Excess Volumes of Tetralin + Cyclohexane, + Hexane, or + 1-Hexanol at 298.15 and 308.15 K

Chun-Hung Yu and Fuan-Nan Tsai*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, Republic of China

Excess volumes of tetralin with cyclohexane, hexane, or 1-hexanol have been measured over the whole composition range at 298.15 and 308.15 K. Excess volumes are positive for the tetralin + cyclohexane mixture, negative for the tetralin + hexane mixture, and negative in mixtures rich in 1-hexanol and positive in those rich in tetralin for the tetralin + 1-hexanol mixture.

Introduction

Excess volumes of binary mixtures are essential for engineering applications. The variations of excess volumes with temperature and composition for mixtures may be complex due to the existence of specific interactions in the mixtures.

Excess volumes of binary mixtures containing one-ring compounds with alkanes (*1, 2*) or alcohols (*3-5*) have been measured by many researchers. However, literature data on excess volumes of two-ring compounds are limited to ambient conditions. In this work, excess volumes of three binary systems containing tetralin + cyclohexane, + hexane, or + 1-hexanol were investigated at atmospheric pressure (nominal value 0.1 MPa) and at 298.15 and 308.15 K over the entire range of mole fraction.

Experimental Section

Tetralin (99+ mass %) and cyclohexane (99.7+ mass %) were purchased from Aldrich, and hexane (99.5+ mass %) and 1-hexanol (99 mass %) were from Fluka. All the substances were used without further purification.

In this work all densities were measured with a Kyoto Electronics vibrating-tube densimeter (model DA-300) with a resolution of 0.0001 $g{\cdot}cm^{-3}$. The densimeter was equipped with a temperature sensor which could keep the temperature within ±0.05 K at 10-30 °C and ±0.1 K at 4-90 °C. This technique requires two density standards; we use freshly boiled, deionized, distilled water and air.

Mixtures were prepared on a mass basis by using a Shimadzu analytical balance (model AEG-120) with an accuracy of ±0.1 mg. The nominal mass of the mixtures prepared was 7 g. To minimize the errors in composition that arise from evaporation during the solution preparation, we charged the heavier component first.

The densities of mixtures ρ are used to calculate the excess volume V^E according to

$$V^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component i, respectively. The estimated uncertainty in V^E was less than 0.005 $cm^3{\cdot}mol^{-1}$.

Results and Discussion

Excess volumes calculated from eq 1 are listed in Table 1 for each binary mixture at 298.15 and 308.15 K. We correlated excess molar volumes as a function of composition using the Redlich-Kister expansion (*6*)

* To whom correspondence should be addressed.

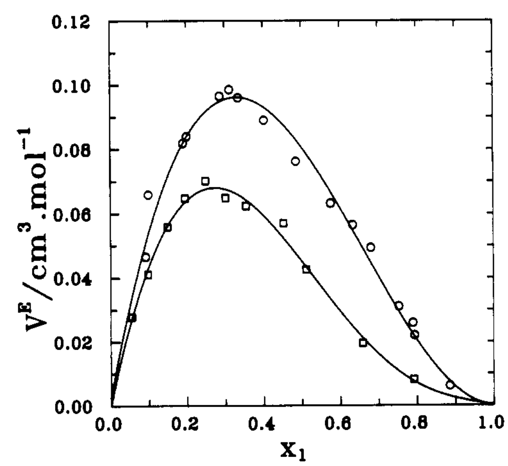

Figure 1. Excess molar volumes V^E of tetralin (1) + cyclohexane (2) as a function of the mole fraction x_1 of tetralin: points, experimental values; ○, 298.15 K; □, 308.15 K; curves, fitted values, eq 2.

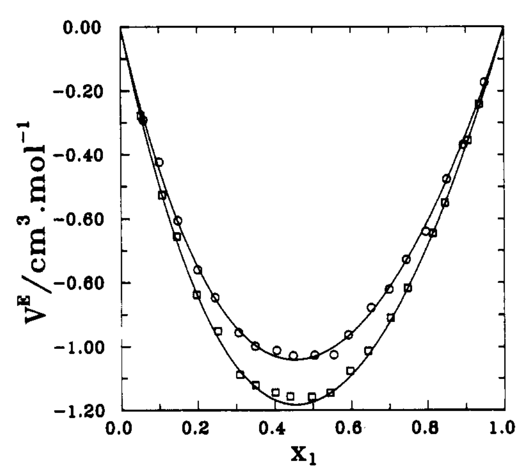

Figure 2. Excess molar volumes V^E of tetralin (1) + hexane (2) as a function of the mole fraction x_1 of tetralin: points, experimental values; ○, 298.15 K; □, 308.15 K; curves, fitted values, eq 2.

