Charge-Transfer Interactions in Nonpolar Solvents in the Presence of Surfactant Aggregates. Ethylpyridinium Bromide Charge-Transfer Complexes in Methylene Chloride Solutions of Dodecylammonium Propionate

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Abstract: Microscopic polarities in the cavities of dodecylammonium propionate (DAP) aggregates in methylene chloride, containing different amounts of water, have been determined spectrophotometrically using the longest wavelength absorption maxima of 1-ethyl-4-carbomethoxypyridinium iodide. The obtained Z values increase linearly with increasing concentrations of solubilized water. Using ^{1}H nmr, water and ethylpyridinium bromide were shown to be localized in the polar cavities of DAP aggregates in methylene chloride. The dissociation constant for the interionic charge-transfer complex of ethylpyridinium bromide, K_d, at given water concentrations, increases with increasing DAP concentrations up to a maximum, after which it remains constant. In 0.20 M DAP in methylene chloride K_d increases logarithmically with increasing concentrations of solubilized water, as expressed in terms of Z values. The increase of K_d values with increasing water concentrations is paralleled by a decrease in the binding constants between the DAP aggregates and ethylpyridinium bromide. The significance of these results is discussed.

Surfactant aggregates in nonpolar solvents are increasingly being utilized as catalytic media for organic and inorganic reactions.[1-7] Significant rate enhancements, with respect to both the bulk apolar solvent and water, have been observed for the mutarotation of 2,3,4,6-tetramethyl-α-D-glucose,[1] for the decomposition of Meisenheimer complexes,[2] for the hydrolysis of 2,4-dinitrophenyl sulfate,[3] for aquation and electron transfer reactions of chromium(III) and cobalt(III) complexes,[4] for the trans-cis isomerization of bis(oxalato)diaquochromate(III) ion,[5] and for ligand exchange reactions at hemin[6] and at aquocobalamin.[7] The observed rate enhancements have been rationalized in terms of substrate solubilization in the polar interior of surfactant aggregates where favorable binding and orientation, proton transfer, and enhanced water activity reduce the overall free energy requirements for the reaction. The nature of the hydrophilic cavity and that of water entrapped therein is clearly of paramount importance in understanding the catalytic mechanisms. Examination of the absorption spectra of interionic charge-transfer complexes in the polar environment of surfactant aggregates in nonpolar solvents provides information on the microscopic polarities of the immediate surrounding of the probe and hence on the nature of the cavity. Additionally, stabilities of charge-transfer complexes are likely to be affected by surfactant aggregates. Our selection of probes was dictated by solubility considerations as well as by the availability of well-documented information.[8-10] The marked solvent sensitivity of the alkylpyridinium salts, whose ground states are ionic and whose excited states are neutral, led Kosower and his coworkers to utilize 1-ethyl-4-carbomethoxypyridinium iodide as the substrate to develop the microscopic solvent polarity parameter Z.[8] Groundwork has also been laid on characterization of effective polarities of aqueous micellar surfactants using charge-transfer interactions of alkylpyridinium ions.[11-13] The dissociation constants of interionic ethylpyridinium bromide charge-transfer complex was found to decrease logarithmically with decreasing bulk dielectric constant.[14] Combining nmr and absorption spectroscopic data on 1-ethyl-4-carbomethoxypyridinium iodide and ethylpyridinium bromide the present paper reports that these probes are solubilized in the interior of dodecylammonium propionate aggregates in methylene chloride where they form charge-transfer complexes whose stabilities are markedly altered by the amount of entrapped water.

Experimental Section

Reagent grade 1-ethyl-4-carbomethoxypyridinium iodide and ethylpyridinium bromide (Eastman) were used as received. Methylene chloride (Aldrich Reagent Grade) was dried by and stored over Linde 4A molecular sieve. The preparation, purification, and characterization of dodecylammonium propionate, DAP, have been described.[15] The critical micelle concentration of DAP in methylene chloride is 3.4×10^{-2} M.[16]

Since solubilized water affects significantly the results, special care was taken to exclude moisture during the preparation of stock solutions. The water content of methylene chloride and of methylene chloride stock solutions was determined and monitored for each set of experiments by gas-liquid-partition chromatography. A Hewlett-Packard 7620A gas chromatograph, equipped with a 6 ft long 0.25 in. i.d. stainless steel Porapak Q (Waters Associates) column was used. The temperature of the column was maintained isothermally at 100°, that of the injection block and the detector at 200°C; helium was used as a carrier and its flow rate was 45 ml/min. The reported water concentrations in the different solutions were prepared by dilution and verified by gas-liquid-partition chromatography using appropriate calibrations.

