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Microemulsion Systems Studied by Positron Annihilation Techniques

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Abstract: The formation of thermalized positronium atoms is greatly reduced if increasing amounts of water become solubilized in reversed micelles formed by sodium bis(2-ethylhexyl) sulfosuccinate in apolar solvents. Similar observations have been made if the surfactant is Triton X-100. The application of the positron annihilation technique to the study of microemulsions consisting of potassium oleate–alcohol–oil–water mixtures indicates, consistent with previous results, that microemulsion formation requires a certain water/oil ratio if the oil is a long-chain aliphatic hydrocarbon such as hexadecane. This ratio is 0.4 in the case of a 1-pentanol- and 0.2 for a 1-hexanol-containing mixture. This minimum water content is strongly reduced if the oil is an aromatic hydrocarbon. The positron annihilation data also sensitively reflect structural rearrangements in these solutions occurring upon further addition of water, such as the transition of spherical aggregates to a disk-like lamellae structure.

Introduction

Microemulsions[1] have recently attracted intense interest because of their potential role in tertiary oil recovery,[2] octane improvement, pollution abatement, and processing aids in chemical processing in general.[3-5] Another new application is a microemulsion-based system that partially imitates early, light-dependent steps occurring in green plants in an effort to convert light energy into chemical fuels.[6]

Microemulsions have been characterized in a great number of publications to which reference is made.[1,7-15] Phenomenologically microemulsions can be described as optically transparent oil–water dispersions, usually produced by mixing a surfactant with a cosurfactant, commonly an alcohol, and water in an oil (hydrocarbon). Microemulsions are thermodynamically stable and in a typical water-in-oil microemulsion the dispersed phase forming spherically shaped droplets containing water molecules with the surfactant and cosurfactant molecules located in the interfacial region may have a diameter in the range of 100–1000 Å.

Several techniques, such as optical property, viscosity, electron microscopy, electrical conductivity, low-angle X-ray, and NMR measurements, were employed in the past for the study of the solubilization and aggregation processes leading to the formation of microemulsions and the structural changes occurring in such solutions upon varying the relative amounts of the various components, especially the water contents.

In previous publications we have reported on the application of the positron annihilation technique to the investigation of micellar aggregation phenomena in reversed micellar systems,[16-21] which are closely related to microemulsions, as well as in aqueous micellar solutions,[22-24] and to the detection of mesomorphic phase transitions in liquid crystals[25] and glass transformations in polymers.[26]

The basis for the employment of this technique to the study of these structural changes is that the mechanism of the positronium atom (Ps), which is the bound state of a positron and an electron, as well as its subsequent reactions is highly dependent on the physical and chemical microstructure of the environment in which these events occur.[27] Positronium formation and positronium reactions can both be easily identified via positron lifetime measurements and variations in these positron annihilation parameters can be correlated with structural changes occurring in the solutions as a function of their composition.

In previous studies we have been able to show that the formation of micelles in aqueous solutions is accompanied by a simultaneous drastic reduction in the positronium formation probability.[22-24] Similar observations were made when the surfactant was added to apolar solvents (reversed micelle formation).[16-23] We interpreted these findings in terms of an effective trapping of (energetic) positrons or positronium atoms by the aggregates or micelles present under these experimental conditions in the solutions, leading to the observed reduction of the number of (thermal) Ps atoms formed.[24]

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Thus the present investigation was carried out to assess the effect which an increasing amount of water solubilized in reverse micelles (leading to the formation of swollen micelles and eventually microemulsions) might have on the positron lifetimes and positronium formation probability and how these parameters might be affected by possible structural changes which these systems undergo at still higher water concentrations.

These studies, which were performed in well-characterized solutions, revealed a distinct correlation between the positronium formation probability and the water contents of the reversed micelles. Consequently, in the second part of this investigation the positron annihilation technique was utilized for a detailed study of several microemulsion systems.

