

Effects of Concentration, Temperature, and Solvent Composition on the Partial Molar Volumes of Sodium Lauryl Sulfate in Methanol (1) + Water (2) Mixed Solvent Media

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ABSTRACT: Precise measurements on the density of sodium lauryl sulfate in pure water and in methanol (1) + water (2) mixed solvent media containing (0.10, 0.20, 0.30, and 0.40) volume fractions of methanol at (298.15, 308.15, 318.15, and 323.15) K are reported. The concentrations are varied from $(0.3 \cdot 10^{-1}$ to $1.3 \cdot 10^{-1})$ mol·kg⁻¹. The results were almost constant on the partial molar volumes with increasing surfactant concentration. Also, the partial molar volumes are found to increase with increasing temperature over the entire concentration range investigated in a given mixed solvent medium and are found to decrease with increasing methanol content in the solvent composition.

INTRODUCTION

The partial molar volume is proved to be a very useful tool in elucidating the interactions occurring in solutions. Studies of partial molar volume of the surfactants have been used to examine the behavior of surfactant solutions.^{1–6} Lee and Hyne⁷ have been determined the partial molar volumes of tetra-alkylammonium chlorides in the ethanol–water mixed solvent system to examine ion–solvent interactions in aqueous solvent mixtures, and they have discussed the structural changes accompanying the addition of ethanol to water.

Recently empirical procedures have been developed to predict the partial molar volume for ionic and nonionic organic compounds in aqueous solutions.^{8,9} However, the evaluation of these procedures for surfactants is limited by the lack of availability of reliable experimental data of a broad variety of chemical structures and macromolecular characteristics. Detailed definitions and an explanation of the partial molar volume have been provided in several papers.^{10–12} Hence, the only basic relation pertaining to the system studied herewith will be dealt. The partial molar volume, V_B , is defined by the following equation;

$$V_B = (\partial V / \partial n)_{T,p} \quad (1)$$

where ∂V represents the change in total volume and n as the number of moles. The partial molar volume is often provided in units of partial molar volume cm³·mol⁻¹. If there is a concentration dependence, the partial molar volumes have to be extrapolated to concentration zero using the following equation which calculate the apparent molar volume at the finite concentrations (C).¹³

$$V_B = \frac{M}{\rho_0} - \frac{10^3}{C} \left(\frac{\rho}{\rho_0} - 1 \right) \quad (2)$$

where M is the molecular weight of the sodium lauryl sulfate, ρ_0 is the density of the solvent, ρ is the density of the solution,

Table 1. Properties of Methanol (1) + Water (2) Mixtures Containing (0.10, 0.20, 0.30, and 0.40) Volume Fraction of Methanol at (298.15, 308.15, 318.15, and 323.15) K

T	ρ_0	η_0	D
K	g·cm ⁻³	mPa·s	
$\phi_1 = 0.10$			
298.15	0.98297	1.0844	75.09
308.15	0.97973	0.8665	71.57
318.15	0.97604	0.7017	68.18
323.15	0.97438	0.6375	66.45
$\phi_1 = 0.20$			
298.15	0.96963	1.3106	71.61
308.15	0.96632	1.0217	68.14
318.15	0.96162	0.8075	64.80
323.15	0.95875	0.7300	63.15
$\phi_1 = 0.30$			
298.15	0.95620	1.4712	67.65
308.15	0.95160	1.1418	64.25
318.15	0.94626	0.8957	60.99
323.15	0.94331	0.8052	59.41
$\phi_1 = 0.40$			
298.15	0.93957	1.4475	63.53
308.15	0.93364	1.2034	60.34
318.15	0.93140	0.9309	57.18
323.15	0.92800	0.8288	55.62

and C is having the unit as the equivalent concentration in mol·kg⁻¹.

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Table 2. Concentration, Density, and Partial Molar Volume of Sodium Lauryl Sulfate in Pure Water and Methanol (1) +Water (2) Mixed Solvent Media at (298.15, 308.15, 318.15, and 323.15) K

