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SOME FACTORS IN SOLUTE PARTITIONING BETWEEN WATER AND MICELLES OR POLYMERIC MICELLE ANALOGUES

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SUMMARY

Micelle–water partition coefficients of p-nitroaniline and p-nitrophenol have been determined for several alkyltrimethylammonium salts including a polymer of undecenyltrimethylammonium bromide. Solubilization depends upon the "concentration" of micellized alkyl carbon atoms regardless of micelle size. Counterion effects are an important aspect of the process. Micelle-like polymers may be useful in theoretical studies by eliminating some of the interactive variables which complicate pseudophase liquid chromatography with ordinary micelles.

INTRODUCTION

Recent reviews describe a growing interest in liquid chromatography (LC) with micellar mobile phases, sometimes termed "pseudophase LC"[1-3]. It is understandable that most studies in this relatively new area have been based upon two surfactants which are readily available in high purity (sodium dodecyl sulfate and hexadecyltrimethylammonium bromide), but optimization cannot be guaranteed unless surfactants with other head groups, chain lengths, and counterions are also evaluated. Micelle–water partition coefficients (K_{MW} values) are important for interpreting solute retention behavior in terms of the three-phase model[4,5]; these values are likewise important in other contexts, *e.g.*, theoretical treatments of micellar catalysis[6]. Armstrong and Stine[7] have described a simple, efficient, and inexpensive method for obtaining K_{MW} values by thin-layer chromatography (TLC): the plot of $R_F/(1 - R_F)$ *vs.* mobile phase micellized surfactant concentration is linear and the ratio of slope to intercept is shown to be $(K_{MW} - 1)\bar{v}$, where $\bar{v}$ is the partial specific volume of the surfactant calculated from density measurements. Results obtained by this method have disclosed several interesting aspects of micellar solubilization with the solutes p-nitroaniline and p-nitrophenol: solubility essentially depends upon the "concentration" of micellized alkyl carbon atoms regardless of micelle size; a micelle-like polymer or "polysoap" accepts solutes in the same manner as do micelles; solubility is lowered by an organic counterion (benzoate) which is highly promotional in regard to

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micelle formation, and becomes lower still at surfactant concentrations above the sphere-to-rod transition.

EXPERIMENTAL

Materials

10-Undecenyltrimethylammonium bromide (UTAB) was prepared by routine alkylation of ethanolic trimethylamine with 10-undecenyl bromide and recrystallized from ethanol–diethyl ether. The critical micelle concentration (CMC) of this material in water was 0.053 M and the aggregation number was 31 as determined by light scattering. Polyundecenyltrimethylammonium bromide (PUTAB) was prepared by irradiation of aqueous 0.5 M UTAB solutions in sealed ampoules with 25 Mrad delivered in 100 h in a ^{60}Co γ source. The chemical shift of the head group methyl protons changed sufficiently upon polymerization to allow the process to be monitored by ^1H NMR spectroscopy; after 100 h, the level of unreacted monomer remained nearly constant at about 30% of the starting material. The pooled solutions were lyophilized and the solid residue was dissolved in ethanol and precipitated with diethyl ether. The latter process was repeated three times. Monomer residue was <2%. (With a comparable compromise between purity and yield, the polymer can also be cleaned up by gel filtration on a Sephadex G-25 column or by dialysis with a cellophane membrane.) The polymerization number by light scattering was 32 and by the luminescence quenching method employed by Turro and Yekta[8] and others, 38. In other words, the polymer molecule is about the same size as the original, unirradiated micelle. This material is a cationic counterpart of the polymerized sodium undecenoate prepared in the same way and characterized as micelle-like by Sprague *et al.*[9].

