

**EFFECT OF DIETHYLSULFOXIDE ON VOLUMETRIC PROPERTIES
OF SODIUM BIS (2-ETHYLHEXYL) SULFOSUCCINATE
MICROEMULSIONS**

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Volumetric properties of reverse micellar system of *n*-heptane/sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/water+diethylsulfoxide (DESO) have been studied by densitometry. The apparent molar volumes (ϕV) were calculated at concentration range of AOT from 0.106 to 1.912 mol/kg, constant degree of AOT hydration ($W=10$) and temperatures of 298.15-313.15 K. The obtained results were compared with those of *n*-heptane/AOT/water+dimethylsulfoxide (DMSO). The ϕV values at different W and constant concentration of AOT were also calculated at temperature range 273.15-298.15 K. The apparent molar volumes at infinite dilution (ϕV^∞) for both DMSO and DESO containing polar phases were calculated using Masson type equation. From the temperature dependence of ϕV Hepler's constants were calculated. The presence of DESO tends to the increase of apparent molar volume of polar phase comparing with DMSO.

Figs. 3, tables 3, references 26.

Introduction

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. Volumetric 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]. Certain amounts of apolar solvent and water containing surfactant molecules are thermodynamically

stable for the formation of surfactant aggregates that are called reverse micelles. They have a polar core which is formed spontaneously when dissolving surfactants in apolar solvents. 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 a great ability to solubilize large amount of water in various organic solvents.

In this work the volumetric properties of reverse micellar systems of *n*-heptane/AOT/water+diethylsulfoxide (DESO) were studied. The results were compared with our previously reported studies of *n*-heptane/AOT/water+dimethylsulfoxide (DMSO) [6,7] to reveal the effect of alkyl chain length of sulfoxide on the properties of *n*-heptane/AOT/water+sulfoxide systems. The use of mixtures as polar solvent is largely used in microemulsions. The mixtures of ionic liquid bmmCl and formamide, glycerol and *N,N*-dimethylformamide, DMSO and water were used as polar solvents by other researchers [8-10]. It was shown that DESO like the widely used DMSO has unique physicochemical properties with possible biomedical applications [11-13].

In this work we report apparent molar volumes, limiting partial molar volumes of the polar phase at different concentrations of both surfactant and polar phase.

Experimental

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT 98%) was obtained from Sigma-Aldrich, USA and was used as received, *n*-heptane was purchased from "Macrochem", Holland. DESO was prepared and purified according to the literature [14]. The double distilled water was used with conductance less than $2 \mu\text{S}/\text{cm}$ at 298.15 K.

The reverse micellar systems were prepared by dissolving calculated amount of AOT in *n*-heptane. In one case 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 remained constant ($W=[\text{polar phase}]/[\text{surfactant}]=10$). In the other case the concentration of AOT was remained constant and equal to 0.106 mol/kg and W was changed from 3 to 14 by adding appropriate amounts of water+DESO mixtures to *n*-heptane/AOT systems. The dependences of ϕV from both molal concentration of AOT and nanopool size (W) for water and DESO+water mixture were demonstrated in graphical abstract. 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 have been chosen as 5/1.

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

Results and discussion

Effect of surfactant concentration. The densities 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 5water/1DESO volume ratio.

The apparent molar volumes (ϕV) were calculated from the measured density values using equation (1) [15]

$$\phi V_3 = \frac{M_3}{\rho} + \frac{\rho_1 - \rho}{\rho \cdot \rho_1} \left(\frac{M_2 m_2 + 1}{W \cdot m_2} \right), \quad (1)$$

where M_3 is the average molar mass of polar phase (for water+DESO mixture 0.02019 kg/mol), ρ_1 and ρ are the densities (kg/dm³) of the systems *n*-heptane/AOT and *n*-hetane/AOT/water+DESO, respectively, M_2 and m_2 are the molar mass (kg/mol) and molality (mol/kg) of surfactant, respectively. The densities of *n*-heptane/AOT/water+DESO system with the apparent molar volume data at 298.15, 303.15, 308.15, 313.15 K are reported in Table 1.