$$V^E/(cm^3{\cdot}mol^{-1}) = x_1(1 - x_1)[a_0 + a_1(2x_1 - 1) + a_2(2x_1 - 1)^2 + a_3(2x_1 - 1)^3] \qquad (2)$$

where a_0, a_1, a_2, and a_3 are adjustable parameters and x_1 is the mole fraction of tetralin. The values of a_0, a_1, a_2, and a_3 are obtained by least-squares analysis with all points weighted equally. The standard deviations are calculated by using the

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Table 1. Densities ρ and Excess Molar Volumes V^E of Binary Mixtures of Tetralin + Cyclohexane, + Hexane, or +1-Hexanol

298.15 K			308.15 K		
x_1	ρ/ (g·cm^{-3})	V^E/ (cm^3·mol^{-1})	x_1	ρ/ (g·cm^{-3})	V^E/ (cm^3·mol^{-1})
Tetralin (1) + Cyclohexane (2)					
1.0000	0.9653	0.0000	1.0000	0.9577	0.0000
0.8855	0.9474	0.0062	0.7917	0.9241	0.0081
0.7939	0.9324	0.0220	0.6581	0.9009	0.0195
0.7897	0.9317	0.0259	0.5116	0.8738	0.0425
0.7530	0.9255	0.0311	0.4529	0.8624	0.0570
0.6804	0.9129	0.0494	0.3549	0.8428	0.0624
0.6333	0.9046	0.0565	0.3012	0.8317	0.0649
0.5755	0.8941	0.0632	0.2495	0.8207	0.0702
0.4863	0.8774	0.0761	0.1959	0.8091	0.0648
0.4025	0.8611	0.0890	0.1507	0.7991	0.0559
0.3351	0.8475	0.0960	0.0984	0.7873	0.0411
0.3123	0.8428	0.0986	0.0556	0.7774	0.0279
0.2872	0.8376	0.0965	0.0000	0.7643	0.0000
0.2007	0.8192	0.0839			
0.1913	0.8172	0.0818			
0.0998	0.7968	0.0659			
0.0920	0.7951	0.0466			
0.0000	0.7738	0.0000			
Tetralin (1) + Hexane (2)					
1.0000	0.9652	0.000	1.0000	0.9577	0.000
0.9491	0.9512	−0.172	0.9356	0.9399	−0.241
0.8936	0.9359	−0.368	0.9058	0.9316	−0.355
0.8501	0.9235	−0.476	0.8460	0.9147	−0.550
0.7954	0.9080	−0.639	0.8142	0.9056	−0.645
0.7445	0.8931	−0.728	0.7481	0.8864	−0.817
0.6991	0.8798	−0.821	0.7034	0.8732	−0.909
0.6520	0.8656	−0.878	0.6439	0.8554	−1.013
0.5923	0.8477	−0.963	0.5964	0.8410	−1.076
0.5543	0.8363	−1.026	0.5448	0.8253	−1.146
0.5042	0.8207	−1.026	0.4968	0.8103	−1.159
0.4486	0.8033	−1.028	0.4403	0.7925	−1.157
0.4056	0.7897	−1.011	0.4019	0.7803	−1.144
0.3492	0.7719	−0.998	0.3502	0.7638	−1.121
0.3061	0.7580	−0.956	0.3093	0.7506	−1.088
0.2451	0.7380	−0.847	0.2527	0.7318	−0.951
0.2002	0.7232	−0.760	0.1977	0.7136	−0.838
0.1485	0.7058	−0.605	0.1461	0.6961	−0.655
0.1004	0.6894	−0.423	0.1074	0.6830	−0.526
0.0590	0.6754	−0.291	0.0528	0.6642	−0.278
0.0000	0.6549	−0.000	0.0000	0.6458	−0.000
Tetralin (1) + 1-Hexanol (2)					
1.0000	0.9653	0.0000	1.0000	0.9577	0.0000
0.9500	0.9581	0.0424	0.9437	0.9495	0.0622
0.8858	0.9491	0.0499	0.8961	0.9428	0.0750
0.8489	0.9439	0.0519	0.8402	0.9350	0.0686
0.8367	0.9422	0.0473	0.7498	0.9223	0.0489
0.7989	0.9369	0.0404	0.6854	0.9131	0.0381
0.7495	0.9299	0.0316	0.5901	0.8993	0.0229
0.7004	0.9229	0.0220	0.5336	0.8911	−0.0015
0.6538	0.9162	0.0095	0.4395	0.8771	−0.0174
0.6202	0.9114	−0.0065	0.3497	0.8636	−0.0390
0.5994	0.9084	−0.0166	0.2779	0.8526	−0.0590
0.5470	0.9007	−0.0235	0.2392	0.8466	−0.0637
0.5033	0.8943	−0.0414	0.1909	0.8390	−0.0634
0.4451	0.8856	−0.0516	0.1149	0.8269	−0.0634
0.3989	0.8786	−0.0549	0.1038	0.8251	−0.0585
0.2974	0.8631	−0.0736	0.0532	0.8168	−0.0357
0.2499	0.8557	−0.0777	0.0000	0.8079	0.0000
0.2017	0.8481	−0.0756			
0.1056	0.8327	−0.0671			
0.0999	0.8417	−0.0540			
0.0516	0.8238	−0.0416			
0.0000	0.8151	0.0000			