C	ρ	V_B	C	ρ	V_B
mol·kg ⁻¹	g·cm ⁻³	cm ³ ·mol ⁻¹	mol·kg ⁻¹	g·cm ⁻³	cm ³ ·mol ⁻¹
T = 298.15 K			T = 308.15 K		
$\phi_1 = 0.00$					
0.11591	1.00171	249.08 ± 0.22	0.11635	0.99799	256.14 ± 0.27
0.09920	1.00107	248.79 ± 0.25	0.09957	0.99746	255.77 ± 0.32
0.08753	1.00063	248.44 ± 0.30	0.08785	0.99709	255.43 ± 0.35
0.07710	1.00024	247.99 ± 0.32	0.07737	0.99676	255.02 ± 0.40
0.05935	0.99950	248.11 ± 0.25	0.05955	0.99613	255.16 ± 0.52
0.04734	0.99903	247.70 ± 0.52	0.04749	0.99573	254.83 ± 0.47
0.04026	0.99874	247.68 ± 0.42	0.04040	0.99548	254.70 ± 0.47
0.03036	0.99833	247.60 ± 0.35	0.03046	0.99513	254.77 ± 0.37
$\phi_1 = 0.10$					
0.12182	0.98867	245.76 ± 0.15	0.12232	0.98472	252.67 ± 0.20
0.10165	0.98773	245.72 ± 0.20	0.10205	0.98392	252.39 ± 0.22
0.08982	0.98721	245.33 ± 0.22	0.09017	0.98345	252.19 ± 0.27
0.07882	0.98670	245.21 ± 0.25	0.07912	0.98300	252.11 ± 0.30
0.06113	0.98588	244.95 ± 0.42	0.06135	0.98229	251.68 ± 0.37
0.04896	0.98529	245.17 ± 0.52	0.04914	0.98177	251.88 ± 0.47
0.04097	0.98492	245.01 ± 0.42	0.04112	0.98144	251.89 ± 0.27
0.03183	0.98449	244.89 ± 0.47	0.03194	0.98106	251.83 ± 0.30
$\phi_1 = 0.20$					
0.11801	0.97567	244.63 ± 0.10	0.11851	0.97169	251.54 ± 0.10
0.10281	0.97490	244.55 ± 0.12	0.10323	0.97100	251.51 ± 0.12
0.08996	0.97427	244.22 ± 0.12	0.09032	0.97045	251.11 ± 0.12
0.07774	0.97366	243.95 ± 0.15	0.07806	0.96990	250.97 ± 0.15
0.05984	0.97275	243.63 ± 0.10	0.06007	0.96910	250.54 ± 0.22
0.04751	0.97210	243.80 ± 0.25	0.04769	0.96853	250.48 ± 0.20
0.04175	0.97181	243.57 ± 0.27	0.04190	0.96827	250.29 ± 0.30
0.03148	0.97128	243.36 ± 0.32	0.03159	0.96778	250.59 ± 0.45
$\phi_1 = 0.30$					
0.12371	0.96301	244.02 ± 0.20	0.12441	0.95778	250.85 ± 0.20
0.10533	0.96204	243.60 ± 0.25	0.10591	0.95688	250.66 ± 0.25
0.09186	0.96130	243.53 ± 0.27	0.09236	0.95624	250.25 ± 0.27
0.07991	0.96066	243.22 ± 0.32	0.08034	0.95565	250.07 ± 0.32
0.05970	0.95956	242.73 ± 0.42	0.06002	0.95463	250.00 ± 0.42
0.04925	0.95896	242.98 ± 0.52	0.04951	0.95410	249.98 ± 0.52
0.04340	0.95864	242.80 ± 0.27	0.04362	0.95380	250.09 ± 0.47
0.03298	0.95806	242.61 ± 0.25	0.03315	0.95329	249.47 ± 0.40
$\phi_1 = 0.40$					
0.12398	0.94697	243.40 ± 0.22	0.12487	0.94045	250.46 ± 0.07
0.10717	0.94599	243.17 ± 0.25	0.10793	0.93955	250.24 ± 0.20
0.09392	0.94520	243.13 ± 0.27	0.09457	0.93883	250.09 ± 0.17
0.08130	0.94447	242.78 ± 0.32	0.08186	0.93817	249.60 ± 0.22
0.05846	0.94311	242.48 ± 0.45	0.05885	0.93692	249.15 ± 0.17
0.04902	0.94255	242.26 ± 0.44	0.04935	0.93638	249.42 ± 0.30
0.04081	0.94205	242.31 ± 0.45	0.04108	0.93593	249.17 ± 0.25
0.03216	0.94153	242.06 ± 0.42	0.03237	0.93545	248.98 ± 0.20