In particular the potassium oleate–hexadecane–pentanol (or hexanol)–water system was investigated, where Shah et al.[1d,12,13] observed striking difference, e.g., in the electrical resistance of the solutions if 1-pentanol was replaced by 1-hexanol. The authors suggested that the system containing 1-pentanol is a cosolubilized system in which one can visualize the surfactant and the cosurfactant forming a liquid which can dissolve both oil and water as a molecular solution, whereas the 1-hexanol-containing system is a true water-in-oil microemulsion in which water is present as spherical droplets. Furthermore, in the hexanol-containing systems the authors claimed to have observed rearrangements in the structure of the solubilized water from water spheres to water cylinders to water lamellae at higher concentrations.[12,13] Such a difference in the behavior of the two systems as well as the postulated structure changes in the hexanol-containing solution should also be sensitively reflected in the positron annihilation parameters and it seemed interesting to evaluate whether this technique could provide independent evidence corroborating the finding by Shah et al.

Another point of interest was to utilize the extreme sensitivity of the positron annihilation process to test Friberg's contention,[14] which was based on light-scattering results, namely, that the three structure-forming components water, pentanol, and potassium oleate form no detectable association aggregates in the concentration range of 5–15% (w/w) water. According to these authors, in this range the water is associated with the surfactant and only if the water content is increased above 15% does gradual association to larger aggregates occur. The presence of up to 50% decane has virtually no effect on this behavior, while in the presence of an aromatic hydrocarbon aggregation takes place even at the lowest water concentrations.

Consequently positron annihilation measurements were also carried out in toluene–potassium oleate–hexanol–water systems in order to clarify this issue and to obtain additional detailed knowledge on the aggregation mechanism in these systems. The results of these experiments will be discussed in the following.

Experimental Section

A. Materials. Triton X-100 purchased from Amersham Corp. was scintillation grade quality. The potassium oleate from ICN Inc. was pharmaceutical grade purity and used without further purification—Aerosol OT (AOT, sodium bis(2-ethylhexyl) sulfosuccinate) obtained from Fisher Scientific Co., with a stated purity of 100%, was recrystallized and dried in accordance with the procedure in ref 28.

Solvents such as toluene, cyclohexane, isooctane, *n*-heptane, and alcohols (1-propanol, 1-pentanol, 1-hexanol) were spectroscopic grade from Fisher Co. The hydrocarbons were further dehydrated by distillation over metallic sodium.

B. Preparation of Solutions for Positron Lifetime Measurements. The various solutions studied in this investigation were prepared by mixing the components in the indicated proportions, to which different amounts of water (triple distilled) were added.

Triton–Cyclohexane–Pentanol. Triton–pentanol (4:1); the mixture (triton–pentanol) is 20% (w/v) in cyclohexane.

Triton–Toluene. (a) Solution: Triton–toluene (v/v) 3:7, 0% alcohol. (b) Solution: (Triton–toluene (v/v) 3:7) 97% (v/v), 1-propanol 3% (v/v). (c) Solution: (Triton–toluene 3:7 (v/v)) 93% (v/v), 1-propanol 7% (v/v). (d) Solution: (Triton–toluene 3:7 (v/v)) 80% (v/v), 1-propanol 20% (v/v).

AOT–Toluene. Solution: AOT (0.565 M) in toluene.

Potassium Oleate–Toluene. (a) Solution: potassium oleate (10 g), toluene (100 mL), hexanol (40 mL).

Potassium Oleate–Hexadecane–Alcohol. Same conditions as in ref 1a, 12, 13. Solutions: potassium oleate (20 g), hexadecane (100 mL), 40 mL of hexanol or pentanol.

C. Positron Lifetime Measurements and Preparation of Samples. Positron lifetime measurements were carried out by a fast coincidence technique. The 1.27-MeV photons resulting from the deexcitation of the excited state of ^{22}Ne, formed in the positron decay of ^{22}Na, are detected by a plastic scintillation detector (Naton 136, 2 × 1 in.) mounted on a RCA 8575 photomultiplier connected to a Ortec 265 base. The output signal is processed in a Ortec 583 differential constant fraction discriminator, which permits only the passage of signals which correspond to a photon energy in the 0.8–1.3-MeV range. These signals provide the starting signal in a Ortec 437A time-pulse height converter (TPHC). The 0.51-MeV photons resulting from the positron annihilation are similarly processed, except that the window in the Ortec 583 differential constant fraction discriminator is set to allow the passage of pulses corresponding to a 0.3–0.52-MeV range. These signals provide the stop signal in the TPHC. Since the energy discrimination is done on the fast signals only valid pulses arrive at the TPHC, and the dead time of this unit is greatly reduced, leading to a much higher coincidence counting rate and thus to significantly shorter counting times.

