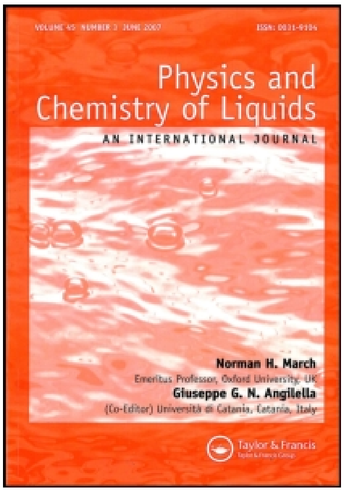
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Volumetric properties of dimethyl sulfoxide with some alcohols at 298.15 K

H. Iloukhani[a]; H. A. Zarei[a]
[a] Faculty of Chemistry, Bu Ali Sina University, Hamadan, Iran

To cite this Article Iloukhani, H. and Zarei, H. A.(2008) 'Volumetric properties of dimethyl sulfoxide with some alcohols at 298.15 K', Physics and Chemistry of Liquids, 46: 2, 154 — 161
To link to this Article: DOI: 10.1080/00319100601124203
URL: http://dx.doi.org/10.1080/00319100601124203

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physics and Chemistry of Liquids
Vol. 46, No. 2, April 2008, 154–161

Volumetric properties of dimethyl sulfoxide with some alcohols at 298.15 K

H. ILOUKHANI* and H. A. ZAREI

Faculty of Chemistry, Bu Ali Sina University, Hamadan, Iran

(*Received 10 May 2006; in final form 17 November 2006*)

Densities ρ, of the binary systems of dimethyl sulfoxide (DMSO) with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, and butan-2-ol have been measured as a function of the composition of DMSO at 298.15 K and atmospheric pressure, using an Anton Paar model DMA 4500 oscillating U-tube densitometer. From the experimental results, excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$, and excess partial molar volumes $\bar{V}_{\mathrm{m},i}^{\mathrm{E}}$, were calculated. Limiting excess partial molar volumes $\bar{V}_{\mathrm{m},i}^{\mathrm{E},0}$, are also calculated by extrapolation of partial excess molar volumes to infinite dilution. The excess molar volumes are negative for methanol, ethanol, propan-1-ol and positive for propan-2-ol, butan-1-ol, and butan-2-ol in the entire composition range. The results are explained in terms of aggregates between unlike molecules through $\mathrm{O}\cdots\mathrm{HO}$ hydrogen bonding.

Keywords: Densities; Excess molar volume; Dimethyl sulfoxide (DMSO); Alcohols

1. Introduction

This article is a continuation of our work related to the study of thermodynamic properties of binary mixtures [1–5]. In recent years, measurements of volumetric properties have been employed in throwing light on the nature of molecular systems and physico-chemical behaviour in liquid mixtures. The non-rectilinear behaviour of volumetric properties of liquid mixtures with changing mole fractions is attributed to the difference in size of the molecules and strength of interactions. DMSO-alcohols systems make particularly interesting systems for study because substituents have a marked effect on the association behaviour. A survey of the literature has shown that no excess molar volume measurement for a mixture of DMSO with studied alcohols exists.

We report, in this article, the densities ρ, the excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$, and excess partial molar volumes $\bar{V}_{\mathrm{m},i}^{\mathrm{E}}$, of binary mixtures containing dimethyl sulfoxide (DMSO) at 25°C and atmospheric pressure. The alcohols used are methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and butan-2-ol.

---

*Corresponding author. Email: iloukhani@basu.ac.ir

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100601124203

Table 1. Source, purity and density of pure components at 298.15 K.

			ρ (g cm^{-3})	
Compounds	Source	Purity/mass (%)	Expt.	Lit.
DMSO	Merck	99.5	1.09538	1.09556[a]
Ethanol	Merck	99.8	0.78650	0.78663[b]
Propan-1-ol	Merck	99.8	0.78516	0.78525[b]
Propan-2-ol	Merck	99.5	0.78086	0.78085[c]
Butan-1-ol	Merck	99.8	0.80575	0.80525[d]
Butan-2-ol	Merck	99	0.80240	0.80239[e]

[a] [10].
[b] [7].
[c] [6].
[d] [9].
[e] [8].

