

VOLUMETRIC PROPERTIES OF DIMETHYLSULFONE
IN ETHANOL–AQUEOUS SOLUTIONS

H. H. GHAZOYAN*

Chair of Physical and Colloids Chemistry YSU, Armenia

In this paper the densities of dimethylsulfone (DMSO₂) solution in ethanol–water mixtures with various compositions have been measured over available concentration range (up to $\sim 1 \text{ mol}\cdot\text{kg}^{-1}$). Densities of solutions and apparent molar volumes were determined over 293.15–323.15 K temperature range. In DMSO₂+ethanol–water systems the strongest interaction between ethanol and water molecules leads to the increase of partial molar volumes for DMSO₂. It was shown that the competitive intermolecular interactions are responsible for the observed phenomena.

Keywords: density; dimethylsulfone, ethanol, appear molar volumes, partial molar volumes.

Introduction. The biomedical and environmental significance for fundamental investigations of aqueous solution of dimethylsulfone (DMSO₂) and influence of the third component on volumetric behavior of the system arises from several reasons.

In the global sulfur cycle dimethylsulfide (DMS) is converted to DMSO₂ leading to an annual atmospheric production of some million tones of DMSO₂, much of which would be deposited by rain and snow [1–3]. In addition, DMSO₂ has been extensively studied from medical point of view [4]. It was established that DMSO₂ are contained in small amounts in human blood and urine [5, 6]. It is also interesting that methionine is transformed into DMSO₂ in living organisms.

In our recent publications a novel and interesting physicochemical properties of aqueous solution of DMSO₂ and its possible biomedical applications have been reported [7, 8].

Aqueous solutions of DMSO₂ are studied by means of densimetry, surface tension and calorimetry.

Obviously, studying the influence of the third component on volumetric behavior of aqueous solution of DMSO₂, it is important to reveal the character of intermolecular interactions.

Moreover, the DMSO₂+ethanol–water systems are interesting, because their components are capable to form hydrogen bonds. Although DMSO₂ are able to form hydrogen bonded complex with water molecule [9], the solution process is endothermic [7]. Obviously, in that case, the endothermic process of crystalline sulfone solution in water is predominated. To make a comparison it is worth

* E-mail: heghine@ysu.am

noticing that the process of mixing ethanol with water is exothermic [10] and very strong hydrogen bonding between ethanol and water takes place [11]. We believe that the competitive intermolecular interactions take place between DMSO2 and components of ethanol–water mixed solvent.

On the basis of densimetric measurements of volumetric properties, i.e. apparent ($V_{\phi,3}$) and standard partial (V_{ϕ}^0) molar volumes of DMSO2 in ethanol–water mixtures over 293.15–323.15 K temperature range have been calculated.

Materials and Methods. DMSO2 is white crystalline powder with maximum solubility in water of $2.3 \text{ mol}\cdot\text{kg}^{-1}$ and insolubility in ethanol at room temperature.

DMSO2 (99.5% purity) as well as ethanol (99.7%) were purchased from “Aldrich Chemical Co” and preliminary dehydrated alcohol distilled two times before measurements.

The densities of solutions DMSO2 with water and ethanol–water mixtures were measured on an Anton Paar DMA 4500 vibrating-tube densimeter at the temperature range 293.15–323.15 K. All solutions were prepared gravimetrically using doubly distilled water. The accuracy of density and temperature measurements was $\pm 1\cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ and $\pm 0.01 \text{ K}$ respectively. The densimeter was calibrated with dry air and doubly distilled water.

Results and Discussion.

Densities and Apparent Molar Volumes. The experimental values of densities of DMSO2–ethanol–water solutions with various compositions of ethanol–water mixture solvents ($X_{\text{ethanol}} = 0.12; 0.46; 0.75$) at the temperature range 293.15–323.15 K are listed in Tab. 1.

