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Temperature Dependence of Molar Excess Volumes for the Dimethyl Sulfoxide + Thiophene System and Thermal Expansion Coefficients between 293.15 and 313.15 K

Silvia B. Aznarez, Lelia Mussari, and Miguel A. Postigo*

Cátedra de Fisicoquímica, Departamento de Química, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, Neuquén 8300, Argentina

Densities were measured with a vibrating-tube densimeter for binary mixtures of dimethyl sulfoxide + thiophene at temperatures from 293.15 to 313.15 K as a function of composition. Molar excess volumes V^E for the mixtures, determined from the density data, are negative and become more negative with an increase in temperature. The coefficients of thermal expansion were also evaluated from the temperature dependence of the density.

Introduction

The temperature dependence of molar excess volumes and the thermal expansion coefficient of binary liquid mixtures are useful quantities in understanding the $P-V-T$ behavior of fluids and fluid mixtures. However, these values are infrequently reported. In this study, both excess volumes and thermal expansion coefficients were calculated from density measurements on dimethyl sulfoxide + thiophene over a temperature range. Their appear to be no previous measurements for this mixture.

Experimental Section

Materials. Dimethyl sulfoxide was supplied by Merk, and thiophene was supplied by Fluka. All solvents were used from freshly opened bottles without further purification. According to the specification of the suppliers, the purities were better than 99.7 mass % for dimethyl sulfoxide and 99.5 mass % for thiophene. All liquids were stored over molecular sieves (Union Carbide Type 4A, from Fluka). The purities of the compounds were checked by determining their refractive indices and densities. Air and bidistilled water were used for the densimeter calibration.

All the solutions were prepared using a Mettler H 315 balance (precision of 1×10^{-4} g) and air-tight stoppered bottles. The more volatile component was directly poured into the bottle. The charged bottle was closed and weighed. The second component was injected into the bottle through the stopper by a syringe. This procedure reduced vapor loss and contamination. The estimated accuracy in the mole fraction is less than $\pm 2 \times 10^{-4}$.

Density Measurements. A digital densimeter (Anton Paar Model DMA 45) was employed for the determination of the densities of the pure components and the binary mixtures. Water and air were used as calibrating fluids. All measurements were carried out at atmospheric pressure. Pressure was measured by a mercury barometer. A Haake constant-temperature bath circulator was used with a temperature control to ±0.01 K.

Temperature was measured with a digital thermometer Digitec calibrated and checked at the water triple point. The accuracy of the densities measured is estimated to be better than ± 0.2 kg m^{-3}. The excess molar volumes V^E were calculated from the density measurements. The accuracy in V^E was estimated to be less than $\pm 2 \times 10^{-9}$ m^3 mol^{-1}.

Table I. Experimental Densities of Pure Substances at Various Temperatures and Comparison with Literature Values

	$\rho \times 10^{-3}/(\mathrm{kg\ m^{-3}})$			
	dimethyl sulfoxide		thiophene	
temp/K	exptl	lit.	exptl	lit.
293.15	1.1002	1.1004[a]	1.0644	1.064 82[b]
298.15	1.0956	1.095 37[b]	1.0583	1.058 84[b]
303.15	1.0906	1.0904[a]	1.0520	
308.15	1.0856		1.0463	
313.15	1.0806	1.0804[a]	1.0409	

[a] Reference 1. [b] Reference 2.

Results and Discussion

The measured densities of dimethyl sulfoxide and thiophene at the various temperatures are given in Table I, together with the values from the literature for comparison.

From the experimental values of densities at different temperatures of the binary systems, the molar excess volume is calculated with the following equation:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - (x_1 V_1 + x_2 V_2) \qquad (1)$$

where M_1 and M_2 are the molecular weights and V_1 and V_2 are the molar volumes of components 1 and 2, respectively, and ρ is the density of the solution.

The densities and the excess molar volumes at different mole fractions of dimethyl sulfoxide at 293.15, 298.15, 303.15, 308.15, and 313.15 K are reported in Table II.

