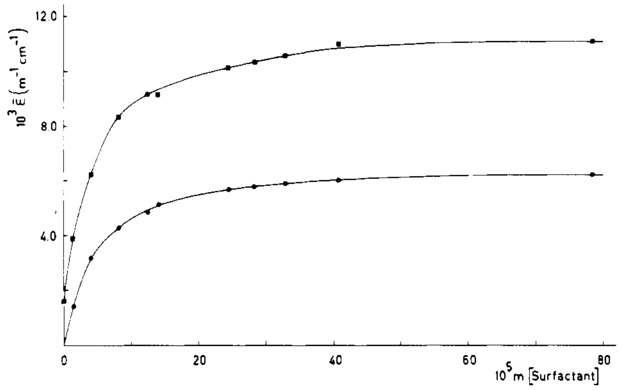

Figure 5. Plots of $\bar{\epsilon}_{app}$ vs. [S$_0$] (cyclohexane solvent, 37 °C): ●, at 420 nm, ■, at 358 nm.

nm against surfactant concentration are shown in Figure 5.[22] These observations indicate that HP is progressively dissociated with increasing surfactant concentration and that a *single* species (most likely the ion pair) is responsible for the increase in absorption at 358 and 420 nm.

The plot of $\bar{\epsilon}_{app}$ at 420 nm vs. surfactant concentration was analyzed in terms of eq 1.

$$S + HP \overset{K'}{\rightleftharpoons} S\cdots HP \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+P^- \qquad (1)$$

Assuming that $k_1 \gg k_{-1}$ and [S] ≈ [S$_0$], it can be easily shown that a plot of $\bar{\epsilon}_{app}^{-1}$ vs. $[S_0]^{-1}$ will give a straight line with a slope of $(K\epsilon_\infty)^{-1}$, where $K = K'k_1/k_{-1}$), and an intercept of ϵ_∞^{-1}. Herein, [S$_0$] is the surfactant concentration, $\bar{\epsilon}_{app}$ the apparent molar extinction coefficient given by OD/[HP$_0$] (OD = optical density), and ϵ_∞ is the molar extinction coefficient of the associate in the plateau region, where HP was found to obey Beer's law. The plot is shown in Figure 6, and the value of ϵ_∞ (6.65×10^3 m^{-1} cm^{-1}) is in satisfactory agreement with the observed value of 7.05×10^3 m^{-1} cm^{-1}. However, further analysis does not support the assumed 1:1 interaction between HP and 1. Since

$$K = [SH^+P^-]/[HP][S] \qquad (2)$$

$$[SH^+P^-] = OD_{obsd}\epsilon_\infty^{-1} \qquad (3)$$

$$[HP] = [HP_0] - [SH^+ \cdot P^-] \qquad (4)$$

$$[S] = [S_0] - [SH^+P^-] \qquad (5)$$

the values of K can be calculated from the individual data.