Table 1

Densities of *n*-heptane/AOT/5water+1DESO (v/v) system and apparent molar volumes of polar phase at W=10 and different temperatures

$m_{\text{AOT}},$ mol/kg	T, K			
	298.15	303.15	308.15	313.15
	$\rho \times 10^{-3}, \text{kg/m}^3$			
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
	$\phi V \times 10^6, \text{m}^3/\text{mol}$			
0.106	22.66	22.77	22.85	22.97
0.227	21.61	21.66	21.92	21.82
0.530	20.94	21.01	21.09	21.17
0.956	20.79	20.86	20.94	21.01
1.275	20.70	20.78	20.85	20.93
1.593	20.57	20.62	20.70	20.78
1.912	20.81	20.88	20.95	21.03

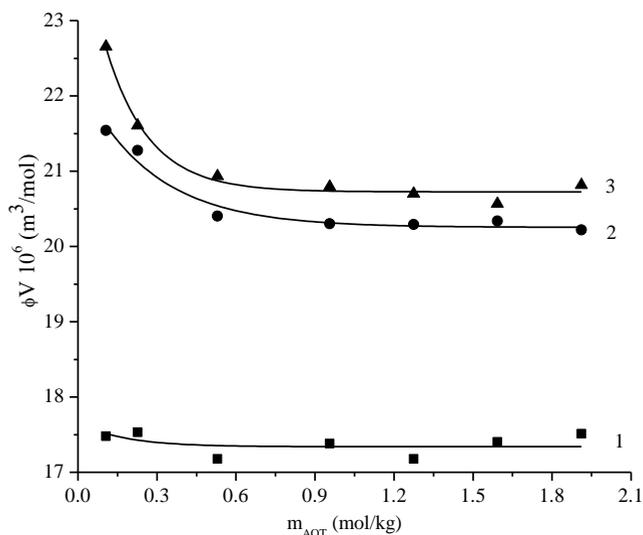


Fig. 1. The apparent molar volume of polar phase plotted against molality of AOT at 298.15 K: 1 – *n*-heptane/AOT/water, 2 – *n*-heptane/AOT/5water+1DMSO (v/v) [6], 3 – *n*-heptane/AOT/5water+1DESO (v/v).

Comparison with our earlier reports [6] shows that the values were increased with addition of DESO to *n*-heptane/AOT/water system (Fig. 1). 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 [16]. 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 [11]. 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 thus higher ϕV values. It is also found that ϕV was decreased with the increase of AOT concentration similar to that of DMSO-water polar solvent. However in the case of DESO-water mixture this decrease is slightly larger than in the case of DMSO-water and pure water as polar phase. This result indicates that with 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 intermicellar interactions were led to the formation of higher aggregates and the effective volume was reduced [17]. The study of conductivity of these systems [18] also confirms the formation of aggregates, where the conductivity of *n*-heptane/AOT/water+DESO system was

much higher comparing with those of *n*-heptane/AOT/water and *n*-heptane/AOT/water+DMSO systems due to formation of infinite clusters.

Effect of polar phase content. The densities of *n*-heptane/AOT/water+DESO system at different contents of polar phase and constant concentration of surfactant ($[AOT]=0.106 \text{ mol/kg}$) were also measured at temperature range from 273.15 K to 298.15 K. The apparent molar volumes of polar phase were calculated according to the equation (1) and together with the measured densities are shown in the Table 2.

The plots of apparent molar volume versus W are depicted in Fig. 2. for the systems of *n*-heptane/AOT/water, *n*-heptane/AOT/water+DMSO [7] and *n*-heptane/AOT/water+DESO at 293.15 K. As it follows from Fig. 2. ϕV values were greater for DESO-water polar phase comparing with water and DMSO-water for each W .

