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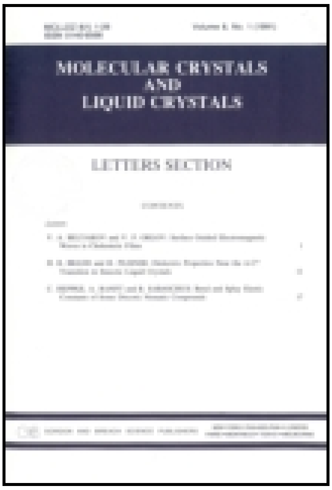

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Positron Lifetime and Electrical Conductivity Studies of Bicontinuous Phase in (TTAB+Pentanol)/Water/n-Octane Reverse Micellar System

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Positron Lifetime and Electrical Conductivity Studies of Bicontinuous Phase in (TTAB+Pentanol)/Water/n-Octane Reverse Micellar System

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Reverse micellar (L2) phase in (TTAB+pentanol)/water/n-octane, mapped by using optical method, was investigated by preparing mixtures of 30%, 40%, 50%, 60% and 70% by weight of (TTAB+pentanol)(1:1) in n-octane. Positron annihilation studies were performed in these mixtures as a function of water concentration. Around water concentrations of 13.8%, 11.1%, 8.4%, 7.9% and 9.1% respectively, ortho-positronium pick-off lifetime $\tau 3$ shows oscillatory behaviour whereas positronium formation I3 exhibits abrupt change. These changes have been attributed to the setting in of bicontinuous phase. Electrical conductivity measurements support these results. Positron annihilation technique can thus distinguish between droplet-like and bicontinuous structures in L2 phase.

Keywords Surfactant; electrical conductivity; bicontinuity; microemulsion; positronium

1. Introduction

There are numerous reports on the formation of bicontinuous structures in microemulsions [1–5]. Transformation from a droplet-like to a bicontinuous structure in a water-in-oil (w/o) microemulsion can occur by suitably changing water content in the system. Despite its existence, detection of a bicontinuous phase experimentally is rather difficult. Scattering techniques using light and x-ray cannot discriminate between droplet-like and bicontinuous structures. Small angle neutron scattering contrast variation technique can throw some light on the existence of bicontinuity from the knowledge of the mean curvature of the surfactant rich film [6], but only to a limited extent. Clausse et al. [7] claims to have used electrical conductivity measurements to demonstrate bicontinuity [7], but again to a limited applicability. While these measurements can throw light on water continuity, they fail to establish oil continuity. On the contrary, fluorescence probe method can be used to

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establish oil continuity. Positron annihilation spectroscopy (PAS) has also been employed in the detection of bicontinuous phase in w/o microemulsions [8].

We here present the results of PAS and electrical conductivity measurements in w/o microemulsion (or L2) phase in (TTAB+Pentanol)/water/n-octane system.

2. Experimental

TTAB (purity $> 98\%$) was procured from Fluka Chemika, Switzerland. Pentanol (purity $> 99\%$) and n-octane (purity $> 99\%$) were obtained from E. Merk, Germany. De-ionised triple-distilled water was used for making ternary solutions. The optimal proportion of TTAB in pentanol for the formation of w/o microemulsion was found to be 1:1 by weight. Subsequently, a phase diagram of (TTAB + pentanol)(1:1)/water/n-octane was mapped out by observing the optical activity of the surfactant solution using crossed polaroids. For detailed study of L2 phase, five mother solutions of (i) 30%, (ii) 40%, (iii) 50%, (iv) 60%, and (iii) 70% by weight of (TTAB + pentanol)(1:1) in n- octane were prepared. By adding water as a third component to these solutions the required (TTAB + pentanol)(1:1)/water/n-octane ternary systems were prepared. Positron annihihation studies were then performed in these systems as a function of the concentration of water using a standard lifetime spectrometer, details of which are described elsewhere [9]. The positron source used was 22Na. The source was prepared by evaporating a few drops of aqueous solution of 22NaCl on a thin Mylar film and then covering it by another similar film. The source was sealed to avoid any leakage when placed in a solution, by using a special grade epoxy resin. The sealed source was placed in the middle of a specially designed glass container which could hold enough sample to stop all the positrons emitted by the source. In each set of measurements, a total of at least 2×10^5 counts were collected. The electrical conductivity measurements were performed using a Delica Impedance Bridge Model 12K.

