Chemistry

CONDUCTIVITY OF REVERSE MICELLAR SYSTEMS OF AOT–n-HEPTANE–WATER+DIMETHYLSULFOXIDE OR DIETHYLSULFOXIDE AT TEMPERATURE RANGE 20–50ºC

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Dependence of conductivity on temperature of sodium bis(2-ethylhexyl) sulfosuccinate (AOT)–n-heptane–water+dimethylsulfoxide (DMSO) or diethyl-sulfoxide (DESO) reverse micellar system has been studied at fixed ratio of molal concentrations of polar phase (water, water+DMSO, water+DESO) to surfactant and at different volume ratios of DMSO (DESO) and water. The threshold percolation temperatures (T_p) for each system have been estimated, the effects of both DMSO and DESO on threshold percolation temperature and percolation process have been discussed. Both DMSO and DESO act as percolation-resisting additives. The presence of mixed solvent has shown a decrease of T_p and tendency to transfer a system from percolating to non-percolating. The activation energy (E_p) for percolation of conductance has also been determined according to Arrhenius equation. The results show that E_p decreases with addition of DMSO or DESO and with an increase of concentration of DMSO.

Keywords: reverse micelles, dimethylsulfoxide, diethylsulfoxide, percolation process, activation energy.

Introduction. Microemulsions are complex systems, where the domains of water and oil are separated by surfactant monolayers. At certain intervals of content and temperature microemulsions consist of discrete surfactant-coated water droplets, which are dispersed in continuous oil phase (water-in-oil microemulsions or reverse micellar systems). Sodium bis (2-ethylhexyl) sulfosuccinate (AOT) is used as a common surfactant, which forms reverse micelles. AOT is a two alkyl chain surfactant it has a comparatively small hydrophilic head group, consisted of a sulfonate ion, a sodium counterion and two ester groups.

Recently reverse micellar systems have attracted attention of many researchers. These systems are in the center of attention, because they are considered to be models of membranes due to their structural similarities with biological membranes [1, 2], they are used as microreactors for enzymatic reactions [3, 4] and for synthesis of nanoparticles [5, 6].

Among different physicochemical properties the electrical conductivity of reverse micellar systems has been extensively investigated. As it is known the

electrical conductivity of such systems is very sensitive to their microstructure [7]. The study of reverse micelles has widely been concentrated on electrical percolation [8–11]. This phenomenon is characterized by sudden increase in electrical conductivity, when the temperature or the volume fraction of dispersed phase reaches a certain threshold value.

The electrical conductivity of AOT–n-heptane–water system has been studied both below the percolation threshold [12, 13] and above percolation [13, 14]. It is interesting to reveal the interactions in the reverse micellar systems, when the polar phase contains not only one pure component, but also the mixed solvents. Such works have been done previously using equimolar mixture of water+formamide [15] and of dimethylsulfoxide (DMSO)+water and diethylsulfoxide (DESO)+water mixtures with different volume ratios [16] as a polar phase. The biological significance not only of DMSO, but also of DESO has been recently recognized [17–20]. Particularly, in [16] the effect of DMSO and its homologue DESO as polar cosolvents on the distribution of vitamin E in AOT–n-heptane–water+DMSO (DESO) reverse micellar systems have been investigated.

In this work the dependence of conductivity on temperature of AOT–n-heptane––water+DMSO or DESO reversed micellar system has been studied at fixed ratio of molal concentrations of polar phase to surfactant (R).

Materials and Methods. AOT (98%) was purchased from "Sigma Aldrich". DMSO was obtained from "LACHEMA N.P." (Brno) and n-heptane obtained from "Macrochem" (Holland). DESO was prepared and purified according to [21]. Double distilled water was used with conductance less than 2 $\mu S \cdot cm^{-1}$ at 25ºC.

The reverse micellar systems were prepared by dissolving calculated amount of AOT in n-heptane changing the molal concentration of AOT from 0.106 to 1.912 *mol/kg*. The ratio of concentrations of different polar solvents (water, water+DMSO, water+DESO) and AOT remained constant (R=[polar phase]/ /[surfactant]=10) by adding appropriate amounts of water and water+sulfoxide mixtures to AOT–n-heptane systems. In works of different authors R varies in wide range of values (2–30), so, we have chosen an approximately average value R=10.

The measurements of electrical conductance of systems were carried out as a function of temperature using Jenway 4330 conductivity & pH meter with uncertainty in measurement within ±0.5%. Dependence of conductivity on temperature was studied at temperature range 20–50ºC and at fixed R using a thermostatic water bath with accuracy ±0.5ºC. The measurements were carried out under electro-magnetic stirring to remove the temperature difference in the conductance cell.

