

Excess Molar volumes of some Binary Mixtures of Dimethyl Sulfoxide (DMSO) at Various temperatures

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Abstract:

Knowledge of physical properties and phase equilibrium for organic solvents is necessary for the design and optimization of the equipment. In this paper the excess molar volume V^E of the binary liquid systems of DMSO (Dimethyl Sulfoxide)+ Benzene , DMSO + o-Xylene , DMSO + 1,4- Dioxane , and DMSO + Tetrahydrofuran, has been calculated from density measurements at 293.15 , 298.15 , and 303.15 K and at atmospheric pressure over the entire composition range. The experimental excess function V^E was fitted to the Redlich-Kister polynomial equation to evaluate the adjustable parameters (A_i) and standard deviation (σ) .

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303.15 , 298.15 , 293.15

Redlich - Kister

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Introduction

In recent years there has been considerable advancement in the experimental investigation of the excess thermodynamic properties (excess molar volumes, partial excess and partial molar volumes, phase equilibrium, excess molar enthalpies, etc.)⁽¹⁻⁴⁾. These factors have been increased in study due to their simplicity as models, having low data requirements and versatility in operational conditions. A survey of the literature shows that very few attempts have been made to study the excess thermodynamic behaviour of binary liquid mixtures containing dimethyl sulfoxide.

Dimethyl sulfoxide, (DMSO), $(\text{CH}_3)_2\text{SO}$, is an important industrial solvent, it is widely used as a therapeutic principle.

It was first introduced to the scientific community in 1963 by a research team headed by Stanley W. Jacob, MD, at the University of Oregon Medical School⁽⁵⁻⁶⁾. Therefore I thought it worthwhile to study excess molar volume of binary solutions of DMSO in polar and nonpolar solvents. The

experimental values of V^E data at 293.15, 298.15, 303.15 K and at atmospheric pressure which are calculated from the density measurements of binary liquid mixtures of DMSO with Benzene, o-Xylene, 1,4-Dioxane, Tetrahydrofuran over the entire composition range are reported in this paper. In general, excess volume depends mainly on two effects: a) the variation of the intermolecular forces when two components come in to contact, and b) the variation of the molecular packing as a consequence of the differences in the size and shape of the molecules of the components⁽⁷⁻⁹⁾.

Experimental

1. Chemicals

The chemicals Dimethyl Sulfoxide, Benzene, o-Xylene, 1,4-Dioxane, Tetrahydrofuran, (all with a purity > 99.8 %) were supplied by Merck. All the chemicals were distilled before use, the purity of these samples was tested by measuring their densities at 293.15, 298.15, 303.15 K. The densities values are in a good agreement with the literature values^(6,10,11,12), as shown in table (1).

Table 1 : Densities of the pure components in the present work and in the literature at (293.15 , 298.15 , and 303.15) K .

Compound	Density g / cm ⁻³					
	Exptl.			Lit.		
	293.15 K	298.15 K	308.15 K	293.15 K	298.15 K	308.15 K
Benzene	0.78441	0.78001	0.77952	0.78452 ^(a)	0.78301 ^(a)	0.77959 ^(a)
0-Xylene	0.89700	0.89691	0.89688	0.89714 ^(b)	0.89698 ^(b)	0.89692 ^(b)
1,4-Dioxane	1.03011	1.0299	1.02971	1.03008 ^(c)	1.0303 ^(c)	1.03000 ^(c)
Tetrahydrofuran	0.88598	0.88581	0.88572	0.88591 ^(a)	0.88588 ^(a)	0.88564 ^(b)
DMSO	0.80010	0.8000	0.79881	0.80050 ^(d)	0.80020 ^(d)	0.79897 ^(d)

(a)= [10]**(b)= [11]****(c)= [12]****(d)= [6]****2. Procedure**

The pure components were stored in the dark at constant humidity and temperature. In order to reduce errors in the mole fraction, the vapour space in the vessels was minimized during preparation of the samples. Densities of the pure liquid and mixtures at different concentrations were measured at 293.15, 298.15, and 308.15 k by using pycnometer (Density bottle), the pycnometer was calibrated with doubly distilled water and dry air at atmospheric pressure. The pycnometer was always kept in a water thermostat ,the thermostat bath was

controlled to within ± 0.01 °C .The details pertaining to calibration , experimental setup , and operational procedures have been described previously ^(13,14) , The mole fraction of each mixture was obtained with an uncertainty of 1×10^{-4} from the measured mass of one the components . All masses were corrected for buoyancy .All molar quantities were based upon the IUPAC table of atomic weights ⁽¹⁵⁾ .