The systems of alcohols with DMSO are of considerable interest from the two counts: (i) breaking of H-bonded structure of alcohols and (ii) formation of new H-bonded molecular complexes between alcohol and DMSO. By extrapolation of excess partial molar volumes to infinite dilution, limiting excess partial molar volumes $\bar{V}_{\mathrm{m},i}^{\mathrm{E},0}$, are also obtained. These values are interesting from a theoretical point of view since at infinite dilution the only interactions present are solute–solvent interactions. No literature data are available on the excess molar volumes of the systems with DMSO analysed in this work.

2. Experimental

2.1. *Materials*

Dimethyl sulfoxide, methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and butan-2-ol were purchased from Merck. No further purification was attempted owing to their high purity grades. Before measurements, chemicals were degassed by cooling and heating at 273.15 K and below boiling point temperature, respectively. The purity of the liquids was further ascertained by comparing the densities at 298.15 K with the values reported in the literature [6–10] (table 1).

2.2. *Apparatus and procedure*

The density of the samples was measured with an Anton Paar DMA 4500 oscillating U-tube densitometer, provided with automatic viscosity correction. The temperature in the cell was regulated to ±0.01 K with solid-state thermostat. The apparatus was calibrated once a day with dry air and double distilled with freshly degassed water. Airtight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle, and the total mass was recorded. Subsequently, the other component was introduced and the mass of the bottle along with the two components was determined. Each mixture was immediately used after it was well mixed by shaking.

All the weightings were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

3. Results and discussion

The experimental results on the excess molar volumes V_m^E, and densities, ρ of binary mixtures of DMSO with alcohols at atmospheric pressure and 298.15 K are listed in table 2 as a function of the mole fraction of DMSO, x_1 and are graphically represented in figure 1. The values of densities ρ, (table 2) have been used to calculate the excess molar volumes V_m^E, with the following equation

$$V_\mathrm{m}^\mathrm{E} = \frac{x_1 M_1 + x_2 M_2}{\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2} \tag{1}$$

where x_i, M_i and ρ_i $(i = 1, 2)$ are the mole fraction, molecular weights, and densities of pure components 1 and 2, respectively, ρ is density of the mixtures.

In all cases, it was possible to represent the dependence of V_m^E on mole fraction using the Redlich–Kister [11] polynomial equation

$$V_\mathrm{m}^\mathrm{E} = x_1(1 - x_1)\sum_{k=0}^{3} B_k(1 - 2x_1)^k. \tag{2}$$

The Redlich−Kister coefficients B_k, with the standard deviation $\sigma(V_\mathrm{m}^\mathrm{E})$, obtained by unweighted least squares associated with the use of equations (2) and (3), respectively, are summarised in table 3. $\sigma(V_\mathrm{m}^\mathrm{E})$ is evaluated from the equation

$$\sigma(V_\mathrm{m}^\mathrm{E}) = \left[\sum_{k=1}^{n} \frac{(V_\mathrm{m,expt.}^\mathrm{E} - V_\mathrm{m,calc.}^\mathrm{E})^2}{n - p}\right]^{1/2} \tag{3}$$

where n is the number of results and p is the number of parameters retained in equation (2).

Comparison of the values of V_m^E for different systems in figure 1 reveals that V_m^E values for the binary mixtures of DMSO with methanol, ethanol, propan-1-ol are negative, while those with butan-1-ol, propan-2-ol and butan-2-ol are positive over the entire composition range studied. The V_m^E *versus* x_1 curves for all the mixtures are almost symmetrical with a minimum or maximum around $x_1 \approx 0.35 - 0.45$. The values of V_m^E at this concentration follow the order:

butan-2-ol > propan-2-ol > butan-1-ol > propan-1-ol > ethanol > methanol.