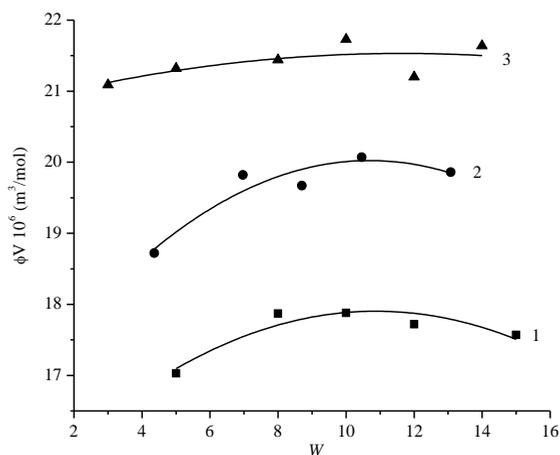


Fig. 2. The plots of the apparent molar volume of polar phase versus W at 293.15 K: 1 – *n*-heptane/AOT/water, 2 – *n*-heptane/AOT/5water+1DMSO (v/v) [7], 3 – *n*-heptane/AOT/5water+1DESO (v/v).

It is also found that ϕV was subtly increased with increasing W up to $W \approx 8-10$ and then reduced. In AOT reverse micelles it was reported that one AOT molecule can be hydrated by as much as 12 water molecules [19]. The counterion Na^+ in AOT can account for 6 water molecules in its solvation shell [20,21]. Thus AOT head group could bind as much as 6 water molecules to get complete hydration, i.e. $W=6$. Similar changeover points were found by the other authors $W=8$ [19], $W=7$ [22]. The reported values of W are quite consistent with our currently observed changeover point around $W \approx 8-10$.

The limiting value of the apparent molar volume (ϕV^0) (equal to the partial molar volume at infinite dilution) was calculated using the empirical Masson-type equation [23]

$$\phi V = \phi V^0 + S_v \sqrt{m}, \quad (2)$$

where S_v is the experimental slope, which is sometimes considered to be the volumetric pairwise interaction coefficient and is the measure of solute-solute/ion-ion interactions, m is the molality of the polar phase. The values of ϕV^0 obtained by least squares fitting of the linear plots of experimental values of ϕV versus the square root of molal concentration (\sqrt{m}) are reported in the Table 3 together with the standard errors.

Table 2

**Densities and apparent molar volumes of polar phase
of *n*-heptane/AOT/5water+1DES0 (v/v) system
at [AOT]=0.106 mol/kg and different temperatures**

W	T, K					
	273.15	278.15	283.15	288.15	293.15	298.15
	$\rho \times 10^{-3}, \text{kg/m}^3$					
3	0.71453	0.71042	0.70623	0.70202	0.69780	0.69354
5	0.71533	0.71121	0.70704	0.70284	0.69861	0.69435
8	0.71655	0.71243	0.70825	0.70405	0.69982	0.69556
10	0.71723	0.71312	0.70894	0.70474	0.70050	0.69625
12	0.71834	0.71424	0.71006	0.70586	0.70163	0.69738
14	0.71878	0.71469	0.71052	0.70634	0.70213	0.69788
	$\phi V \times 10^6, \text{m}^3/\text{mol}$					
3	20.86	20.87	21.01	21.15	21.29	21.44
5	21.10	21.17	21.21	21.29	21.32	21.56
8	21.16	21.23	21.31	21.39	21.44	21.62
10	21.43	21.49	21.57	21.65	21.73	21.87
12	20.90	20.94	21.01	21.09	21.14	21.27
14	21.45	21.49	21.55	21.61	21.64	21.77

Table 3

Limiting apparent molar volumes of polar phases at different temperatures

T, K	$\phi V_0 \times 10^6, \text{m}^3/\text{mol}$		
	Water	5water/1DMSO	5water/5DES0
273.15	16.38 ± 0.07	16.81 ± 0.05	20.60 ± 0.04
278.15	16.55 ± 0.09	17.03 ± 0.09	20.64 ± 0.04
283.15	16.74 ± 0.10	17.23 ± 0.09	20.77 ± 0.04
288.15	16.88 ± 0.11	17.42 ± 0.09	20.85 ± 0.04
293.15	16.91 ± 0.09	17.49 ± 0.09	20.95 ± 0.04
298.15	17.01 ± 0.09	17.81 ± 0.09	21.36 ± 0.04