Measurements under these experimental conditions required typically 15–20 min. Random coincidences were further suppressed by requiring coincidence between the output pulses of the discriminators, utilizing a Ortec 414 fast coincidence unit, whose output pulse was used as gating signal at the TPHC. The output of the TPHC was stored in the usual way in a multichannel analyzer. The resolution of the system, as measured by the prompt time distribution of ^{60}Co source and without changing the 1.27- and 0.511-MeV bias, was found to be 0.390 ns fwhm. Corrections for the source component, which had an intensity of less than 4%, were made in the usual way by using conventional computational methods. Specially designed cylindrical sample vials (Pyrex glass 100 mm long and 10 mm i.d.) were filled with about 2 mL of the sample solution. The positron sources consisted of 5–20 Ci ^{22}Na, prepared by diffusing carrier-free ^{22}NaCl into a thin, soft glass foil. The sources were placed inside the vials and completely immersed in the liquid sample. The vials were degassed and subsequently sealed off and counted at room temperature.

D. General Method of Data Analysis. Positron lifetimes and distributions were obtained by standard computational techniques. The lifetime spectra were resolved as previously described[29] into two components, a short-lived component, which is the result of *p*-Ps annihilation, free positron annihilation, and epithermal Ps interactions, and the long-lived component, with a decay constant λ_2 and its associated intensity I_2 which originates from the reactions and subsequent annihilation of thermalized or nearly thermalized *o*-Ps.

Results and Discussion

A. Correlation between Water Contents of Reversed Micelles and Positron Annihilation Parameters. In order to assess the effect of the water contents in reversed micelles on the positron annihilation process we carried out positron lifetime measurements in some well-characterized reversed micellar systems such as sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) and Triton X-100 dissolved in various apolar solvents.

The AOT system has been studied by various investigators,[9,11,28,30-43] most recently by Thomas et al.,[44-46] who probed

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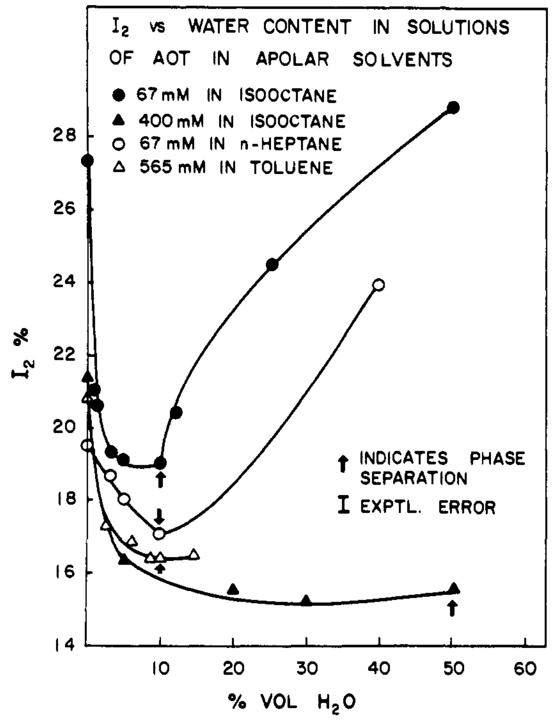

Figure 1. I_2 vs. water contents in solutions of AOT in apolar solvents at room temperature.

the structure and state of water solubilized in the reversed micelles formed by AOT in hydrocarbons by fluorescence techniques and pulse radiolysis.

Water is accommodated in the polar centers of the AOT aggregates where it forms spherical pools the sizes of which are controlled by the AOT/H_2O ratios. The experimental results obtained by these investigators seem to indicate that in smaller water pools the water molecules are highly immobilized owing to strong ion–dipole interactions with counterions. On completion of the solvation shell of the counterion ($H_2O/Na^+ \simeq 6$) the rigidity of the micellar core is greatly reduced and the properties of the additional water molecules approach that of bulk water.