For short-chain alcohols, the negative values of V_m^E suggested the specific intermolecular interaction such as order formation of strong hydrogen bonding (through $\mathrm{O} \cdots \mathrm{HO}$) between the more polar DMSO and hydroxyl group of the alcohols. The negative values of excess molar volumes also mean that the mixture is less compressible than the corresponding ideal mixture. Therefore, in the systems, a compression in free volume is considered to occur, making the mixtures less compressible than the ideal mixture, which ultimately culminates into the negative

Table 2. Densities, ρ (g cm^{-3}), excess molar volumes, $V_{\mathrm{m}}^{\mathrm{E}}$ (cm^3 mol^{-1}), in equation (1) and excess partial molar volumes, $\bar{V}_{\mathrm{m},i}^{\mathrm{E}}$ (cm^3 mol^{-1}), in equation (4) for binary mixtures DMSO with alcohols at 298.15 K.

x_1	ρ	$V_{\mathrm{m}}^{\mathrm{E},}$	$\bar{V}_{\mathrm{m},1}^{\mathrm{E},}$	$\bar{V}_{\mathrm{m},2}^{\mathrm{E},}$	x_1	ρ	$V_{\mathrm{m}}^{\mathrm{E},}$	$\bar{V}_{\mathrm{m},1}^{\mathrm{E},}$	$\bar{V}_{\mathrm{m},2}^{\mathrm{E},}$
DMSO(1) + methanol(2)									
0.0773	0.83106	−0.2630	−2.8712	−0.0452	0.5566	1.00831	−0.5453	−0.2028	−0.9837
0.1555	0.87027	−0.4425	−1.9945	−0.1590	0.6406	1.02862	−0.4808	−0.1076	−1.1245
0.2343	0.90499	−0.5679	−1.3527	−0.3129	0.7178	1.04518	−0.3863	−0.0540	−1.2370
0.3142	0.93526	−0.6078	−0.8905	−0.4861	0.8013	1.06166	−0.2834	−0.0210	−1.3404
0.3954	0.96261	−0.6164	−0.5650	−0.6638	0.8847	1.07665	−0.1678	−0.0052	−1.4235
0.4805	0.98817	−0.6012	−0.3371	−0.8400	0.9604	1.08919	−0.0590	−0.0004	−1.4780
DMSO(1) + ethanol(2)									
0.0837	0.81739	−0.0905	−0.9452	−0.0128	0.5554	0.97548	−0.2195	−0.1251	−0.3356
0.1585	0.84509	−0.1525	−0.7216	−0.0435	0.6336	0.99835	−0.1985	−0.0847	−0.3945
0.2329	0.87151	−0.1920	−0.5396	−0.0875	0.7271	1.02472	−0.1669	−0.0505	−0.4672
0.3127	0.89878	−0.2189	−0.3859	−0.1449	0.7881	1.04121	−0.1328	−0.0334	−0.5210
0.3999	0.92738	−0.2328	−0.2614	−0.2134	0.8778	1.06485	−0.0887	−0.0133	−0.6222
0.4861	0.95446	−0.2298	−0.1747	−0.2819	0.9578	1.08504	−0.0336	−0.0019	−0.7526
DMSO(1) + propan-1-ol(2)									
0.0793	0.82195	−0.0092	−0.1506	−0.0007	0.5630	0.96255	−0.0232	−0.0154	−0.0615
0.1583	0.84461	−0.0279	−0.1254	−0.0042	0.6464	0.98750	−0.0237	−0.0075	−0.0729
0.2315	0.86580	−0.0453	−0.0987	−0.0107	0.7164	1.00853	−0.0189	−0.0035	−0.0811
0.3078	0.88757	−0.0222	−0.0703	−0.0213	0.8045	1.03537	−0.0228	−0.0015	−0.0873
0.3992	0.91419	−0.0211	−0.0444	−0.0356	0.8725	1.05614	−0.0167	−0.0008	−0.0911
0.4779	0.93730	−0.0201	−0.0266	−0.0496	0.9570	1.08203	−0.0027	−0.0001	−0.0982
DMSO(1) + propan-2-ol(2)									
0.0735	0.80173	0.0645	0.8311	0.0034	0.5566	0.94816	0.1437	0.0324	0.3669
0.1568	0.82575	0.1236	0.6592	0.0264	0.6447	0.97664	0.1085	0.05111	0.3935
0.2472	0.85230	0.1734	0.4364	0.0832	0.7118	0.99867	0.0795	0.0449	0.3796
0.3151	0.87271	0.1864	0.2700	0.1443	0.7969	1.02694	0.0437	0.0259	0.3199
0.3934	0.89668	0.1879	0.1322	0.2550	0.8785	1.05426	0.0186	0.0089	0.2312
0.4718	0.92117	0.1726	0.0290	0.3030	0.9604	1.08192	0.0052	0.0007	0.1402
DMSO(1) + butan-1-ol(2)									
0.0772	0.82308	0.0345	0.4016	0.0026	0.5552	0.94690	0.1109	0.0753	0.1557
0.1560	0.84149	0.0590	0.3367	0.0112	0.6327	0.97009	0.1040	0.0459	0.1986
0.2406	0.86204	0.0849	0.2695	0.0279	0.7084	0.99382	0.0885	0.0248	0.2413
0.3134	0.88041	0.1019	0.2156	0.0485	0.8003	1.02401	0.0623	0.0089	0.2898
0.3968	0.89968	0.1110	0.1660	0.0753	0.8807	1.05173	0.0398	0.0021	0.3246
0.4787	0.92489	0.1158	0.1121	0.1163	0.9602	1.08048	0.0142	0.0001	0.3464
DMSO(1) + butan-2-ol(2)									
0.0779	0.81921	0.1262	1.5775	0.0051	0.5646	0.94468	0.3668	0.1234	0.6889
0.1624	0.83817	0.2531	1.3199	0.0415	0.6368	0.96702	0.3167	0.0522	0.7949
0.2456	0.85790	0.3407	1.0036	0.1232	0.7236	0.99512	0.2553	0.0120	0.8783
0.3241	0.87758	0.3893	1.7100	0.2402	0.7953	1.01957	0.1901	0.0018	0.9092
0.3800	0.89218	0.4105	0.5246	0.3408	0.8813	1.05031	0.1089	0.0006	0.9144
0.4906	0.92281	0.4037	0.2437	0.5554	0.9621	1.08062	0.0349	0.0003	0.9204

