Excess molar volumes of sulfolane in binary mixtures with six aromatic hydrocarbons at 298.15 K

Yang-Xin Yu, Yi-Gui Li *

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract

Excess molar volume data on mixing for binary mixtures of sulfolane with toluene, o-xylene, m-xylene, p-xylene, ethylbenzene and 1,2,4-trimethyl benzene have been measured over the entire composition range at 298.15 K and atmospheric pressure in order to investigate interactions between molecules. A vibrating tube density meter was used. All mixtures exhibit negative excess volumes with a minimum which occurs approximately at $x = 0.5$. The experimental results have been correlated using the Redlich–Kister equation and have been qualitatively discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The extraction of aromatic hydrocarbons from aliphatic hydrocarbons by means of sulfolane is an important industrial process. Therefore, it is necessary to have complete thermodynamic data for these mixtures. Jannelli and Sacco [1] have studied the viscosity, dielectric constant and solid liquid phase diagram of sulfolane–benzene binary mixtures. Several other researchers [1–5] have studied the vapor–liquid and liquid–liquid equilibrium for binary and ternary mixtures containing sulfolane and aromatic hydrocarbons (benzene, toluene or ethylbenzene).

Whereas, experimental densities for the systems involving sulfolane and aromatic hydrocarbons, with the exception of sulfolane–ethylbenzene binary mixture [5], are not available. In the present investigation, we report experimental excess molar volume data for binary systems of sulfolane with toluene, o-xylene, m-xylene, p-xylene, ethylbenzene and 1,2,4-trimethyl benzene at 298.15 K and atmospheric pressure. The experimental results have been correlated using the Redlich–Kister equation and have been qualitatively discussed.

---

* Corresponding author.

2. Experimental

2.1. Materials

Toluene and 1,2,4-trimethylbenzene are analytical reagents. Ethylbenzene, *p*-xylene, *o*-xylene and *m*-xylene are chemical reagents. These aromatic hydrocarbon compounds were repurified by distillation and their middle fractions were collected. Then they were dried using activated type 0.5 nm molecular sieves, and the water content was found to be less than 0.01 mass% as determined by Mitsubishi moisture meter (Model CA-05). Sulfolane was supplied by Beijing Chemical Engineering Plant (chemical reagent) and was twice vacuum distilled at a pressure below 2.7 kPa to yield a colorless and odorless product. To minimize the contact of this deliquescent reagent with moist air, all the purified chemicals were kept in sealed bottles in desiccators.

In order to check the purity of compounds, density and refractive index values were measured in this work and reported in Table 1 in comparison with the literature data taken from Refs. [6–8] at 298.15 K and at atmospheric pressure.

2.2. Density measurements

An Anton Paar DMA60 vibrating tube density meter (Graz, Austria), in combination with one DMA602 remote cell, was used to measure densities of the binary mixtures at 298.15 K. The temperature of the U-shaped tube was checked continuously using a calibrated digital thermometer (Anton Paar DT100-20) with an accuracy of ± 0.01 K. An external Hetotherm bath circulator (Heto, type CB7) was used with a temperature control interval of ± 0.005 K. All the measurements were carried out at atmospheric pressure. Pressure was measured by means of a mercury barometer.

Table 1
Physical properties of the pure components at 298.15 K

Substance	Density (g/cm^3)		Refractive index	
	Experiment	Literature[a]	Experiment	Literature[a]
Toluene	0.86198	0.86219	1.4941	1.49413
o-Xylene	0.87567	0.87594	1.5029	1.50295
m-Xylene	0.85988	0.86009	1.4947	1.49464
p-Xylene	0.85648	0.85661	1.4932	1.49325
Ethylbenzene	0.86289	0.86253	1.4932	1.49320
1,2,4-Trimethylbenzene	0.87170	0.87174[b]	1.5024	1.50240
Sulfolane	(1.26654)[f]	(1.2640)[a,f]	1.4819[c]	1.4816[c]
		(1.26705)[d,f]		

[a]Ref. [6].
[b]Ref. [7].
[c]Data at 303.15 K.
[d]Ref. [8].
[f]Extrapolated value.