In the first series of experiments positron lifetime measurements were performed in solutions of AOT (67 and 400 mM) in isooctane, to which increasing amounts of water were added. For comparison similar measurements were made with *n*-heptane (67 mM AOT) and toluene (535 mM AOT) as solvent.

As can be seen from Figure 1, where I_2, the intensity of the long-lived component in the positron lifetime spectra which is indicative of the number of thermalized *o*-Ps formed,[27,29] is plotted as a function of the water contents, I_2 is drastically reduced in all four solutions even in the presence of a relatively small amount of water (<1%), which corresponds roughly to 8–9 molecules of water per AOT molecule in the 67 mM AOT and to 1–2 water molecules per AOT molecule in the higher concentrated AOT solutions.

At higher water concentrations, phase separation, as indicated in the figure, occurs, which makes further evaluation of the positron annihilation data difficult. The drastic decrease of I_2 with the water contents is accompanied by a small simultaneous increase of λ_2. The annihilation rate λ_2 can be considered in the solutions to be the weighted average of the rates of the annihilation of the thermalized Ps atoms residing in the various environments and should therefore be less affected by the trapping of positrons.

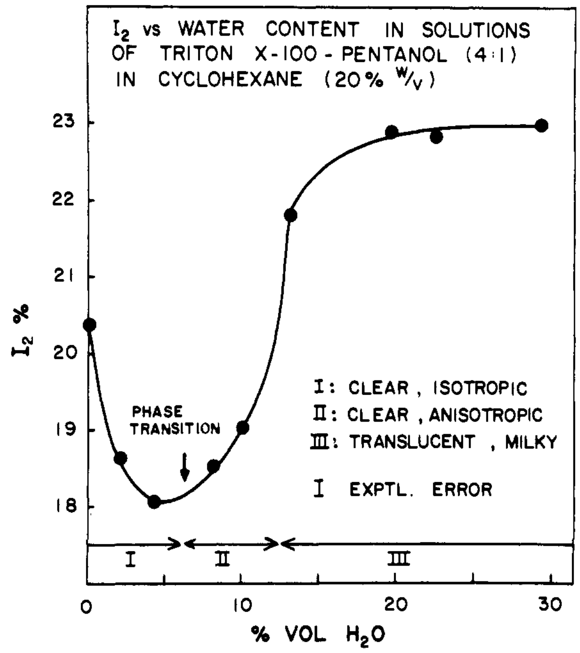

Figure 2. I_2 vs. water contents in solutions of Triton X-100–pentanol (4:1) in cyclohexane (20% w/v) at room temperature.

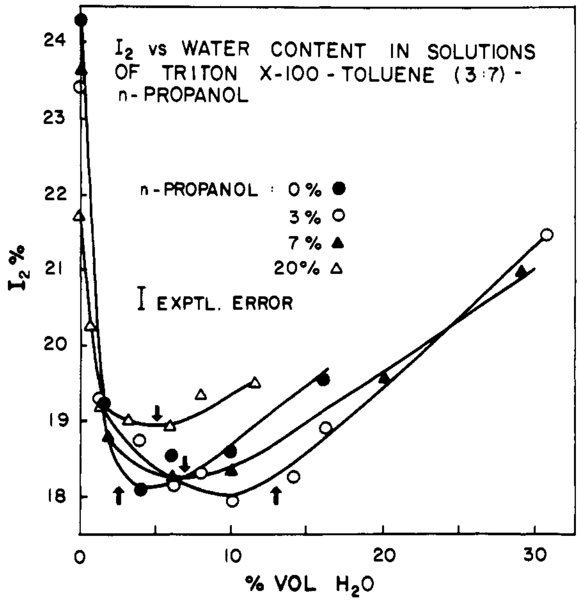

Figure 3. I_2 vs. water contents in solutions of Triton X-100–1-propanol in toluene at room temperature.