Decyltrimethylammonium bromide ($D_{10}TAB$) and the tetradecyl salt (TTAB) were prepared and purified in a conventional manner[10]. Eastman dodecyltrimethyl-ammonium bromide ($D_{12}TAB$) was recrystallized from ethanol–diethyl ether. Baker reagent hexadecyltrimethylammonium bromide (HTAB) was used as received. Bromides were converted to chloride (HTAC) or benzoate (HTABz) salts by ion exchange on Bio-Rad AG1-X8 columns; a bromide ion-selective electrode was used to confirm the adequacy of the exchange process. The solutes *p*-nitroaniline and *p*-nitrophenol were Aldrich materials. TLC plates, 5 × 20 cm, were cut from the Macherey-Nagel Polyamid-6 UV_{254} product distributed by Brinkmann.

Methods

Chromatography was performed at ambient temperature of 22 ± 0.5°C. Samples were pipetted onto the plates 2 cm from the bottoms, and the solvent was allowed to migrate about 15 cm. R_F values were determined visually from the diminished luminescence of the stationary phase fluorophore at the solute spots. Partial molar volumes were obtained by a standard method as described, for example, by Güvelli *et al.*[11]. Light scattering measurements were performed as described earlier[10].

With pure water as the mobile phase, the values of $R_F/(1 - R_F)$ for *p*-nitroaniline and *p*-nitrophenol are 0.07 and 0.05, respectively. As surfactant is added, the values at first hold at these levels and then break upward, suggesting that CMC values are obtainable from the abrupt slope changes. The study of Armstrong

and Stine[7] suggests that, for cationic surfactants, this behavior is not an artifact resulting from mobile phase concentration changes as the solvent wets the plate. Furthermore, CMC values obtained in this manner are close to literature values where the latter are available; for example, the recommended value in a critical compilation[12] for $D_{12}TAB$ in water is $1.59 \cdot 10^{-2} M$, while the value from our plots is $1.7 \cdot 10^{-2} M$. Because the intercept is very sensitive to CMC, and K_{MW} to the intercept, CMC values from the TLC data were preferred to those from other sources, which may vary considerably with the method of measurement[12], for calculating micellized surfactant concentrations. Slopes were obtained from a standard program for linear regression of $R_F/(1 - R_F)$ on micellized surfactant concentration.

RESULTS

Fig. 1 shows typical data sets obtained with the solute p-nitroaniline and several mobile phase surfactants, including the polymer, with bromide counterions. To avoid clutter, actual data points are shown for only one of the lines. Each point represents the average of eight individual R_F measurements on four separate plates. The correlation coefficients were as follows: $D_{10}TAB$, 0.99; PUTAB, 0.99; UTAB, 0.91; $D_{12}TAB$, 0.99; TTAB, 0.98 and HTAB, 0.97. The limited concentration range of the HTAB data reflects the low solubility of this material[13]; solutions near the upper end of the curve were probably, in fact, supersaturated.

The lines shown in Fig. 2 were generated by multiplying micellized surfactant concentrations by the numbers of carbon atoms in the alkyl chains (*e.g.*, by 16 in the case of HTAB). The "spread" in the slopes is clearly decreased by this operation, although not all of the confidence intervals of the slopes at a probability level of 0.95 overlap. Statistically, at this probability level, one cannot quite say that the slopes are identical, but they are very nearly so; of the six lines, two different sets of five meet the test.

Lines similar to those in Figs. 1 and 2 are obtained with the solute p-nitrophenol,
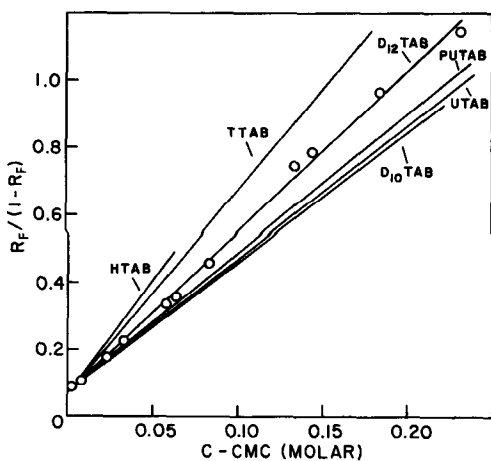