It is evident from the Table 3 that ϕV^0 values increase with an addition of DASO and with an increase in temperature. Moreover the ϕV^0 values increase in the following order: water<DMSO<DES0 mainly due to the increase of $V_{V,W}$ and V_{void} as it is known the ϕV^0 values can alternatively be thought of as arising from four constituents [23,24]:

$$\phi V^0 = V_{v,W} + V_{void} + V_{h-philic} + V_{h-phobic} , \quad (3)$$

where $V_{v,W}$ and V_{void} are van der Waals volumes and volume of empty spaces present therein. $V_{h-philic}$ and $V_{h-phobic}$ represent contributions due to hydrophilic and hydrophobic hydration respectively.

The comparison of the values of partial molar volumes of water presented in Table 3 with the same values reported in [16] shows that the volume of water in micellar system is smaller than that of bulk water. This can be explained by the difference of properties of water within organized and bulk media.

The temperature dependence of ϕV^0 can be expressed as [23-25]:

$$\phi V^0 = a + bT + cT^2 , \quad (4)$$

where T is the temperature in Kelvin, a , b and c are empirical parameters.

The sign of second derivative of the limiting apparent molar volume with respect to temperature at constant pressure $\left(\frac{\partial^2 \phi V^0}{\partial T^2}\right)_p$, which is also known as

Hepler's constant, characterizes the long range structure making and structure breaking ability of the solute in the solution [25,26]. If $\left(\frac{\partial^2 \phi V^0}{\partial T^2}\right)_p$ value is positive it

means the solute is structure maker, if it is negative, the solute is structure breaker. The values of Hepler's constant may be determined by least squares fitting of $\phi V^0 = f(T)$ plots (Fig. 3.) and were positive for both quaternary systems of *n*-heptane/AOT/water+DMSO and *n*-heptane/AOT/water+DESO, respectively, which indicates that DMSO and DESO act as structure makers.

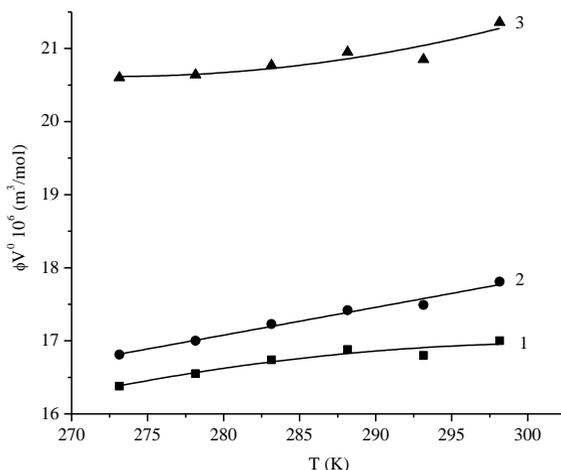


Fig. 3. The plots of limiting apparent molar volume against temperature: 1 - *n*-heptane/AOT/water, 2 - *n*-heptane/AOT/5water+1DMSO (v/v), 3 - *n*-heptane/AOT/5water+1DESO (v/v)

Conclusion

In this paper data of density of *n*-heptane/AOT/water+DESO reverse micellar system were reported. Derived properties such as apparent molar volume and partial molar volume at infinite dilution were 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 effective volume of micellar core was increased and thus the apparent molar volume of polar phase was raised. The positive values of Hepler's constant suggested that both DMSO and DESO act as structure makers in reverse micellar system.

We believe that the results from these studies can be utilized for better understanding the interactions within the organic polar solvent containing aqueous microemulsions.