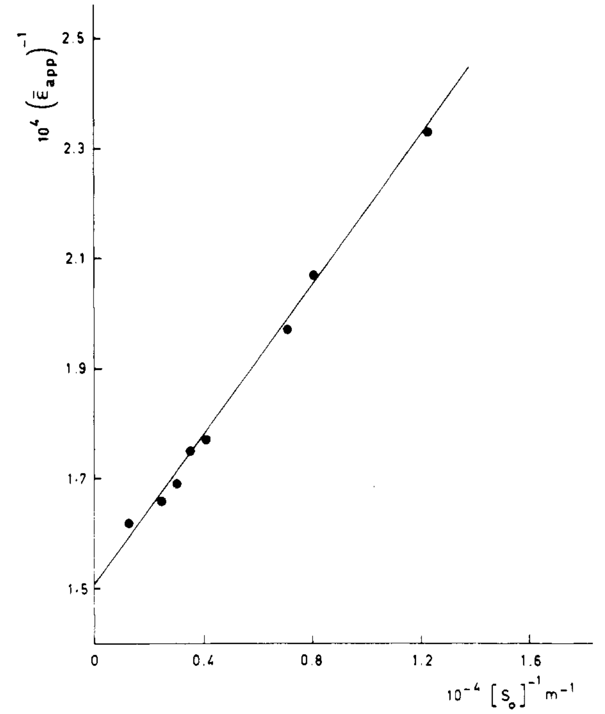

Figure 6. Plot of $(\bar{\epsilon}_{app})^{-1}$ vs. $[S_0]^{-1}$ for solutions of HP in cyclohexane in the presence of 1 (37 °C).

The results, listed in Table II, show that K decreases with increasing surfactant concentration. This apparent discrepancy can be readily understood in terms of surfactant aggregation to form reversed micelles. A semiquantitative analysis can be made of the binding of HP to these aggregates based on the following assumptions: (i) the association of 1 is so strong that in the surfactant concentration range used for the binding of HP the monomer concentration can be neglected; (ii) there is a 1:1 interaction between HP and the reversed micelles, and the binding constant is independent of $\bar{N}_{NA}$; (iii) eq 3 holds for all $\bar{N}_{NA}$ values; that is, the molar extinction coefficient ϵ_∞ does not vary significantly with the size of the surfactant aggregate.

Support for the latter assumption is found in recent work by Schwartz et al.[23] and in our observation that ϵ_∞ is very similar for cyclohexane ($\epsilon_\infty = 9.0 \times 10^3$ M^{-1} cm^{-1}), and chloroform ($\epsilon_\infty = 8.8 \times 10^3$ M^{-1} cm^{-1}) as the solvent.

For the binding of HP to the reversed micelle (S$_n$) we can write

$$S_n + HP \overset{K}{\rightleftharpoons} S_nH^+P^-$$

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[22] The linear plot of $\bar{\epsilon}_{358}$ vs. $\bar{\epsilon}_{420}$ has an intercept in accord with $\bar{\epsilon}_{358}$ at zero surfactant concentration.

$$K = \frac{[S_nH^+P^-]}{[S_n][HP]} = \frac{[S_nH^+P^-]}{[HP](S_0n^{-1} - [S_nH^+P^-])} \qquad (6)$$

and we obtain

$$S_0n^{-1} = \frac{[S_nH^+P^-]}{K[HP]} + [S_nH^+P^-] \qquad (7)$$

In these equations, n stands for the aggregation number of the reversed micelle. The value of K at $n = 1$ ($2.55 \times 10^5\ m^{-1}$) was obtained by extrapolating the plot of K_{calcd} vs. [S] to infinite dilution ($[S_0] = 0$). The n values were then calculated from the known $[S_0]$ values by using eq 7 (Table II). For comparison, a set of n values was calculated from $[S_0]$ values and the K value ($1.33 \times 10^5\ m^{-1}$) obtained from the $\bar{N}_{NA}$ value ($\bar{N}_{NA} = 17$, $[S_0] = 1.97 \times 10^{-3}\ m$) as determined by VPO measurements (Table II). On consideration of the fact that the VPO measurements were carried out at 50 °C where $\bar{N}_{NA}$ is expected to be smaller[13c,d] than at 37 ° C,the two sets of aggregation numbers appear to present a fairly good physical picture of the aggregation behavior.

A similar analysis was carried out with the data obtained in the chloroform solutions. Somewhat surprisingly, a plot of $\epsilon_{app}{}^{-1}$ vs. $[S_0]^{-1}$ was not linear. In fact, two straight lines were obtained with a break point at about $[S_0] = 9 \times 10^{-4}\ m$ (Figure 7). Extrapolation of both lines provides two ϵ_∞ values of $6.25 \times 10^3\ m^{-1}\ cm^{-1}$ and $13.2 \times 10^3\ m^{-1}\ cm^{-1}$, respectively. The second is close to the experimental value ($\epsilon_\infty = 13.1 \times 10^3\ m^{-1}\ cm^{-1}$). The ratio of the two ϵ_∞ values suggests that the surfactant is dissociated at low concentrations in chloroform. VPO measurements on the iodide counterpart of 1 in dichloromethane strongly support this conclusion.[13c]