The excess molar volumes of the binary systems can be represented by a Redlich–Kister form of the type

$$V^E = x_1 x_2 \sum_{k=0}^{n} a_k (2x_1 - 1)^k \qquad (2)$$

The method of least squares was used to determine the values of the coefficients a_k. The optimum number of coefficients was ascertained from an examination of the standard deviation defined by the equation

$$\sigma = [\sum (V^E_{\mathrm{obsd}} - V^E_{\mathrm{calcd}})^2/(n_{\mathrm{obsd}} - n)]^{1/2} \qquad (3)$$

where n_{obsd} is the number of experimental points and n is the number of parameters.

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Table II. Experimental Densities and Excess Volumes V^E for Dimethyl Sulfoxide (1) + Thiophene (2) Mixtures between 293.15 and 313.15 K

x_1	$\rho \times 10^{-3}$/(kg m^{-3})	$V^E \times 10^6$/(m^3 mol^{-1})		($V^E_{exptl} - V^E_{calcd}$)/(10^{-6} m^{-3} mol^{-1})	x_1	$\rho \times 10^{-3}$/(kg m^{-3})	$V^E \times 10^6$/(m^3 mol^{-1})		($V^E_{exptl} - V^E_{calcd}$)/(10^{-6} m^{-3} mol^{-1})
		exptl	calcd(eq 3)				exptl	calcd(eq 3)	
T = 293.15 K									
0.0482	1.0668	–0.062	–0.055	–0.007	0.5513	1.0865	–0.228	–0.232	0.004
0.0999	1.0692	–0.114	–0.116	0.002	0.5985	1.0879	–0.205	–0.202	–0.003
0.1492	1.0716	–0.169	–0.171	0.002	0.6499	1.0892	–0.164	–0.166	0.002
0.1985	1.0740	–0.222	–0.218	–0.004	0.6839	1.0902	–0.145	–0.143	–0.002
0.2491	1.0761	–0.249	–0.255	0.006	0.7483	1.0919	–0.097	–0.101	0.004
0.3063	1.0785	–0.279	–0.282	0.003	0.7972	1.0934	–0.073	–0.073	0.000
0.3517	1.0803	–0.294	–0.292	–0.002	0.8372	1.0947	–0.057	–0.054	–0.003
0.3972	1.0819	–0.294	–0.292	–0.002	0.8975	1.0966	–0.029	–0.030	0.001
0.4487	1.0836	–0.284	–0.281	–0.003	0.9486	1.0984	–0.015	–0.014	–0.001
0.4967	1.0850	–0.261	–0.261	0.000					
T = 298.15 K									
0.0482	1.0609	–0.073	–0.085	0.012	0.5513	1.0818	–0.273	–0.267	–0.006
0.0999	1.0637	–0.150	–0.163	0.013	0.5985	1.0831	–0.238	–0.241	0.003
0.1492	1.0662	–0.208	–0.224	0.016	0.6499	1.0846	–0.205	–0.209	0.004
0.1985	1.0686	–0.257	–0.270	0.013	0.6839	1.0856	–0.183	–0.187	0.004
0.2491	1.0709	–0.293	–0.302	0.009	0.7483	1.0874	–0.133	–0.146	0.013
0.3063	1.0733	–0.317	–0.323	0.006	0.7972	1.0888	–0.097	–0.114	0.017
0.3517	1.0750	–0.320	–0.328	0.008	0.8372	1.0900	–0.070	–0.090	0.020
0.3972	1.0767	–0.322	–0.325	0.003	0.8975	1.0921	–0.047	–0.054	0.007
0.4487	1.0784	–0.307	–0.312	0.005	0.9486	1.0937	–0.015	–0.026	0.011
0.4967	1.0800	–0.292	–0.294	0.002					
T = 303.15									
0.0482	1.0551	–0.107	–0.122	0.015	0.5513	1.0766	–0.306	–0.305	–0.001
0.0999	1.0579	–0.178	–0.217	0.039	0.5985	1.0781	–0.279	–0.283	0.004
