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Densities, Viscosities, and Excess Volumes of Isopropyl Acetate + Cyclohexane Mixtures at 298.15 and 308.15 K

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Measurements of density and viscosity for binary mixtures of isopropyl acetate with cyclohexane are reported at 298.15 and 308.15 K over the entire range of composition. Derived excess volumes are positive at both temperatures. The viscosity data are analyzed on the basis of both the corresponding states approach and the Grunberg and Nissan treatment.

Introduction

Excess properties of binary systems are of considerable interest in understanding the existence of specific interactions such as dispersion forces, hydrogen bonding interactions, and others. In a system such as isopropyl acetate + cyclohexane, although there is no hydrogen bonding, dispersion, dipolar, and induction forces contribute to the nonidealities of liquid and vapor phases. It is also possible that when a globular molecule such as cyclohexane is mixed with a branched long chain molecule like isopropyl acetate, there will be orientational disorders. Besides these physicochemical aspects, isopropyl acetate and cyclohexane are important in chemical industry, and any data would be useful. A literature search did not reveal any data on this system. We report here measurements of density and viscosity as a function of composition at 298.15 and 308.15 K for the system isopropyl acetate + cyclohexane.

Experimental Section

Materials. The chemicals used in the present study were purified by using standard procedures (*1*). Isopropyl acetate (Aldrich) was allowed to stand over anhydrous calcium chloride overnight and then fractionally distilled in an all-glass 0.8-m distillation column. Cyclohexane (Aldrich, HPLC grade) was fractionally distilled over sodium. The middle fraction boiling within ±0.1 K was collected for use in density and viscosity measurements. The purity of the chemicals was checked by measuring and comparing densities, boiling points, and refractive indexes. Refractive index was measured by using Abbe refractometer Mark II Model 104828/N with an accuracy of ±0.0001. The results are given in Table I. The purity of the chemicals is assessed to be better than 99.9 mol %. The density of isopropyl acetate measured in this work at 298.15 K is 0.866 47 g cm^{-3}, where as the literature value quoted by Riddick et al. is 0.870 20 g cm^{-3} at 298.15 K. The data available in other sources (*2-4*) [ρ(293.15 K) = 0.8718 g cm^{-3}; ρ(277.15 K) = 0.8913 g cm^{-3}; ρ(291.15 K) = 0.8732 g cm^{-3}; ρ(293.15 K) = 0.870 g cm^{-3}] are in better agreement with our value when all these values are correlated with temperature.

Table I. Properties of Pure Components[a]

component	density[b]/(g cm^{-3})		boiling point/K		refractive index[b]	
	exp	lit.	exp	lit.	exp	lit.
isopropyl acetate	0.866 47	0.870 20	361.73	361.75	1.3747	1.3750
cyclohexane	0.773 88	0.773 89	353.85	353.88	1.4236	1.4235

[a] Literature values are from ref 1. [b] At 298.15 K.

Apparatus. Densities of liquids and liquid mixtures were measured by using a bicapillary pycnometer of volume 8.2299 cm^3 at 298.15 K and 8.2320 cm^3 at 308.15 K. The pycnometer was calibrated with deionized double-distilled water [ρ(298.15 K) = 0.997 0475 g cm^{-3}; ρ(308.15 K) = 0.994 0313 g cm^{-3}] (*1*). Density values are reproducible to ±5 × 10^{-5} g cm^{-3}. Excess volumes were computed from density and composition with the equation

$$V^{E} = [xM_1 + (1 - x)M_2]/\rho_m - xM_1/\rho_1 - (1 - x)M_2/\rho_2 \qquad (1)$$

where x is the mole fraction of isopropyl acetate, M_1, M_2 represent molecular masses, and ρ_m, ρ_1, ρ_2 are the densities of the mixture, component 1, and component 2, respectively.