Because of the relative small changes of λ_2 observed with a variation in the water contents, we will in the following only try to correlate the I_2 values with the structural changes occurring in the systems.

Other systems which have been widely investigated are Triton X-100 solutions. Kumar et al.[47] determined the water uptake in Triton–cyclohexane solutions and observed a distinct increase of water solubilization upon addition of alcohols, which the authors explain in terms of the formation of spherical swollen micelles similar to those discussed previously for the AOT system.

Figure 2 shows the results of positron lifetime measurements in a 20% (w/v) solution of Triton–pentanol (4:1 by weight) in cyclohexane to which different amounts of water were added. In accordance with the results obtained in the AOT systems, I_2 drops as a function of increasing amount of water solubilized in the Triton–pentanol aggregates up to about 7–8% H_2O, at which the

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appearance of an anisotropic phase can be observed accompanied by an increase of I_2, leveling off at about 13% H_2O, at which point phase separation occurs. The transition from the clear to the anisotropic phase has previously been associated with a transition from swollen micelles to a disk-like lamellae structure.

We also included into this investigation positron lifetime measurement in Triton–toluene mixtures (3:7) with various amounts of propanol present. The addition of water resulted again in a pronounced decrease of I_2 until an anisotropic phase or phase separation occurred (Figure 3), at which point I_2 sharply increased.

Summarizing, it can be said that the results observed in all the systems discussed so far show a consistent trend, namely, a drastic decrease of I_2 with the amount of water solubilized in the reversed micelles.

Previously[18–24] we have explained a similar drop in I_2 upon aggregate formation in solutions of surfactants in aqueous and apolar solvents by an efficient trapping of energetic Ps atoms leading to rapid annihilation in these aggregates or by a trapping of the precursors of Ps (kinetically excited positrons or electrons) by these aggregates inhibiting Ps formation.

The further decrease of I_2 in the same solutions, e.g., AOT–isooctane, upon addition of water (Figure 3) may, therefore, be rationalized in a similar way, by assuming that the presence of water in the reversed micelles enhances the capability of these aggregates to trap the precursors of Ps, or energetic Ps itself, thus reducing the yield of thermalized Ps atoms. The reason for this trapping enhancement may be the increase of the polarity of the aggregate and the fluidity of the water molecules if a larger water pool is present in the micelles. This would be an obvious analogy to the results of Thomas et al.,[46] who observed a distinct increase in the rate constants for electron capture in these solutions with larger water pools present above the value one can reasonably expect from the increase of the geometric cross sections of the reversed micelles with increasing water contents. These results led the author to believe that larger water bubbles exert an attractive force on e^-.

In the case of Ps formation, the species which are trapped in these aggregates could be the electrons formed in the positron track, thus reducing effectively the number of electrons available for recombination with the positron at the end of its track, if one prefers to explain the results in terms of the spur reaction model,[48] which assumes that Ps is formed via positron–electron recombination within the positron spur. On the other hand, if it is the polarity of the aggregate which creates an attractive environment for such a small charged particle and the mobility of the water molecules which may contribute to an effective trapping by providing the hydration energy for such a small charged entity, then there is reason to believe that a positively charged particle, i.e., the positron, which has approximately the same hydration energy, would be equally well captured—i.e., thermalized—and, if mobile water is available, hydrated, thus rendering it incapable of forming Ps. The third possibility is the trapping of kinetically excited Ps. Since Ps can be assumed to be highly polarizable an environment of high polarity would also constitute a good trapping site for such a species. Subsequent rapid annihilation could explain the observed reduction of I_2.

While the details of the trapping mechanism are still not exactly understood and the subject of ongoing investigation in this laboratory, the present evidence clearly indicates the great potential of the positron annihilation technique for the investigation of reversed micelles containing water molecules, i.e., microemulsions.