The positron lifetime spectra were analysed using the software package PC-PATFIT developed by Riso National Laboratory, Denmark [10]. For determining the resolution function of the lifetime spectrometer, benzophenone single crystal was grown from a solution of benzophenone in methanol. The resolution function was extracted from the lifetime data using the software RESOLUTION. This resolution function was then used to deconvolute the lifetime spectra obtained for a sample. The most suitable fit to a lifetime spectrum was obtained by using the software POSITRONFIT which can fit a given data set to a two-, three-, or four-component multi-exponential fit with several constraints. A three-component fit constraining the shortest component τ_1 to para-positronium (p-Ps) lifetime, 0.125 ns, and the intensities I_1 and I_3 fixed in the ratio of 1:3 produced the best fit to all lifetime spectra. The longest component τ_3 was associated with the pick-off annihilation of ortho-positronium (o-Ps) with electrons bound to the molecules of the samples. The relative intensity I_3 of this component is proportional to the positronium (Ps) formation in the samples. Both these parameters exhibit significant sensitivity to structural changes taking place in the samples. The intermediate component, τ_2, has been attributed to the free annihilation of positrons with electrons of the samples without forming any bound state with them. This component did not show any appreciable sensitivity to any structural change occurring in the systems.

3. Results and Discussion

Figure 1 shows the phase diagram of (TTAB + pentanol)(1:1)/water/n-octane ternary system. A w/o microemulsion (L_2) phase extending over wide range of concentrations of

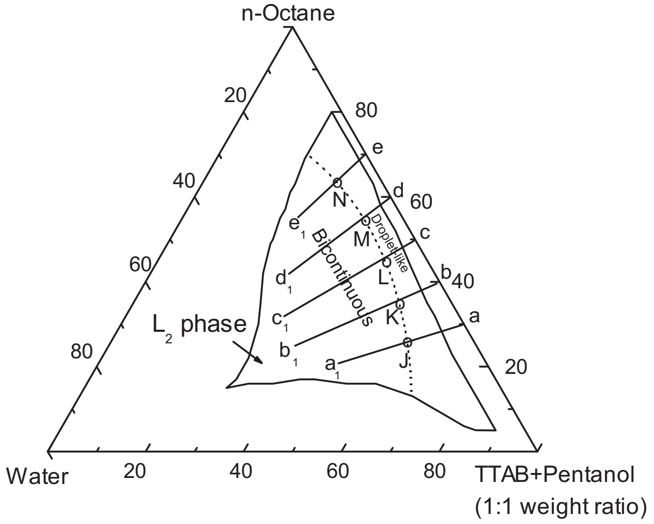

Figure 1. Phase diagram of (TTAB + pentanol)(1:1)/water/n-octane system.

the constituents is seen in this figure. The lines aa_1, bb_1, cc_1, dd_1, and ee_1 shown represent the directions along which positron lifetime and electrical conductivity measurements were performed on the ternary solutions obtained by gradually adding water to the mother solutions of (TTAB + pentanol)(1:1)/n-octane prepared.

Figure 2 shows the typical graphs of the dependence of τ_3 and I_3 on the concentration of water in (TTAB + pentanol)(1:1)/water/n-octane system prepared from the mother solution containing 40% (TTAB + pentanol)(1:1), that is, as we move along bb1. It can be noted from these graphs that positron annihilation parameters τ_3 and I_3 exhibit monotonous changes up to a certain concentration of water. However, at a water concentration of about 11.1%, these parameters exhibit either an abrupt or an oscillatory change indicating thereby the onset of a phase transformation.

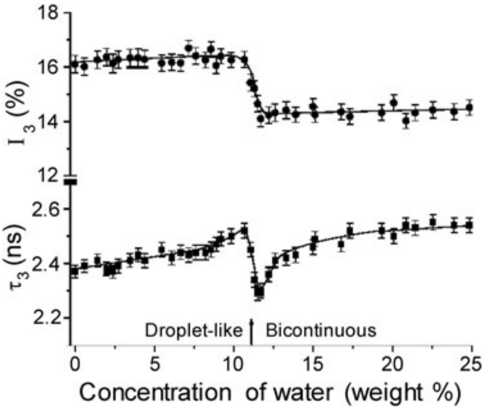

Figure 2. Dependence of τ_3 and I_3 on water concentration for (TTAB + pentanol)(1:1)/water/n-octane system initially containing 40% (TTAB + pentanol)(1:1) and 60% n-octane.