Viscosities were measured with an Ubbelohde viscometer. The viscometer was calibrated by using distilled water [η(298.15 K) = 0.890 25 cP; η(308.15 K) = 0.719 03 cP] (*1*). The viscometer constant, k, was calculated from the viscosity, η_w, density, ρ_w, and flow time, t_w, of water by using the relation $k = \eta_w/\rho_w t_w$. The k values are 3.9744 × 10^{-3} cm^2 s^{-2} at 298.15 K and 3.9712 × 10^{-3} cm^2 s^{-2} at 308.15 K. These are the mean values of 10 calculated k values, which did not differ by more than ±0.0005. An electronic stopwatch capable of measuring time to ±0.01 s was used for the time measurement. Kinetic energy corrections were negligible. The estimated error in viscosity was ±5 × 10^{-4} cP. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure components with those reported in the literature.

A thermostatically controlled, well-stirred water bath with temperature controlled to ±0.02 K was used for all the measurements. Temperature was measured by using a quartz thermometer with a resolution of better than ±0.01 K. Mixtures were prepared on a mass basis by using a Sortorius analytical balance series R with RS 232-C port and an accuracy of ±0.1 mg. Precautions were taken to minimize evaporation losses during the preparation of mixtures and measurement.

Theoretical Correlations

On the basis of the corresponding states treatment for mixture compressibility factors (*5*, *6*), Teja and Rice (*7*, *8*) proposed the following expression for liquid mixture viscosity

$$\ln (\eta_m \xi_m) = x \ln (\eta_1 \xi_1) + (1 - x) \ln (\eta_2 \xi_2) \qquad (2)$$

where $\xi = (V_c)^{2/3}/(T^c M)^{1/2}$; T^c, V^c, and M are critical temperature, critical volume, and molecular mass, respectively. The values of critical temperature, critical volume, and molec-

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Table II. Data on Density (ρ), Excess Volume (V^E), and Viscosity (η) for Isopropyl Acetate (1) + Cyclohexane (2) at 298.15 K

x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	η/cP
0.0000	0.773 88	0.0000	0.9006
0.0846	0.779 83	0.4151	0.8036
0.1126	0.781 38	0.5230	0.7518
0.1665	0.785 51	0.6868	0.7050
0.2671	0.793 63	0.9148	0.6360
0.3555	0.801 28	1.0254	0.5940
0.4881	0.813 65	1.0324	0.5485
0.5911	0.823 52	0.9747	0.5241
0.6773	0.832 36	0.8311	0.5099
0.7902	0.843 91	0.6252	0.4951
0.8873	0.854 03	0.4054	0.4932
0.9593	0.862 12	0.1532	0.4903
1.0000	0.866 47	0.0000	0.4900

Table III. Data on Density (ρ), Excess Volume (V^E), and Viscosity (η) for Isopropyl Acetate (1) + Cyclohexane (2) at 308.15 K

x_1	ρ/(g cm^{-3})	V^3/(cm^3 mol^{-1})	η/cP
0.0000	0.763 81	0.0000	0.7634
0.0846	0.771 44	0.3554	0.6718
0.1126	0.781 38	0.4764	0.6494
0.1665	0.785 16	0.6830	0.6120
0.2671	0.782 80	0.9519	0.5559
0.3555	0.790 18	1.0713	0.5212
0.4881	0.802 42	1.0483	0.4824
0.5911	0.812 45	0.9262	0.4620
0.6773	0.820 91	0.8060	0.4512
0.7902	0.832 93	0.5726	0.4410
0.8873	0.842 29	0.3377	0.4366
0.9593	0.849 84	0.1277	0.4349
1.0000	0.854 15	0.0000	0.4342

ular mass of the mixture at each composition were evaluated by using the equations (*5*, *6*)

$$V_m^c = x^2 V_1^c + (1 - x)^2 V_2^c + 2x(1 - x) V_{12}^c \qquad (3)$$

$$T_m^c = [x^2 T_1^c V_1^c + (1 - x)^2 T_2^c V_2^c + 2x(1 - x) T_{12}^c V_{12}^c] / V_m^c \qquad (4)$$

$$M_m = x M_1 + (1 - x) M_2 \qquad (5)$$

$$V_{12}^c = [\{(V_1^c)^{1/3} + (V_2^c)^{1/3}\}/2]^3 \qquad (6)$$

$$T_{12}^c V_{12}^c = \epsilon_{12} (T_1^c T_2^c V_1^c V_2^c)^{1/2} \qquad (7)$$

where ϵ_{12} is an interaction parameter of order unity and the value was obtained from the viscosity value at $x = 0.5$.