After measuring the densities of the pure fluids and binary liquid mixtures , the excess molar volumes were calculated from the following equation ⁽¹⁶⁻¹⁸⁾:

$$V^E = \frac{X_1 M_1 + X_2 M_2}{P} - \frac{X_1 M_1}{P_1} - \frac{X_2 M_2}{P_2} \quad \dots\dots\dots 1$$

Where X1 and X2 mole fraction, M1 and M2 denote the molecular weights and P1 and P2 stand for the densities of the pure components “1”and “2”, respectively. The values of V^E determined from density measurement are accurate within ± 0.0005 cm³ .mol⁻¹ .

Results and discussion

The density and excess molar volume data , evaluated to eq. (2) , for the binary liquid mixtures are listed in Table 2 , 3 ,4 , and 5 .

Table 2: Densities and excess molar volumes V^E of binary mixtures of DMSO(X₁) – benzene (X₂) at 293.15, 298.15 and 308.15 K.

293.15 K			298.15 K			303.15 K		
X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)	X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)	X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)
0.0000	0.78441	0.0000	0.0000	0.78001	0.0000	0.0000	0.77952	0.0000
0.1226	0.78693	-0.0766	0.1226	0.78292	-0.0639	0.1226	0.78221	-0.0488
0.2392	0.78882	-0.0880	0.2392	0.78524	-0.0642	0.2392	0.78453	-0.0594
0.3502	0.79060	-0.0964	0.3502	0.78753	-0.0768	0.3502	0.78672	-0.0689
0.4561	0.79221	-0.0893	0.4561	0.78965	-0.0755	0.4561	0.78874	-0.0643
0.5571	0.79375	-0.0783	0.5571	0.79153	-0.0601	0.5571	0.79061	-0.0580
0.6536	0.79514	-0.0629	0.6536	0.79340	-0.0549	0.6536	0.79232	-0.0367
0.7459	0.79652	-0.0551	0.7459	0.79521	-0.0476	0.7459	0.79402	-0.0238
0.8342	0.79781	-0.0424	0.8342	0.79683	-0.0229	0.8342	0.79571	-0.0203
0.9188	0.79901	-0.0243	0.9188	0.79852	-0.0199	0.9188	0.79733	-0.0125
1.0000	0.80010	0.0000	1.0000	0.80000	0.0000	1.0000	0.79881	0.0000

Table 3: Densities and excess molar volumes V^E of binary mixtures of DMSO(X₁) – o-Xylene (X₂) at 293.15, 298.15 and 308.15 K.

293.15 K			298.15 K			303.15 K		
X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)	X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)	X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)
0.0000	0.89700	0.0000	0.0000	0.89691	0.0000	0.0000	0.89688	0.0000
0.0649	0.89237	-0.0810	0.0649	0.89235	-0.0902	0.0649	0.89228	-0.0942
0.2942	0.87291	-0.0908	0.2942	0.87287	-0.0977	0.2942	0.87253	-0.0996
0.4168	0.86183	-0.0983	0.4168	0.86174	-0.0999	0.4168	0.86047	-0.00107
0.5264	0.85140	-0.0950	0.5264	0.85132	-0.0969	0.5264	0.85071	-0.0984
0.6251	0.84156	-0.0841	0.6251	0.84150	-0.0886	0.6251	0.84081	-0.0946
0.7145	0.83232	-0.0749	0.7145	0.83228	-0.0820	0.7145	0.83151	-0.0905
0.7956	0.82358	-0.0588	0.7956	0.82353	-0.0641	0.7956	0.82267	-0.0743
0.8697	0.81522	-0.0480	0.8697	0.81534	-0.0549	0.8697	0.81436	-0.0613
0.9376	0.80778	-0.316	0.9376	0.80760	-0.0449	0.9376	0.80656	-0.0541
1.0000	0.8001	0.0000	1.0000	0.8000	0.0000	1.0000	0.79881	0.0000

