Thermophysical Properties of Binary Mixtures of Cyclohexane + Nitrobenzene, Cyclohexanone + Nitrobenzene, and Cyclohexane + Cyclohexanone at (298.15, 303.15, and 308.15) K

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The experimental values of density, viscosity, and ultrasonic velocity for the binary mixtures of cyclohexane + nitrobenzene, cyclohexanone + nitrobenzene, and cyclohexane + cyclohexanone are determined at (298.15, 303.15, and 308.15) K over the entire composition range. The excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), and excess isentropic compressibility (K_S^E) have been calculated.

Introduction

In recent years, there has been considerable interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures. In principle, the interaction between the molecules can be established from the study of the characteristic departure from ideal behavior of some physical properties (i.e., volume, compressibility, and viscosity). Viscosity data for liquid mixtures have also yielded information regarding the nature of interaction forces operating within and between the molecules and the existence of a complex,[1] if any.

Cyclohexane is a versatile solvent with properties of a good binder, blowing agent, and dispersion media for a broad range of liquids, and the other two polar solvents used are cyclohexanone and nitrobenzene. They also have numerous applications both in pure chemistry and industry, so it was of interest to investigate the thermodynamic properties of binary mixtures comprising these three chemicals.

Experimental values of the density, dynamic viscosity, and ultrasonic velocity at three temperatures, (298.15, 303.15, and 308.15) K, for the systems cyclohexane + nitrobenzene, cyclohexanone + nitrobenzene, and cyclohexane + cyclohexanone have been determined over the entire composition range. From the given data, the excess molar volume (V^E), deviation in viscosity ($\Delta\eta$), and excess compressibility (K_S^E) have been calculated.

Experimental Section

Nitrobenzene (Qualigens, India), cyclohexanone (SD Fine Chemicals, India), and cyclohexane (SD Fine Chemicals, India) were purified by distillation and stored over activated 4-Å molecular sieves (Union Carbide). The physical properties of pure components were measured experimentally and are compared with literature values whenever available as given in Table 1. Densities were measured by using a calibrated bicapillary pycnometer having an uncertainty of $\pm 1 \times 10^{-4}$ g·cm^{-3}. The mole fraction of each mixture was obtained with an uncertainty of $\pm 1 \times 10^{-4}$. Viscosities were determined using a modified Ubbelohde viscometer as described earlier.[2] From the measured values of density ρ and efflux time t, the viscosity η was calculated using the relation

$$\frac{\eta}{\rho} = At + \frac{B}{t} \tag{1}$$

where A and B are viscometer constants.

The values of the constants were obtained by measuring the flow time with twice-distilled benzene and carbon tetrachloride. The flow measurements were made with an electronic stopwatch with a precision of ±0.01 s. An average of two or three sets of flow times for each liquid or liquid mixture was taken for the purpose of calculating the viscosity. The uncertainty of the viscosity estimates is found to be within ±0.003 mPa·s.

The speed of sound was measured with an ultrasonic time intervalometer (UTI-101) with uncertainty of 0.1

Table 1. Properties of Pure Components at Different Temperatures

		ρ/g·cm^{-3}		η/mPa.s	
component	T/K	exptl	lit	exptl	lit
nitrobenzene	298.15	1.1985	1.1983[4]	1.6860	
	303.15	1.1936	1.1934[4]	1.6187	1.6190[4]
	308.15	1.1911		1.5543	1.5500[5]
cyclohexane	298.15	0.7739	0.7738[4]	0.8945	0.8980[4]
	303.15	0.7686	0.7684[6]	0.8284	0.8200[4]
	308.15	0.7612		0.7637	
cyclohexanone	298.15	0.9410		2.0212	2.0205[4]
	303.15	0.9374	0.9376[4]	1.8057	1.8100[4]
	308.15	0.9365		1.5849	