values of $V_{\mathrm{m}}^{\mathrm{E}}$. Whereas, with longer-chain alcohols disruption of the ordered structure of pure component during formation of the mixture leads to positive effect on excess volume. Negative values of $V_{\mathrm{m}}^{\mathrm{E}}$ for methanol, ethanol, and propan-1-ol, and positive values for butan-1-ol, propan-2-ol, and butan-2-ol support this explanation.

The excess partial molar volumes, $\bar{V}_{\mathrm{m},i}^{\mathrm{E}}$ of a component in a binary mixture can be determined from excess molar volume data using

$$\bar{V}_{\mathrm{m},i}^{\mathrm{E}} = V_{\mathrm{m}}^{\mathrm{E}} + (1 - x_i)\left(\frac{\partial V^{\mathrm{E}}}{\partial x_i}\right)_{x_{j\neq i}p,T} \tag{4}$$

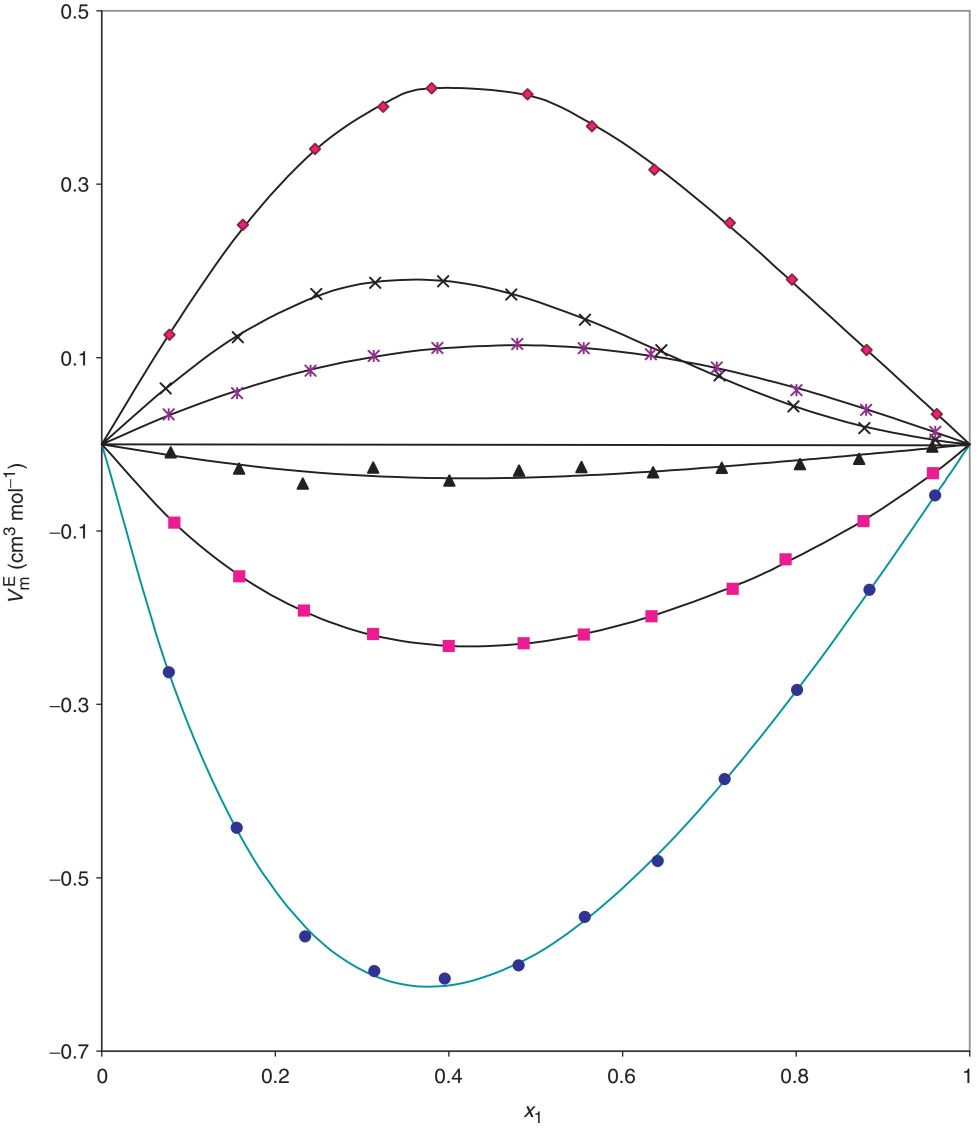


Figure 1. Excess molar volumes at 298.15 K of DMSO (1) with alcohols (2). Solid curves were calculated from coefficients of equation (2) given in table 3. (●) Methanol, (■) ethanol, (▲) propan-1-ol, (×) propan-2-ol, (✳) butan1-ol, (◆) butan-2-ol.