Table 4: Densities and excess molar volumes V^E of binary mixtures of DMSO(X₁) – 1,4-Dioxane (X₂) at 293.15, 298.15 and 308.15 K.

293.15 K			308.15 K			303.15 K		
X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)	X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)	X ₁	P (g cm ⁻³)	V ^E (cm ³ mol ⁻¹)
0.0000	1.03011	0.0000	0.0000	1.02990	0.0000	0.0000	1.02971	0.0000
0.1777	0.99931	0.0349	0.1177	0.99923	0.0276	0.1177	0.99892	0.0218
0.2308	0.97095	0.0470	0.2308	0.97083	0.0405	0.2308	0.97042	0.0303
0.3397	0.94442	0.0567	0.3397	0.94431	0.0512	0.3397	0.94380	0.0379
0.4446	0.91954	0.0765	0.4446	0.91943	0.0718	0.4446	0.91902	0.0569
0.5456	0.89655	0.0632	0.5456	0.89643	0.0594	0.5456	0.89561	0.0541
0.6429	0.87484	0.0617	0.6429	0.87472	0.0585	0.6429	0.87393	0.0438
0.7369	0.85453	0.0435	0.7369	0.85442	0.0414	0.7369	0.85340	0.0394
0.8277	0.83533	0.0310	0.8277	0.83522	0.0295	0.8277	0.83421	0.0198
0.9154	0.81714	0.0267	0.9154	0.81705	0.0259	0.9154	0.81602	0.0086
1.0000	0.80010	0.0000	1.0000	0.80000	0.0000	1.0000	0.79881	0.0000

Table 5: Densities and excess molar volumes V^E of binary mixtures of DMSO(X_1) – Tetrahydrofuran (X_2) at 293.15, 298.15 and 308.15 K.

293.15 K			298.15 K			303.15 K		
X_1	P (g cm^{-3})	V^E (cm^3 mol^{-1})	X_1	P (g cm^{-3})	V^E (cm^3 mol^{-1})	X_1	P (g cm^{-3})	V^E (cm^3 mol^{-1})
0.0000	0.88598	0.0000	0.0000	0.88581	0.0000	0.0000	0.88572	0.0000
0.1130	0.87430	0.0280	0.1130	0.87420	0.0223	0.1130	0.87398	0.0192
0.2228	0.86360	0.0396	0.2228	0.86350	0.0344	0.2228	0.86320	0.0250
0.3295	0.85370	0.0433	0.3295	0.85358	0.0413	0.3295	0.85310	0.0359
0.4332	0.84450	0.0627	0.4332	0.84428	0.596	0.4332	0.84368	0.0454
0.5342	0.83580	0.0479	0.5342	0.83576	0.0457	0.5342	0.83499	0.0394
0.6324	0.82781	0.0363	0.6324	0.82776	0.03294	0.6324	0.82691	0.0258
0.7279	0.82022	0.0342	0.7279	0.82013	0.0291	0.7279	0.81925	0.0225
0.8210	0.81314	0.0241	0.8210	0.81303	0.0194	0.8210	0.81203	0.0142
0.9117	0.80643	0.0137	0.9117	0.80633	0.0095	0.9117	0.80525	0.0042
1.0000	0.8001	0.0000	1.0000	0.8000	0.0000	1.0000	0.79881	0.0000