0.1492	1.0607	–0.255	–0.281	0.026	0.6499	1.0797	–0.247	–0.255	0.008
0.1985	1.0631	–0.299	–0.323	0.024	0.6839	1.0806	–0.213	–0.236	0.023
0.2491	1.0652	–0.322	–0.349	0.027	0.7483	1.0826	–0.170	–0.196	0.026
0.3063	1.0676	–0.335	–0.362	0.027	0.7972	1.0839	–0.127	–0.163	0.036
0.3517	1.0695	–0.354	–0.363	0.009	0.8372	1.0853	–0.109	–0.134	0.025
0.3972	1.0712	–0.351	–0.357	0.006	0.8975	1.0871	–0.059	–0.087	0.028
0.4487	1.0731	–0.345	–0.344	–0.001	0.9486	1.0887	–0.021	–0.044	0.023
0.4967	1.0748	–0.331	–0.328	–0.003					
T = 308.15									
0.0482	1.0495	–0.115	–0.116	0.001	0.5513	1.0718	–0.348	–0.337	–0.011
0.0999	1.0527	–0.215	–0.211	–0.004	0.5985	1.0731	–0.305	–0.311	0.006
0.1492	1.0554	–0.283	–0.278	–0.005	0.6499	1.0747	–0.270	–0.277	0.007
0.1985	1.0577	–0.318	–0.326	0.008	0.6839	1.0759	–0.256	–0.253	–0.003
0.2491	1.0602	–0.362	–0.359	–0.003	0.7483	1.0777	–0.195	–0.202	0.007
0.3063	1.0625	–0.371	–0.381	0.010	0.7972	1.0794	–0.171	–0.161	–0.010
0.3517	1.0645	–0.390	–0.387	–0.003	0.8372	1.0804	–0.124	–0.127	0.003
0.3972	1.0663	–0.391	–0.386	–0.005	0.8975	1.0822	–0.070	–0.075	0.005
0.4487	1.0681	–0.376	–0.377	0.001	0.9486	1.0840	–0.043	–0.035	–0.008
0.4967	1.0698	–0.361	–0.361	0.000					
T = 313.15 K									
0.0482	1.0444	–0.135	–0.130	–0.005	0.5513	1.0669	–0.374	–0.380	0.006
0.0999	1.0475	–0.233	–0.235	0.002	0.5985	1.0686	–0.356	–0.354	–0.002
0.1492	1.0503	–0.305	–0.308	0.003	0.6499	1.0703	–0.323	–0.321	–0.002
0.1985	1.0530	–0.366	–0.360	–0.006	0.6839	1.0713	–0.299	–0.297	–0.002
0.2491	1.0553	–0.393	–0.395	0.002	0.7483	1.0732	–0.239	–0.244	0.005
0.3063	1.0577	–0.412	–0.418	0.006	0.7972	1.0747	–0.196	–0.199	0.003
0.3517	1.0597	–0.427	–0.425	–0.002	0.8372	1.0760	–0.173	–0.161	–0.012
0.3972	1.0615	–0.432	–0.425	–0.007	0.8975	1.0775	–0.093	–0.100	0.007
0.4487	1.0634	–0.419	–0.417	–0.002	0.9486	1.0790	–0.048	–0.049	0.001
0.4967	1.0651	–0.400	–0.403	0.003					

Table III. Coefficients a_k from Equation 3 and Standard Deviations, σ, for the Binary System at Different Temperatures

T/K	a_0/(10^{-6} m^3 mol^{-1})	a_1/(10^{-6} m^3 mol^{-1})	a_2/(10^{-6} m^3 mol^{-1})	a_3/(10^{-6} m^3 mol^{-1})	a_4/(10^{-6} m^3 mol^{-1})	$\sigma(V^E)$/(10^6 m^3 mol^{-1})
293.15	−1.0394	0.9689	0.3636	–0.5645		0.0037
298.15	−1.1700	0.8876	0.1212	–0.1788	0.1184	0.0038
303.15	−1.3060	0.7643	–0.5827	0.2464		0.0058
308.15	−1.4403	0.7819	–0.2170	0.2697		0.0069
313.15	−1.6066	0.7279	–0.3808	0.3625		0.0055

The values for the coefficients are given in Table III, along with the standard deviation, σ, and Figure 1 shows the fitted V^E curves together with the experimental points.