According to Grunberg and Nissan (*9*), the low-temperature viscosity for the mixture is given as

$$\ln \eta_m = x \ln \eta_1 + (1 - x) \ln \eta_2 + x(1 - x) d_{12} \qquad (8)$$

where d_{12} is an interaction parameter that is a function of the chemical nature of the components and temperature. The value of d_{12}, obtained from a fit of eq 8 to the viscosity at $x = 0.5$, was used to compute the viscosities over the entire composition range.

Results

The experimental densities and viscosities and the derived excess volumes are given in Tables II and III at 298.15 and 308.15 K, respectively. The dependence of V^E on mole fraction is expressed in terms of an empirical equation of the form

$$V^E \text{ (cm}^3 \text{ mol}^{-1}) = x(1 - x) \sum_{i=0}^{3} [a_i (2x - 1)^i] \qquad (9)$$

where a_is are empirical constants. The values of the constants, obtained by the least-squares analysis, are included in Table IV, along with the standard deviation, σ.

Table IV. Values of the Parameters of Equation 9 and the Standard Deviation, σ

temp K	a_0	a_1	a_2	a_3	σ (cm^3 mol^{-1})
298.15	4.1172	−1.0029	0.7049	0.3033	0.0115
308.15	4.1951	−1.7440	−0.1415	1.4218	0.0106

Table V. Experimental and Calculated Values of Viscosity for Isopropyl Acetate (1) + Cyclohexane (2) at 298.15 and 308.15 K

	298.15 K			308.15 K		
x_1	η(exp)	η(eq 2)	η(eq 8)	η(exp)	η(eq 2)	η(eq 8)
0.0000	0.9006	0.9006	0.9006	0.7634	0.7634	0.7634
0.0846	0.8036	0.7981	0.8049	0.6718	0.6828	0.6880
0.1126	0.7518	0.7696	0.7775	0.6495	0.6602	0.6663
0.1665	0.7050	0.7209	0.7298	0.6120	0.6215	0.6283
0.2671	0.6360	0.6485	0.6564	0.5559	0.5636	0.5696
0.3555	0.5940	0.6006	0.6060	0.5212	0.5250	0.5291
0.4881	0.5485	0.5493	0.5500	0.4824	0.4832	0.4835
0.5911	0.5241	0.5225	0.5199	0.4620	0.4613	0.4589
0.6773	0.5099	0.5070	0.5023	0.4512	0.4485	0.4445
0.7902	0.4951	0.4946	0.4888	0.4410	0.4382	0.4333
0.8873	0.4932	0.4898	0.4852	0.4365	0.4341	0.4303
0.9593	0.4903	0.4892	0.4871	0.4349	0.4336	0.4319
1.0000	0.4900	0.4900	0.4900	0.4342	0.4342	0.4342

Table VI. Values of Interaction Parameters (ϵ_{12}, d_{12}) and Average Absolute Deviation (AAD)[a] at 298.15 and 308.15 K

	ϵ_{12}	d_{12}	AAD	
temp K	eq 7	eq 8	eq 2	eq 8
298.15	0.923	−0.785	0.0055	0.0091
308.15	0.927	−0.726	0.0042	0.0077

[a] Average absolute deviation = $|\eta_{exp} - \eta_{calcd}|/n$, where n is the number of measurements.

The values of V^E are positive over the entire range of composition at both temperatures. The behavior of this mixture may be attributed to the dispersion forces and the loss of dipolar association of polar isopropyl acetate on dilution with nonpolar cyclohexane. Further, the data included in Tables II and III indicate that there is no significant effect of temperature on excess volumes. Viscosity data, computed on the basis of the corresponding states principle and Grunberg and Nissan equation, are given in Table V, along with experimental results. The values of the interaction parameters and the average absolute deviation (AAD) are included in Table VI. A comparison of the data indicates that viscosity data of this mixture can be adequately represented by the corresponding states method and the Grunberg and Nissan relation.

Registry No. Isopropyl acetate, 108-21-4; cyclohexane, 110-82-7.

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