Table 2. Continued

C	ρ	V_B	C	ρ	V_B
$\text{mol}\cdot\text{kg}^{-1}$	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$
$T = 318.15 \text{ K}$			$T = 323.15 \text{ K}$		
$\phi_1 = 0.00$					
0.11688	0.99363	262.04 ± 0.32	0.11718	0.99118	265.00 ± 0.22
0.10001	0.99317	261.77 ± 0.37	0.10026	0.99076	264.71 ± 0.25
0.08824	0.99285	261.50 ± 0.42	0.08845	0.99047	264.40 ± 0.27
0.07771	0.99257	261.11 ± 0.47	0.07790	0.99021	264.06 ± 0.32
0.05980	0.99203	261.27 ± 0.50	0.05995	0.98971	264.18 ± 0.42
0.04769	0.99169	260.73 ± 0.27	0.04780	0.98939	263.91 ± 0.52
0.04056	0.99147	260.84 ± 0.35	0.04066	0.98919	264.05 ± 0.40
0.03059	0.99117	260.79 ± 0.47	0.03066	0.98891	264.24 ± 0.47
$\phi_1 = 0.10$					
0.12289	0.98036	259.39 ± 0.25	0.12314	0.97843	262.15 ± 0.32
0.10251	0.97965	259.33 ± 0.32	0.10271	0.97778	261.92 ± 0.40
0.09057	0.97925	259.09 ± 0.37	0.09074	0.97738	261.95 ± 0.42
0.07946	0.97888	258.77 ± 0.42	0.07962	0.97700	262.09 ± 0.47
0.06161	0.97824	258.79 ± 0.52	0.06173	0.97643	261.86 ± 0.12
0.04934	0.97778	258.88 ± 0.24	0.04943	0.97602	261.89 ± 0.20
0.04128	0.97751	258.97 ± 0.27	0.04136	0.97576	261.71 ± 0.25
0.03207	0.97720	258.64 ± 0.51	0.03213	0.97546	261.48 ± 0.45
$\phi_1 = 0.20$					
0.11918	0.96638	258.35 ± 0.17	0.11959	0.96325	261.54 ± 0.17
0.10380	0.96581	257.91 ± 0.15	0.10415	0.96267	261.52 ± 0.10
0.09082	0.96528	257.98 ± 0.17	0.09112	0.96221	261.17 ± 0.15
0.07848	0.96478	258.01 ± 0.15	0.07873	0.96177	260.77 ± 0.17
0.06039	0.96408	257.53 ± 0.17	0.06058	0.96106	261.02 ± 0.22
0.04794	0.96357	257.59 ± 0.15	0.04809	0.96060	260.68 ± 0.27
0.04212	0.96335	257.19 ± 0.20	0.04225	0.96039	260.30 ± 0.17
0.03176	0.96292	257.34 ± 0.20	0.03185	0.95998	260.51 ± 0.17
$\phi_1 = 0.30$					
0.12521	0.95185	257.56 ± 0.25	0.12565	0.94863	260.82 ± 0.10
0.10658	0.95106	257.14 ± 0.27	0.10695	0.94785	260.71 ± 0.12
0.09294	0.95044	257.22 ± 0.25	0.09326	0.94730	260.36 ± 0.15
0.08084	0.94989	257.28 ± 0.25	0.08111	0.94681	259.97 ± 0.17
0.06038	0.94900	256.74 ± 0.25	0.06058	0.94592	260.03 ± 0.20
0.04980	0.94852	256.76 ± 0.40	0.04997	0.94547	259.88 ± 0.20
0.04388	0.94826	256.54 ± 0.42	0.04402	0.94523	259.47 ± 0.15
0.03334	0.94777	256.87 ± 0.32	0.03345	0.94476	259.75 ± 0.12
$\phi_1 = 0.40$					
0.12527	0.93754	256.99 ± 0.15	0.12578	0.93390	260.21 ± 0.22
0.10826	0.93676	256.46 ± 0.15	0.10869	0.93313	259.89 ± 0.20
0.09486	0.93609	256.55 ± 0.22	0.09523	0.93251	259.75 ± 0.20
0.08211	0.93546	256.52 ± 0.22	0.08242	0.93193	259.39 ± 0.22
0.05902	0.93435	255.95 ± 0.25	0.05925	0.93082	259.51 ± 0.30
0.04948	0.93387	256.02 ± 0.27	0.04967	0.93038	259.12 ± 0.27
0.04119	0.93347	255.67 ± 0.25	0.04135	0.92999	258.90 ± 0.30
0.03246	0.93302	256.04 ± 0.25	0.03258	0.92956	259.18 ± 0.25

The aim of the present work is to analyze the influence of concentration, medium, and temperature on the surfactant solution in methanol (1) + water (2) mixed solvent media by partial molar volumes. The solution densities

are systematically measured for sodium lauryl sulfate, and the partial molar volume of the surfactant is computed at the temperatures (298.15, 308.15, 318.15, and 323.15) K.