Fig. 1. Armstrong plots for p-nitroaniline, bromide counterions. To avoid clutter, data points are shown for $D_{12}TAB$ only.
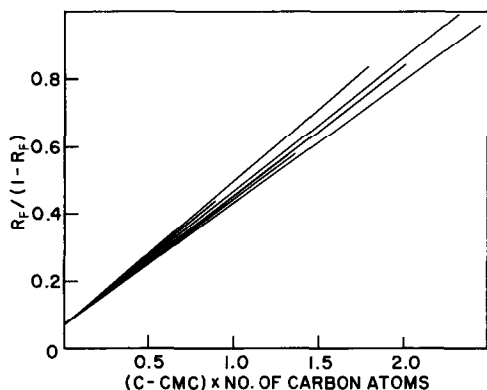
Fig. 2. Armstrong plots for p-nitroaniline, bromide counterions, normalized for the number of carbon atoms in the surfactant alkyl chain. In order from largest to smallest slope: TTAB, HTAB, D_{12}TAB, D_{10}TAB, PUTAB, UTAB.

although, of course, the slopes are numerically different. Fig. 3 shows an interesting effect of the benzoate counterion which is discussed below in relation to the superimposed light scattering curve obtained with solutions of HTABz. Data and calculated partition coefficients are given in Table I, and the latter are displayed in Fig. 4.

DISCUSSION

For the four cases common to both studies, our K_{MW} values agree reasonably with those of Armstrong and Stine[7] except for p-nitrophenol in HTAC, where ours is unaccountably 48% larger. It is seen in Table I and Fig. 4 that the K_{MW} values for both solutes are the same with D_{10}TAB as with UTAB, perhaps reflecting the fact that the terminal unsaturation of the latter is expected to have about the same effect upon micellar properties as removal of one methylene unit from a saturated alkyl chain[14].

Armstrong's review[2] provides an excellent summary of the manner in which the interpretation of solute retention behaviour is complicated by the complexity of micellar LC systems. Some of the problems relate to the inevitable presence of unmicellized surfactant ions in solutions of ordinary micelles, including head group interactions with ionic solutes and modification of the stationary phase by monomer accumulation. Others arise in the use of mobile phase modifiers such as methanol, which introduce additional confusion by their generally unknown effects upon micellar properties. We suggest that polymeric micelle analogues may help chromato-graphers sort out some of these effects. Solutions of PUTAB give a linear light scattering curve which rises from the origin. There is no CMC, nor monomer to form ion pairs or to coat a surface, yet the polymer points in Fig. 4 lie in the same domain as those for micelles. It should also be noted that "pure" counterion effects can be studied using such polymers, without the intrusion of the changes in CMC and aggregation number which often attend the substitution of one counterion for another with ordinary micelles. One expects, for example, that cationic micelles with bromide counterions will be larger than their chloride counterparts[15], but the size here remains

TABLE I

DATA SUMMARY AND CALCULATED PARTITION COEFFICIENTS

Surfactant*	Partial molar volume	Slope** (Fig. 1)	Slope*** (Fig. 2)	Intercept	K_{MW} §	K_{MW}^{*} §§
p-Nitroaniline solute						
$D_{10}TAB$	0.2607	3.865	0.387	0.070	213	22
UTAB	0.2699	4.007	0.364	0.070	213	20
PUTAB	0.2491	4.138	0.376	0.070	238	23
$D_{12}TAB$	0.2950	4.760	0.397	0.070	232	20
TTAB	0.3271	6.025	0.430	0.070	264	20
HTAB	0.3555	6.787	0.424	0.070	274	18
$D_{10}TAC$	0.2496	3.395	0.340	0.070	195	20
PUTAC	0.2351	3.569	0,324	0.070	218	21
$D_{12}TAC$	0.2877	4.649	0.387	0.070	232	20
HTAC	0.3479	6.559	0.410	0.070	269	18
TTABz	0.3855	3.362	0.240	0.070	126	10
HTABz	0.4182	3.537§§§	0.221§§§	0.070	122§§§	9§§§
p-Nitrophenol solute						
$D_{10}TAB$	0.2607	3.871	0.387	0.050	298	31
UTAB	0.2699	4.006	0.364	0.050	298	28
PUTAB	0.2491	4.681	0.426	0.050	377	35
$D_{12}TAB$	0.2950	5.619	0.468	0.050	383	33
TTAB	0.3271	7.546	0.539	0.050	462	34
HTAB	0.3555	9.039	0.565	0.050	510	33
$D_{10}TAC$	0.2496	4.221	0.422	0.050	339	35
PUTAC	0.2351	4.786	0.435	0.050	408	38
$D_{12}TAC$	0.2877	6.844	0.570	0.050	477	41
HTAC	0.3479	10.716	0.670	0.050	617	40
TTABz	0.3855	5.851	0.418	0.050	305	23
HTABz	0.4182	3.806§§§	0.238§§§	0.050	183§§§	12§§§