Absorption maxima of 8.0×10^{-5} M 1-ethyl-4-carbomethoxypyridinium iodide in the different systems were determined in the thermostated cell compartment of a Cary-118C spectrophotometer at a scan rate of 0.05 nm/sec and 2.0 nm/in. There was a small (<2 nm) time-dependent shift in the absorption maxima. Values of absorption maxima, used in calculating solvent polarity parameter Z, were taken at zero time by extrapolations from plots of λ_{max} *vs.* time. Z values were calculated from $Z = 2.859 \times 10^5/\lambda_{max}$ in Å[8] and are accurate to ±0.02. Absorbancies of ethylpyridinium bromide ($(1.4\text{-}38)10^{-3}$ M) in the different systems were determined at 290 nm using 0.10-cm cells in the thermostated cell compartment of the Cary-118C spectrophotometer. The temperature for all absorbance measurements was maintained at 25.0 ± 0.05° by water circulation from a precision thermostat.

The ^{1}H nuclear magnetic resonance spectra were obtained on a modified Varian Associates HA-100 spectrometer with a Hewlett-Packard Model 200 ABR audio oscillator and frequency counter. All spectra were determined at ambient probe temperature (*ca.* 34°) on freshly prepared solutions in methylene chloride and were measured relative to neat tetramethylsilane (TMS) contained in a Wilmad 520-2 internal coaxial capillary tube. Chemical shifts were obtained from spectra recorded at 500 MHz sweep widths and are given in hertz or on the δ scale in ppm (δ_{TMS} 0 ppm) relative to the "external" TMS. Individual measurements are accurate to ±0.002 ppm. The resonance frequency of solvent CH_2Cl_2 rela-

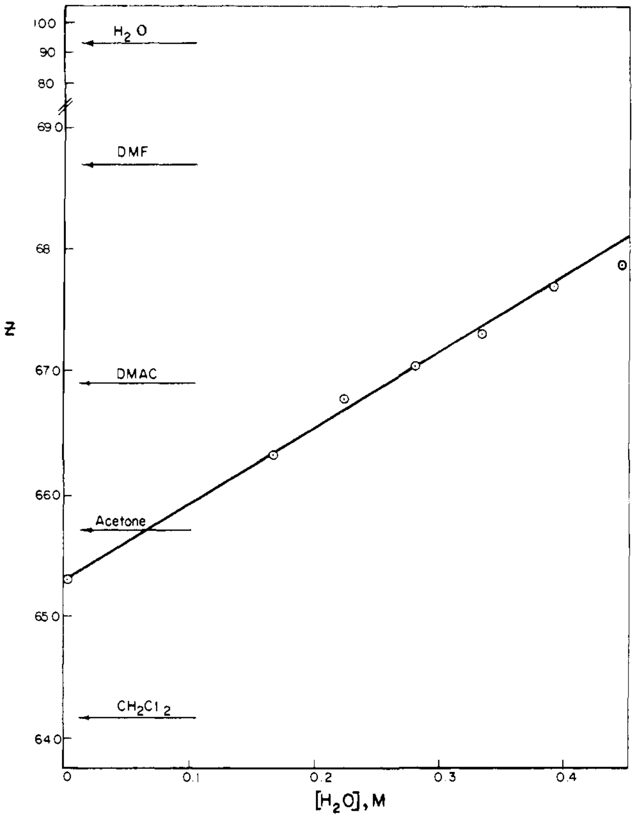

Figure 1. Plot of determined Z values in 0.20 M DAP in methylene chloride *vs.* solubilized water concentrations. Z values of some solvents are indicated by arrows.

tive to the standard exhibited a negligible shift over the surfactant and solubilizate concentration ranges employed and consequently bulk susceptibility corrections were not applied. However, they are predictably small and would not affect the obtained results appreciably.

