Studies on microemulsions

Part 1: Scattering studies on water-in-oil microemulsions

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Abstract: The microemulsions formed in the 4-component system water-potassium oleate-hexanol-dodecane have been investigated by time-average light scattering and small angle neutron scattering. A constant volume fraction ratio water: potassium oleate of 1.44 was used and at this constant composition, which gave a pseudo 3-component system, a wide region of the microemulsion domain was examined. In order to interpret the scattering data at finite volume fractions of the dispersed phase, water, allowance had to be made for interactions between the water-in-oil microemulsion droplets. This was carried out using a hard sphere model for the interaction. It is shown that using this model self-consistent results are obtained by light scattering and neutron scattering and an estimate can be made of the size of the particles in concentrated colloidal dispersions.

Key words: microemulsions, light scattering, neutron scattering, particle interactions.

Introduction

Microemulsions can be considered as concentrated colloidal dispersions which are optically transparent owing to the small diameter of the droplets which are usually less than 100 Å. Their transparency has rendered them amenable to study by light scattering and several studies [1, 2] have been reported since they were first investigated in this manner by Hoar and Schulman [3]. A basic difficulty with such studies to determine the particle size of the droplets is that the theory of scattering in its simplest form cannot be applied since extrapolation to infinite dilution is required and this constitutes a condition where microemulsions do not exist. Consequently, any studies on microemulsions which are made must be carried out at finite concentrations in the regions of 3-component or 4-component mixtures in which they exist as stable colloidal entities. Hence scattering theories must be used which apply under these conditions and take into account the particle-particle interactions which are of necessity present in such systems [2, 4]. Multiple scattering must also be avoided.

In a previous study a theoretical basis was developed for the interpretation of scattering data obtained on microemulsions and it was applied to results obtained by time-average light scattering, photon correlation spectroscopy and small angle neutron scattering [5]. However, in the system examined, sodium dodecyl benzene sulphonate-hexanol-p-xylene-water, measurements were confined to a limited range of samples along a composition line with a constant molar ratio of hexanol:sodium dodecyl benzene sulphonate of 3.28:1.0. It was concluded from these experiments that the HARD SPHERE model gave a self consistent interpretation of the results from the scattering techniques used. Moreover, it was possible to confirm that the water-in-oil microemulsion droplet consisted of a water core stabilised by an adsorbed layer of the surfactant (sodium dodecyl benzene sulphonate) and the co-surfactant (hexanol). In this system the dispersion medium, p-xylene, had a higher refractive index than the hydrocarbon chains of the surfactant and co-surfactant thus introducing the need for a concentric sphere model to interpret the results by light scattering.

In the present work we have investigated the system, potassium oleate-hexanol-dodecane-water, chosen so that the refractive index of the dispersion medium matched that of the surfactant and co-surfactant components; the latter constitute the stabilising moieties in the water-in-oil microemulsions formed. A similar quaternary system, potassium oleate-pentanol-benzene-water, has been investigated by Sjöblom and Friberg [6] and they have produced a tetrahedral phase diagram showing the location of the oil-in-water microemulsion region. It is likely that our
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Experimental

Materials

The distilled water used throughout the investigation was doubly distilled from an all-Pyrex apparatus. The refractive index was $n_{\text{D}}^2 = 1.3401$ and the density, $\rho_{\text{D}} = 0.9982$. The deuterium oxide used was Fluorochem material containing 99.8% D$_2$O.

The hexanol used was B. D. H. analytical grade material with $n_{\text{D}}^{36} = 1.4179$ and $\rho_{\text{D}} = 0.8186$.

The oleic acid used was fresh Eastman Kodak technical grade material (98% by titration) which was stored in a tightly stoppered bottle in the dark.

Dodecane was B. D. H. analytical grade material with $n_{\text{D}}^{36} = 1.4296$.

Preparation of microemulsion

All the systems were prepared in order to have a constant water to oleate volume ratio of 1.44. This value was chosen since it was deduced from earlier work [6] that this ratio would produce a transparent region extending over a wide area of the diagram, bounded on one side by macroemulsions and liquid crystalline regions and on the other by a solution region (see figs. 1b and 2).

For initial exploration of the regions of the phase diagram the minimum hexanol content of the interphase was estimated by the technique of Bowcott and Schulman [7]. Mixtures of dodecane, potassium oleate and water were titrated with hexanol until a transparent, homogeneous system was obtained; additional dodecane was then added and the titration repeated. After repeating...