The density determination is based on measuring the period of oscillation of a vibrating U-shaped sample tube, which is filled with sample solution. The relationship between the period τ and the density ρ is

$$\rho = A(\tau^2 - B) \qquad (1)$$

where A and B are instrument constants which are determined by calibration with redistilled, degassed water and dry air. Characteristic vibration period τ of the instrument with dry air and pure water were checked after every one and three measurements, respectively. The uncertainty in the measured vibration period τ is 1×10^{-6} s, which leads to a precision in densities and excess molar volumes of $\pm 5 \times 10^{-5}$ g cm^{-3} and 3×10^{-3} cm^3 mol^{-1}, respectively.

The procedure to prepare samples by mass was analogous to Ref. [9]. The aromatic hydrocarbon components was directly poured into an air-tight stoppered bottle. The charged bottle was closed and weighed. The sulfolane was injected into the bottle through the stopper by means of a syringe. The possible error in the mole fraction is estimated to be 1×10^{-4}.

The densities, ρ, of mixtures were used to calculate the excess molar volumes V^E, according to

$$V^E = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \qquad (2)$$

3. Results and discussion

The experimental excess molar volume data as a function of mole fraction of sulfolane are shown in Table 2 and are graphically represented in Fig. 1. For each binary mixture, excess molar volume data were fitted to the Redlich–Kister equation to correlate the composition dependence of the excess property.

$$V^E = x_1 x_2 \sum_{k=0}^{3} a_k (x_1 - x_2)^k \qquad (3)$$

The values of a_k, obtained by a least-squares method with all points weighted equally, correspond to the minimum value of the standard deviation σ defined as

$$\sigma = \left[\Sigma \left(V_c^E - V_e^E \right)^2 / (N - n) \right]^{1/2} \qquad (4)$$

Results of least-squares analysis are reported in Table 3.

The excess molar volumes included in Table 2 show that the V^E values are negative over the entire mole fraction range for all binary mixtures studied in present work. They may be explained in terms of two opposing effects [10]: (1) expansion in volume due to mutual loss of dipolar association and the difference in size and shape of the component molecules; (2) contraction in volume comes from dipole-induced dipole and dipole–dipole interactions and donor–acceptor interactions between unlike molecules. The experimental results suggest that the latter effect is dominant in the binary sulfolane–aromatic hydrocarbon mixtures. The V^E values for equimolar mixtures are found to vary in the following order (in the absolute values):

Toluene $> p-$ xylene $> m-$ xylene $>$ ethylbenzene $> o-$ xylene $> 1,2,4-$ trimethyl benzene

Assuming that energy associated with orientational order for all pure aromatic hydrocarbons is of the same order, the variation in V^E of these mixtures will be due to the variation in magnitude of

specific interaction energy in these mixtures. There are specific electron donor–acceptor interactions between sulfolane and aromatic hydrocarbons. Although the introduction of methyl (or ethyl) groups in the ring will increase the donator–acceptor interaction, there is steric repulsion among the atoms of

Table 2
Experimental excess molar volumes for binary system at 298.15 K[a]