Results and Discussion

***Z* Values of the Cavities of DAP Aggregates.** 1-Ethyl-4-carbomethoxypyridinium iodide is an ideal probe for determining effective polarities of the interior of DAP aggregates in methylene chloride. The ionic nature and high-water solubility of this probe[8] ensure its predominent localization in the polar interior of the surfactant aggregates. Its structural similarity to ethylpyridinium bromide renders it a good model for the interionic charge-transfer interactions of the latter. Equally importantly, 1-ethyl-4-carbomethoxypyridinium iodide has been extensively used for the determination of Z values for a large number of solvents.[8] Z values of methylene chloride solutions of DAP, containing different amounts of solubilized water, were calculated from the determined longest wavelength absorption maxima of 1-ethyl-4-carbomethoxypyridinium iodide (see Experimental Section). A good linear correlation is obtained between the determined Z values in 0.20 M DAP in methylene chloride and the concentration of solubilized water entrapped therein (Figure 1). It is seen that at all concentrations of solubilized water, the microscopic environment of the probe is more polar than that of neat methylene chloride. Increasing the amount of solubilized water, as expected, results in an increase of the apparent polarity of the cavity. Although solubility restrictions did not allow the examination of microscopic polarities of larger volumes than 0.44 M surfactant entrapped water, the range of Z values in the present system is considerably smaller and indicates lower apparent polarities than those obtained using vitamin B_{12} as a probe in DAP solubilized water in benzene.[6] This is not unexpected, since we have demonstrated that solubilization of such a large molecule as vitamin B_{12} results in the enlargement of surfactant aggregates, containing *ca.* 300 monomers,[6] in the cavities of which appreciable variation of effective solvent polarities is feasible. Conversely, aggregates of DAP in methylene chloride, even in the presence of alkylpyridinium ions, are likely to remain relatively small and hence they impose effective polarity restrictions on the entrapped water.

^{1}H Nmr Investigations of Water and Ethylpyridinium Bromide Solubilization. Dynamic interactions of water and ethylpyridinium bromide with DAP have been investigated by ^{1}H nmr spectroscopy. Two different types of experiments were performed. In the first set of experiments, chemical shifts of magnetically discreet protons of 0.20 M DAP were determined at different concentrations of added solubilizates. In the second set of experiments, chemical shifts of ethylpyridinium bromide protons were followed as functions of DAP concentrations in the presence of different amounts of water. These latter data were utilized for calculating the surfactant aggregate–solubilizate binding constant.

Table I summarizes the chemical shifts, δ_0, of 0.20 M DAP protons in the absence of ethylpyridinium bromide, at different concentrations of solubilized water. Plots of the observed chemical shifts of the magnetically discreet protons *vs.* the concentration of solubilized water result in a considerable upfield shift of the NH_3^+ protons, and in somewhat smaller downfield shift of the $CH_2NH_3^+$ and $CH_2CO_2^-$ protons. Significantly, chemical shifts of other surfactant protons are unaffected (Figure 2). These data clearly indicate that water predominantly interacts with the charged polar headgroups of the dodecylammonium propionate aggregates, which form, of course, the interior of "reversed micelles."[16] In other words, the present ^{1}H nmr data substantiate that solubilized water forms "pools" in the cavities of surfactant aggregates in nonpolar solvents.

At given constant water concentrations, the observed chemical shifts (δ) of the magnetically discreet protons of DAP are linear functions of added ethylpyridinium bromide. This relationship is expressed by[17-19]

$$\delta = \delta_0 + a[x] \qquad (1)$$

where δ and δ_0 are the observed and limiting chemical shifts and $[x]$ is the concentration of ethylpyridinium bromide. Values for a were calculated from the linear plots of δ *vs.* [ethylpyridinium bromide], as illustrated in Figure 3, and are collected in Table I. It is seen that addition of ethylpyridinium bromide affects appreciably only the chemical shifts of NH_3^+ protons. Once again, the observed data are compatible with solubilization of the substrate at the polar interior of the DAP aggregates in methylene chloride. Considering the ionic nature of ethylpyridinium bromide, these results are hardly surprising.