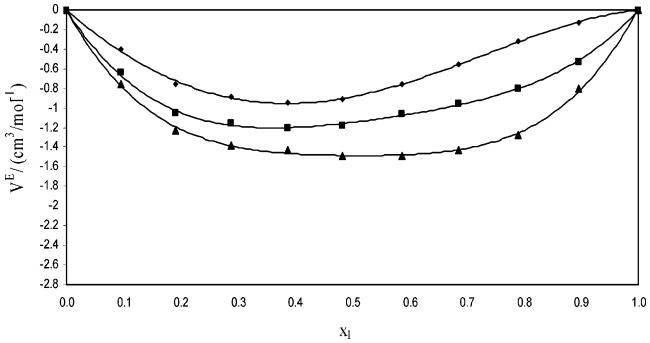

Figure 1. Excess molar volume V^E for the system cyclohexane (1) + nitrobenzene (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

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Table 2. Density, ρ, Excess Molar Volume, V^E, Viscosity, η, Deviation in Viscosity, $\Delta\eta$, Speed of Sound, u, and Excess Isentropic Compressibility, K_S^E, for the Cyclohexane (1) + Nitrobenzene (2) System at Different Temperatures

x_1	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	$\Delta\eta$/mPa·s	u/m·s^{-1}	$10^{12}K_S^E$/Pa^{-1}
			T = 298.15 K			
1.0000	0.7739	0.0000	0.8945	0.0000	1871.0	0.0000
0.8960	0.8169	−0.1308	0.9338	−0.0430	1849.0	−4.5600
0.7901	0.8616	−0.3163	0.9712	−0.0893	1823.0	−6.8400
0.6850	0.9072	−0.5604	1.0224	−0.1214	1797.9	−8.5700
0.5865	0.9504	−0.7605	1.0831	−0.1386	1776.2	−9.9400
0.4828	0.9960	−0.9071	1.1670	−0.1368	1754.2	−10.7700
0.3866	1.0379	−0.9495	1.2604	−0.1196	1735.7	−11.2800
0.2875	1.0805	−0.8850	1.3687	−0.0896	1717.6	−11.2000
0.1908	1.1218	−0.7543	1.4824	−0.0525	1698.6	−9.9500
0.0951	1.1604	−0.3994	1.5885	−0.0222	1675.9	−6.1500
0.0000	1.1985	0.0000	1.6860	0.0000	1648.4	0.0000
			T = 303.15 K			
1.0000	0.7686	0.0000	0.8284	0.0000	1993.0	0.0000
0.8960	0.8144	−0.5263	0.8740	−0.0365	1967.2	−2.9300
0.7901	0.8600	−0.8073	0.9142	−0.0800	1945.2	−5.4400
0.6850	0.9050	−0.9541	0.9680	−0.1092	1927.0	−7.7400
0.5865	0.9476	−1.0643	1.0325	−0.1226	1910.2	−9.1300
0.4828	0.9930	−1.1772	1.1171	−0.1200	1893.5	−10.1200
0.3866	1.0350	−1.2069	1.2101	−0.1030	1879.2	−10.6200
0.2875	1.0780	−1.1631	1.3132	−0.0782	1863.4	−10.0500
0.1908	1.1197	−1.0530	1.4230	−0.0448	1845.3	−8.1000
0.0951	1.1580	−0.6382	1.5270	−0.0165	1826.9	−4.8500
0.0000	1.1936	0.0000	1.6187	0.0000	1806.0	0.0000
			T = 308.15 K			
1.0000	0.7612	0.0000	0.7637	0.0000	2092.0	0.0000
0.8960	0.8091	−0.7982	0.8182	−0.0276	2061.3	−0.8400
0.7901	0.8566	−1.2721	0.8626	−0.0670	2041.5	−2.9700
0.6850	0.9023	−1.4317	0.9182	−0.0944	2027.8	−4.9700
0.5865	0.9450	−1.4902	0.9873	−0.1032	2018.8	−6.8000
0.4828	0.9900	−1.4832	1.0739	−0.0986	2009.6	−7.8500
0.3866	1.0319	−1.4315	1.1680	−0.0807	1998.6	−7.4900
0.2875	1.0755	−1.3835	1.2765	−0.0504	1985.0	−6.0589
0.1908	1.1176	−1.2280	1.3854	−0.0180	1973.2	−4.3100
0.0951	1.1560	−0.7556	1.4890	0.0099	1963.3	−1.9000
0.0000	1.1911	0.0000	1.5543	0.0000	1960.0	0.0000

m·s^{-1}. All of the measurements were made at constant temperature with the help of a circulating-type cryostat (MK 70 - MLW), where the uncertainty in temperature was ±0.02 K.

