Study of Micelle Formation in Solutions of Alkylammonium Carboxylates in Apolar Solvents by Positron Annihilation Techniques[1]

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Abstract: The positron annihilation technique was applied to the study of the self-association process in solutions of alkylammonium carboxylates in apolar solvents, such as cyclohexane and benzene. The results indicate that the positronium formation probability responds very sensitively to changes in the microenvironment in these solutions. A distinct cooperative effect of the solution resulting in abrupt changes in the number of thermal ortho-positronium atoms formed was observed and studied as a function of the length and structure of the hydrocarbon chain in the cationic and anionic parts of the surfactant molecules. While the chain length in the cationic portion of the surfactant seems to have little effect on the positronium formation probability, distinct differences can be observed when the structure of the carboxylate ion is changed. Furthermore, a profound effect in the physical property of the solutions was recognized when cyclohexane was replaced by benzene as a solvent. The results are discussed in terms of the existing models for self-association.

Introduction

Because of the increasing importance of reversed micelles as catalysts in chemical and biological reactions[3,4] it is essential to obtain additional information on the properties of these surfactant aggregates in organic solvents and the effect of additives on the formation and structure of the reversed micelles.

While there is ample evidence that in aqueous micellar system the aggregation can best be characterized by a monomer $\rightleftarrows$ n-mer type association,[3] there still exists considerable uncertainty whether this mechanism, also called the pseudophase model, prevails in the case of the reversed micellar systems, or whether the multiple equilibrium model applies, which assumes stepwise formation of aggregation in an indefinite association process, monomer $\rightleftarrows$ dimer $\rightleftarrows$ trimer $\rightleftarrows \ldots n$-mer.[4]

Evidence for the latter mechanism was, e.g., derived from vapor pressure osmometry measurements on solutions of dodecylammonium propionate in benzene and cyclohexane.[5] On the other hand, experiments in our own laboratory utilizing the positron annihilation technique,[6] which show unambiguously discontinuities in a physical property of the solution, namely, the thermal ortho-positronium (Ps) formation probability, as a function of surfactant concentration,[7-10] indicate the appearance of a cooperative effect (reducing the Ps formation) at certain surfactant concentrations. This observation was recently confirmed by Eicke et al.,[11] who also recognized abrupt changes in physical properties of reversed micellar solutions by measuring the dielectric increment.

An attempt to find a unified interpretation of the self-association of ionic surfactants in solvents of low dielectric constant has been recently described by Muller.[4] His model calculations suggest that, when the solvent has a relatively high dielectric constant, ϵ, or the sum of the radii of the ionic head groups, d, is large, association is best represented by stepwise sequential formation of open-chain oligomers with approximately equal equilibrium constants for the binding of additional monomers. When ϵ and d are both small, compact clusters are preferred. Their electrostatic binding energy increases with increasing aggregation number, n, but their growth is eventually limited at $n = n_{\max}$ by the steric demand of the hydrocarbon chains. When $n_{\max} \geq 16$ most of the aggregated surfactant should be present in the form of clusters with $n \simeq n_{\max}$, and then the association process is much more nearly analogous to micellization in aqueous solutions.

In order to test these predictions we carried out several series of positron annihilation experiments in solutions of alkylammonium propionates, in which the alkyl group in the alkylammonium ion was varied from butyl to hexyl, octyl, decyl, and dodecyl.

We also investigated the effect of the nature and size of the hydrocarbon chain of the carboxyl ion, i.e., replacing the propionate by butanoate, benzoate, and p-nitrobenzoate on the aggregation mechanism. Another parameter studied was the nature of solvent; both cyclohexane and benzene were used in these experiments.

Experimental Section

A. Purity of Materials. Butyl- (BAP), hexyl- (HAP), octyl- (OAP), decyl- (DeAP), and dodecyl- (DAP) ammonium propionates were prepared by neutralization of their respective amines (obtained from Aldrich Co.) with propionic acid (Fisher Scientific Co.) in n-hexane.[12,13] Dodecylammonium butanoate (DAB) was prepared by neutralization of dodecylamine with butyric acid (Fisher Scientific Co.) in n-hexane. BAP, HAP, and OAP were purified by distillation at reduced pressure. Repeated recrystallization of DeAP and DAP from n-hexane resulted in products with a melting point in agreement with the values published in the literature.[12] The commercially available amines had been purified by distillation under reduced pressure.