* For abbreviations, see section on Materials. Counterions are: B, Br⁻; C, Cl⁻; Bz, benzoate $(C_6H_5CO_2^{-})$.

** Concentration is molarity of micellized surfactant, i.e., $(M_{surf} - CMC)$, as plotted in Fig. 1.

*** Concentration is "molarity" of surfactant alkyl chain CH_3- and $-CH_2-$ groups, i.e., $(M_{surf} - CMC)$ × number of C atoms in alkyl chain, as plotted in Fig. 2.

§ K_{MW} is the usual dimensionless micelle–water partition coefficient as defined by Armstrong and Nome[4] and others.

§§ K_{MW}^{*} values are obtained using slopes as seen in Fig. 2 rather than those of Fig. 1. See Discussion.

§§§ Calculated from data for surfactant concentrations below the sphere-to-rod transition. See Fig. 3 and Discussion.

the same because the chloride was prepared from the bromide after polymerization. Further, the polymer will not be disrupted by solvents such as methanol and acetonitrile.

A striking counterion effect is seen in the decreased K_{MW} values for both solutes attending the substitution of benzoate for chloride or bromide. Hydrophobic counterion substituents promote micelle formation in a fairly predictable manner[16],
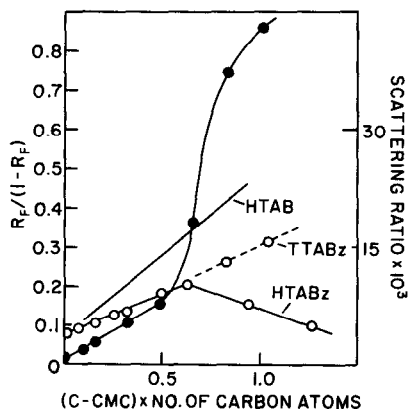
Fig. 3. Effect of benzoate counterions with p-nitroaniline. The HTAB curve from Fig. 2 is shown for comparison; solid circles show ratios of scattered radiant power (90°) to incident power for light scattering on aqueous HTABz solutions.

acting somewhat as solubilizates. In terms of the Menger micelle model[17-19], they readily infiltrate the porous, open, highly disordered surface region, perhaps displacing water and creating a higher degree of organization than would simple inorganic counterions. The Hartley micelle[20], despite its more clearly differentiated interior and surface regions, is considered sufficiently fluid to accept hydrophobic insertions whose removal from bulk water is highly favorable. In either case, it is reasonable that a counterion which possesses qualities of an organic solubilizate may induce changes in micellar organization that diminish hospitality toward additional guest molecules.