It should be noted that while water shifts the ammonium protons of the surfactants upfield, ethylpyridinium bromide shifts them downfield. The upfield shift is likely to be the consequence of stronger hydrogen bonding between the oxygen atom of water and the NH_3^+ protons of DAP than that between the hydrogen atom of water and the CO_2^- group of the surfactant. Alternatively, effective hydrogen bonding between water and the polar groups of the surfactant might offset the electrostatic field effect which would manifest in the downfield shifts of $\delta_{NH_3^+}$. Similar results have been observed in the solubilization behavior of methanol, DMSO, imidazole, pyrazole, and 2-pyridone in benzene in the presence of DAP.[20] Of these solubilizates, only methanol, a solvent capable of forming strong hydrogen bonds, induced upfield shifts of the ammonium protons of DAP. Addition of DMSO, pyrazole, imidazole, and 2-pyridone to

Table I. Chemical Shifts of 0.20 *M* DAP in CH_2Cl_2 and Their Dependence on the Concentration of Added Water and Ethylpyridinium Bromide[a]

$[H_2O]$, *M*		NH_3^+	$CH_2NH_3^+$	$CH_2CO_2^-$	$-CH_2-$	CH_3
0.002	δ_0	869.1	324.6	258.6	177.5	153.2
0.111	δ_0	733.5	326.6	259.7	177.5	154.0
	a	8.02×10^3				
0.167	δ_0	692.5	327.7	259.8	177.4	154.0
	a	6.35×10^3				
0.222	δ_0	662.7	328.4	259.8	177.4	154.1
	a	5.05×10^3				
0.278	δ_0	633.4	329.6	260.3	178.0	154.2
	a	4.58×10^3				
0.333	δ_0	623.7	330.5	260.3	177.5	153.9
	a	3.48×10^3				

[a] Obtained at 100 MHz and 34°; see Experimental Section. Values of *a* were obtained from linear plots of data according to eq 1, each containing at least eight different concentrations of ethylpyridinium bromide. Changes of chemical shifts of protons other than NH_3^+ as a function of ethylpyridinium bromide concentration is negligible.

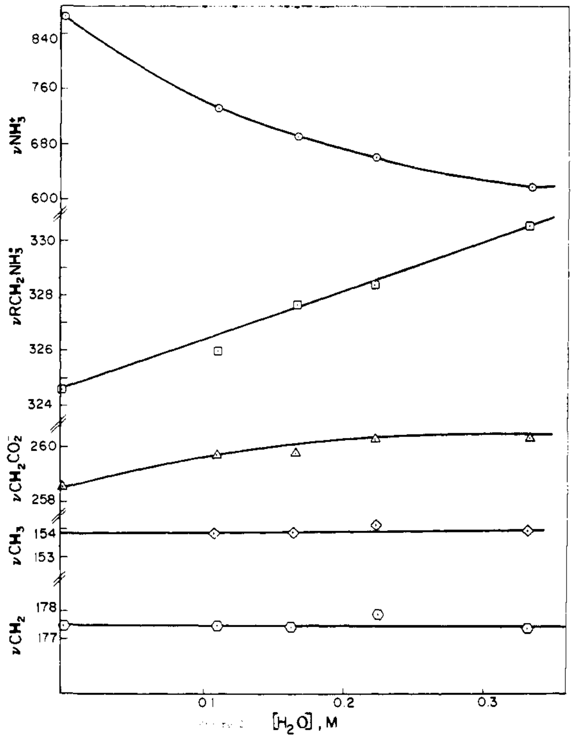

Figure 2. Chemical shifts of DAP protons in methylene chloride as functions of solubilized water concentrations. Notice the scale difference for the different protons.

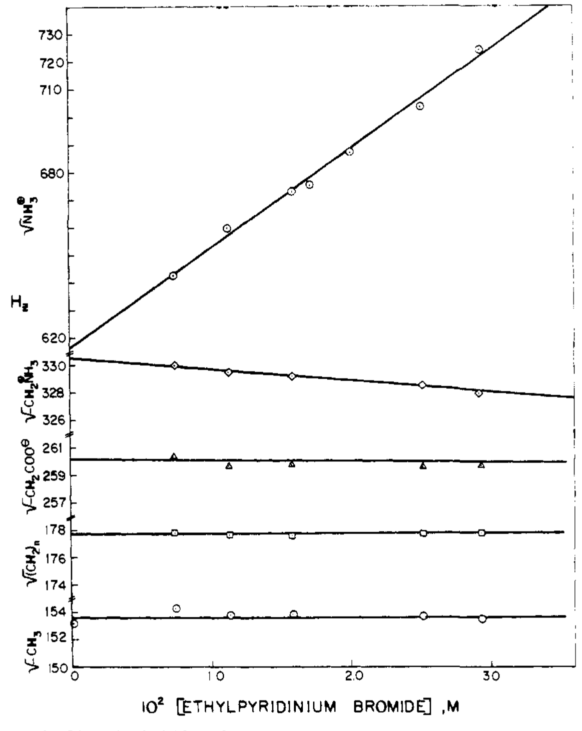

Figure 3. Chemical shifts of DAP protons in methylene chloride, in the presence of 0.333 *M* solubilized water, as functions of ethylpyridinium bromide concentrations. Notice the scale difference for the different protons.