Employing $\bar{N}_{NA} = 1.3$ ($[S_0] = 1.96 \times 10^{-3}\ m$; VPO), we now calculate $K = 7.48 \times 10^2\ m^{-1}$. The n values calculated with this K and a variety of $[S_0]$ values are listed in Table III. These n values are again in reasonable agreement with those obtained from VPO measurements (Figure 1), provided that $[S_0] > 9 \times 10^{-4}\ m$. Below this surfactant concentation, appreciable dissociation of 1 occurs, and the treatment in terms of eq 2–5 is expected to break down. Nevertheless, the analysis provides n values around 0.5 ± 0.1, consistent with the assumed dissociation of 1.

In conclusion we note that our observations in the two solvent systems shed further light on some uncertainties in Schelly's description[12] of the solubilization of picric acid in reversed micelles of Aerosol-OT in benzene. We observe that picric acid dissociates into ion pairs even at very low surfactant concentrations; in fact, it dissociates in practially all systems that provide a suitable proton acceptor. This situation may be contrasted with Schelly's conclusion[12] that "only a small fraction of the micelles are eligible to accommodate picric acid in their polar interior". Furthermore, an analysis in terms of a monomer concentration increasing with surfactant concentration and finally reaching a limiting value appears artificial. Instead, the behavior may be better described by assuming an increasing aggregation number that reaches a limiting value. Interestingly, the value of K ($2.55 \times 10^5\ m^{-1}$) defined in terms of eq 1 for solubilization of HP in cyclohexane solutions of 1 is of the same order of magnitude as that found by Schelly[12] ($K = 6.8 \times 10^5\ M^{-1}$) for solubilization of HP in solutions of reversed micelles of Aerosol-OT in benzene.

Our results further substantiate the notion that equilibrium studies employing indicator dyes like picric acid may yield useful information about the physicochemical properties of reversed micelles. However, care should be taken in the interpretation of the data particularly at low surfactant concentrations where the aggregation process is not well-defined.

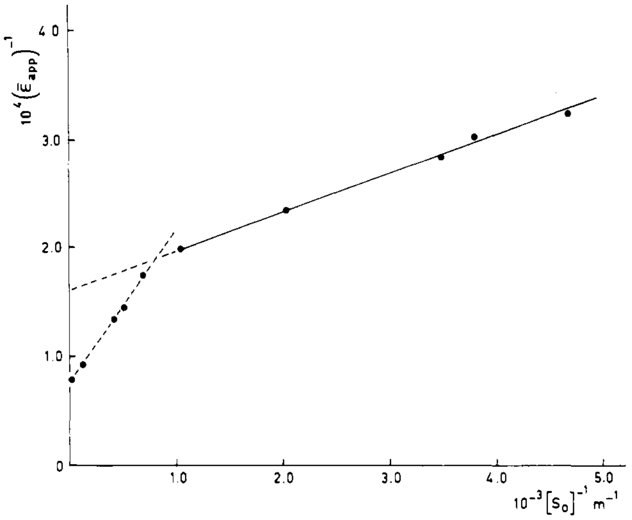

Figure 7. Plot of $(\bar{\epsilon}_{app})^{-1}$ vs. $[S_0]^{-1}$ for solutions of HP in chloroform in the presence of 1 (37 °C).