In the systems studied, the excess volumes are negative throughout the whole mole fraction range and the curves are asymmetric with a minimum at $x_1 \cong 0.4$. Studies reported in the literature show also negative excess volumes for the benzyl alcohol + dimethyl sulfoxide system (*3*) and 2-pyrrolidinone + dimethyl sulfoxide system (*4*).

We have compared the experimental data at 298.15 K with the results calculated by applying the Prigogine–Flory–Patterson theory (*5*). The expression for V^E from Prigogine–Flory–Paterson can be separated into three terms. The first one, which is negative, is due to the difference between the

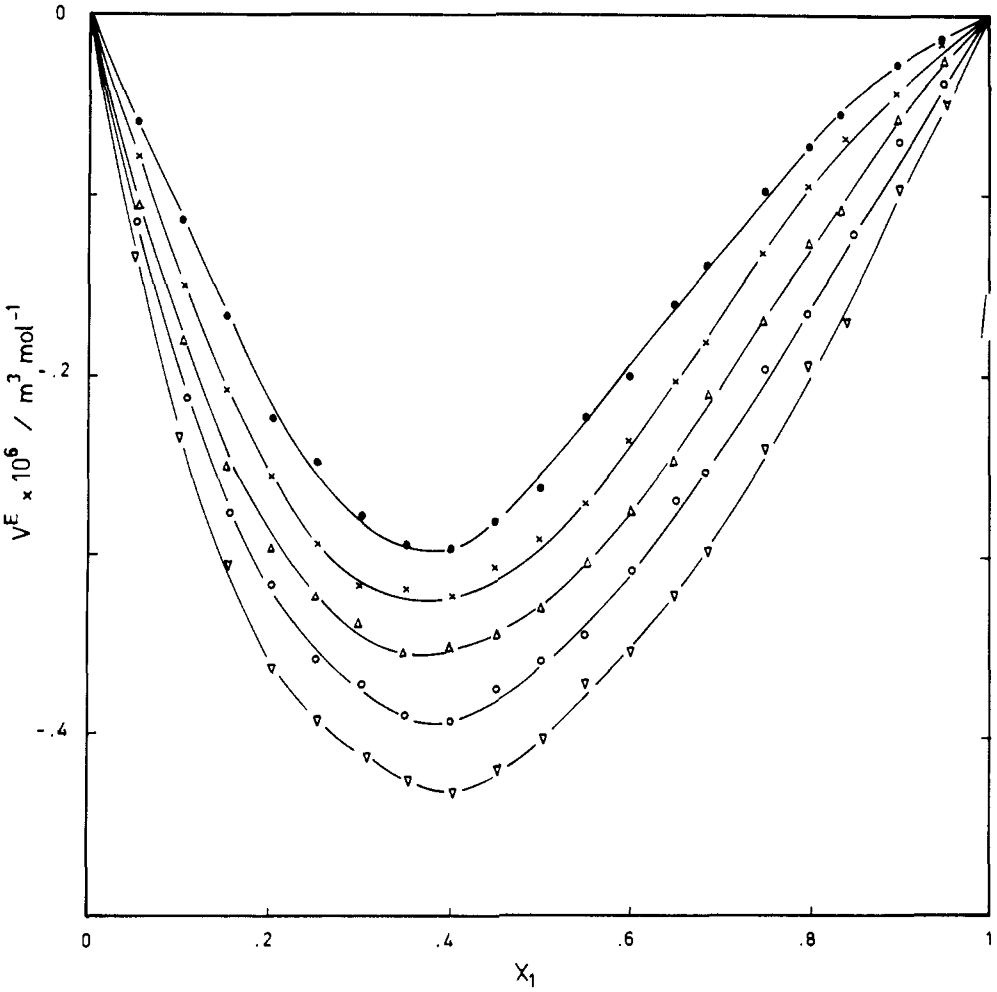

Figure 1. Experimental results of V^E: (●) 293.15 K, (×) 298.15 K, (▵) 303.15 K, (○) 308.15 K, (▿) 313.15 K, (curves) eq 3 with parameters from Table III.