equation

$$\sigma(V^E) = \left[\frac{\sum(V^E_{\rm exptl} - V^E_{\rm calcd})^2}{n-p}\right]^{1/2} \qquad (3)$$

where n is the number of measurements and p is the number of parameters.

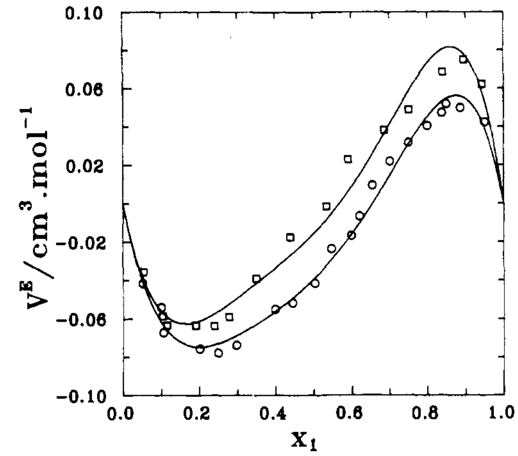

Figure 3. Excess molar volumes V^E of tetralin (1) + 1-hexanol (2) as a function of the mole fraction x_1 of tetralin: points, experimental values; ○, 298.15 K; □, 308.15 K; curves, fitted values, eq 2.

Table 2. Values of the Parameters a_i (Equation 2) and the Standard Deviation $\sigma(V^E)$ (Equation 3) for Tetralin (1) + Cyclohexane (2), + Hexane (2), or + 1-Hexanol (2)

component 2	a_0/ (cm^3·mol^{-1})	a_1/ (cm^3·mol^{-1})	a_2/ (cm^3·mol^{-1})	a_3/ (cm^3·mol^{-1})	$\sigma(V^E)$/ (cm^3·mol^{-1})
298.15 K					
cyclohexane	0.3173	−0.2960	0.0470	−0.1022	0.0043
hexane	−4.1264	0.7430	−0.3210		0.0130
1-hexanol	−0.1572	0.3906	0.1829	0.6521	0.0051
308.15 K					
cyclohexane	0.1810	−0.3144	0.1146	0.0472	0.0026
hexane	−4.6492	0.8173	−0.2152		0.0100
1-hexanol	−0.0627	0.3994	0.2931	0.8120	0.0093

The values of the parameters, along with the standard deviations $\sigma(V^E)$, are given in Table 2. Curves calculated from eq 2 are shown in Figures 1–3.

Figures 1 and 2 indicate that excess volumes are positive for tetralin + cyclohexane and negative for tetralin + hexane, respectively, over the whole range of composition. The data show that the values of the temperature coefficient $(\partial V^E/\partial T)_p$ are negative for both mixtures.

Figure 3 indicates that excess volumes of tetralin + 1-hexanol are negative in mixtures rich in 1-hexanol and positive in those rich in tetralin. The trend between excess volume and composition is similar to that observed for mixtures of 1,2,4-trichlorobenzene with five 1-alkanols (7).

Literature Cited

(1) Rice, P.; Teja, A. S. *J. Chem. Eng. Data* **1980**, *25*, 346.
(2) Qin, A.; Hoffman, D. E.; Munk, P. *J. Chem. Eng. Data* **1992**, *37*, 61.
(3) Mallu, B. V.; Chalapati Rao, Y. V. *J. Chem. Eng. Data* **1990**, *35*, 444.
(4) Ortega, J.; Pena, J. A.; Paz Andrade, M. I.; Pintos, M.; Romani, L. *J. Chem. Thermodyn.* **1985**, *17*, 321.
(5) Gama, L.; Tojo, J. *J. Chem. Eng. Data* **1992**, *37*, 20.
(6) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(7) Vijayalakshmi, T. S.; Naidu, P. R. *J. Chem. Eng. Data* **1992**, *37*, 368.

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