Dodecylammonium benzoate (DABz) was prepared by the neutralization of dodecylamine with benzoic acid (Fisher Scientific Co.) at about 70 °C. The crystalline salt was washed with reagent grade acetonitrile in order to remove any free benzoic acid.[16]

Dodecylammonium nitrobenzoic (DABzNO$_2$) acid was prepared, as its analogues DAP and DABz, by neutralization of dodecylamine with p-nitrobenzoic acid. All surfactants were checked by elemental analysis. Since some of the surfactants were very hygroscopic, appropriate care had to be taken to avoid any hydration.

Solvents such as n-hexane, benzene, and cyclohexane were glass-distilled spectroscopic grades from Burdick and Jackson Laboratories. These solvents were further dehydrated by distillation over metallic sodium. The redistilled solvents were stored in desiccators to avoid any further contamination with water.

B. Positron Lifetime Measurements and Preparation of the Sample. Positron lifetime measurements were carried out by the usual delayed coincidence method as previously described.[15] The resolution of the system as measured by the fwhm of the prompt coincidence spectrum of a ^{60}Co source without changing the 1.27 and 0.511 MeV bias was found to be less than 0.4 ns fwhm. Specially designed cylindrical sample vials (Pyrex glass, 100 mm and 10 mm i.d.) were filled with about 2 mL of the appropriate solution. The positron sources consisted of ~3-5 μCi ^{22}Na diffused into a thin foil of soda lime glass.

The relative amount of positron annihilation occurring in the glass

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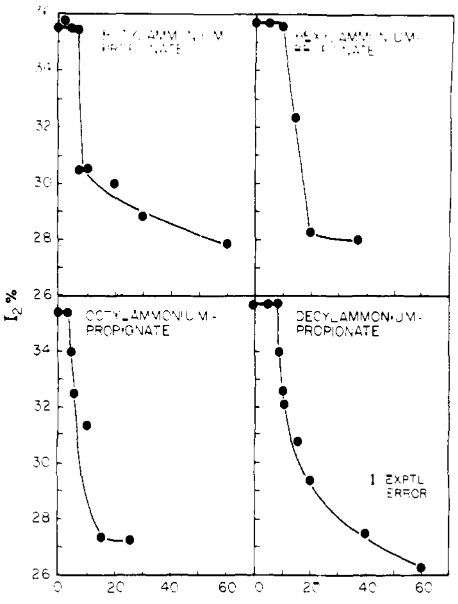

Figure 1. I_2 vs. surfactant concentration in various alkylammonium carboxylates in cyclohexane at room temperature.

was found to be less than 2%, for which corrections were made. The radioactive sources were suspended in the center of the ampule and all solutions were carefully degassed by freeze-thaw techniques to remove oxygen. The vials were subsequently sealed under vacuum and the measurements carried out at the desired temperature in a specially designed thermostat which allowed control of the temperature within ±0.5 °C. All measurements were carried out at room temperature, with the exception of the $DABzNO_2$ experiments, which were done at 54 °C.

C. General Method of Data Analysis. The lifetime spectra under investigation were separated into two components.[16] The short-lifetime component with a mean life τ_1 is the result of *p*-Ps annihilation, free positron annihilation, and epithermal Ps interactions. The long-lifetime component with a mean life τ_2 and its associated intensity I_2 results from the reactions and subsequent annihilation of thermalized *o*-Ps.

Results and Discussion

In the first series of experiments the length of the hydrocarbon chain in the alkylammonium ion of the alkylammonium propionates was successively increased from 4 to 6, 8, 10, and 12 carbon atoms going from BAP to HAP, OAP, DeAP, and DAP.

While λ_2, the annihilation rate of the *o*-Ps atoms in the cyclohexane solution of these various systems, does not change significantly over the surfactant concentration range studied, I_2, which is related to the (thermal) *o*-Ps formation probability, shows abrupt changes at certain surfactant concentrations similar to those previously reported for DAP in cyclohexane and benzene. As the results in Figure 1 indicate (for comparison see also Figure 2, where the DAP data are shown), the surfactant concentration at which the drastic changes occur falls into a relatively small range of about 7–9 mM, with the exception of OAP, for which a smaller concentration of about 3 mM was observed. This appears to be somewhat at variance with the results of earlier experiments by Fendler et al.,[13,14] who observed discontinuities in a plot of the chemical shifts of the different photons obtained by ^1H NMR spectroscopy in benzene solutions of these systems. The breaks in the curves occur in their investigation generally at higher concentrations than those observed in our experiments, especially in shorter chain hydrocarbons, whereas good agreement between their and our measurements exists in the case of DAP.