Table 1

Densities of DMSO2+ethanol–water ternary mixtures at various temperatures

T, K	293.15	298.15	303.15	308.15	313.15	318.15	323.15
$m, \text{ mol}\cdot\text{kg}^{-1}$	$\rho, \text{ g}\cdot\text{cm}^{-3}$						
<i>DMSO2+ethanol–water, $X_{\text{ethanol}} = 0.1237$</i>							
0.0000	0.96289	0.96028	0.95747	0.95452	0.95142	0.94819	0.94483
0.1986	0.96365	0.96077	0.95773	0.95456	0.95127	0.94785	0.94433
0.3007	0.96578	0.96290	0.95985	0.95667	0.95335	0.94992	0.94644
0.3904	0.96788	0.96497	0.96190	0.95870	0.95536	0.95197	0.94843
0.5494	0.97273	0.96989	0.96689	0.96376	0.96051	0.95714	0.95365
0.6457	0.97477	0.97185	0.96882	0.96567	0.96238	0.95896	0.95550
0.7357	0.97641	0.97353	0.97045	0.96723	0.96393	0.96034	0.95685
0.8000	0.97767	0.97479	0.97171	0.96851	0.96500	0.96125	0.95803
0.8945	0.97965	0.97677	0.97371	0.97054	0.96725	0.96384	0.96033
1.0009	0.98190	0.97899	0.97592	0.97272	0.96942	0.96600	0.96248
<i>DMSO2+ethanol–water, $X_{\text{ethanol}} = 0.4613$</i>							
0.0000	0.87350	0.86956	0.86522	0.86087	0.85645	0.85196	0.84740
0.1009	0.87642	0.87223	0.86794	0.86358	0.85916	0.85467	0.85011
0.2005	0.87892	0.87473	0.87043	0.86607	0.86164	0.85715	0.85259
0.2980	0.88114	0.87694	0.87264	0.86827	0.86384	0.85935	0.85479
0.4003	0.88360	0.87943	0.87512	0.87075	0.86632	0.86183	0.85726
0.4959	0.88619	0.88198	0.87767	0.87330	0.86887	0.86438	0.85981
0.5925	0.88851	0.88430	0.87997	0.87562	0.87121	0.86671	0.86214
0.7472	0.89212	0.88791	0.88357	0.87921	0.87477	0.87027	0.86570
0.8919	0.89562	0.89141	0.88709	0.88270	0.87826	0.87375	0.86917
0.9839	0.89649	0.89217	0.88781	0.88354	0.87914	0.87461	0.87004

<i>DMSO2+ethanol–water, $X_{ethanol}=0.7495$</i>							
0.0000	0.82462	0.82033	0.81592	0.81147	0.80695	0.80238	0.79774
0.1005	0.82662	0.82231	0.81790	0.81344	0.80892	0.80434	0.79970
0.2004	0.82946	0.82515	0.82073	0.81626	0.81174	0.80716	0.80251
0.3007	0.83243	0.82811	0.82369	0.81922	0.81469	0.81011	0.80545
0.3956	0.83434	0.83002	0.82559	0.82112	0.81659	0.81200	0.80735
0.5004	0.83707	0.83274	0.82831	0.82384	0.81930	0.81470	0.81005
0.5958	0.83949	0.83514	0.83070	0.82622	0.82168	0.81708	0.81242
0.7044	0.84254	0.83839	0.83388	0.82938	0.82483	0.82022	0.81555

As it is evident from experimental data, the increase of temperature leads to by reduction of density.

Apparent molar volumes of DMSO2 in ternary systems have been calculated by the following equation according to the procedure developed in [12]:

$$V_{\phi,3} = \frac{M_3}{\rho} + \frac{\rho_o - \rho}{\rho \cdot \rho_o} \left(\frac{M_2 m_2 + 1}{a \cdot m_2} \right), \quad (1)$$

where M_3 , M_2 are the molar weights of DMSO2 and ethanol respectively; ρ_o , ρ are the mixture solvent (ethanol–water) and ternary solution densities; m_2 is the molal concentration of ethanol in ethanol–water mixture and $a = n_3/n_2$, where n_3 and n_2 are numbers of moles of DMSO2 and ethanol respectively.