x_1	V^E	x_1	V^E	x_1	V^E
x_1 Sulfolane + (1 − x_1) toluene					
0.0634	−0.320	0.3980	−1.052	0.7371	−0.780
0.1104	−0.510	0.4507	−1.079	0.7854	−0.675
0.1638	−0.681	0.5042	−1.072	0.8366	−0.533
0.2250	−0.839	0.5796	−1.019	0.8931	−0.362
0.3081	−0.980	0.6159	−0.981	0.9187	−0.277
0.2814	−0.939	0.6553	−0.932	0.9626	−0.129
0.3406	−1.010	0.6903	−0.874		
x_1 Sulfolane + (1 − x_1) o-xylene					
0.0548	−0.207	0.4096	−0.726	0.7419	−0.593
0.0932	−0.310	0.4384	−0.733	0.7837	−0.532
0.1528	−0.446	0.4716	−0.742	0.8315	−0.435
0.2094	−0.543	0.5373	−0.756	0.8795	−0.326
0.2479	−0.588	0.5853	−0.736	0.9056	−0.258
0.3118	−0.659	0.6547	−0.695	0.9400	−0.162
0.3445	−0.684	0.7182	−0.627	0.9569	−0.120
x_1 Sulfolane + (1 − x_1) m-xylene					
0.0477	−0.209	0.4086	−0.931	0.6721	−0.807
0.1022	−0.407	0.4498	−0.944	0.7159	−0.731
0.1570	−0.558	0.4943	−0.948	0.7512	−0.668
0.1898	−0.639	0.5459	−0.920	0.8012	−0.561
0.2432	−0.751	0.5757	−0.910	0.8587	−0.426
0.2839	−0.816	0.5779	−0.899	0.8964	−0.317
0.3478	−0.895	0.6095	−0.875	0.9321	−0.217
x_1 Sulfolane + (1 − x_1) p-xylene					
0.0633	−0.300	0.3733	−0.920	0.6776	−0.849
0.1167	−0.488	0.4357	−0.960	0.7232	−0.777
0.1459	−0.579	0.4552	−0.961	0.7684	−0.690
0.2087	−0.719	0.5032	−0.975	0.8222	−0.559
0.2758	−0.818	0.5445	−0.967	0.8950	−0.348
0.3094	−0.869	0.6136	−0.922	0.9247	−0.253
0.3321	−0.882	0.6238	−0.916	0.9570	−0.148
x_1 Sulfolane + (1 − x_1) ethylbenzene					
0.0742	−0.319	0.4188	−0.891	0.6606	−0.843
0.1200	−0.456	0.4403	−0.899	0.7113	−0.775
0.1737	−0.587	0.4984	−0.922	0.7625	−0.678
0.2294	−0.691	0.5202	−0.921	0.8195	−0.541
0.2743	−0.750	0.5712	−0.906	0.8647	−0.427
0.3588	−0.841	0.6018	−0.895	0.9005	−0.321
0.3968	−0.879	0.6301	−0.869	0.9473	−0.166

Table 2 (continued)

x_1	V^E	x_1	V^E	x_1	V^E
x_1 Sulfolane + (1 − x_1) 1,2,4-trimethylbenzene					
0.0577	−0.124	0.4255	−0.557	0.6921	−0.490
0.1259	−0.257	0.4642	−0.563	0.7270	−0.466
0.1668	−0.317	0.4941	−0.566	0.7632	−0.431
0.1994	−0.370	0.5312	−0.562	0.7758	−0.408
0.2503	−0.427	0.5761	−0.560	0.8211	−0.354
0.3080	−0.478	0.6116	−0.544	0.8721	−0.274
0.3694	−0.524	0.6408	−0.534	0.9265	−0.173

[a] Unit of V^E is cm^3/mol.

sulfolane and the two or three bulky methyl (or one ethyl) groups, which hinders the proper orientation of sulfolane to interact with xylenes, ethylbenzene or trimethylbenzene and results in a more positive or less negative excess volume. Therefore, the V^E values for xylene, ethylbenzene or 1,2,4-trimethylbenzene mixtures should be more than that for toluene mixture and the V^E value for 1,2,4-trimethylbenzene mixture should be the biggest. This is substantiated by our experimental data. For xylenes, the specific interaction energy between the two unlike molecules is affected by the relative position of two methyl groups in the ring.
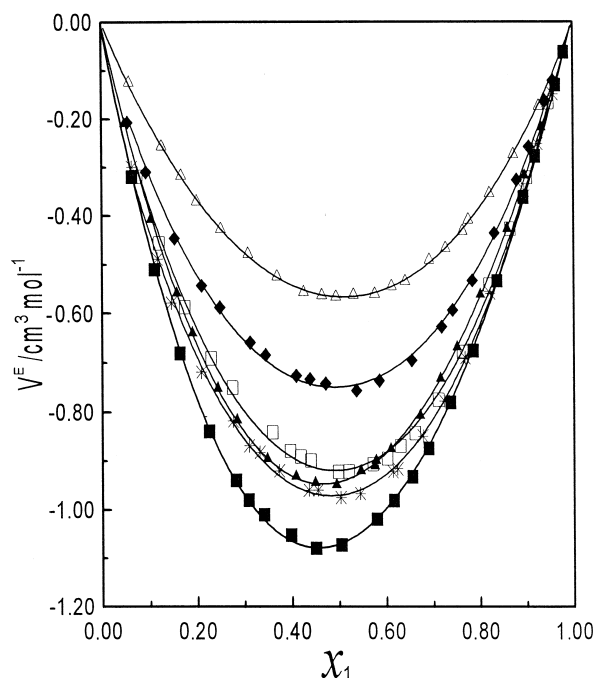