Results and Discussion. The electrical conductivity of systems of AOT–n-heptane–water+dialkylsulfoxide (DASO) has been measured at temperature range 20–50ºC and surfactant molal concentration range 0.106 to 1.912 *mol/kg*. The volume ratios of components of polar phase (DASO+water) were 1:1; 1:3 (DMSO) and 1:5 (DMSO, DESO). In our case, when DASO+water mixed solvent has been used instead of water as a polar phase, the question regarding to the location of organic cosolvent is rising. The results obtained by [22], where as a polar phase water+methanol (ethanol) mixed solvents were used instead of water alone, show that the higher is the polarity of organic cosolvent, the more alcohol remains in core of micelles. Taking into account that the location of cosolvent depends on its polarity and the fact, that DMSO and DESO are more polar than

above mentioned alcohols according to their values of dielectric constants (ε): 46.6 for DMSO and 44.1 for DESO [23], which are higher than those of methanol and ethanol: 32.6 and 24.5 respectively at 20°C, one can surely insist that DASO remains in the micellar core. Moreover, DMSO and DESO have a negligible solubility in n-heptane, which in its turn supports above mentioned suggestion.

It should be noted that DESO contrary to DMSO has limited solubility in AOT–n-heptane–water reverse micellar system. The solutions become heterogeneous for more contents of DESO. The most available composition for DESO was mixture with volume ratio 1:5.
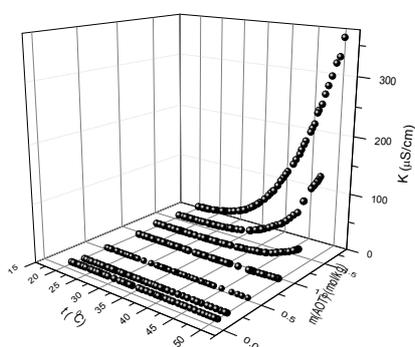

Fig. 1. Conductivity as a function of temperature for AOT–n-heptane–water reverse micellar system at different concentrations of AOT and *R*=10.
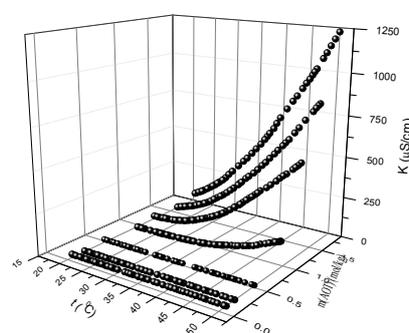

Fig. 2. Conductivity as a function of temperature for AOT–n-heptane–water+DMSO (5:1) reverse micellar system at different concentrations of AOT and *R*=10.
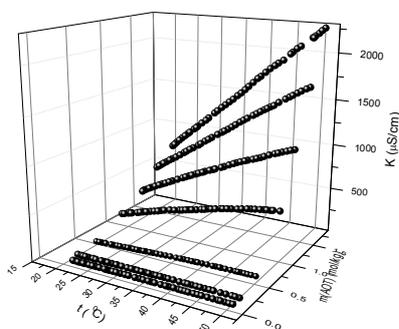

Fig. 3. Conductivity as a function of temperature for AOT–n-heptane–water+DESO (5:1) reverse micellar system at different concentrations of AOT and *R*=10.

To compare the effect of DASO on the conductivity of these systems the plots of conductivity versus temperature are shown in Fig. 1–3, where the volume ratios for both DMSO and DESO were the same.

It is known, that microemulsions are stable solutions of polar phase, surfactant and oil. They usually have low viscosity and conductivity, where the average size of disperse phase (micelles) is 10–50 *nm*. But water-in-oil type micro emulsions may have a significant rise in conductance (100–1000 fold or more) whether volume fraction of particles or temperature reaches a certain threshold value this process is known as percolation [8]. The percolation process describes sigmoidal type dependence of conductivity from temperature (or volume fraction of micelles) [24].

From Fig. 1, 2 it can be seen, that at low concentrations of AOT and at given temperature range (until 1.275 *mol/kg* in absence of DMSO and until 0.956 *mol/kg* in presence of DMSO) there is no percolation in the systems. Moreover, in presence of DMSO and with an increase of its concentration (figures not shown) the threshold percolation temperature decreases and the percolation becomes not clear, i.e. conductivity increases not sharp as in the case of water alone, but subtly. Fig. 3 shows, that percolation hinders in the case of DESO.

As it is known the electrical conductivity of microemulsions is caused by the motion of charged water droplets, when the temperature or volume fractions of water droplets are low [25, 26]. The ionization of neutral water droplets takes place due to charging mechanism, which is driven by spontaneous thermal fluctuations. According to this mechanism droplets approach each other, fuse to form a short-lived droplet dimer and then redisperse and during their fusion the content of water droplets exchanges. The main cause of observed conductivity in dilute microemulsions is the migration of charged droplets in an external electric field.