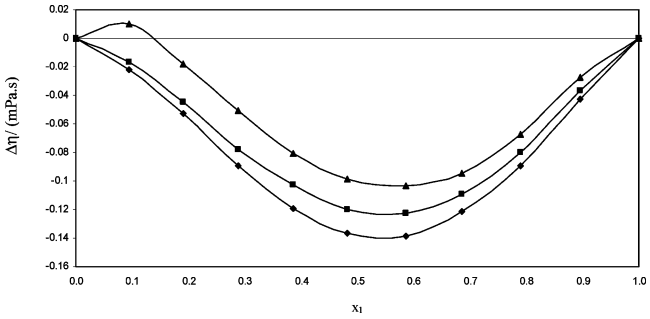

Figure 2. Deviation in viscosity $\Delta\eta$ for the system cyclohexane (1) + nitrobenzene (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

Experimental Results and Correlations

Experimental values of viscosity η, density ρ, and speed of sound u and calculated values of excess molar volumes, deviation in viscosity, and excess isentropic compressibility of all of the three binary mixtures are reported in Tables 2−4.

The excess molar volume V^E was calculated by the relation

$$V^E = x_1M_1\left(\frac{1}{\rho_m} - \frac{1}{\rho_1}\right) + x_2M_2\left(\frac{1}{\rho_m} - \frac{1}{\rho_2}\right) \qquad (2)$$

where x_1 and x_2, M_1 and M_2, and ρ_1 and ρ_2 are the mole fractions, molecular weights, and densities of pure components 1 and 2, respectively. ρ_m is the mixture density.

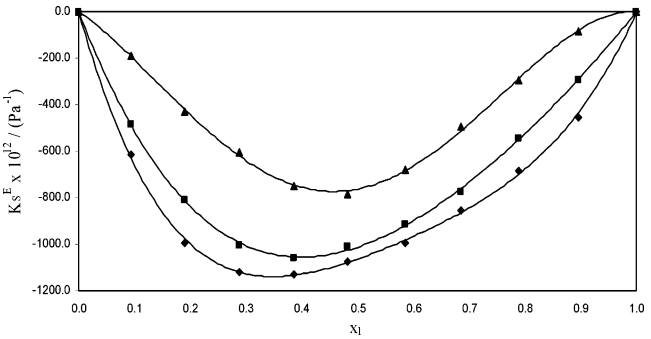

Figure 3. Excess isentropic compressibility K_S^E for the system cyclohexane (1) + nitrobenzene (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

Deviations in viscosity $\Delta\eta$ were obtained by using the relation

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \qquad (3)$$

where η_1 and η_2 are the viscosities of pure components 1 and 2, respectively, whereas η_m is the viscosity of the mixture.

Values of the speed of sound u and mixture density ρ_m were used to calculate the isentropic compressibility K_S by using the relation

$$K_S = u^{-2}\rho_m^{-1} \qquad (4)$$

Table 3. Density, ρ, Excess Molar Volume, V^E, Viscosity, η, Deviation in Viscosity, $\Delta\eta$, Speed of Sound, u, and Excess Isentropic Compressibility, K_S^E, for the Cyclohexanone (1) + Nitrobenzene (2) System at Different Temperatures