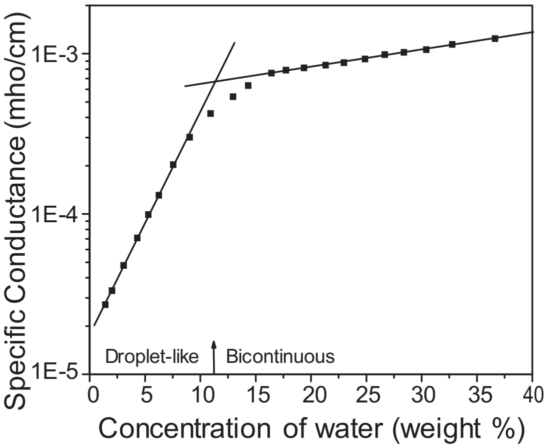

Figure 3. Dependence of specific conductance on the concentration of water for (TTAB + pentanol)(1:1)/water/n-octane system initially containing 40% of (TTAB + pentanol)(1:1).

Optical study reveals turbidity in this system for water concentration less than about 4.5%. At water concentration of 4.5% the solution turns clear and exhibits isotropic character indicating the formation of w/o microemulsion. The microemulsion phase exists till about 11.1% of water concentration. In this region, the positron annihilation parameters τ_3 and I_3 do not show any characteristic changes. At water concentration of about 11.1%, I_3 undergoes an abrupt decline in its value while τ_3 exhibits an oscillatory behaviour. Similar changes in the positron annihilation parameters were also observed in CTAB/water/hexanol system [8], and are suggestive of the setting in of a structural transformation in the system. It can be noted however that optically the system still continues to remain clear and isotropic. In case of CTAB/water/hexanol system, such characteristic changes of positron annihilation parameters, supported by electrical conductivity measurements, have been attributed to the onset of bicontinuous phase in the microemulsion phase. On further addition of water in the system beyond these characteristic changes, τ_3 and I_3 become almost constant again till the occurrence of phase separation at a water concentration of about 50%. The system continues to remain optically clear and isotropic until the phase separation occurs. Positron annihilation studies performed on other (TTAB + pentanol)(1:1)/water/n-octane systems, along bb_1, cc_1, dd_1, and ee_1 directions, also produced an abrupt change in I_3 and an oscillatory change in τ_3 when the systems transform into bicontinuous phase. The transition points indicating these transformations from droplet-like to bicontinuous phase are marked in figure 1 as J, K, L, M, and N.

Figure 3 shows the corresponding variation in the electrical conductivity values as a function of water concentration in (TTAB + pentanol)(1:1)/water/n-octane system which initially contains 40% (TTAB + pentanol)(1:1) and 60% n-octane. It is observed in this figure that, with the formation of w/o microemulsion, the specific conductance increases rapidly with increasing water concentration, a phenomenon characteristic of percolation [11–13]. When the water concentration is further increased in the system, the specific conductance plot tends to saturate out at a nearly constant level. This change in specific conductance plot has been explained on the basis of occurrence of percolation transition or onset of bicontinuity [7] in the system. The behavior of the conductivity near this transition shows a smooth changeover from the conductivity associated with percolation to the conductivity of the bicontinuous phase. The water concentration at which the bicontinuity appears in the system corresponds to the point of intersection of the two linear portions of the specific conductance plot.

In water-in-oil microemulsion, water droplets are usually dispersed in bulk oil medium. At low water concentrations, the electrical conductivity of the system is very low as the counter-ions, locked inside the water droplets, are not able to contribute to electrical conduction. When these electrically conducting droplets are randomly distributed within the insulating oil matrix, the sample is non-conducting, until the volume fraction of the conducting phase reaches the so- called percolation threshold. Close to the percolation threshold, the electrical properties show a nonlinear (critical) behaviour: small variations in the physical parameters, such as composition, voltage or temperature, result in large variations of electrical properties [14–16]. Thus the electrical conductivity of the present system can increase manifold, perhaps over many orders of magnitude, when the water concentration of the system is increased. Such large changes in the electrical conductivity have been observed in the present work (Fig. 3). The electrical conductivity behaviour of w/o microemulsions has been explained on the basis of percolative and effective medium theories [17–20]. However, the mechanism leading to percolation and the charge transport process has not so far been understood fully. One approach attributes percolation to the appearance of a "bicontinuous structure", that is, an open water channel responsible for electrical conduction – the static percolation picture [10, 21]. The other approach considers the attractive interaction between water globules as responsible for the formation of percolation clusters; here the charge transport is via hopping of the atomic surfactant on the clusters which also rearrange in time – the dynamic percolation picture [18, 22]. Evidences in support of both the percolation approaches can be found in literature. Frequency dependent electrical conductivity and dielectric measurements performed in an AOT/water/decane system [11] support the dynamic percolation model. Eicke et al. [23] also used the dynamic percolation model to explain the experimental results on AOT/water/isooctane microemulsions, wherein the conductivity is related to the migration of charged nanodroplets, which are nanometer-sized water droplets coated with surfactant monolayer, in the electric field.