When the temperature or volume fraction of polar phase is higher, the clusterization process occurs and different transport mechanisms appear. Particularly charge hopping mechanism (surfactant hopping model) or formation of transient water channels cause a sharp increase in conductivity. According to the second mechanism, water droplets need to have an effective collision, fuse together, exchange the matter and then redisperse. Moreover, "hopping" mechanism of surfactant ion transfer has a minor contribution to the conductance and it is fusion-mass transfer-fission mechanism that is responsible for the sharp increase in conductivity [12, 14]. This process has been discussed as a percolation process and is caused by the motion of surfactant counter-ions (Na^+ ions) through water channels or by the movement of surfactant anions through connected clusters of water droplets. In its turn the last process promotes the clusterization process by opening the surfactant layers [11, 12].

The percolation process may be discussed as a transition from water-in-oil droplet like form to connected clusters of droplet like microstructure. The conductivity of reverse micellar systems of AOT is due to the motion of cations through temporary water channels formed by the fusion of droplets. The most important factors for determination of exchange rate of water molecules and ions during their collision are the rigidity of interface and attractive interactions between clusters [11]. The size and shape of micelles depend on the flexibility of interface of droplet, which is related to the molecular packing parameter (*P*) defined as

$$P = v_0/al_0 \ ,$$

where v_0 and l_0 are the volume and chain length of surfactant, *a* is the area of head group at the interface of the hydrophilic core hydrophobic media. The lower is the value of *P*, the higher is flexibility of interface and thus percolation process will be facilitated [11, 27]. It is obvious, that v_0 and l_0 are the intrinsic properties of surfactant and are constant at given surfactant. Whereas *a* may be changed by modifying the solution conditions and, thus, *P* will be changed.

It is known that different types of additives may affect the percolation process and act as percolation-assistant or percolation-resistant. Their assistance is explained by the way of promoting the fusion of droplets, whereas resistance is modeled as blocking of fusion process [14].

From Fig. 1–3 it can be seen, that both DMSO and DESO have percolation-resisting effect. In the case of DESO conductivity vs temperature curves do not show sigmoidal type dependence. However threshold percolation temperature (T_p) decreases in the presence of DMSO and with increase of its concentration. On the one hand, T_p should increase, as far as DMSO is considered as percolation-resisting additive, on the other hand, our previous study [28] shows, that with addition of DMSO and with an increase of its concentration the apparent molar volume of polar phase, i.e. the volume of micelles due to interactions existing inside the system increases. It makes micelles easily collide and fuse together and, thus, T_p decreases. As a result, the first effect is suppressed by the second and as a whole T_p decreases.

The percolation resisting effect of DMSO may be explained by the fact, that DMSO has a capacity to solubilize cation [29, 30]. In AOT based micellar system Na^+ operates as counter-ion and DMSO captures this ion. The formed complex of DMSO and Na^+ ions may penetrate into the interface deeply and, thus, increase the screening effect of the interface comparing with the absence of DMSO. As a result the area of polar groups *a* of surfactant decreases and packing parameter increases. This means that the rigidity of interface of micelles increases and as a result percolation hinders. This explanation is supported by the authors of [11], who explain the resisting effect of crown ethers in the same way. It follows from Fig. 3, that DESO acts as stronger percolation-resisting additive than DMSO. Therefore, it can be supposed that DESO captures cations (particularly Na^+ ions) stronger than DMSO.

The activation energy for percolation of conductance is determined according to Arrhenius equation [11, 14]:

$$\kappa = A\exp(-E_p/RT) \quad \text{or} \quad \ln\kappa = \ln A - E_p/RT,$$

where *A* is constant, *R* and *T* are gas constant and absolute temperature respectively, κ is conductivity.

The values of E_p can be obtained from the slope of $\ln k$ vs $1/T$. The mentioned plot is depicted in Fig. 4 for AOT–n-heptane–water+DMSO (1:1) system. For the other systems the Figures are not shown in order to avoid the repetition and taking into account that for all the systems E_p determines in the same way.
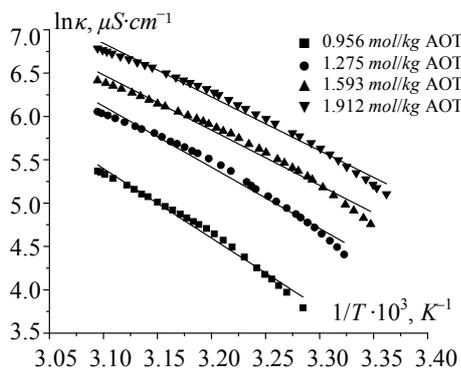

Fig. 4. Plots of $\ln \kappa$ vs $1/T$ to evaluate E_p of AOT–n-heptane–water+DMSO (1:1) reverse micellar system at different [AOT] and *R*=10.