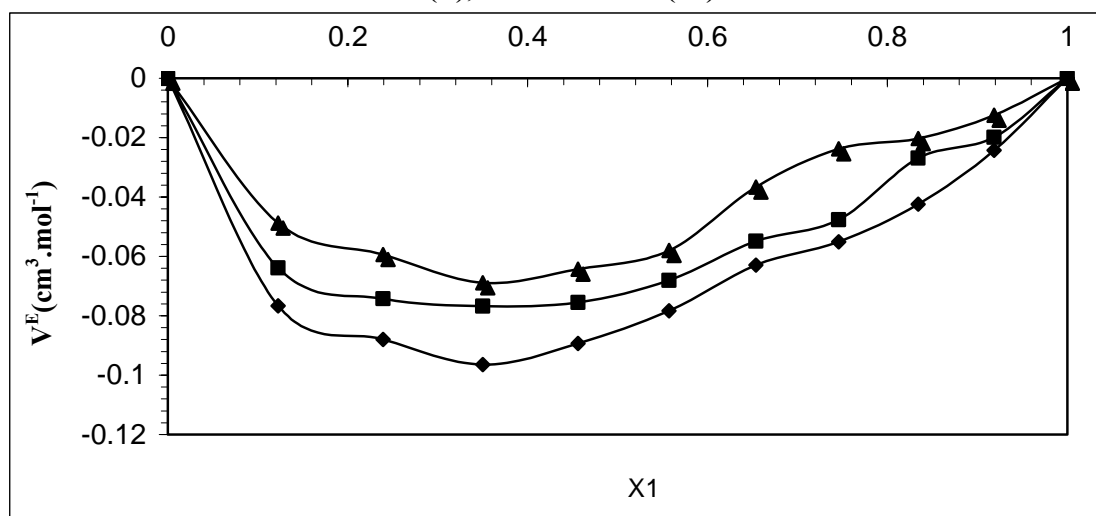
Fig. 1. Represented the relationship between the excess molar volume of the binary mixtures DMSO + Benzene and the molar fraction of DMSO at 293.15 K (\blacklozenge), 298.15 K (\blacksquare), and 303.15 K (\blacktriangle).

Fig. 2. Represented the relationship between the excess molar volume of the binary mixtures DMSO + o-xylene and the molar fraction of DMSO at 293.15 K (◆), 298.15 K (■), and 303.15 K (▲)

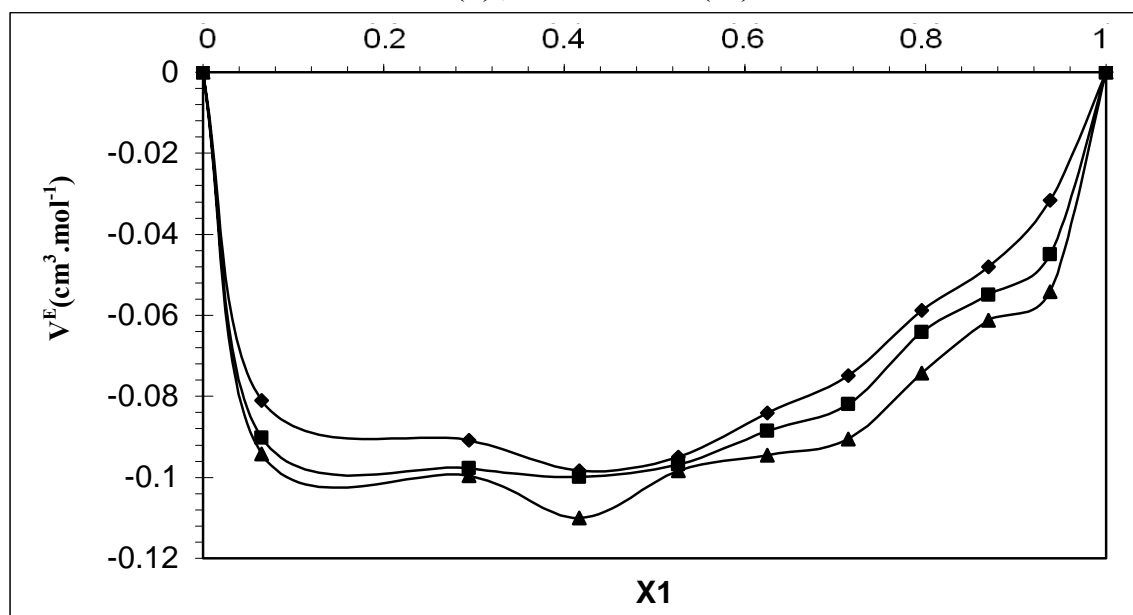


Fig. 3. Represented the relationship between the excess molar volume of the binary mixtures DMSO + 1-4 Dioxane Benzene and the molar fraction of DMSO at 293.15 K (◆), 298.15 K (■), and 303.15 K (▲).