The calculated values of $V_{\phi,3}$ for ternary systems are reported in Tab. 2. As it follows from the data, apparent molar volumes increase with temperature increasing.

Table 2

Apparent molar volumes of DMSO2 in ethanol–water mixtures at temperature range 293.15–323.15 K

<i>T, K</i>	293.15	298.15	303.15	308.15	313.15	318.15	323.15
<i>m, mol · kg⁻¹</i>	<i>V_φ, cm³ · mol⁻¹</i>						
<i>DMSO2+ethanol–water, X_{ethanol}=0.1237</i>							
0.1986	96.585	97.263	97.905	98.552	99.174	99.815	100.429
0.3007	94.719	95.252	95.779	96.312	96.855	97.395	97.866
0.3969	93.694	94.167	94.638	95.119	95.585	96.076	96.584
0.5494	91.687	92.061	92.432	92.811	93.189	93.575	93.970
0.6457	91.358	91.755	92.124	92.498	92.884	93.284	93.650
0.7357	91.210	91.570	91.950	92.346	92.725	93.198	93.572
0.8000	91.221	91.415	91.786	92.164	92.631	93.165	93.410
0.8945	90.807	92.120	92.498	92.883	93.263	93.655	94.049
1.0009	90.527	91.197	91.539	91.885	92.240	92.601	92.969
<i>DMSO2+ethanol–water, X_{ethanol}=0.4613</i>							
0.1009	81.391	83.911	83.751	84.140	84.444	84.755	85.072
0.2005	82.856	84.272	84.388	84.738	85.096	85.414	85.739
0.2980	83.902	84.987	85.171	85.546	85.897	86.224	86.558
0.4003	84.030	84.843	85.081	85.440	85.782	86.108	86.466
0.4959	83.468	84.251	84.497	84.841	85.173	85.493	85.840
0.5925	83.477	84.180	84.466	84.772	85.067	85.403	85.746
0.7472	83.502	84.120	84.423	84.742	85.080	85.414	85.754
0.8919	83.281	83.844	84.122	84.470	84.802	85.142	85.490
0.9839	84.461	85.119	85.452	85.687	98.931	86.360	86.708

DMSO ₂ +ethanol–water, $X_{ethanol}=0.7495$							
0.1005	87.974	88.560	88.897	89.374	89.725	90.220	90.586
0.2004	82.159	82.554	82.893	83.306	83.589	83.946	84.311
0.3007	79.518	79.886	80.175	80.513	80.812	81.116	81.472
0.3956	81.146	81.501	81.831	82.166	82.473	82.821	83.139
0.5004	80.482	80.836	81.146	81.460	81.781	82.134	82.438
0.5958	80.151	80.530	80.852	81.178	81.487	81.824	82.144
0.7044	79.245	79.210	79.644	79.986	80.296	80.630	80.950

The influence of ethanol on the volumetric behavior has been taken into account by changing the apparent molar volume compared with the apparent molar volume of the binary aqueous solutions of DMSO₂. To compare, the corresponding literature data for DMSO₂+water binary solutions are depicted in Fig. 1. Likely DMSO₂+water binary solutions the apparent molar volumes in ternary systems also irregularly change with molality of solutions. It is interesting that the effect of ethanol on the values of apparent molar volumes does not change monotonic with increasing the ethanol quantity in ethanol–water mixture (Fig. 1).

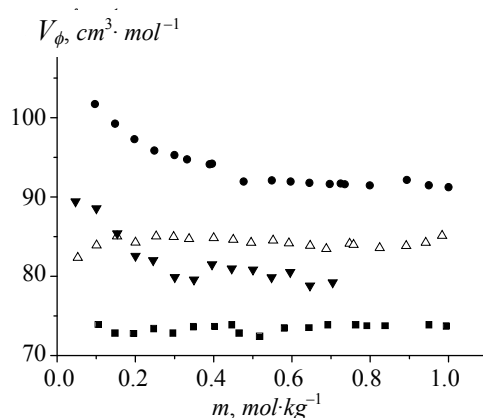


Fig. 1. Apparent molar volumes, plotted against molality of solutions for DMSO₂+water: (■ – data from [7]), DMSO₂+ethanol–water ($X_{ethanol}=0.12$ (●), $X_{ethanol}=0.46$ (▼), $X_{ethanol}=0.75$ (Δ)); $T = 298.15$ K.