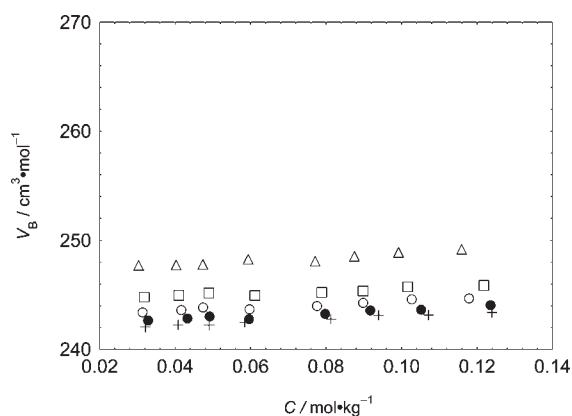


Figure 1. Concentration independence of partial molar volume for sodium lauryl sulfate at 298.15 K, in pure water (Δ) and different methanol (1) + water (2) mixtures (\square , 0.10 methanol; \circ , 0.20 methanol; \bullet , 0.30 methanol; $+$, 0.40 methanol).

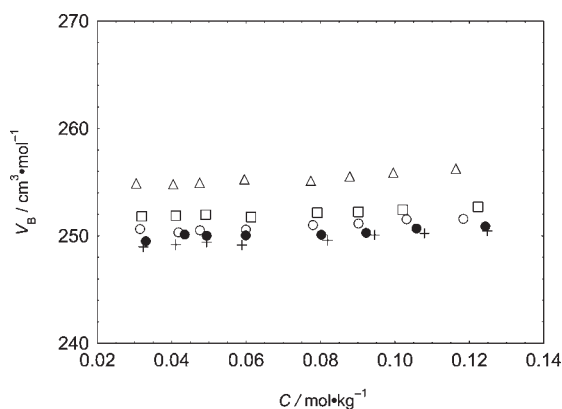


Figure 2. Concentration independence of partial molar volume for sodium lauryl sulfate at 308.15 K, in pure water (Δ) and different methanol (1) + water (2) mixtures (\square , 0.10 methanol; \circ , 0.20 methanol; \bullet , 0.30 methanol; $+$, 0.40 methanol).

EXPERIMENTAL SECTION

Methanol (Merck, India) was distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.77723 \pm 0.00004 \text{ g} \cdot \text{cm}^{-3}$ and a coefficient of viscosity of $0.47424 \pm 0.00005 \text{ mPa} \cdot \text{s}$ at 308.15 K; these values are in good agreement with the literature values.¹³ Triply distilled water with a specific conductance less than $10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The physical properties of methanol (1) + water (2) mixed solvents used in this study at (298.15, 308.15, 318.15, and 323.15) K are shown in Table 1, and those values are matched with the published works.^{14,15} The following literature data for the density of pure water,^{16,17} were taken to calculate the partial molar volume of sodium lauryl sulfate in pure water. The relative permittivity of methanol (1) + water (2) mixtures at the experimental temperatures were obtained by regressing the relative permittivity data as a function of solvent composition from the literature.¹⁸

Sodium lauryl sulfate employed in these investigations was purchased from Merck Specialties Private Limited, Mumbai,

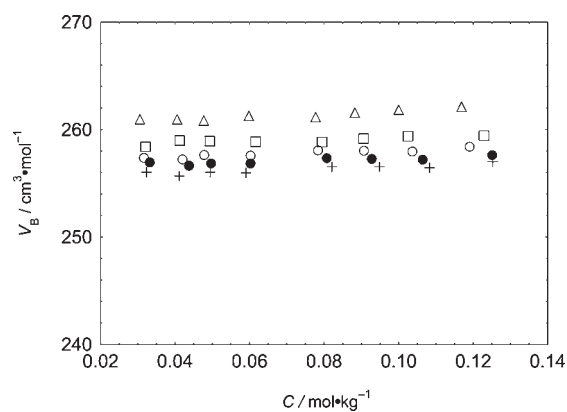


Figure 3. Concentration independence of partial molar volume for sodium lauryl sulfate at 318.15 K, in pure water (Δ) and different methanol (1) + water (2) mixtures (\square , 0.10 methanol; \circ , 0.20 methanol; \bullet , 0.30 methanol; $+$, 0.40 methanol).