x_1	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	$\Delta\eta$/mPa·s	u/m·s^{-1}	$10^{12}K_S^E$/Pa^{-1}
			$T = 298.15$ K			
1.0000	0.9410	0.0000	2.0212	0.0000	1847.7	0.0000
0.8973	0.9634	0.3953	1.9705	−0.0163	1853.5	−8.7100
0.7966	0.9875	0.5550	1.9215	−0.0315	1848.3	−14.0000
0.6945	1.0116	0.7417	1.8791	−0.0397	1839.8	−17.9500
0.5920	1.0369	0.8156	1.8484	−0.0360	1825.7	−20.2500
0.4950	1.0613	0.8519	1.8269	−0.0250	1811.2	−21.9400
0.3938	1.0875	0.8159	1.8120	−0.0060	1790.0	−21.7700
0.2933	1.1145	0.7041	1.8023	0.0180	1764.1	−20.0000
0.1946	1.1418	0.5348	1.7852	0.0340	1733.0	−16.2859
0.0980	1.1696	0.2891	1.7518	0.0330	1696.0	−10.2520
0.0000	1.1985	0.0000	1.6860	0.0000	1648.4	0.0000
			$T = 303.15$ K			
1.0000	0.9374	0.0000	1.8057	0.0000	1970.1	0.0000
0.8973	0.9619	0.1487	1.7778	−0.0087	1964.1	−3.5400
0.7966	0.9857	0.3349	1.7494	−0.0183	1963.0	−7.9125
0.6945	1.0096	0.5345	1.7206	−0.0280	1962.0	−12.0609
0.5920	1.0345	0.6469	1.7042	−0.0252	1957.0	−15.1327
0.4950	1.0589	0.6700	1.6945	−0.0168	1945.0	−16.1567
0.3938	1.0856	0.5819	1.6849	−0.0075	1927.7	−16.0800
0.2933	1.1134	0.3946	1.6781	0.0046	1901.5	−13.7340
0.1946	1.1408	0.2067	1.6661	0.0110	1873.0	−10.5031
0.0980	1.1676	0.0458	1.6450	0.0080	1842.8	−6.4296
0.0000	1.1936	0.0000	1.6187	0.0000	1806.0	0.0000
			$T = 308.15$ K			
1.0000	0.9365	0.0000	1.5849	0.0000	2090.0	0.0000
0.8973	0.9614	0.0998	1.5770	−0.0047	2081.5	−1.7000
0.7966	0.9850	0.2858	1.5710	−0.0076	2080.0	−4.4847
0.6945	1.0086	0.5068	1.5670	−0.0085	2080.5	−7.4305
0.5920	1.0334	0.6199	1.5648	−0.0076	2076.4	−9.3510
0.4950	1.0579	0.6159	1.5622	−0.0072	2069.7	−10.6020
0.3938	1.0849	0.4847	1.5611	−0.0052	2058.6	−11.1152
0.2933	1.1129	0.2616	1.5586	−0.0047	2041.5	−10.3953
0.1946	1.1403	0.0598	1.5572	−0.0030	2019.9	−8.4650
0.0980	1.1668	−0.0872	1.5556	−0.0017	1991.0	−4.6825
0.0000	1.1911	0.0000	1.5543	0.0000	1961.0	0.0000

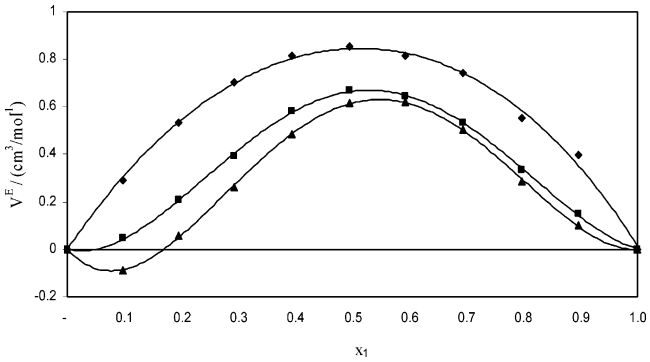

Figure 4. Excess molar volume V^E for the system cyclohexanone (1) + nitrobenzene (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

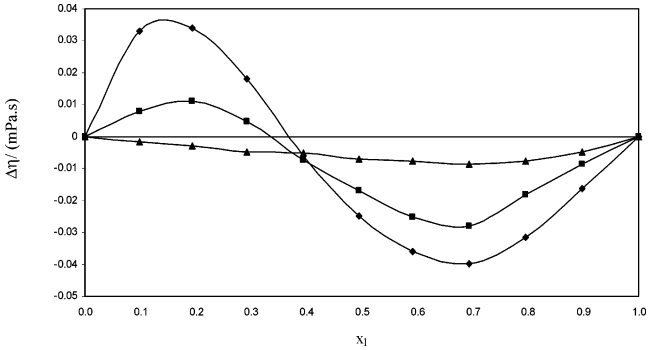

Figure 5. Deviation in viscosity $\Delta\eta$ for the system cyclohexanone (1) + nitrobenzene (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

The excess isentropic compressibility K_S^E was obtained from the relation

$$K_S^E = K_S - (K_{S1}x_1 + K_{S2}x_2) \quad (5)$$

where K_S is the experimental value of the isentropic compressibility of the mixture and K_{S1} and K_{S2} are isentropic compressibilities of components 1 and 2, respectively.

