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P. Hossein Khani, A. Maitra, P. Jain. Phase transformation studies in (TTAB + pentanol)/water/n-octane system. Journal de Physique IV Proceedings, 1993, 03 (C4), pp.C4-321-C4-323. 10.1051/jp4:1993452 . jpa-00251495

HAL Id: jpa-00251495

<https://hal.science/jpa-00251495>

Submitted on 1 Jan 1993

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Phase transformation studies in (TTAB + pentanol)/water/n-octane system

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Abstract

Phase transformation studies have been carried out in (TTAB+pentanol)/water/n-octane system using optical and positron lifetime spectroscopic methods. TTAB and pentanol were mixed in 1:1 proportion by weight. The phase diagram for this system was constructed by birefringence measurements. It exhibits a well defined isotropic L_2 phase. Positron lifetime measurements carried out in this phase show its inhomogeneity. These measurements have made it possible to demark the boundary between the droplet like and the bicontinuous structures in this phase. The results are supported by electrical conductivity measurements.

Introduction

Tetra decyl trimethyl ammonium bromide(TTAB) is a cationic surfactant which when dissolved in different solvents, gives rise to several aggregated phases. TTAB/water/pentanol system is found to exhibit two isotropic microemulsion phases, L_1 and L_2 , and two mesophases[1,2]. In recent years interest in the structure of microemulsion phase has considerably increased[3-5]. In a w/o microemulsion, with increasing water content the system may transform from a droplet like to a bicontinuous structure. The phase boundary between these two structures is of interest, both from theoretical as well as application points of view. Experimental detection of bicontinuity is rather difficult. Scattering techniques, light and X-ray, fail to discriminate between droplet like and bicontinuous structures. Small angle neutron scattering(SANS) contrast-variation technique is able to provide some estimate about the mean curvature of the surfactant-rich film[6], the demonstration of a microemulsion with a mean curvature, on the average zero, is a strong indication of bicontinuity. Electrical conductivity measurements have been claimed to demonstrate bicontinuity[7], but it has limited applicability. They can indicate water continuity but fail to establish oil continuity. On the otherhand, a fluorescence probe method can be employed to establish oil continuity. Thus a combination of two techniques can provide a better indication of the existence of bicontinuity. Recently, positron annihilation technique has been employed in the detection of bicontinuity in CTAB/water/hexanol system[8,9]. In the present work, this technique has been employed to investigate the (TTAB+pentanol)/water/n-octane system. Optical birefringence has been employed for mapping the phase diagram of this system. The results of this investigation are presented in this paper.

Experimental

TTAB, pentanol and n-octane having purities better than 98% were procured from Fluka A.G. and BDH Chemicals, respectively and used without any further purification. Deionised triple distilled water was used for making various aqueous solutions. In the present work, pentanol has been used as a co-surfactant and was mixed with TTAB in 1:1 proportion by weight. For obtaining the phase diagram of (TTAB+pentanol)/water/n-octane system, a given weight percentage of (TTAB+pentanol) in n-octane was prepared and then it was titrated with water. The existence of a transparent isotro-

pic monophasic region was determined through visual as well as observation through crossed polaroids. The weight fractions of the constituents for the extrimities of this region were calculated and plotted on a triangular plot. This procedure was repeated for varying amounts of (TTAB+pentanol) dissolved in n-octane and thus a complete phase diagram was obtained.

Positron lifetime measurements were carried out using a standard lifetime spectrometer. The positron source used was ^{22}Na . A sealed positron source sandwich was prepared using thin Kapton films and a special grade epoxy resin. The sealed source and sample were contained in a suitably designed sample holder. Positron lifetime measurements were performed in (TTAB+pentanol)/water/n-octane solutions having fixed initial weight fractions of (TTAB+pentanol) dissolved in n-octane, as a function of the concentration of water. In these solutions, low frequency electrical conductivity was also measured as a function of water concentration. All measurements were performed at 20°C .

Results and discussions

The phase diagram for (TTAB+pentanol)/water/n-octane system as obtained by birefringence measurements is shown in Figure 1. This system exhibits an isotropic L_2 micro-emulsion phase. The optical measurements indicate that this phase has a homogeneous character.

Positron lifetime spectra obtained were analysed using a software PC-PATFIT developed by Riso National Laboratory, Denmark[10]. Details of analysis procedure are described elsewhere[8]. Each lifetime spectra could be decomposed into three lifetime components, τ_1 , τ_2 and τ_3 . The shortest component,

τ_1 , was fixed to 0.125 ns, the p-Ps lifetime. The intermediate component, τ_2 , was ascribed to free annihilation of positrons and the longest component,

τ_3 , represents the pick-off lifetime of o-Ps. The relative intensity, I_3 , of the longest component is, therefore, a measure of Ps formation in the medium. The parameters, τ_3 and I_3 , are found to exhibit sensitivity to structural changes occurring in the medium. The dependence of these parameters on the concentration of water in a typical (TTAB+pentanol)/water/n-octane solution, initially containing 35% by weight of (TTAB+pentanol) in n-octane, as obtained in the present work is shown in Figure 2. It is seen that at a water concentration of about 7% by weight, the I_3 value increases abruptly indicating a structural transformation occurring in the system. The τ_3 value, on the other hand, exhibits an oscillatory behaviour around this concentration of water. In CTAB/water/hexanol system, it has been shown that such

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

Fig.2: Dependence of τ_3 and I_3 in a typical (TTAB+pentanol)/n-octane/water system on water concentration.

a behaviour of τ_3 value indicates the onset of bicontinuity[9]. It may further be noted(Fig.2) that for water concentrations >11 mM the lifetime τ_3

value remains nearly constant till the phase separation occurs. This observation indicates that beyond this concentration of water the system continues to be in the bicontinuous phase. The dependence of electrical conductivity on the concentration of water in a typical (TTAB+pentanol)/water/n-octane system having the same initial weight percent of (TTAB+pentanol) in n-octane as in case of the positron lifetime measurements, mentioned above, is shown in Figure 3. The initial rapid increase in conductivity with increasing water concentration is due to percolation[11,12] in microemulsion droplets or aggregates. A flattening of the increase in conductivity at a water concentration of about 8%, by weight, indicates the onset of water continuity in the microemulsion. Thus at this concentration of water, the droplet like structure of the microemulsion seems to transform to a bicontinuous structure. Such a situation is represented by a point P_1 on the phase diagram(Fig.1). Similar points representing transformation from droplet to bicontinuity were obtained from positron lifetime and electrical conductivity measurements for (TTAB+pentanol)/water/n-octane solutions having varying amounts of (TTAB+pentanol) initially dissolved in n-octane. The curve PQS joining such points, thus gives the boundary between regions where the w/o microemulsion has droplet like and bicontinuous structures, respectively. The present work, thus, demonstrates that employing positron lifetime and electrical conductivity measurements the existence of bicontinuity in microemulsions can be detected. These methods further make it possible to delineate the boundary between the droplet like and bicontinuous phases of a microemulsion.

Fig.3: Dependence of sp.conductance in a typical (TTAB+pentanol)/n-octane/water system on water concentration.

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