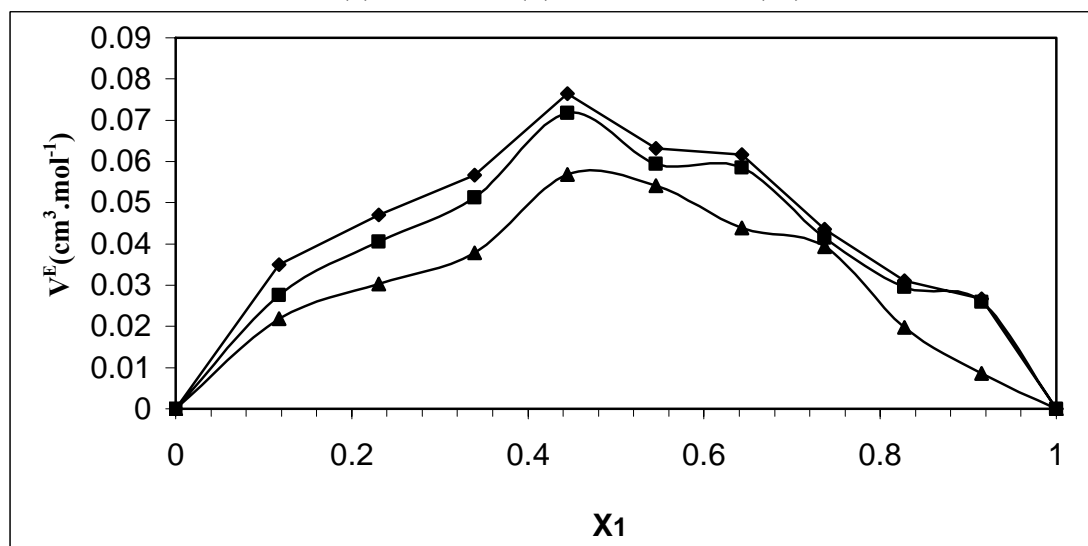
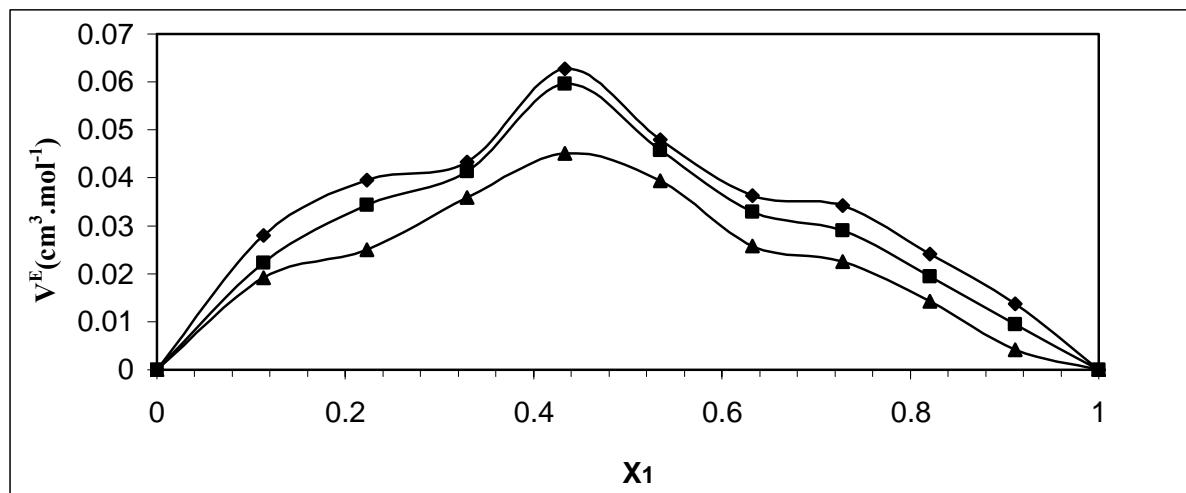