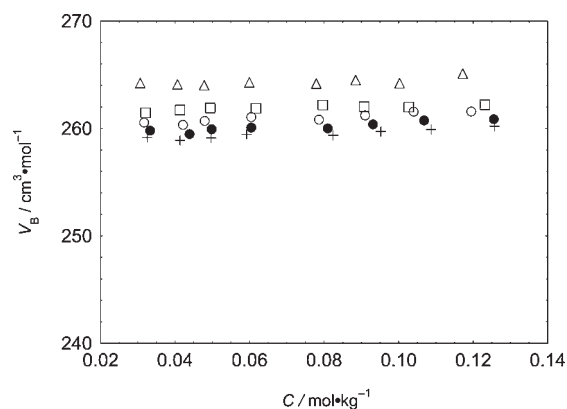


Figure 4. Concentration independence of partial molar volume for sodium lauryl sulfate at 323.15 K, in pure water (Δ) and different methanol (1) + water (2) mixtures (\square , 0.10 methanol; \circ , 0.20 methanol; \bullet , 0.30 methanol; $+$, 0.40 methanol).

India. To measure density, the pycnometric method was used. The stock solutions were freshly prepared for each concentration series to avoid problems of aging and microorganism contamination, which was found to occur with diluted surfactant solutions.¹⁹

The densities of solutions were determined by the use of an Ostwald-Sprengel type pycnometer of about 25 cm^3 capacity. The sample solution was transfused into the pycnometer by using a medical syringe. The pycnometer was then tightly fixed in a thermostat at the experimental temperatures within $\pm 0.005 \text{ K}$. After thermal equilibrium was attained, the mass of the pycnometer was measured with an electronic balance, and the density was calculated. Density measurements are precise within $\pm 0.00005 \text{ g} \cdot \text{cm}^{-3}$, which is satisfactory for our purpose. To avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed in three replicates. The partial molar volumes at different molalities of the solutions are given in Table 2 along with the standard error at the 95 % confidence interval.

RESULTS AND DISCUSSION

When alcohol and water are mixed, there is a minute but measurable heat of solution that is evident. The hydrogen bonding and closer packing of the molecules by the attraction allow a larger number of molecules of the hydrated alcohol to fit into the same space, thus decreasing the overall volume. The density is decreased with the increase of alcohol content for the methanol (1) + water (2) mixed solvent system (Table 1).

However, the density of the system increases with the addition of surfactant (Table 2). This behavior has been found to be similar in the literature.^{20,21} As the liquid becomes warmer, the molecules spread out more. When the molecules are more spread out, the substance is less dense, as the specific gravity is lower (Tables 1 and 2).

The partial molar volumes for the sodium lauryl sulfate in pure water and four other different methanol (1) + water (2) mixtures containing (0.10, 0.20, 0.30, and 0.40) volume fraction of methanol at (298.15, 308.15, 318.15, and 323.15) K are shown in Table 2. Representative plots (Figures 1 to 4) show the variation of partial molar volumes of the investigated solution as a function of the surfactant concentration. From these figures, the partial molar volumes exhibit almost independent behavior with increasing concentration within the examined concentration ranges in this study. The partial molar volume data for pure water of sodium lauryl sulfate at 298.15 K above critical micelle concentration (cmc) are almost the same as that of reported by Durchschlag and Zipper.⁸ Obviously, the concentration independence of partial molar volumes follows the same pattern at all temperatures and solvent compositions investigated.

The effects of temperature and relative permittivity on the partial molar volume values have been shown in Table 2. At each temperature, the partial molar volume values are found to decrease with decreasing relative permittivity by increasing the methanol content in the system. On the other hand, the partial molar volume is increased in the given system with increasing temperature. This is mostly due to the weakening of surfactant–solvent binding energy with increasing temperature. The same pattern has been also reported by Iqbal et al.²²

The relative permittivity of the medium is decreased with increasing in the methanol content at a given temperature and similar findings were reported in the previous study also.¹⁴ Because lower relative permittivity promotes greater counterion-binding, and hence a lower amount of uncondensed counterions in going from (0.10 to 0.40) volume fraction of methanol in the mixed solvent media over the entire range of temperatures investigated.

CONCLUSIONS

Effects of concentration, temperature, and solvent composition on the partial molar volumes of sodium lauryl sulfate in methanol (1) + water (2) mixed solvent media have been studied by measuring density through pycnometric method. The following conclusions have been drawn from the above results and discussion. The densities decrease with increase of alcohol content for the studied methanol (1) + water (2) mixed solvent system. However, density is increased with the addition of sodium lauryl sulfate. The partial molar volumes are found to be increased with increasing temperature over the entire concentration range investigated in the given mixed solvent system. Furthermore, at a particular temperature, the partial molar volumes are found almost same even at the different

concentrations, and these values are found to be decreased as the relative permittivity of the medium decreases.

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