where $(\partial V^E/\partial x_i)_{x_{j\neq i},p,T}$ is calculated from equation (2) using the parameters in table 3. The excess partial molar volumes of DMSO, $\bar{V}^E_{m,1}$ and of alcohols, $\bar{V}^E_{m,2}$ for all composition can be calculated by using the Redlich–Kister coefficients, B_k (table 3) in equation (4). Results of densities, excess molar volumes and excess partial molar volumes at 298.15 K are also listed in table 2. Figure 2 shows $\bar{V}^E_{m,1}$ *versus* x_1 for the six systems.

Table 3. Values of the adjustable coefficients, B_k in equation (2) and standard deviations, $\sigma(V_m^E)$ (cm^3 mol^{-1}), in equation (3) for DMSO with alcohols at 298.15 K.

System	B_0^a	B_1^a	B_2^a	B_3^a	$\sigma(V_m^E)^a$
DMSO + methanol	−2.351	1.1618	−0.4160	0.1085	0.016
DMSO + ethanol	−0.9126	0.2588	−0.1315	−0.0595	0.005
DMSO + propan-1-ol	−0.1521	0.0595	0.0171	−0.0291	0.023
DMSO + propan-2-ol	0.6612	0.6488	−0.1570	0.2541	0.005
DMSO + butan-1-ol	0.4560	0.0516	−0.0477	−0.0059	0.005
DMSO + butan-2-ol	1.5976	0.6957	−0.2942	0.3311	0.009

Table 4. Excess partial molar volumes at infinite dilution, $\bar{V}_{m,i}^{E,0a}$ (cm^3 mol^{-1}), in equations (5) and (6) at 298.15 K.