Fig . 4 . Represented the relation-ship between the excess molar volume of the binary mixtures DMSO + Tetrahydrofuran and the molar fraction of DMSO at 293.15 K (◆) , 298.15 K (■) , and 303.15 K (▲) .



The values of V^E for mixture were correlated to the Redlich –Kister polynomial equation⁽¹⁹⁾ .

$$V^E = X_1(1-X_1) \sum_{i=1}^K A_i(2X_1-1)^{i-1} \quad \text{.....2}$$

Where X_1 represent the mole fraction of DMSO , A_i are fitting parameters obtained by the least square method , k is the degree of the polynomial expansion used .Values of coefficients

A_i and standard deviations σ are summarized in table 6, together with the standard deviation of the fit σV^E is defined as:

$$\sigma V^E = [\sum (V^E - V^E_{cal})^2 / (N-k)]^{1/2} \quad \text{.....3}$$

Where N represent the number of the experimental data points and K is the number of coefficients.

Table 6 : Coefficients A_i from equation (2) and standard deviations σV^E from equation (3) of (DMSO+ benzene , + o-xylene , + 1,4-Dioxane ,+ Tetrahydrofuran) at various temperatures .

Mixture	T(K)	A_0	A_1	A_2	A_3	σV^E
DMSO + benzene	293.15	-0.33051	-0.19891	-0.27306	-0.07385	0.0058
	298.15	-0.26966	-0.1171	-0.17832	-0.18493	0.0014
	303.15	-0.23583	-0.21825	-0.05579	0.05997	0.0159
DMSO+ o-xylene	293.15	-0.36179	0.07323	0.38919	0.2817	0.0039
	298.15	-0.35381	0.05249	-0.72718	0.56886	0.0020
	303.15	-0.23074	-0.33355	-1.11822	1.26504	0.0033
DMSO +1,4- Dioxane	293.15	-0.23583	-0.21825	-0.05579	0.05997	0.0003
	298.15	0.25186	-0.03642	-0.04174	0.08731	0.0006
	303.15	0.21075	0.04527	-0.10377	-0.15901	0.0003
DMSO +Tetrahydrofuran	293.15	0.20124	-0.08792	-0.00104	0.05811	0.014
	298.15	0.19245	-0.10105	-0.06671	0.09646	0.012
	303.15	0.15697	-0.06834	-0.07469	0.00735	0.025

The excess molar volume of both mixtures DMSO +1,4-Dioxane , + Tetrahydrofuran are positive throughout .However , they are significantly smaller for DMSO + Tetrahydrofuran mixture , which is nearly ideal solution , than for the DMSO + 1,4- Dioxane system .Positive values can be explained by the predominance of expansion in volume , caused by the loss of dipolar association and difference in size and shape of component molecules , over contraction in volumes , due to the dipole – dipole and dipole – induced dipole interaction .The excess molar volume show negative deviation over the whole mole fraction for binary mixtures of DMSO + Benzene , + o-Xylene and decreases negativity in the sequence of

o-xylene > benzene , and decreased negativity as the temperature increased . The V^E obtained could be qualitatively explained by the dipole – induce dipole interaction between DMSO and benzene ring of the aromatic hydrocarbon, which was greater than the dispersive and dipole – dipole breaking interaction. Due to the electron donor ability of the DMSO, a weak charge transfer complex would be formed. Methyl substituted benzene had a greater electron donor ability than benzene (inductive effect of the methyl group), this would give a stronger charge transfer complex and the highest negative V^E (20-23) .

The excess molar volume V^E of all mixtures decreases negativity deviation as the temperature increase.

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