Table III. Optical Absorption Behavior of Picric Acid[a] in Solutions of 1 in Chloroform at 37 °C

10^4[1], m	$10^{-3}\bar{\epsilon}_{app}$ (420 nm), m^{-1} cm^{-1}	$10^{-3} \times K_{calcd}$,[b] m^{-1}	n_{calcd}[c]
0.631	1.44		
0.837	1.75		
0.935	1.87		
2.163	3.09		
2.635	3.31		
2.875	3.53		
4.931	4.27		
9.598	5.03	0.66	1.15
14.64	5.74	0.54	1.37
19.52	6.88	0.57	1.30
23.99	7.46	0.55	1.33
94.66	10.9	0.55	1.36
920.1	12.7	0.37	2.01
1020	13.1		

[a] $[HP] = 5.4 \times 10^{-5}\ m$. [b] Calculated from eq 2 by using eq 3–5 and $\epsilon_\infty = 13.1 \times 10^3\ m^{-1}\ cm^{-1}$. [c] Calculated from eq 7 using $[S_0]$ values and $K = 7.48 \times 10^2\ m^{-1}$ (from VPO: $\bar{N}_{NA} = 1.3$, $[S_0] = 1.96 \times 10^{-3}\ m$).

Experimental Section

Materials. The amphiphile 1 was prepared according to the method described previously[24] [mp [mp 68 °C (lit.[24] mp 64 °C)]. Picric acid ("pro-analysi"; VCB, Brussels) was crystallized three times from methanol and dried in vacuo. All solvents were "pro-analysi" (Merck). All solutions were made up by weight and concentrations are expressed in molal concentrations (moles per kilogram, m), unless otherwise stated.

VPO Measurements. The VPO measurements were performed at 37 °C in chloroform and at 50 °C in cyclohexane on a Hewlett-Packard Model 302B osmometer equipped with a variable temperature controller, Model 18575A. The apparatus was calibrated according to the manufacturer's instructions by using triphenylphosphine ($CHCl_3$) and biphenyl ($c\text{-}C_6H_{12}$).

Optical Absorption Measurements. The optical absorption spectra were taken at 37 °C on a Cary 210 spectrophotometer (automatic base-line correction) equipped with a thermostated

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(24) Sudhölter, E. J. R.; Engberts, J. B. F. N.; de Jeu, W. H. *J. Phys. Chem.* **1982**, in press.

cell compartment. All measurements were made in the same set of 1-cm quartz cells. Samples were thermostated at least 15 min before recording the spectra. Near-infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer at ca. 40 °C. Cells with NaCl windows (optical path length of 10 mm) were used. All spectral measurements were performed at least in duplicate.

Acknowledgment. We thank Mr. J. Ebels for carrying out the VPO measurements.

Registry No. 1, 80243-88-5; picric acid, 88-89-1.

Carbanions. 21. Reactions of 2- and 3-*p*-Biphenylylalkyl Chlorides with Alkali Metals. Preparation of Labile Spiro Anions[1,2]