Fig. 1. Excess molar volumes for the sulfolane(1) + aromatic hydrocarbon(2) systems (solid lines refer to the fitted values; symbols refer to the experimental values: ■, toluene; *, p-xylene; ▲, m-xylene; □, ethylbenzene; ◆, o-xylene; △, 1,2,4-trimethylbenzene).

Table 3
Values of the parameters a_0, a_1, a_2 and a_3 of Eq. (3) and standard deviations at 298.15 K[a]

System	a_0	a_1	a_2	a_3	σ
Sulfolane + toluene	−4.27961	0.56434	−0.35758	0.55084	0.0035
Sulfolane + o-xylene	−3.00015	−0.17402	−0.55286	0.90743	0.0033
Sulfolane + m-xylene	−3.76886	0.42838	−0.22191	0.25511	0.0038
Sulfolane + p-xylene	−3.88061	0.02891	−0.62198	1.10095	0.0038
Sulfolane + ethylbenzene	−3.67271	−0.22720	−0.49877	1.24700	0.0034
Sulfolane + 1,2,4-trimethylbenzene	−2.26456	−0.08506	−0.20910	−	0.0035

[a]Unit of the parameters is cm^3/mol.

Because the excess volume data on mixing only give information about the packed structure, the intermolecular interactions concluded from volume effects directly is not always correct and they must be validated by the excess enthalpy data on mixing for the studied binary systems. To give better insight into the nature of interactions between sulfolane and aromatic hydrocarbons, the enthalpies on mixing and the spectroscopic data of these mixtures should be determined further.

4. List of symbols

A, B	instrument constants in Eq. (1)
a_k	polynomial coefficients in Eq. (3), cm^3/mol
M	molar mass of pure component, g/mol
N	experimental data points
n	number of coefficients in Eq. (3)
V^E	excess molar volume, cm^3/mol
x	mole fraction

Greek letters

ρ	density, g/cm^3
σ	standard deviation defined as Eq. (4)
τ	vibration period, s

Subscripts

c	calculated value
e	experimental value

Acknowledgements

References

 [1] L. Jannelli, A. Sacco, J. Chem. Thermodyn. 4 (1972) 715–722.
 [2] M. Karvo, J. Chem. Thermodyn. 12 (1980) 1175–1181.
 [3] R.M. De Fre, L.A. Verhoeye, J. Appl. Chem. Biotechnol. 26 (1976) 469–487.
 [4] S.J. Ashcroft, A.D. Clayton, R.B. Shearn, J. Chem. Eng. Data 24 (1979) 195–199.
 [5] T. Hanschild, H. Knapp, J. Solution Chem. 20 (1991) 125–138.
 [6] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents. Wiley-Interscience, New York, 1986.
 [7] A. Anderko, J. Chem. Thermodyn. 22 (1990) 55–60.
 [8] A. Lopez, L. Jannelli, L. Silvestri, J. Chem. Eng. Data 27 (1982) 183–186.
 [9] M. Fermeglia, J. Lapasin, J. Chem. Eng. Data 33 (1988) 415–417.
[10] V. Verma, D.C. Spah, K.C. Kalra, K.C. Singh, J. Solution Chem. 19 (1990) 85–93.