In the present work also, the dependence of specific conductance on the concentration of water in (TTAB + pentanol)(1:1)/water/n-octane systems exhibits percolation transition. It can be noted that the specific conductance in the conducting phase in the present system is about 10-3 mho/cm which is much higher than those in AOT/water/isooctane and AOT/water/decane systems [11, 23]. The higher conductivity values in the conducting phase of (TTAB + pentanol)(1:1)/water/n-octane observed in the present work suggest that in this system the mechanism of percolation is perhaps of the static type i.e. the system undergoes a structural change from droplet-like to bicontinuous structure. This conjecture is also strongly supported by the results of the positron lifetime measurements.

The sensitivity of positron annihilation parameters τ_3 and I_3 to phase or structural transformations occurring in the system has been observed in various systems [24, 25]. In several systems, an abrupt or oscillatory change in the values of these parameters is a signature indicative of a structural change or phase transformation occurring in the system. Such an abrupt change in I_3 and a relaxational variation in τ_3 were also observed during a glass transition in the liquid crystal forming compound, n-p-cyano-p-heptylbiphenyl [26]. The abrupt or oscillatory change exhibited by τ_3 and I_3 at a certain water concentration in the present (TTAB + pentanol)(1:1)/water/n- octane systems therefore indicates a structural or phase transformation undergoing in these systems. The values of water concentrations at which such a transformation is detected by positron annihilation parameters are in close agreement with those determined from conductivity measurements. This agreement is a strong evidence for the observed changes in positron annihilation parameters and the electrical conductivity to represent the same phenomenon, namely the percolation transition, taking place in the system.

In general, the micelles formed initially in CTAB/water and TTAB/water binary systems are of spherical structure which gradually transforms to extended, rod-like, and finally to entangled rod-like structures. The surface free energy considerations applied to TTAB and CTAB micelles, normal or reverse, favour formation of cylindrical structures [27–29]. The formation of endless conduit-like structures in these systems permits the counter-ions to move in these conduits and hence enhances the electrical conductivity above the percolation threshold. This model is supported in the present investigation by the high value of specific conductance observed above the percolation threshold. Positron lifetime studies in the present work also detect the occurrence of a structural or phase transformation in the systems at a particular concentration of water. The positronium (Ps) formed in these systems is a hydrogen-like structure having dimensions of about $1\text{Å}'$. Positron annihilation in molecular materials is highly localized, thereby sensing variations in local electron or charge densities. This makes the positron annihilation parameters to be sensitive to structural or phase transformations. If the dynamic approach were to be accepted, the change in positron annihilation parameters is expected to be gradually varying with increasing water concentration rather than abrupt or oscillatory, a change characteristic of a structural transformation. Thus the positron annihilation study supports the static percolation approach i.e. the formation of a bicontinuous structure.

4. Conclusion

Positron lifetime and electrical conductivity measurements have been carried out to study the fine structure of w/o microemulsion (L_2) phase, mapped out by using optical method, for (TTAB + pentanol)(1:1)/water/n-octane. Both the positron annihilation parameters τ_3 and I_3 exhibit characteristic changes that indicate the existence of a phase boundary dividing the L_2 phase into droplet-like and bicontinuous structures. Thus the present work demonstrates that positron, as a non-destructive probe, can be used to reveal the existence of two structurally different regions in the L_2 phase which is otherwise considered to be a single phase. The changes observed in τ_3 and I_3 during the transformation from droplet-like to bicontinuous phase are identical in nature to those observed during glass transition in thermotropic liquid crystals. Combined application of positron annihilation technique with electrical conductivity measurements can yield a more detailed information on the transformation from droplet-like to bicontinuous structures. This study also reveals that the static model for percolation is more suitable for describing the phenomenon observed in the present system.

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