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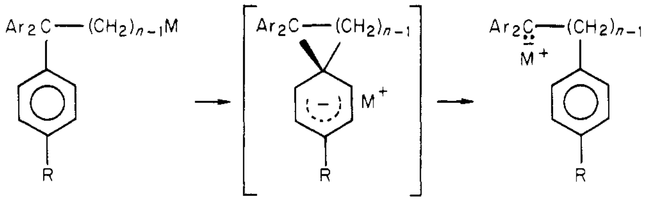
The present work was undertaken to see if (3-*p*-biphenylylpropyl)- and (2-*p*-biphenylethyl)cesium cyclize like (4-*p*-biphenylbutyl)cesium to stable spiro anions. Reaction of 1-*p*-biphenylyl-3-chloropropane (**5**) with Cs–K–Na alloy in THF at −75 °C gave, under the optimum conditions found, 36% of 7-phenylspiro[3.5]nona-6,5-dien-5-yl anion (**8**) besides 3-*p*-biphenylylpropyl (**7**), 1-*p*-biphenylylpropyl (**9**), and *p*-biphenylylmethyl (**10**) anions, according to the products of carbonation. The spiro anion **8** (Cs^+ as the counterion) has a half-life of about 13 min at −75 °C. In contrast, **5** reacts with lithium to give predominantly (3-*p*-biphenylylpropyl)lithium. Reaction of 1-*p*-biphenylyl-2-chloroethane with Cs–K–Na alloy gave no appreciable spiro anion under conditions which were successful with **5**. In the reaction of 1-*p*-biphenylyl-2-chloro-2-methylpropane (**28**) with Cs–K–Na alloy the α-*gem*-dimethyl group accelerates [1,2] migration of the *p*-biphenylyl group to give products similar to those from 2-*p*-biphenylyl-1-chloro-2-methylpropane (**24**); however, the expected intermediate spiro anion **26** was undetectable by the carbonation technique. With both α- and β-*gem*-dimethyl groups, 2-*p*-biphenylyl-3-chloro-2,3-dimethylbutane (**41**) reacts with Cs–K–Na alloy to give 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-5,7-dien-4-yl anion (**43**) and 2-*p*-biphenylyl-1,1,2-trimethylpropyl anion (**42**) in about a 2:1 ratio according to the results of carbonation. The open anion **42** and the spiro anion **43** appear to be in mobile equilibrium (Cs^+ as the counterion) with half-lives of about 22 min in THF at −75 °C. With lithium as the counterion, only the open product (2-*p*-biphenylyl-1,1,2-trimethylpropyl)lithium (**50**) was detectable by carbonation.

Spiro anions **1** have been suggested as intermediates or transition states in [1,*n*] sigmatropic migrations of aryl groups in organoalkli metal compounds.[3] The preparation of the stable spiro anion **2a** by reaction of 4-chloro-1-*p*-biphenylylbutane with alkali metals[4] lends support to the interpretation of spiro anions as intermediates as does also the preparation[5] of the nitrogen analogue **2b**. Yet reaction of spiro[2.5]octa-4,7-diene with potassium amide in liquid ammonia at −65 °C or with *n*-butyllithium in tetrahydrofuran–hexane at room temperature gave no observable spiro anion **3a** but only products in which the cyclopropane ring was open. The related species[6a] **4** was, however, stable in liquid ammonia even at −30 °C. These results were explained on the basis that the product from cyclopropyl ring opening of **3a** contains an aromatic benzene ring and is therefore readily formed whereas that from similar ring opening of **4** contains a nonaromatic cyclooctatetraene ring. Attempts to prepare the nitrogen analogue **3b** were similarly unsuccessful and gave only the product of cyclopropyl ring opening, the [2-(4-pyridyl)ethyl]magnesium reagent,[5b] as did similar attempts to prepare the *gem*-dimethyl analogue[5c] **3c**. The present work was undertaken to probe the question as to what anions, containing only carbon and hydrogen, related in structure to **1** and **3a** may be stable species.



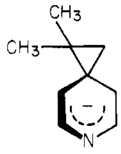
1

2a

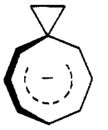
2b

3a

3b



3c



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Results and Discussion

Reactions of 1-*p*-Biphenylyl-3-chloropropane (5) with Alkali Metals. In view of the successful preparation of the spiro anion **2a**, the preparation of the lower homologue **8** by reaction of 1-*p*-biphenylyl-3-chloropropane (**5**) with Cs–K–Na alloy was studied (see Scheme I) with the results reported in Table I. For reactions run for a few minutes in tetrahydrofuran (THF) at −75 °C and then carbonated, the acidic products which were volatile as

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(1) Based upon the Ph.D. Thesis of P.-C. L., Georgia Institute of Technology, Sept 1977, which should be consulted for more complete experimental details.

(2) A preliminary account of a portion of this work has appeared: Bertrand, J. A.; Grovenstein, E.; Lu, P.-C.; VanDerveer, D. *J. Am. Chem. Soc.* **1976**, *98*, 7835–7836. This publication should be consulted for some of the properties of 14, 41, and 44.

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