Table IV. Equation of State Parameters for the Pure Liquids at 298.15 K

liquid	$V \times 10^6$/ ($m^3\,mol^{-1}$)	$\alpha \times 10^3/K^{-1}$	$\gamma \times 10^{-6}$/ ($J\,m^{-3}\,K^{-1}$)	$P^* \times 10^{-6}$/ ($J\,m^{-3}$)	$V^* \times 10^6$/ ($m^3\,mol^{-1}$)
dimethyl sulfoxide	71.312	0.904	1.586	712.7	58.087
thiophene	79.501	1.110	0.949	456.2	62.607

free volumes of the components. The second one is due to the difference of internal pressures, and the third one, which is generally positive, is due to the interactional contribution. X_{12} is the interactional parameter.

$$\frac{V^E}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}}{(4/3)\tilde{V}^{-1/3} - 1}\psi_1\theta_2\frac{X_{12}}{P_1^*}$$

interactional contribution

$$-\frac{(\tilde{V}_1 - \tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3} - 1]}{[(4/3)\tilde{V}^{-1/3} - 1]\tilde{V}}\psi_1\psi_2$$

free volume contribution

$$+\frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{P_1^*\psi_2 + P_2^*\psi_1}\psi_1\psi_2 \qquad (4)$$

internal pressure contribution

where the surface fraction θ_2 is given by

$$\theta_2 = \frac{\theta_2 s_2}{\theta_1 s_1 + \theta_2 s_2} \qquad (5)$$

where s is the molecular surface/volume ratio for the components, ψ is a composition variable given by

$$\psi_1 = \frac{\phi_1P_1^*}{\phi_1P_1^* + \phi_2P_2^*} = 1 - \psi_2 \qquad (6)$$

and the hard core volume fraction is given by

$$\phi_1 = \frac{x_1V_1^*}{x_1V_1^* + x_2V_2^*} \qquad (7)$$

The interaction parameter $X_{12} = 4.5\,10^6$ J m^{-3}, obtained from the equimolar value of the enthalpy of mixing (*6*), was used to predict the V^E values.

All parameters needed for the calculations are given in Table IV. Figure 2 shows the V^E values calculated by the Prigogine–Flory–Patterson theory and the experimental values at 298.15 K. Data prediction of the V^E value based on the Prigogine–Flory–Patterson theory predicts our experimental values of V^E well.

Density data have been fitted to polynomials

$$\rho/(\mathrm{kg\ m^{-3}}) = \sum_{k=0}^{4} B_k x_1^k \qquad (8)$$

where x_1 is the molar fraction of the dimethyl sulfoxide. The coefficients B_k are assumed to be functions of temperature