In this context it seems important to point out that in the shorter chain systems (BAP, HAP, OAP, and DeAP) in our experiments, after an initially sharp drop, the I_2 values (Figures 1 and 2) display a much less pronounced decline followed by a leveling off at surfactant concentrations between 20 and 60 mM, depending on the system, whereas in the case of DAP the sharp decline in I_2 is characterized by an equally sudden leveling off at 9–10 mM. It might be that the ^1H NMR measurements are indicative of the situation which corresponds to the one at which our positron annihilation parameter, I_2, has leveled off. This in turn may reflect the different sensitivity of the two techniques to two or more different types of species present.

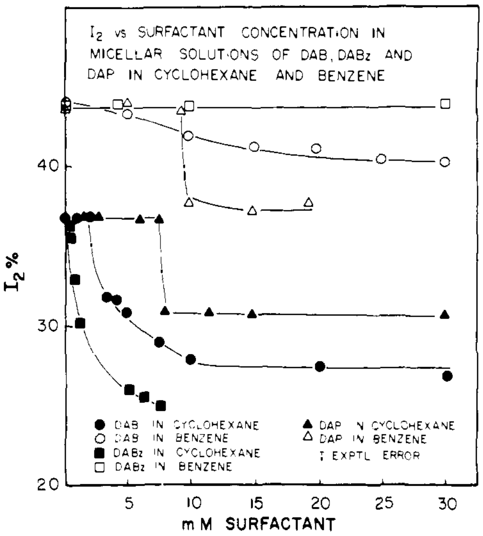

Figure 2. I_2 vs. surfactant concentration in DAP, DAB, and DABz in cyclohexane and benzene solutions at room temperature.

While the present results confirm the sudden appearance of a cooperative effect in these systems at a given surfactant concentration, the results also indicate that the length of the hydrocarbon chain in the alkylammonium ion has relatively little effect on (1) the type of aggregation mechanism and (2) the surfactant concentration at which the cooperative effect appears.

In the second series of experiments the length and the structure of the hydrocarbon chain in the carboxylate ion of the surfactant molecule were varied from propionate to butanoate and benzoate.

While, as shown in Figure 2, the results observed for DAB in cyclohexane solution vary only slightly from those obtained for DAP, the corresponding I_2 values for DABz display a definitely different trend. The apparent surfactant concentration at which a drop in I_2 occurs is shifted to a very low concentration, well below 1.0 mM, and it remains doubtful whether a discontinuity in the I_2 vs. surfactant concentration plots can be clearly defined at all.

The effect of the nature of the solvent on the appearance of a cooperative effect in these solutions, as indicated by a sudden change in the thermal *o*-Ps formation probability (I_2), was studied by replacing the cyclohexane as solvent by benzene in the above systems. The results, which are shown in Figure 2, where I_2 is plotted as a function of surfactant concentration, exhibit a rather dramatic effect. While DAP in benzene shows the familiar behavior, namely, a sharp drop at about 8.7 mM, no such discontinuity could be observed either in DAB or in DABz–benzene solutions. The DAB system shows a slight monotonous decline of the I_2 values with increasing surfactant concentrations from 0 to 30 mM, and the I_2 values observed in DABz–benzene solutions remain essentially constant over the whole concentration range studied, i.e., up to 50 mM.

In order to further evaluate the aspect of the influence of the

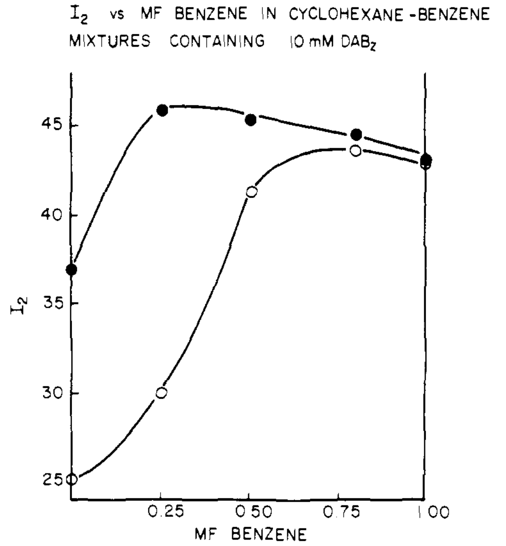

Figure 3. I_2 vs. mole fraction benzene in cyclohexane-benzene mixtures without (●) or with 10 mM DABz (○) present (at room temperature).