benzene solutions of DAP resulted in downfield shifts of the ammonium protons of the surfactant.[20]

Slopes of the $\delta_{NH_3^+}$ *vs.* [ethylpyridinium bromide] plots, *a* values in Table I, increase with decreasing concentrations of solubilized water. These results indicate, not unexpectedly, that the interaction of ethylpyridinium bromide with DAP becomes stronger as the size of the solubilized "water pool" decreases. The determined ethylpyridinium bromide-DAP binding constants, K_{MS}, also substantiate these observations. The observed chemical shifts of the methyl protons of ethylpyridinium bromide, δ, as functions of aggregated DAP concentrations (Table II) were utilized for the calculation of K_{MS} from eq 2, where δ, δ_0, and δ_{MS} are the chemical shifts of the methyl protons of ethylpyridinium bromide at given DAP concentrations, in the uncomplexed form and in the complexed form, respectively.

$$\frac{1}{\delta - \delta_0} = \frac{1}{K_{MS}(\delta_{MS} - \delta_0)}\left(\frac{1}{[M]}\right) + \frac{1}{\delta_{MS} - \delta_0} \qquad (2)$$

The aggregate concentration, [M] is calculated from eq 3, where C_D is the stoichiometric DAP concentration, CMC is the operational critical micelle concentration, and *N* is the aggregation number.

$$[M] = \frac{C_D - CMC}{N} \qquad (3)$$

Values of 3.4×10^{-2} *M* and 6 were used for the CMC and *N* of DAP in methylene chloride.[16] Plots of the left-hand side of eq 2 *vs.* [M] give good straight lines (Figure 4) from which values of K_{MS} have been calculated. The magnitude of binding ethylpyridinium bromide to DAP aggregates, K_{MS}, in methylene chloride (Table II) is of the same order as those previously determined for the interaction of methanol, pyrazole, imidazole, DMSO, and 2-pyridone with DAP in benzene.[21] More significantly, K_{MS} values increase logarithmically with increasing concentration of water, *i.e.*, decreasing *Z* values (Figure 5). The tighter the grip of the surfactant, *i.e.*, the smaller the "water pool," the stronger the binding between the surfactant aggregates and ethylpyridinium bromide.

Dissociation Constants of Ethylpyridinium Bromide Charge-Transfer Complexes. The absorbancies of ethylpyridinium bromide at 290 nm in all the solvent systems investi-

Table II. Effect of DAP on the Chemical Shifts of Ethylpyridinium Bromide in CH_2Cl_2[a]

$[H_2O]$, *M*	[DAP], *M*	δ_{CH_3}, ppm	K_{MS}, M^{-1} [b]
0.111	0.091	221.2	23.4
	0.105	220.7	
	0.125	220.2	
	0.154	219.6	
	0.199	218.3	
	0.333	216.5	
0.222	0.090	221.0	3.84
	0.158	219.9	
	0.198	219.1	
	0.244	218.7	
	0.327	217.4	
	0.413	216.5	
	0.514	215.2	
0.278	0.154	219.4	2.71
	0.201	218.9	
	0.237	218.4	
	0.297	217.6	
	0.402	216.3	
	0.497	215.2	
	0.697	212.9	
0.333	0.194	220.6	2.47
	0.311	219.1	
	0.398	218.2	
	0.515	217.0	
	0.680	215.1	
	0.779	213.9	

[a] Obtained at 100 MHz and 34°; concentration of ethylpyridinium bromide is 2.88–0.96 × 10^{-2} *M*. [b] Calculated from eq 2.