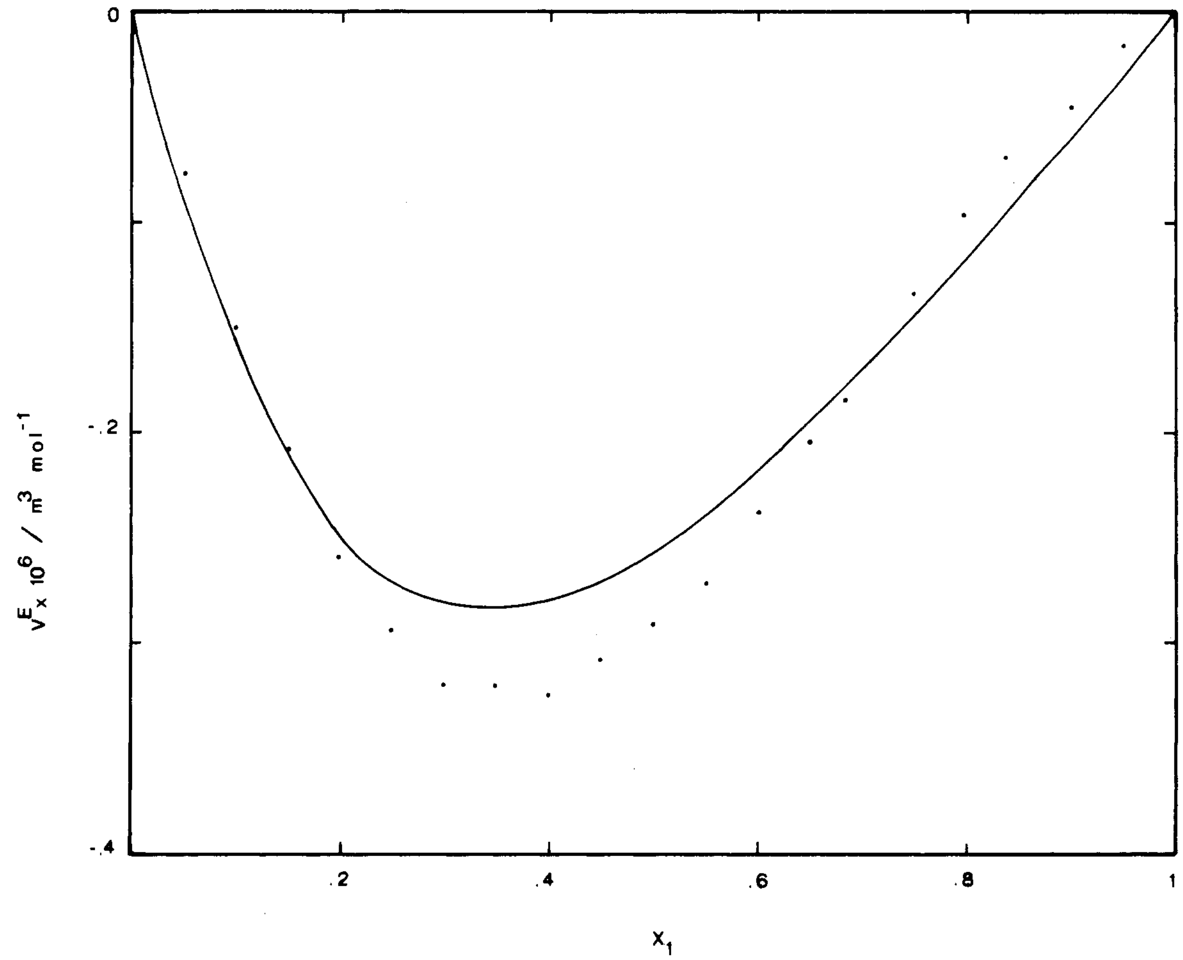

Figure 2. Excess molar volume for the dimethyl sulfoxide + thiophene system at 298.15 K: experimental results (●). The solid curve was calculated by the Prigogine–Flory–Patterson theory.

Table V. Parameters B_{kj} of Equation 10

	B_{kj}		
k	$j = 0$	$j = 1$	$j = 2$
0	1461.65	-1.5324	0.000 601
1	-308.88	1.462	-0.000 785
2	967.02	-3.761	0.001 440
3	-1568.55	6.103	0.002 92
4	797.83	-2.980	0.001 96

and have been fitted with polynomials of the form

$$B_k = \sum_{j=0}^{2} B_{kj} T^j \qquad (9)$$

The values of B_{kj} are listed in Table V. The density obtained above can be used to calculate the coefficient of thermal expansion $\alpha = \rho[\partial(1/\rho)/\partial T]_P$ of the binary system in the range of temperatures investigated. In Table VI are given the values obtained in the present study for the pure components at different temperatures.

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Table VI. Calculated Thermal Expansion Coefficient α for the Pure Components

	$\alpha \times 10^3$/K^{-1}				
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
dimethyl sulfoxide	0.896	0.904	0.912	0.921	0.930
thiophene	1.109	1.110	1.110	1.110	1.111

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