System	$\bar{V}_{m,1}^{E,0}$	$\bar{V}_{m,2}^{E,0}$
DMSO + methanol	67.2895	39.2433
DMSO + ethanol	70.0835	57.8312
DMSO + propan-1-ol	71.1615	75.0619
DMSO + propan-2-ol	72.2257	77.0702
DMSO + butan-1-ol	71.7926	92.3448
DMSO + butan-2-ol	72.9949	93.3146

The behaviour of $\bar{V}_{m,1}^E$ for DMSO with alcohols differs from one mixture to another. With methanol, ethanol, and propan-1-ol the values of $\bar{V}_1^E$ are negative and increase over the whole range of DMSO. With propan-2-ol, butan-1-ol, and butan-2-ol, the values of $\bar{V}_{m,2}^E$ are positive over the whole range of DMSO concentration. The $\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$values which are related by equation (4) can differ in sign, size and slope, but both values *versus* composition plots show a similar trend.

The excess partial molar volume at infinite dilution, $\bar{V}_{m,i}^{E,0}$ appears to be of particular interest. In the limit of infinite dilution, solute–solute interactions disappear. Thus, the values of the excess partial molar volumes at infinite dilution provide insight into solute–solvent interactions. We can consider DMSO at infinite dilution ($x_1 = 0$) in alcohols and of alcohols at infinite dilution ($x_1 = 1$) in DMSO. Setting ($x_1 = 0$) in equation (4) leads to

$$\bar{V}_{m,1}^{E,0} = \sum_{k=0} B_k. \tag{5}$$

Similarly, setting ($x_1 = 1$) in equation (4) leads to

$$\bar{V}_{m,2}^{E,0} = \sum_{k=0} B_k(-1)^{k-1}. \tag{6}$$

In equations (5) and (6), $\bar{V}_{m,1}^{E,0}$ and $\bar{V}_{m,2}^{E,0}$ represent the excess partial molar volumes of DMSO at infinite dilution in alcohols and the excess partial molar volume of alcohols at infinite dilution in DMSO, respectively. All excess partial molar volumes at infinite dilution, $\bar{V}_{m,i}^{E,0}$ were calculated using the Redlich–Kister coefficients, B_k (table 3) in equations (5) and (6) listed in table 4.