The activation energy has been determined from the slopes of the curves and together with the corr. coefficients are presented in Tab. 1 and 2. It should be mentioned that the observation of percolation at low concentrations of AOT

requires higher temperatures, than are used in our work. This suggestion can be supported by the fact, that in the presence of DMSO, when threshold percolation temperature decreases, percolation process occurs at 0.956 *mol/kg* molal concentration of AOT, whereas in the case of pure water percolation is observed only at 1.275 *mol/kg*.

Activation energy for percolation of conductance for AOT–n-heptane–water and AOT–n-heptane––water+DMSO reverse micellar systems at different volume ratios of water+DMSO and R=10

C_{AOT}, mol/kg	AOT–n-heptane––water		AOT–n-heptane––water+DMSO, 5:1		AOT–n-heptane––water+DMSO, 3:1		AOT–n-heptane––water+DMSO, 1:1	
	E_p, kJ/mol	corr. coeff.	E_p, kJ/mol	corr. coeff.	E_p, kJ/mol	corr. coeff.	E_p, kJ/mol	corr. coeff.
0.956	–	–	103	0.9973	78	0.9936	67	0.9866
1.275	160	0.9939	82	0.9751	70	0.9839	59	0.9845
1.593	146	0.9982	74	0.9750	61	0.9865	53	0.9829
1.912	112	0.9919	67	0.9769	56	0.9838	51	0.9872

Activation energy for percolation of conductance for AOT–n-heptane–water and AOT–n-heptane–water+DMSO (DESO) (5:1) reverse micellar systems at R=10

C_{AOT}, mol/kg	AOT–n-heptane–water		AOT–n-heptane––water+DMSO (5:1)		AOT–n-heptane––water+DESO (5:1)	
	E_p, kJ/mol	corr. coeff.	E_p, kJ/mol	corr. coeff.	E_p, kJ/mol	corr. coeff.
0.956	–	–	103	0.9973	30	0.9546
1.275	160	0.9939	82	0.9751	30	0.9708
1.593	146	0.9982	74	0.9750	30	0.9812
1.912	112	0.9919	67	0.9769	29	0.9825

As can be seen from Tab. 1 the activation energy for percolation is higher in the absence of DMSO. Authors of [14] have determined the activation energy for percolation of AOT–n-heptane–water system. The value of E_p was much higher comparing with our results. But one must take into account that in [14] all experiments were carried out at $R=25$, and as mentioned in [24] $\Delta \lg \kappa$ increases with increasing R, which means, that E_p also increases as it is calculated from the slope of $\ln \kappa$ vs $1/T$.

Table 1 shows, that E_p decreases with the increase of DMSO concentration, i.e. in the presence of percolation-resisting additive activation energy is lower compared with water. But the similar results were obtained by the authors of [11, 14] for percolation-assisting and percolation-resisting additives. They considered that separation of the fused micelles was the rate determining step in dynamic percolation process. The additives that facilitate the aggregation of micelles may reduce T_p, but it is their fission that defines the magnitude of E_p.

It must be mentioned that AOT–n-heptane–water+DESO system does not produce percolation, but we have determined activation energy as E_p and the values are presented in Tab. 2. This quantity is not the activation energy of percolation, but we discuss it as activation energy for conductivity assuming that clusterization process also takes place in this system. The study that is carried out at present

shows, that in the case of DESO the apparent molar volume is higher than in case of DMSO, it means that with replacing DMSO by DESO the formation of aggregates takes place easier.

The low values of E_p may appear, because of strong interactions between water and DMSO (DESO) molecules [31, 32], which cause a weakening of rival polar phase-surfactant interactions and, hence, the fission of micellar aggregates takes place easier than in the case of pure water. In addition, the polarity inside micellar core decreases according to dielectric constant values of DMSO and DESO mentioned above, which in turn may simplify the separation of aggregates. Moreover it is also known that DESO+water interactions are stronger than DMSO+water interactions [32]. As a result, the fission of micellar aggregates requires less energy and E_p reaches its lowest value.

Conclusion. On the basis of conductivity results the effect of DMSO and DESO on percolation process of AOT–n-heptane–water reverse micellar system has been revealed. The threshold percolation temperature and activation energy for percolation in absence and presence of DASO have been evaluated. With the addition of DMSO (DESO) the percolation process is retarded and threshold percolation temperature decreases. The activation energy for percolation of conductance decreases with addition of DMSO and DESO. More appropriate mechanism for percolation phenomenon in AOT–n-heptane–water+DMSO (DESO) systems has been discussed.

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