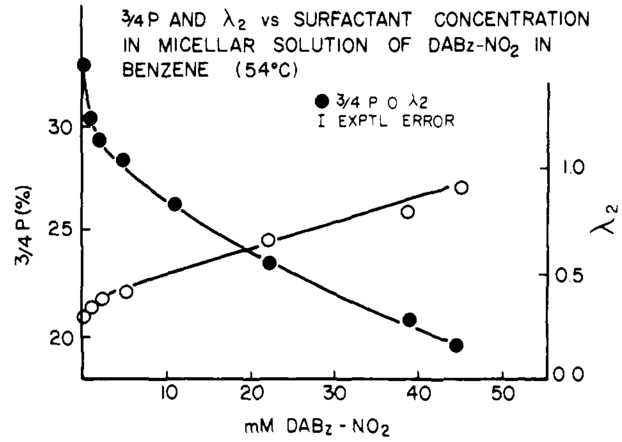

Figure 4. $\frac{3}{4}P$ (●) and λ_2 (○) vs. DABzNO$_2$ concentration in benzene solution at 54 °C.

nature of the solvent on the appearance of a cooperative effect, a third series of experiments was performed in which I_2 was measured in cyclohexane-benzene mixtures of various composition without any surfactant and with 10 mM DABz surfactant present. The latter concentration was chosen since the previous data in cyclohexane-DABz solutions revealed that at this concentration I_2 levels off (Figure 2).

The results of these latter experiments are shown in Figure 3, where I_2 is plotted as a fraction of the mole fraction of benzene. In the neat benzene-cyclohexane mixture, the I_2's vary only slightly over the whole range, leading to a maximum at ~0.25 mf benzene which indicates the nonideal behavior of the mixture, the maximum probably caused by some benzene-cyclohexane clusters, etc., formed at this composition. The I_2 values observed with 10 mM DABz, on the other hand, increase rapidly with the mole fraction benzene and become (at 0.5 mf benzene) almost indistinguishable from those measured in a neat benzene-DABz solution.

These latter data certainly demonstrate the dominating influence of the benzene and clearly indicate that the changes of I_2 are not an additive effect of the two solvents.[17]

The introduction of a nitro group in the para position of the benzene ring in DABz leads again to a completely different behavior. If DABzNO$_2$ is dissolved in benzene (because of the limited solubility of DABzNO$_2$ the measurements were carried out at 54 °C), the thermal *o*-Ps formation probability drops significantly with the surfactant concentration as shown in Figure 4, without displacing any discontinuities. Since in this system the surfactant reacted strongly with *o*-Ps as indicated by a significant change in λ_2, the number of thermal *o*-Ps formed ($\frac{3}{4}P$) had to be calculated from I_2, the intensity of the long-lived component in the positron lifetime spectra, by using the correlation between I_2, λ_2, and $\frac{3}{4}P$ as previously discussed:[18]

$$I_2 = \tfrac{3}{4}P(1 + K_1[\mathrm{M}])/(\lambda_\mathrm{F} - \lambda_\mathrm{p} - K_1[\mathrm{M}])$$

where K_1 is the observed rate constant of *o*-Ps with the surfactant, [M] is the surfactant concentration, λ_P is the positron annihilation rate in the neat solvent, and λ_F corresponds to the annihilation rate of the free positrons in these solutions. It was approximated as $2.5 \times 10^9\ \mathrm{s}^{-1}$.

Such a correction was not necessary in the other systems, where thermal *o*-Ps interacted only very weakly with the surfactant and no significant change in λ_2 could be observed as a function of surfactant concentration. Consequently I_2 remained proportional to the number of thermal *o*-Ps atoms formed independent of surfactant concentration.

Muller[4] has postulated that most surfactant-solvent systems fall into one of two classes showing different aggregation behavior and he considers DAP in benzene or cyclohexane as a prototype for what he calls type 1 aggregation, which has the following characteristics: (1) small average aggregation number ($\bar{n}$);[3-7] (2) no well-defined critical micelle concentration (cmc); (3) $\bar{n}$ progressively increases with increasing surfactant concentration without reaching a limiting constant value; (4) the dependence of the micellar molecular weight on the surfactant concentration is accounted for by using a stepwise sequential multiple-equilibrium model.

The second class of surfactants according to Muller[4] is characterized by (1) a large aggregation number (12-30); (2) aggregation appears to commence at a moderately well defined cmc; (3) at fairly high surfactant concentrations, $\bar{n}$ reaches a constant limiting value which depends on the nature of the surfactant and solvent; (4) aggregation is better described by a single equilibrium or monomer $\leftrightharpoons n$-mer model. A typical example for this second category would be the alkali dialkylsulfosuccinates in solvents of low dielectric constants.