B. Study of Properties of Microemulsions via the Positron Annihilation Techniques. Using a combination of physical techniques such as electrical resistance, high-resolution NMR, etc., Shah et al.[1d,12,13] have postulated that two isotropic clear systems consisting of a surfactant, potassium oleate, a cosurfactant, which is an alcohol, hexadecane, and water, with identical compositions, except that one contains 1-pentanol and the other 1-hexanol, are structurally quite dissimilar systems. They proposed a structure for the pentanol-containing system, which can be characterized as a state of cosolubilization, in which the surfactant and cosurfactant form a liquid which can dissolve both oil or water as a molecular solution, whereas the hexanol-containing system is a true water-in-oil microemulsion in which water is present as spherical droplets.

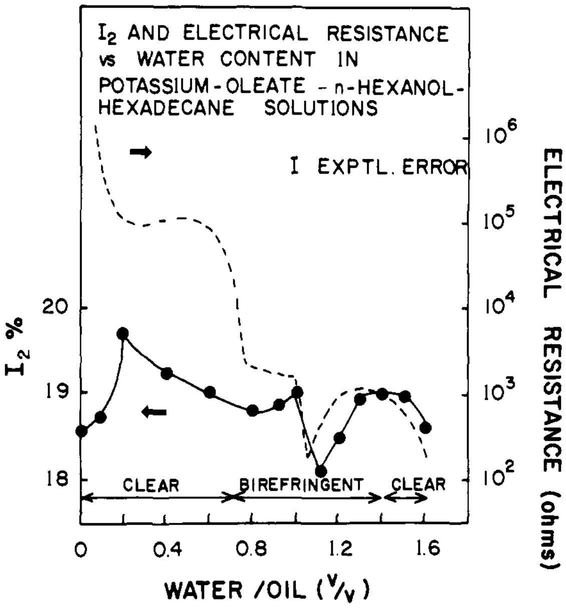

Figure 4. I_2 and electrical resistance vs. water content in potassium oleate–1-hexanol–hexadecane solutions at room temperature. (Composition of solution: 100 mL of hexadecane, 20 g of potassium oleate, 40 mL of hexanol.) Electrical resistance data were taken from ref 12.

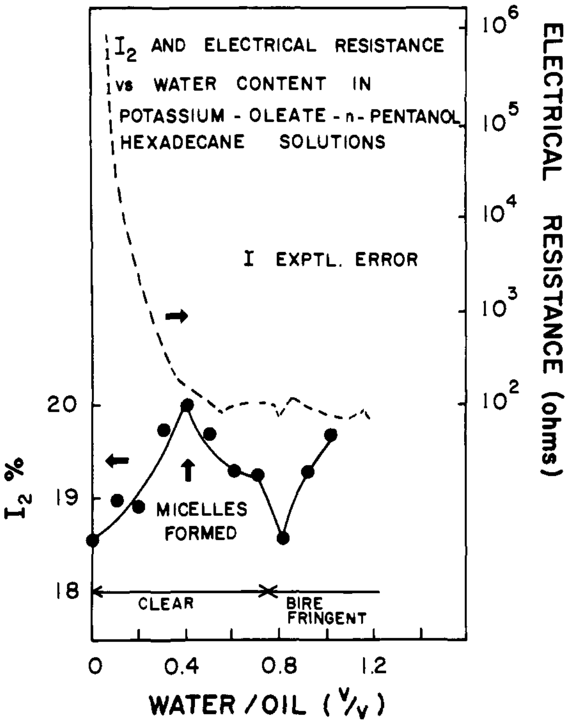

Figure 5. I_2 and electrical resistance vs. water content in potassium oleate–1-pentanol–hexadecane solutions at room temperature. (Composition of solution: 100 mL of hexadecane, 20 g of potassium oleate, 40 mL of pentanol.) Electrical resistance data were taken from ref 12.

