

EFFECT OF DIETHYL SULFOXIDE ON RHEOLOGICAL PROPERTIES OF AOT MICROEMULSIONS

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Transport properties of reverse micellar system of *n*-heptane–sodium bis (2-ethylhexyl) sulfosuccinate (AOT)–water + diethyl sulfoxide (DESO) have been studied by densitometry and viscosimetry. The relative viscosities (η_r) of the systems were calculated at concentration range of AOT from 0.106 to 1.912 *mol/kg*, constant degree of AOT hydration ($W=[\text{polar phase}]/[\text{AOT}]=10$) and at temperature range 298.15–313.15 *K*. Based on the plots of η_r against volume fractions of dispersed particles, the probable interactions between micelles were discussed. The obtained results were compared with those of *n*-heptane–AOT–water + dimethyl sulfoxide (DMSO). The presence of DESO tends to the formation of micellar aggregates at smaller concentrations of surfactant comparing with DMSO.

Keywords: relative viscosity, reverse micelles, dimethyl sulfoxide, diethyl sulfoxide.

Introduction. It is well known that reverse micelles are nanopools of polar solvent surrounded by surfactant monolayer and dispersed in continuous oil phase. The polar head groups of surfactant are pointing inward to polar solvent and hydrocarbon tails pointing towards nonpolar organic solvent. Aerosol OT (AOT) or sodium bis(2-ethylhexyl) sulfosuccinate is the best known sample of this class of surfactants. AOT is used to form reverse micelles, because of the great ability to solubilize large amount of water in various organic solvents.

Physicochemical studies of aqueous ternary systems are gaining importance, sometimes it is difficult to arrive at a definite conclusion regarding structure and properties of solutions from studies of binary systems alone. Viscometric and related thermodynamic parameter values in binary systems are abundantly available, whereas data of thermodynamic parameters of ternary systems are limited [1, 2].

Reverse micelles having a number of technological applications have attracted considerable attention in recent years. They are considered to be models of biological membranes [3], they can be used for the preparation of nanoparticles [4] and provide nano-sized reactors for the enzymatic reactions [5]. In this work the transport properties of reverse micellar systems of *n*-heptane–AOT–water + diethyl sulfoxide (DESO) were studied. To calculate the volume fraction of micelles the

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densities of micellar systems were measured. The results were compared with our previously reported studies of n-heptane–AOT–water + dimethyl sulfoxide (DMSO) [6] to reveal the effect of alkyl chain length of sulfoxide on the properties of n-heptane–AOT–water + sulfoxide systems. It is known that DESO, like widely used, DMSO, has unique physicochemical properties with possible biomedical applications [7–9].

In this work we report the relative viscosities of the system and volume fractions of micelles at different concentrations of surfactant.

Materials and Methods. AOT (98%) was obtained from “Sigma-Aldrich” (USA), and was used as soon as was received, n-heptane was purchased from “Macrochem” (Holland). DESO was prepared and purified according to [10].

The reverse micellar systems were prepared by dissolving calculated amount of AOT in n-heptane. The molal concentration of AOT was changed from 0.106 to 1.912 mol/kg and the ratio of concentrations of polar solvent (water+DESO) and AOT was kept constant ($W=[\text{polar phase}]/[\text{surfactant}]=10$). It should be noted that for high content of DESO the system is not suitable for density measurements, because of non-homogeneity of solutions, therefore, the most optimal volume ratio of water to DESO has been chosen as 5 : 1.

The densities of the solutions were measured using Anton Paar DMA 4500 vibrating tube densimeter with precision of $1.0 \cdot 10^{-2} \text{ kg/m}^3$ and uncertainties of $5.0 \cdot 10^{-2} \text{ kg/m}^3$. The temperature was kept constant at each measurement with uncertainties of $\pm 0.01 \text{ K}$. Before and after each measurement the densimeter was calibrated with deionized double-distilled water and dry air.

The flow times of reverse micellar systems were measured using Ubbelohde capillary viscometer. The relative viscosities of solutions were calculated from the relations of the flow times.

Results and Discussion. The densities and flow times of reverse micellar systems of n-heptane–AOT–water + DESO were measured at temperature range from 298.15 to 313.15 K, surfactant concentration range from 0.106 to 1.912 mol/kg, $W=10$ and water : DESO = 5 : 1 volume ratio.

For a dilute solution of non-interacting spherical particles the viscosity (η) depends on the volume fraction (ϕ) of the particles according to the relation derived by Einstein [11]:

$$\eta = \eta_0 (1 + 2.5\phi), \quad (1)$$

where η_0 is the viscosity of pure solvent.

Since this expression is only valid at infinite dilution without any interaction between the particles, one has to expand it to a virial form to treat finite concentration [6, 11]:

$$\eta_r = \frac{\eta_s}{\eta_0} = 1 + a\phi + b\phi^2 + c\phi^3 + \dots, \quad (2)$$

where a , b , c are empirical parameters.

The volume fraction of dispersed particles is the relation of its volume to the volume of entire solution. Since, all the samples were prepared by weight and the interactions inside the system will be neglected by summarizing the volumes of components, the volume fraction of the micellar phase was calculated using the equation [2, 12]:

$$\phi = \frac{V_m}{V} = 1 - (1 - W_m) \frac{\rho}{\rho_0}, \quad (3)$$

where W_m is the weight fraction of the micellar phase; V_m and V are the volumes of micelles and the system respectively; ρ and ρ_0 are the densities of microemulsion and pure solvent (n-heptane) respectively.

The relative viscosities, densities of n-heptane–AOT–water + DESO system and volume fractions of micelles are shown in Table.