A comparison of the present results obtained with the alkylammonium carboxylates such as BAP, HAP, OAP, DeAP, DAP, and DAB in cyclohexane solutions, which all show the appearance of a cooperative effect at a well-defined surfactant concentration, with the previously reported results for AOT benzene or cyclohexane solutions, however, reveals no qualitatively different behavior.[7-9] Furthermore, measurements of the dielectric increment in AOT-benzene and DAP-benzene solutions carried out by Eicke et al.[11] as a function of surfactant concentration show abrupt changes in this parameter in both systems at a surfactant concentration range at which I_2 in the positron annihilation studies also sharply declines.

Thus it appears that the process which is recognized by both of these techniques occurs with surfactants falling into either one of Muller's classifications.

Furthermore, it seems reasonable to assume that this sudden change in these two physical parameters is related to the formation of a new species via a pseudophase transition. This new species may be a trimer or another cyclic aggregate as previously postulated by several authors.[19,20]

This does not exclude, however, that this pseudophase transition leading to the appearance of the cooperative effect is followed by a continuous concentration-dependent aggregation. Judging from the shape of the I_2 vs surfactant concentration plots as shown in Figures 1 and 2 the latter process seems to be more pronounced in the shorter chain surfactants BAP, HAP, OAP, and DeAP than in DAP, which would emphasize the steric effect involved in the aggregation step. This becomes even more evident if the anionic part of the surfactant molecule contains an aromatic ring system, as in DABz (in cyclohexane), in which case this initial pseudophase transition cannot be observed at all. On the other hand, the simple extension of the hydrocarbon chain of the anion by one C atom seems to have little influence on the aggregation behavior (Figure 3).

Of special interest is the effect of the nature of the solvent on the positronium formation probability with DAP, DAB, or DABz in cyclohexane as compared to benzene solutions of these components.

While in the cyclohexane solutions of all three systems the thermal o-Ps formation is clearly affected by the presence of different amounts of surfactant, in benzene solutions this is true only for the DAP system and to a much lesser degree for the DAB surfactant, while no change at all in I_2 can be observed in the case of DABz over the total micelle concentration range (Figure 3) studied.

These differences are somewhat puzzling and will demand further investigation. Tentatively one might want to consider that this different behavior is inherent to the system, and perhaps a result of strong intermolecular interaction between the solvent benzene molecules with the aromatic ring in the benzoate portion of the surfactant molecules which prevents sudden rearrangements or pseudophase transitions, as, e.g., postulated by Eicke.[21] This author has suggested that in the DAP solutions at low surfactant concentrations the surfactant molecules are lined up in an open-chain-like structure and undergo at a certain concentration a pseudophase transition to a multipolar structure, which would explain the drastic drops in the I_2 values at a certain surfactant concentration. As pointed out above, this sudden transition might be hindered by strong intermolecular interaction between the benzoate ion and the solvent, benzene. This would be consistent with the previously made observation that certain additives, such as nitrobenzenes or tetracyanoethylene, which form molecular complexes with DAP eliminate the drastic changes of I_2 giving rise to a more gradual drop of I_2.[8]

While this presents a possible explanation of the differences between the DAP and DABz systems, an open question still remains: the drastic variation of I_2 in DAB–cyclohexane while hardly any change in I_2 can be seen over the same surfactant concentration range in DAB–benzene systems.

Qualitatively this solvent effect may be also expected on the basis of Muller's model,[4] which would predict a preference of open-chain oligomers which might not be detectable by the positron annihilation technique if the product ϵd is large (ϵ: cyclohexane (2.0 D) vs. benzene (2.3 D), although, as our experiments show, steric factors will play a significant role.

Interesting is the observation that the DABzNO$_2$ surfactants show a distinctly different behavior in benzene as compared to DAB or DABz in the same solvent. In line with the above assumption one would have to postulate that the presence of the polar nitro group favors the formation of cyclic aggregates which in turn can be recognized by the positron annihilation method.

The general picture which emerges from this study is that the aggregation behavior of these surfactants is governed in a rather subtle way by the nature of surfactant and solvent. An attempt to develop a general model for the aggregation process will be further complicated by the fact that small amounts of water or other impurities which cannot by completely excluded in the experiments may have a profound effect on the association mechanism.[11,22,23]

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(2) Visiting Scientist from Instituto Nacional de Energia Nuclear, Mexico.
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