The light scattering curve in Fig. 3 shows, near about 0.6 on the abscissa, a steepening associated with micellar growth. The simultaneous appearance of
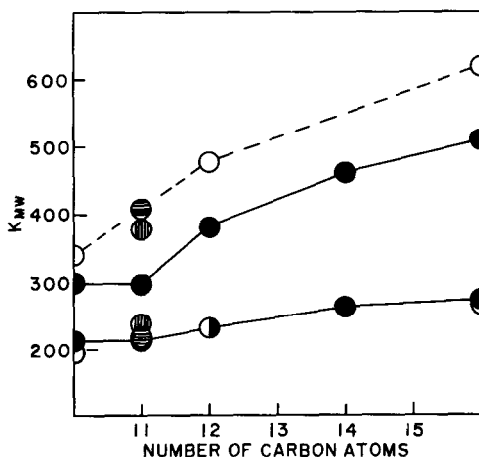

Fig. 4. Pictorial summary of data from Table I. Open circles, Cl^- counterions; solid circles, Br^- counterions; vertically hatched circles, PUTAB; horizontally hatched circles, PUTAC; lower solid line, p-nitroaniline solute; upper solid and dotted lines, p-nitrophenol solute.

dissymmetry (based upon measurements at scattering angles of 45 and 135°) suggests that the larger aggregates are rod-like. In other words, a sphere-to-rod transition, not seen with the other surfactants in this study at the concentrations employed, occurs in this region. (Some writers have designated the transition a "second CMC", but IUPAC has attempted to discourage this usage.) The corresponding transition for HTAB occurs at much higher concentrations[21]. It is plausible that closer packing in rod-like micelles may diminish solute intrusion, perhaps even to the degree that surfactant increments above the sphere-to-rod transition scarcely increase a solute's mobile phase solubility. This alone does not explain, however, the negative slope seen in Fig. 3 for p-nitroaniline in HTABz, since presumably spherical micelles, on thermodynamic grounds, coexist with rods in this region. (p-Nitrophenol exhibits a similar slope change in the same HTABz concentration region.) The magnitudes of other terms are such that negative slopes correspond to physically meaningless negative K_{MW} values.

The mobile phases were unbuffered (to avoid the introduction of extraneous counterions), and questions were raised during manuscript review regarding possible pH effects upon the charge status of the solutes as discussed by Arunyanart and Cline-Love[22]. However, protonation of p-nitroaniline ($pK_b \approx 13$) would require solutions far more acidic than ours, particularly in the face of the pK shifts known to result from incorporation in micelles[23]. Further, although benzoate solutions are more alkaline than those with Br^- or Cl^-, increasing ionization of p-nitrophenol ($pK_a = 7.15$) would presumably increase its mobility as it became itself an effective counterion. Nor is it clear how the abrupt divergence of the TTABz and HTABz plots near the sphere-to-rod transition (Fig. 3), seen with both solutes, could relate to poor pH control. Thus the negative slopes at higher HTABz concentrations remain difficult to explain and attest to the complexity of micellar LC.

The K_{MW}^* values in Table I were calculated using slopes based upon the abscissa units shown in Fig. 2. Although we do not wish to exaggerate their obviously limited usefulness, in principle, taken with $\bar{v}$ values and carbon chain lengths, they could be used to calculate equivalent concentrations in substituting one surfactant for another. The striking feature, however, is how nearly independent of surfactant chain length are the K_{MW}^* values. It has been known for many years that, *ceteris paribus*, micellar aggregation numbers increase with chain length; for example, in one study the "molecular weights" of the micelles in water were 10 200 for $D_{10}TAB$, 15 500 for $D_{12}TAB$, and 25 300 for TTAB[24]. Yet, carbon atom for micellized carbon atom, the larger micelles are no more effective solubilizers than are smaller ones.

Chain length and counterion effects seen in Table I and Fig. 4 are far from insignificant, and are complicated by their dependence upon the nature of the solute. With p-nitroaniline, for example, K_{MW} increases by only 29% when HTAB replaces $D_{10}TAB$, whereas with p-nitrophenol there is a 71% increase. The ratio of K_{MW} values for the two solutes ($K_{MW_{PNP}}/K_{MW_{PNA}}$) ranges from 1.4 with $D_{10}TAB$ to 2.3 with HTAC. With HTA^+, replacing Br^- with Cl^- has virtually no effect upon $K_{MW_{PNA}}$ but increases the value for p-nitrophenol by over 20%. Thus even a study limited to two solutes and three counterions leads one to suppose that many reported pseudophase LC separations are probably not optimized.

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