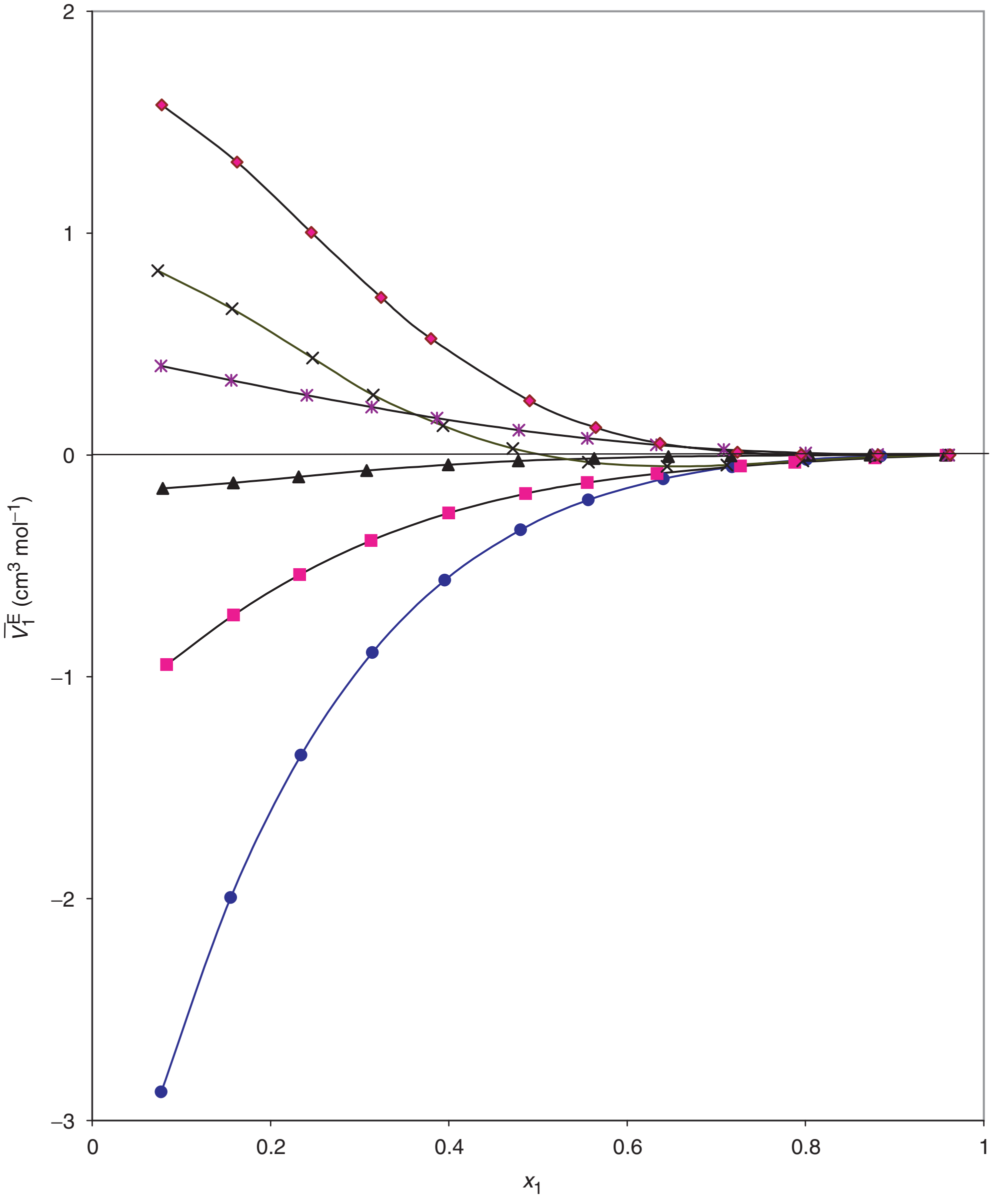


Figure 2. Excess partial molar volumes at 298.15 K of DMSO in mixtures of DMSO (1) with alcohols (2). (—●—) Methanol, (—■—) ethanol, (—▲—) propan-1-ol, (×) propan-2-ol, (—✳—) butan-1-ol, (—◆—) butan-2-ol.

Acknowledgements

The authors thank the University authorities for providing the necessary facilities to carry out the work.

References

[1] H. Iloukhani, M. Rezaei-Sameti, J.B. Parsa. *J. Chem. Thermodyn.*, **38**, 975 (2006).
[2] H. Iloukhani, Z. Rostami. *J. Sol. Chem.*, **32**(5), 451 (2003).
[3] H. Iloukhani, H.A. Zarei. *J. Chem. Eng. Data*, **47**, 195 (2002).
[4] H. Iloukhani, H.A. Zarei. *Phys. Chem. Liq.*, **40**, 449 (2002).
[5] H. Iloukhani, J.B. Parsa. *J. Sol. Chem.*, **30**(9), 807 (2001).
[6] G. Ouyang, Z. Huang, J. Ou, W. Wu, B. Kang. *J. Chem. Eng. Data*, **48**, 195 (2003).
[7] A.G. Marigliano, H.N. Solimo. *J. Chem. Eng. Data*, **47**, 796 (2002).
[8] M. Dominguez, S. Santafe, H. Artigas, F.M. Royo. *Themochem. Acta*, **381**(9), 181 (2002).
[9] J.A. Riddick, W.B. Bunger, T.K. Sakano. *Organic Solvents Techniques of Chemistry*, 4th Edn, Vol. II, Wiley, New York (1986).
[10] T. Kimura, S. Takagi. *J. Chem. Thermodyn.*, **18**, 447 (1986).
[11] O.J. Redlich, T. Kister. *Ind. Eng. Chem.*, **40**, 345 (1948).