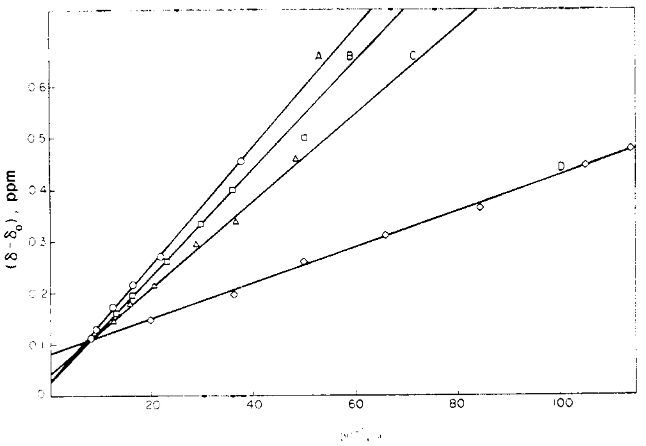

Figure 4. Binding constant plots for the interaction of ethylpyridinium bromide with DAP aggregates in methylene chloride (eq 2), in the presence of 0.333 *M* (A), 0.278 *M* (B), 0.222 *M* (C), and 0.111 *M* (D) solubilized water.

gated increase exponentially as a function of substrate concentration. This spectral behavior for alkylpyridinium halides is well documented[8-10] and has been interpreted to be due to the equilibrium formation of interionic charge-transfer complexes between the alkylpyridinium cation and the halide anion[8-16]

$$RPy^+X^- \overset{K_d}{\rightleftharpoons} RPy^+ + X^- \tag{4}$$

where RPy^+X^- represents *all* ion pairs irregardless of the extent and nature of solvent participation. The dissociation constant of ion pairs, K_d, is given by

$$K_d = \frac{([C] - [RPy^+Y^-])^2}{[RPy^+Y^-]} \tag{5}$$

where [C] is the stoichiometric total concentration of alkylpyridinium halides. Since absorption of the free ions at 290 nm is negligible, the observed absorbancies, *A*, are related to the extinction coefficient, ϵ, of all ion pairs by Beer's law ($\epsilon = A/[RPy^+Y^-]$). Neglecting activity coefficients, combination of eq 5 with Beer's law and appropriate rearrangements lead to eq 6, which has been successfully utilized for

$$A/[C] = \epsilon - \sqrt{K_d}(\sqrt{A}/[C]) \tag{6}$$

the calculation of K_d and ϵ for interionic alkylpyridinium halide charge-transfer complexes in a variety of media.[8-14] Indeed, good straight lines were obtained, as illustrated in Figure 6, on plotting $A/[C]$ *vs.* $\sqrt{A}/[C]$ for ethylpyridinium bromide charge-transfer complexes in all the systems investigated. Obtained values of K_d and ϵ are given in Table III. At a constant concentration of solubilizated water (0.111 *M*) increasing concentrations of DAP increase the dissociation constant of the ethylpyridinium bromide charge-transfer complex up to a maximum after which K_d remains constant. This type of saturation kinetics has often been observed both for aqueous[22-24] and nonaqueous[1,2] micellar systems.

Table III. Dissociation Constants, K_d, and Molar Extinction Coefficients, ϵ, of Ethylpyridinium Bromide Charge-Transfer Complexes in Methylene Chloride at 25.0°

[DAP], *M*	$[H_2O]$, *M*	10^3K_d, M^{-1}	ϵ_{290nm}, M^{-1} cm^{-1}	Z[a]
0	55.5	1100 (950)[b]	39.3 (40)[b]	94.6[c]
0	0.002	1.42	840	64.2[c]
0.010	0.111	1.62	799	
0.020	0.111	1.72	746	
0.030	0.111	1.75	726	
0.040	0.111	2.52	767	
0.050	0.111	3.45	782	
0.080	0.111	4.47	790	
0.10	0.111	4.52	758	
0.20	0.111	4.75	585	65.9
0.20	0.002			65.3
0.30	0.111	4.74	595	
0.20	0.167	10.6	761	66.3
0.20	0.222	29.0	1100	66.8
0.20	0.278	51.7	1430	67.0
0.20	0.333	85.1	1670	67.3
0.20	0.389			67.7
0.20	0.444			67.9

[a] Determined in the present work, unless stated otherwise. [b] Determined in ref 14. [c] Taken from ref 8.