Standard Partial Molar Volumes. The standard partial molar volumes V_{ϕ}^0 , which are taken to be apparent molar volumes at the infinite dilution, were estimated from the plots of V_{ϕ}^0 versus molality for DMSO₂ by extrapolation using the equation

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

where V_{ϕ}^0 is the infinite dilution apparent molar volume that equals the standard partial molar volume and S_v is an experimentally determined parameter (slope constant). Partial molar volumes at infinite dilution are considered of particular interest, because of their usefulness in examining solute-solvent interactions, as solute-solute interactions can be assumed to be eliminated at infinite dilution. At infinite dilution, the partial molar volume and apparent molar volume are equal.

Standard partial molar volumes for DMSO₂ solutions in water [7] and ethanol–water mixtures at 293.15–313.15 K temperature range are presented in Tab. 3.

Table 3

Standard partial molar volumes of DMSO2 in binary and ternary systems at temperature range 293.15–323.15 K

T, K	$V_{\phi}^0, m^3 \cdot mol^{-1}$			
	DMSO2 + water*	DMSO2+ethanol–water		
		$X_{ethanol}=0.1237$	$X_{ethanol}=0.4613$	$X_{ethanol}=0.7495$
293.15	73.66	98.11	82.01	86.39
298.15	74.17	98.70	84.27	87.08
303.15	74.84	99.42	84.21	87.37
308.15	75.45	100.00	84.57	87.86
313.15	76.89	100.85	83.58	88.11
318.15	76.90	101.54	85.20	88.60
323.15	77.59	102.22	85.55	88.98

* Reference [7]

As it follows from the Table, the values of standard partial molar volumes increase with the increase of temperature for all cases (Fig. 1). In addition, V_{ϕ}^0 for DMSO2 in water is less than for solutions in ethanol–water mixed solvent.

It is known that V_{ϕ}^0 comprises four contributions [13]:

$$V_{\phi}^0 = (V_{VW} + V_V) + (V_S + V_h), \quad (3)$$

where V_{VW} is the intrinsic van der Waals volume, V_V is the void volume, V_S is the contribution from solute-solvent interactions and V_h is the hydrophobic hydration.

We believe that the latter has the main contribution in the increase of V_{ϕ}^0 for ternary solution when compared with binaries. The results obtained show that the values of standard partial molar volumes for DMSO2+water mixture are less than that of DMSO2+ethanol–water mixtures (Fig. 2).

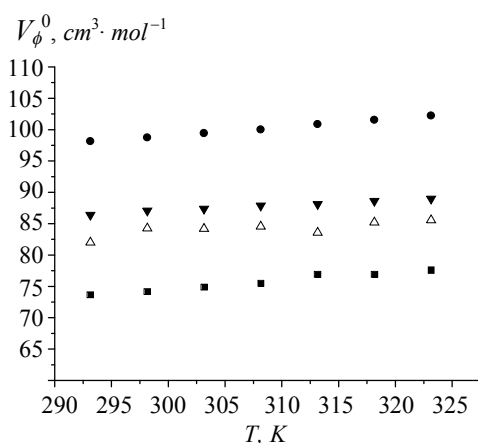


Fig. 2. Standard partial molar volumes, plotted against molality of solutions for: DMSO2+water (■ data from [7]); DMSO2 + ethanol–water ($X_{ethanol}=0.12$ (●), $X_{ethanol}=0.46$ (▼), $X_{ethanol}=0.75$ (▲)).

We believe that competitive intermolecular interactions are responsible for the observed phenomena. In the DMSO2+ethanol–water system the strongest

interaction between ethanol and water molecules leads to the increase of partial molar volumes for DMSO₂. Moreover, the strongest interaction between molecules of DMSO₂ with ethanol and water molecules by hydrogen bonding take place in ternary systems when the mixed solvent has $X_{ethanol}=0.46$ mole fraction.