Friberg et al.[14,15] more recently studied the same system (pentanol only) by light scattering and electron microscopy and came to the conclusion that a certain water concentration is a necessary ingredient in these and similar systems to achieve the formation of micelles and, with increasing water contents, microemulsions. They identified in the pentanol-containing system a water/oil ratio of about 0.4 (v/v) as the point at which inverse micelle formation occurs, a concentration which incidentally co-

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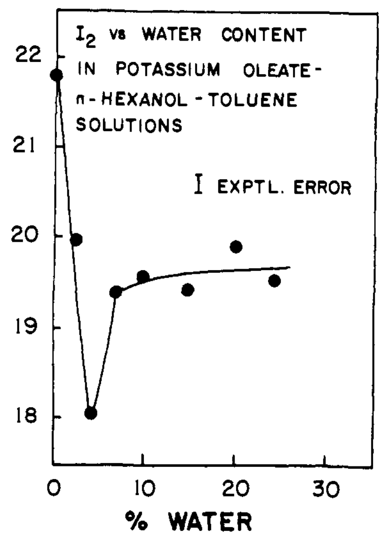

Figure 6. I_2 vs. water content in potassium oleate–1-hexanol–toluene solutions at room temperature. (Composition of solution: 100 mL of toluene, 40 mL of hexanol, 10 g of potassium oleate.)

incides with a change of slope on Shah's conductivity curve.

We reinvestigated these two systems by utilizing the positron annihilation technique, expecting that on the basis of the results discussed in the preceding section the formation of water-containing micelles or microemulsions could be detected by a significant drop in the positron annihilation parameter I_2 (vide supra). The results for the 1-hexanol-containing system are shown in Figure 4 where I_2 is plotted as a function of the water contents. For comparison, Shah's electrical resistance measurements[12] were included.

The plot clearly shows an increase of I_2 up to a water/oil ratio of 0.2, which is the opposite of that one would expect for micelle formation and thus provides no evidence for micelle formation. We, therefore, suggest that in this region a state of cosolubilization as assumed by Shah exists. If the water/oil ratio increases beyond 0.2, I_2 shows a significant drop. We would like to associate this concentration in accordance with the AOT results with the onset of microemulsion formation. A comparison with Shah's data[12] shows that at this ratio the electrical resistance undergoes a distinct change of slope. In the pentanol-containing system a similar situation prevails (Figure 5) except that the drop of I_2 occurs at the higher water/oil ratio of 0.4, which is identical with the ratio at which Friberg[14] observes large aggregate formation in his light-scattering experiments.

Friberg[14] noted that the replacement of the aliphatic by an aromatic hydrocarbon caused pronounced changes in the initial association, resulting in micelle formation even at very small concentration. This is also borne out in the positron annihilation data obtained in the toluene–potassium oleate–1-hexanol–water system. As can be seen from Figure 6, I_2 decreases sharply when small amounts of water are added. In contrast to the systems containing aliphatic hydrocarbons the plot provides no evidence for the existence of cosolubilization at low water concentrations. On the basis of the present positron annihilation data we would, therefore, concur with Friberg[14,15] that in the potassium oleate–hexadecane–1-hexanol or 1-pentanol–water systems below a water/oil ratio of 0.2 and 0.4, respectively, water is cosolubilized, whereas at higher water concentrations these solutions form true microemulsions. In potassium oleate–toluene–1-hexanol–water solutions, on the other hand, no such obvious minimum water concentration is required for micelle formation.

The effect of the nature of the oil phase, or a polar solvent, in this case aliphatic vs. aromatic hydrocarbon, is interesting and may be related to strong intermolecular interaction between the solvent molecules and the surfactant molecules, similar to the one which we suggested for the dodecylammonium benzoate system in benzene solution.[18] Another point of interest is the characteristic behavior of I_2 at higher water concentrations in the potassium oleate–hexadecane–1-hexanol–water system. Shah interpreted his electrical resistance, viscosity, and NMR measurements in the birefringent region, i.e., at a water/oil ratio between 0.7 and 1.3, in terms of a change in the structure of water from water spheres to water cylinders to water lamellae.

Our positron annihilation data in this system (Figure 4) seem to indicate, as presented by the change of the slope in the I_2 vs. water/oil ratio plot, a phase transition or separation at 0.8 and again at 1.1, coinciding with clear breaks in Shah's[12,13] electrical resistance, viscosity, and NMR plots. Whether these results indeed signal, as suggested by Shah, structural changes, or the existence of mixtures of a liquid-crystalline phase and one or two liquids as postulated by Friberg,[14,15] cannot be answered; however, they again demonstrate the sensitivity of the positron annihilation technique toward subtle rearrangements in liquid systems.

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