ԴԻԵԹԻԼՍՈՒԼՖՕՔՍԻԴԻ ԱԶԴԵՅՈՒԹՅՈՒՆԸ ՆԱՏՐԻՈՒՄԻ ԲԻՍ (2-ԷԹԻԼՆԵՔՍԻԼ) ՍՈՒԼՖՈՍՈՒԿՅԵՆԱՏԻ ՄԻԿՐՈԷՄՈՒԼՍԻՍԵՆՆԵՐԻ ԾԱՎԱԼԱՅԻՆ ՆԱՏԿՈՒԹՅՈՒՆՆԵՐԻ ՎՐԱ

Գ. Ա. ՇԱԿԻՆՅԱՆ, Ն. Ո. ՍԱՐԳՍՅԱՆ, Ա. Մ. ԿՈԼԿԵՐ և Շ. Ա. ՄԱՐԳԱՐՅԱՆ

Ն-Հեպտան/նատրիումի բիս (2-էթիլհեքսիլ) սուլֆոսուլֆինատ (AOT)/ջուր+դիէթիլսուլֆօքսիդ (ԴԵՍՕ) շրջված միցելային համակարգի ծավալային հատկություններն ուսումնասիրվել են խտաչափության մեթոդով: Թվացյալ մոլային ծավալը (ϕV) հաշվարկվել է AOT-ի 0.106-ից 1.912 մոլ/կգ կոնցենտրացիոն տիրույթում, AOT-ի հաստատուն հիդրատացիայի աստիճանում ($W=10$) և 298.15-ից 313.15 Կ ջերմաստիճաններում: Ստացված արդյունքները համեմատվել են ն-Հեպտան/AOT/ջուր+դիէթիլսուլֆօքսիդ (ԴՄՍՕ) համակարգի նույն արդյունքների հետ: ϕV -ի արժեքները հաշվարկվել են նաև տարբեր W -երի և AOT-ի հաստատուն կոնցենտրացիայի պայմաններում 273.15-ից 298.15 Կ ջերմաստիճանային տիրույթում: ԴՄՍՕ և ԴԵՍՕ պարունակող բեկուային ֆազերի համար հաշվարկվել են թվացյալ մոլային ծավալներն (ϕV^0) անասՀման նոսր լուծույթում՝ օգտագործելով Մեսսոնի հավասարումը: ϕV -ի ջերմաստիճանային կախումից որոշվել են Հեպլերի հաստատունները: ԴԵՍՕ-ի առկայությունը հանգեցնում է բեկուային ֆազի թվացյալ մոլային ծավալի մեծացմանը ԴՄՍՕ-ի համեմատ:

ВЛИЯНИЕ ДИЭТИЛСУЛЬФОКСИДА НА ОБЪЕМНЫЕ СВОЙСТВА МИКРОЭМУЛЬСИЙ НАТРИЕВОЙ СОЛИ БИС(2-ЭТИЛГЕКСИЛОВОГО) ЭФИРА СУЛЬФОЯНТАРНОЙ КИСЛОТЫ

Г. А. ШАГИНЯН, А. Р. САРКИСЯН, А. М. КОЛКЕР и Ш. А. МАРКАРЯН

Методом денситометрии исследованы объемные свойства обращенной мицеллярной системы *n*-гептан/натриевая соль бис(2-этилгексилового) эфира сульфоянтарной кислоты (AOT)/вода+диэтилсульфоксид (ДЭСО). Кажущиеся молярные объемы вычислены при концентрационном интервале AOT от 0.106 до 1.912 моль/кг, постоянной степени гидратации AOT ($W=10$) и температурах от 298.15 до

313.15 К. Полученные результаты сравнивались с таковыми, полученными для системы *n*-гептан/АОТ/ вода+диметилсульфоксид (ДМСО). Значения ϕV вычислены также при разных *W* и постоянной концентрации АОТ в температурном интервале от 273.15 до 298.15 К. С помощью уравнения Массона вычислены кажущиеся объемы полярных фаз, содержащих ДМСО и ДЭСО при бесконечном разбавлении (ϕV^0). Из температурной зависимости ϕV определены постоянные Геплера. По сравнению с ДМСО наличие ДЭСО приводит к повышению кажущегося молярного объема полярной фазы.

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