The excess properties (V^E and K_S^E) and the deviation in viscosity ($\Delta\eta$) were fit to a Redlich−Kister-type equation.[3]

$$A^E = x_1x_2\sum_{i=1}^{n} A_{j-1}(x_1 - x_2)^{(j-1)} \quad (6)$$

where A^E is the excess property, A_j represents the parameters, and n is the degree of the polynomial equation.

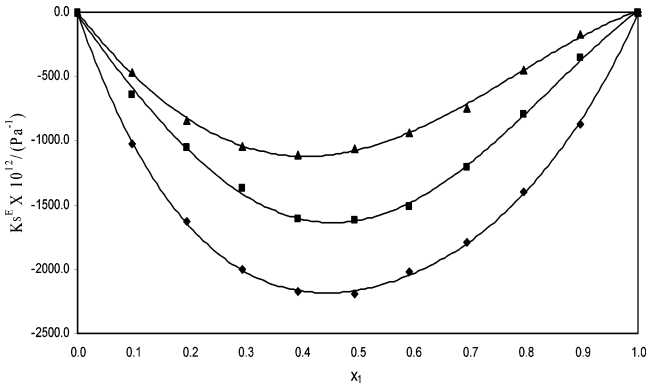

Figure 6. Excess isentropic compressibility K_S^E for the system cyclohexanone (1) + nitrobenzene (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

Table 4. Density, ρ, Excess Molar Volume, V^E, Viscosity, η, Deviation in Viscosity, $\Delta\eta$, Speed of Sound, u, and Excess Isentropic Compressibility, K_S^E, for the Cyclohexane (1) + Cyclohexanone (2) System at Different Temperatures

x_1	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	$\Delta\eta$/mPa·s	u/m·s^{-1}	$10^{12}K_S^E$/Pa^{-1}
			$T = 298.15$ K			
0.0000	0.9410	0.0000	2.0212	0.0000	1847.7	0.0000
0.0964	0.9216	0.3030	1.8524	−0.0601	1849.5	0.3550
0.2003	0.9013	0.5950	1.6823	−0.1132	1851.9	0.6592
0.2916	0.8838	0.8392	1.5406	−0.1520	1854.4	0.8696
0.3895	0.8660	1.0104	1.4029	−0.1794	1857.0	1.0445
0.4895	0.8489	1.0800	1.2749	−0.1949	1859.3	1.1760
0.5887	0.8325	1.0933	1.1630	−0.1949	1861.7	1.2570
0.6957	0.8154	1.0447	1.0634	−0.1739	1864.5	1.2800
0.7951	0.8003	0.9022	0.9917	−0.1337	1867.0	1.1891
0.8969	0.7865	0.5540	0.9386	−0.0722	1869.0	0.8402
1.0000	0.7739	0.0000	0.8945	0.0000	1871.0	0.0000
			$T = 303.15$ K			
0.0000	0.9374	0.0000	1.8057	0.0000	1970.1	0.0000
0.0964	0.9179	0.2880	1.6614	−0.0500	1972.3	0.1275
0.2003	0.8976	0.5531	1.5219	−0.0880	1974.2	0.4431
0.2916	0.8802	0.7648	1.4056	−0.1151	1976.2	0.6640
0.3895	0.8628	0.8677	1.2941	−0.1309	1978.0	0.8560
0.4894	0.8455	0.9292	1.1837	−0.1437	1980.1	1.0110
0.5886	0.8287	0.9672	1.0836	−0.1468	1982.7	1.0720
0.6957	0.8116	0.8988	0.9925	−0.1333	1985.4	1.0712
0.7951	0.7963	0.7650	0.9237	−0.1049	1988.1	0.9354
0.8968	0.7818	0.4914	0.8707	−0.0585	1990.8	0.6255
1.0000	0.7686	0.0000	0.8284	0.0000	1993.0	0.0000
			$T = 308.15$ K			
0.0000	0.9365	0.0000	1.5849	0.0000	2090.0	0.0000
0.0964	0.9166	0.2474	1.4849	−0.0208	2090.2	−0.1162
0.2003	0.8957	0.4960	1.3842	−0.0362	2090.5	−0.1318
0.2916	0.8783	0.6182	1.2958	−0.0496	2090.7	−0.2325
0.3895	0.8603	0.7077	1.2034	−0.0617	2090.8	−0.2579
0.4894	0.8426	0.7345	1.1122	−0.0708	2090.9	−0.2699
0.5886	0.8256	0.7123	1.0255	−0.0760	2091.0	−0.2428
0.6957	0.8075	0.6730	0.9408	−0.0728	2091.2	−0.0810
0.7951	0.7913	0.5959	0.8704	−0.0616	2091.4	0.1703
0.8968	0.7755	0.4063	0.8101	−0.0383	2091.8	0.2520
1.0000	0.7612	0.0000	0.7637	0.0000	2092.0	0.0000