Conclusion. The volumetric results obtained show that the values of standard partial molar volumes for DMSO₂+water mixture are less in comparison with DMSO₂+ethanol–water mixtures. We believe that the competitive intermolecular interactions are responsible for the observed phenomena. In the DMSO₂+ethanol–water system the strongest interaction between ethanol and water molecules leads to the increase of partial molar volumes for DMSO₂.

Received 23.02.2015

REFERENCES

1. **De Bruyn W.J., Shorter J.A., Davidovits P., Worsnop D.R., Zahniser M.S., Kolb C.E., Geophys J.** Uptake of Gas Phase Sulfur Species Methanesulfonic Acid, Dimethylsulfoxide and Dimethyl Sulfone by Aqueous Surfaces. // J. Geophys. Res., 1994, v. 99, p. 16927–16932.
2. **Borodina E., Kelly D.P., Rainey F.A., Ward-Rainey N.L., Wood A.P.** Dimethylsulfone as a Growth Substrate for Novel Methyltrophic Species of Hyphomicrobium and Arthrobacter. // Arch. Microbiol., 2000, v. 173, p. 425–437.
3. **Barnes I., Hjorth J., Mihalopoulos N.** Dimethyl Sulfide and Dimethyl Sulfoxide and Their Oxidation in the Atmosphere. // Chem. Rev., 2006, v. 106, p. 940–975.
4. **Herschler R.J.** Methylsulfonylmethane and Methods of Use. US Patent 1981, 4, 296, 130.
5. **Jacob S.W., Lawrence R.M., Zucker M.** The Miracle of MSM. The Natural Solution for Pain. NY: G.P. Putnam's Sons, 1999.
6. **Hucker H.B., Miller J.K., Hochberg A., Brobyn R.D., Riordan F.H., Calesnick B.** Studies on the Adsorption, Excretion and Metabolism of Dimethylsulfoxide (DMSO) in Man. // J. Pharmacol. Exp. Ther., 1967, v. 155, p. 309–317.
7. **Markaryan Sh.A., Aznauryan M.G., Kazoyan E.A.** Physicochemical Properties of Aqueous Solutions of Dimethyl- and Diethylsulfones. // Russ. J. Phys. Chem. A, 2011, v. 85, № 12, p. 2138–2141.
8. **Ghazoyan H.H., Markarian Sh.A.** Densities and Thermochemical Properties of Dimethylsulfone in Dimethylsulfoxide and Dimethylsulfoxide–Water. // The Journal of Molecular Liquids, 2013, v. 183, p. 85–88.
9. **Givan A., Grothe H., Loewenschuss A., Nielsen C.J.** Infrared Spectra and *ab initio* Calculations of Matrix Isolated Dimethyl Sulfone and Its Water Complex. // Physical Chemistry Chemical Physics, 2002, v. 4, p. 255–263.
10. **Costigan M.J., Hodges L.J., Marsh K.N., Stokes R.H., Tuxford C.W.** The Isothermal Displacement Calorimeter: Design Modifications for Measuring Exothermic Enthalpies of Mixing. // Australian J. Chem., 1980, v. 33, № 10, p. 2103–2119.
11. **Nose A., Hojo M.** Hydrogen Bonding of Water–Ethanol in Alcoholic Beverages. // J. Biosci. Bioengin., 2006, v. 102, p. 269–280.
12. **D'Aprano A., Donato I.D., Goffedi M., Liveri V.T.** Volumetric and Transport Properties of Aerosol-OT Reversed Micelles Containing Light and Heavy Water. // J. Sol. Chem, 1992, v. 21, p. 323–331.
13. **Kumar A., Singh M., Gupta K.C.** An Estimation of Hydrophilic and Hydrophobic Interaction of Aqueous Urea, Methylurea, Dimethylurea and Tetramethylurea from Density and Apparent Molal Volume at 30.0°C. // Phys. Chem. Liq., 2010, v. 48, № 1, p. 1–6.