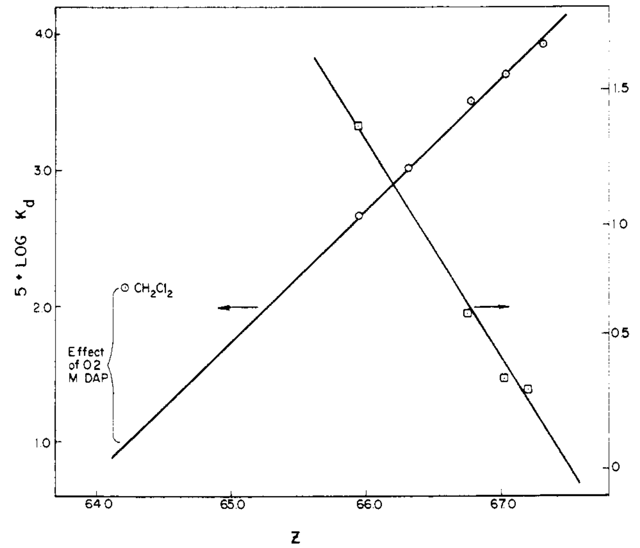

Figure 5. Plot of the logarithm for the dissociation constant of ethylpyridinium bromide charge-transfer complex in CH_2Cl_2 in the presence of 0.2 *M* DAP, K_d, and that for the DAP bromide binding constant, K_{MS}, at different amounts of solubilized H_2O *vs.* solvent polarity parameter *Z*.

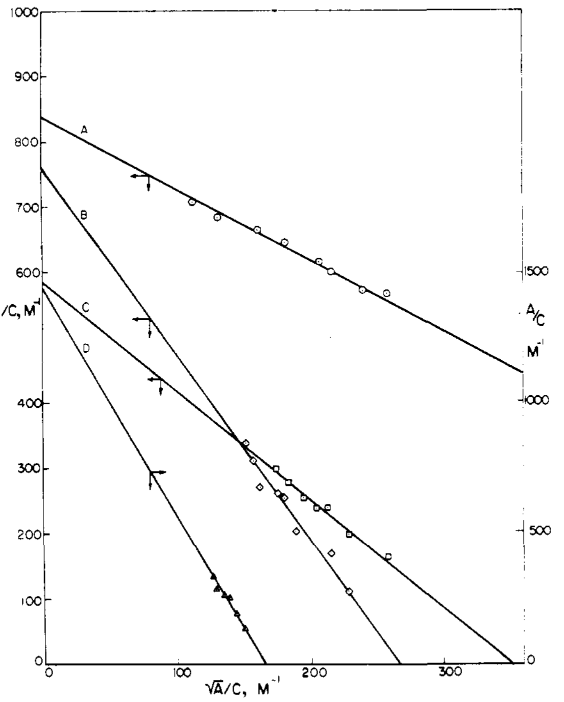

Figure 6. Plots of data according to eq 6 for the ethylpyridinium bromide charge-transfer complex formation in methylene chloride at 25.0°. Absorbancies are taken at 290 nm. A = neat CH_2Cl_2; B = 0.20 *M* DAP in CH_2Cl_2 in the presence of 0.167 *M* H_2O; C = 0.20 *M* DAP in CH_2Cl_2 in the presence of 0.111 *M* H_2O; and D = 0.20 *M* DAP in CH_2Cl_2 in the presence of 0.278 *M* H_2O.

Dissociation constants for and extinction coefficients of the interionic ethylpyridinium bromide charge-transfer complexes in methylene chloride in the presence of 0.20 *M* DAP increase with increasing amounts of solubilized water. A good linear relationship has in fact been obtained between the logarithm of K_d values and the determined solvent polarity parameter *Z* (Figure 5). Extrapolation of this line to a *Z* value corresponding to that of neat methylene chloride indicates that 0.20 *M* DAP decreases the dissociation constant of ethylpyridinium bromide by 15-fold (Figure 5). Analogous extrapolation of the binding constant between ethylpyridinium bromide and aggregates of DAP (not shown) results in $K_{MS} = 400\ M^{-1}$, an appreciable value. Favorable interactions between the polar surfactant headgroups and the solubilized ethylpyridinium bromide result, evidently, in stabilization of the interionic charge-transfer complex. Increasing the concentration of entrapped water in the cavities of DAP aggregates results in logarithmic decrease of substrate surfactant association and charge-transfer complex stability (Figure 5).

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