The root-mean-square (σ) deviations presented in this paper were computed using

$$\sigma = \left[\frac{\sum(X_{\text{exptl}} - X_{\text{calcd}})^2}{N - n}\right]^{1/2} \quad (7)$$

where N is the number of data points and n is the number of coefficients. The values of the coefficients of eq 6 as determined by least squares along with the standard deviations for all three systems are reported in Table 5.

Discussion

The excess molar volumes V^E for all three systems at three temperatures are shown in Figures 1, 4, and 7. The V^E for all of the systems except for [cyclohexane (CH) + nitrobenzene (NB)] are positive and decrease with an increase in temperature, which indicates the decrease in repulsive forces. The V^E value for the [CH + NB] system is negative and increases with increasing temperature, indicating the presence of intermolecular forces.

The deviations in viscosity $\Delta\eta$ for all three systems are shown in Figures 2, 5, and 8. The deviations are negative for systems containing [CH + NB] and [CH + cyclohexanone (CHO)], and with increasing temperature, $\Delta\eta$ decreases, whereas for the [CHO + NB] system it shows a different trend. The S-shaped curves at 298.15 and 303.15 K shifting from positive to negative at a mole fraction of 0.3938 for cyclohexanone indicate the increase in interaction forces between components, which may be qualitatively interpreted in terms of the closer approach of unlike molecules leading to a reduction in viscosity.[1]

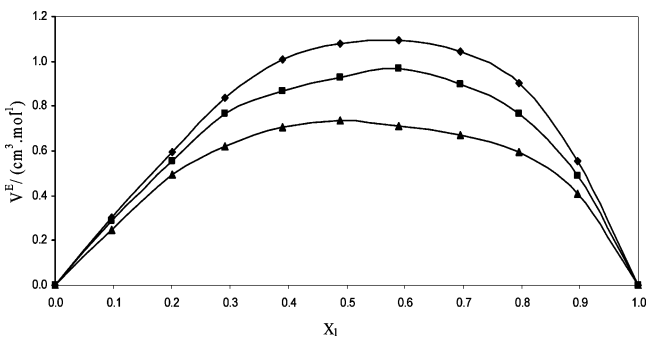

Figure 7. Excess molar volume V^E for the system cyclohexane (1) + cyclohexanone (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

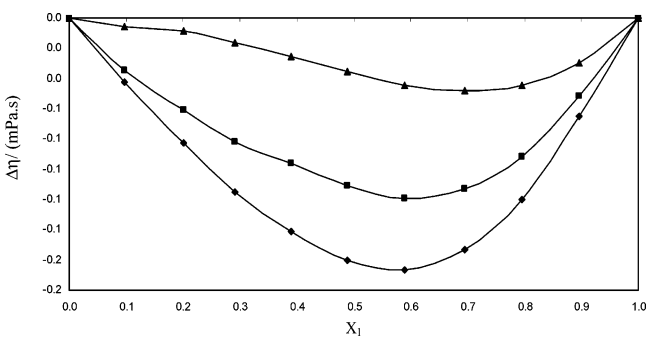

Figure 8. Deviation in viscosity $\Delta\eta$ for the system cyclohexane (1) + cyclohexanone (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

Table 5. Values of the Coefficients of the Redlich−Kister Equation (Eq 6) and Standard Deviation (Eq 7) at Different Temperatures