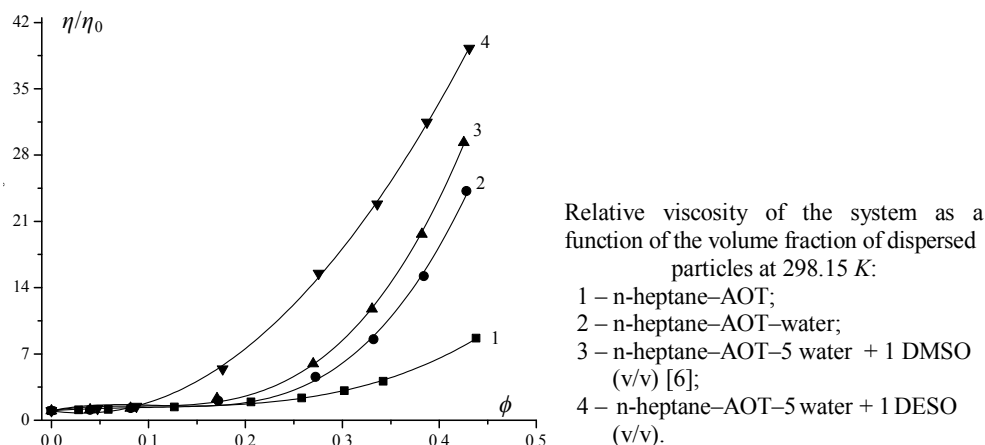
Densities, relative viscosities of n-heptane–AOT–5 water +1 DESO (v/v) system and volume fractions of dispersed particles at $W=10$ and different temperatures

$m_{\text{AOT}},$ mol/kg	T, K			
	298.15	303.15	308.15	313.15
	$\rho \cdot 10^{-3}, \text{ kg/m}^3$			
0.106	0.69908	0.69478	0.69046	0.68610
0.227	0.71706	0.71274	0.70842	0.70405
0.530	0.75481	0.75048	0.74612	0.74174
0.956	0.79664	0.79232	0.78799	0.78362
1.275	0.82075	0.81647	0.81216	0.80781
1.593	0.84198	0.83772	0.83342	0.82903
1.912	0.85929	0.85506	0.85079	0.84650
	ϕ			
0.106	0.04752	0.04745	0.04740	0.04735
0.227	0.08760	0.08742	0.08723	0.08704
0.530	0.17661	0.17621	0.17583	0.17542
0.956	0.27562	0.27504	0.27446	0.27386
1.275	0.33596	0.33529	0.33463	0.33395
1.593	0.38727	0.38656	0.38586	0.38518
1.912	0.43084	0.43010	0.42937	0.42861
	η/η_0			
0.106	1.22446	1.23042	1.23077	1.2466
0.227	1.45789	1.48802	1.48546	1.51262
0.530	5.40099	5.33226	5.18715	5.10825
0.956	15.52285	15.48986	15.70356	15.95146
1.275	22.82706	22.59447	22.10600	21.86893
1.593	31.47401	31.27189	30.64728	30.85922
1.912	39.26971	39.82488	38.04409	36.04369

The obtained results were compared with our previous reports [6], where pure water and the mixture of DMSO and water with the same volume ratio were used as a polar phase. In Figure the ϕ dependence of relative viscosity of n-heptane–AOT–5 water + 1DESO (v/v) microemulsion at 298.15 K temperature is compared with that of the reverse micellar systems of n-heptane–AOT, n-heptane–AOT–water and n-heptane–AOT–5 water + 1DMSO (v/v).

To fit the experimental results for each system the Eq. (2) was used with only four parameters. As it follows from Figure, the plots of η_r versus ϕ are linear at low concentrations of AOT. It can be suggested that the reverse micelles have spherical shape. However, for the system of n-heptane–AOT–water + DESO the positive deviation was displayed at lower concentrations of AOT comparing with

other systems and the system was characterized with higher viscosity. It may be explained in terms of evolution of intermicellar interactions with concentration of AOT. At presence of DESO the system tends to the formation of micellar aggregates at smaller concentrations of AOT comparing with DMSO and water.



It is known that both DMSO–water and DESO–water mixtures exhibit strong deviations from ideality. The excess molar volumes of these solutions are negative over the whole range of composition [13]. Therefore, it is expected that the polar DESO–water mixture encapsulated within the reversed micelles is characterized with less volume. On the other hand, the existing competitive strong intermolecular interactions between molecules of water and sulfoxide affects the hydration of surfactant head groups leading to the promotion of the solubilization of vitamin E [7]. It can be suggested that due to sulfoxide–water strong interactions the surfactant head groups were less hydrated and the weakened AOT–polar phase interactions were led to the increase of effective volume of polar phase [14]. The increase of surfactant concentration, consequently the content of polar phase, as their ratio was remained constant the concentration of dispersed particles was increased. Therefore, the probability of their collision and hence the aggregation was increased. The study of conductivity of these systems [15] also confirms the formation of aggregates, where the conductivity of n-heptane–AOT–water + DESO system was much higher comparing with n-heptane–AOT–water and n-heptane–AOT–water + DMSO systems due to formation of infinite clusters.

Conclusion. In this paper data of density and relative viscosity of n-heptane–AOT–water + DESO reverse micellar system were reported. From the density data the volume fraction of micelles was calculated. These parameters were compared with those of n-heptane–AOT–water + DMSO reverse micellar system to reveal the influence of alkyl chain length. The comparison shows that in the presence of DESO the surfactant head groups were less hydrated due to competitive sulfoxide–water strong interactions. Therefore, the formation of micellar aggregates due to intermicellar interactions occurs at smaller concentrations of AOT.

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