T/K	A_o	A_1	A_2	A_3	σ
Cyclohexane (1) + Nitrobenzene (2)					
		V^E/cm^3·mol^{-1}			
298.15	−3.5465	7.6213	2.2709	−9.0294	0.1686
303.15	−5.6157	4.3677	3.0889	−5.1284	0.0962
308.15	−7.7524	−0.3250	4.7099	0.5094	0.0084
		$\Delta\eta$/mPa·s			
298.15	−0.6348	−0.6391	0.5983	0.7776	0.0143
303.15	−0.5611	−0.6391	0.5983	0.7776	0.0138
308.15	−0.4698	−1.0134	0.5497	1.2226	0.0225
		$10^{12}K_S^E$/Pa^{-1}			
298.15	−50.8525	55.7332	26.7553	−65.7677	1.2147
303.15	−44.8366	53.5215	28.0781	−63.0961	1.2469
308.15	−30.1762	25.5633	26.4473	−29.7991	0.5593
Cyclohexanone (1) + Nitrobenzene (2)					
		V^E/cm^3·mol^{-1}			
298.15	−5.6157	4.3677	3.0889	−5.1284	0.0962
303.15	2.7508	2.7003	−2.7887	−3.2591	0.0289
308.15	2.3813	4.8667	−2.9080	−5.8468	0.0520
		$\Delta\eta$/mPa·s			
298.15	−0.5611	−0.6391	0.5983	0.7776	0.0138
303.15	−0.0797	−0.5162	0.1071	0.6176	0.0055
308.15	−0.0374	−0.7930	0.0279	0.0951	0.0008
		$10^{12}K_S^E$/Pa^{-1}			
298.15	−50.8525	55.7332	26.7553	−65.7677	1.2147
303.15	−70.9314	60.4718	54.6959	−71.4937	0.6411
308.15	−46.5318	74.5000	34.7531	−88.4945	0.8411
Cyclohexane (1) + Cyclohexanone (2)					
		V^E/cm^3·mol^{-1}			
298.15	5.4297	5.6934	−4.1589	−6.8467	0.0628
303.15	4.7320	4.3232	−3.5232	−5.2041	0.0180
308.15	3.7131	2.7473	−2.6207	−3.3125	0.0303
		$\Delta\eta$/mPa·s			
298.15	−0.7857	−0.1275	0.0675	0.1071	0.0008
303.15	−0.5809	−0.1260	−0.0454	0.1406	0.0011
308.15	−0.2861	−0.1396	−0.0542	0.0419	0.0005
		$10^{12}K_S^E$/Pa^{-1}			
298.15	6.3705	10.7154	−4.4907	−12.8391	0.1191
303.15	5.2114	10.8647	−4.3267	13.0149	0.1198
308.15	−0.5507	6.9818	0.8601	−8.3121	0.0767

The values of K_S^E are negative for the systems [CH + NB] and [CHO + NB] as shown in Figures 3 and 6, which indicate the presence of strong interaction forces between the molecules.[7] However, for the system [CH + CHO], K_S^E values are positive at 298.15 and 303.15 K, whereas they are slightly negative at 308.15 K as shown in Figure 9.

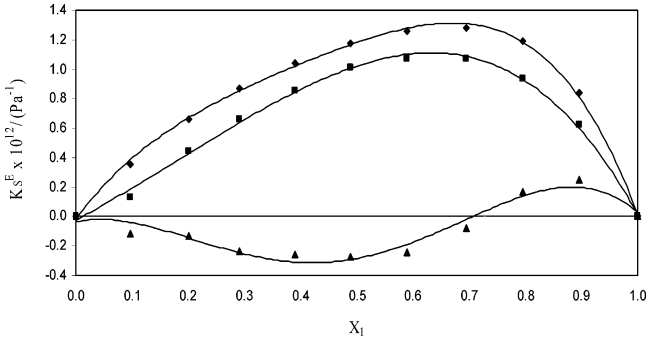

Figure 9. Excess isentropic compressibility K_S^E for the system cyclohexane (1) + cyclohexanone (2) at ◆, 298.15 K; ■, 303.15 K; and ▲, 308.15 K.

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