Relative Permittivities, Speeds of Sound, Viscosities, and Densities of Cyclohexanone + *cis*-Decalin and Cyclohexanone + *trans*-Decalin Mixtures at 283.15, 293.15, and 303.15 K

Nikos G. Tsierkezos and Ioanna E. Molinou*

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64004, 157 10 Zografou, Athens, Greece

George A. Polizos

Department of Physics, National Technical University of Athens, Zografou Campus, 157 80 Athens, Greece

Relative permittivities, speeds of sound, viscosities, and densities for the binary mixtures of cyclohexanone + *cis*-decalin and cyclohexanone + *trans*-decalin have been measured over the whole composition range at (283.15, 293.15, and 303.15) K. The excess volumes and the deviations in viscosity, speed of sound, isentropic compressibility, and molar polarization were calculated. The results were fitted to a Redlich−Kister type polynomial equation, and the corresponding parameters have been derived. The Kirkwood correlation factor was also calculated.

Introduction

Studies on excess functions of binary mixtures are of considerable importance in understanding the nature of molecular interactions. Continuing our work for the study of thermodynamic properties of binary organic solutions,[1,2] we report in this paper the relative permittivities, speeds of sound, viscosities, and densities for the binary mixtures of cyclohexanone + *cis*-decalin and cyclohexanone + *trans*-decalin at (283.15, 293.15, and 303.15) K. From these results the excess volumes and the deviations in viscosity, speed of sound, isentropic compressibility, and molar polarization have been derived. The Kirkwood correlation factor was also calculated using relative permittivity data. All materials used in this work are of industrial interest.

Cyclohexanone is a polar cyclic ketone having relative permittivity $\epsilon = 16.3$ (293.15 K) and dipole moment $\mu = 3.01$ D, and it is used as a solvent for vinyl resins, crude rubber, waxes, fats, and shellac. It also is used for the production of adipic acid and resins. *cis*-Decalin and *trans*-decalin are diastereomer cycloalkanes with zero dipole moment and almost identical relative permittivities, $\epsilon_{cis} = 2.5$ and $\epsilon_{trans} = 2.4$ (293.15 K). Decalin is used as a solvent for naphthalene, fats, resins, oils, and waxes and is often a replacement for turpentine in lacquers, shoe polishes, and floor waxes and also for motor fuel and lubricants. The aim of this work is to test whether the presence of polar molecules of cyclohexanone induces dipoles in the decalin molecules.

Thermodynamic properties of cyclohexanone with alkanes[3] and aromatic hydrocarbons[4] have been reported in the literature. A survey in the literature showed that mixtures of cyclohexanone + *cis*-decalin and cyclohexanone + *trans*-decalin have not been studied.

Experimental Section

Materials. Cyclohexanone (Riedel-de Häen, >99.8%), *cis*-decalin (Merck, >98.0%), and *trans*-decalin (Merck,

* E-mail: imolinou@cc.uoa.gr.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of the Pure Liquids with Literature Values at 293.15 K

liquid	$\rho_{(exp)}$/g·cm^{-3}	$\rho_{(ref)}$/g·cm^{-3}	$n_{D(exp)}$	$n_{D(ref)}$
cyclohexanone	0.940 20[a]	0.937 4[a−c]	1.446 1[a]	1.446 3[a−c]
cis-decalin	0.896 71	0.896 60[d]	1.481 3	1.481 1[d]
		0.896 71[e]		1.480 98[e]
trans-decalin	0.870 01	0.869 00[d]	1.469 5	1.469 3[d]
		0.869 71[e]		1.469 32[e]

[a] Values at 303.15 K. [b] Aralaguppi et al., 1999 (ref 3). [c] Aralaguppi et al., 1999 (ref 4). [d] Korosi and Kovats, 1981 (ref 5). [e] Camin and Rossini, 1955 (ref 6).

>98.0%) were used without purification. The purity of the liquids was assessed by comparing the experimental densities and refractive indices with the literature values (Table 1).

The binary mixtures were prepared by mass using an electronic balance (Mettler A210P, ±0.01 mg). The mole fractions were known from ±0.0001 to ±0.0005 in all cases.

Measurements. Densities were measured with an Anton Paar (DMA 58) microcomputer controlled precision densimeter with a built-in solid state thermostat. The estimated uncertainty of the measured densities was ±0.000 01 g·cm^{-3}. The DMA cell was calibrated with dry air and doubly distilled water at atmospheric pressure. The sample thermostat was controlled to ±0.01 K.

Flow times of the solvent mixtures were measured with a viscosity measuring unit (Schott Geräte AVS 310), equipped with an Übbelohde capillary viscometer. The time measurement tolerance was ±0.005%, and the display accuracy was ±0.01 s. The temperature was maintained constant within ±0.03 K. The viscosities were averaged from four readings. The uncertainty in the viscosity values was ±0.001 mPa·s.

Relative permittivities were measured by a Hewlett-Packard impedance analyzer (HP 4291A RF). The frequency range was 1 MHz to 1.8 GHz, and the precision in the relative permittivity values was 1%. The calibration

Table 2. Experimental Densities (ρ), Viscosities (η), Speeds of Sound (u), Isentropic Compressibilities (k_s), Relative Permittivities (ϵ), and Kirkwood Correlation Factors (g) of Cyclohexanone (1) + Decalin (2) Mixtures at 283.15, 293.15, and 303.15 K

x_1	ρ/g·cm⁻³	η/mPa·s	u/m·s⁻¹	k_s/TPa⁻¹	ϵ	g	x_1	ρ/g·cm⁻³	η/mPa·s	u/m·s⁻¹	k_s/TPa⁻¹	ϵ	g
						Cyclohexanone (1) + *cis*-Decalin (2)							Cyclohexanone (1) + *trans*-Decalin (2)
			283.15 K							283.15 K			
0.0000	0.904 40	4.092	1499.4	492	2.4		0.0000	0.877 39	2.578	1439.0	550	2.4	
0.0500	0.905 89	3.971	1495.6	494	2.6	0.520	0.0500	0.879 76	2.562	1438.0	550	2.6	0.534
0.1446	0.908 46	3.788	1488.6	497	3.4	0.803	0.1500	0.884 46	2.540	1435.3	549	3.3	0.721
0.2281	0.911 34	3.643	1483.7	498	4.0	0.767	0.2415	0.889 59	2.534	1435.0	546	4.1	0.780
0.3500	0.916 18	3.458	1477.1	500	5.1	0.774	0.3447	0.896 02	2.543	1435.3	542	5.1	0.803
0.4482	0.920 81	3.332	1473.7	500	6.3	0.814	0.4511	0.903 37	2.570	1436.7	536	6.0	0.767
0.5559	0.926 34	3.218	1470.5	499	8.3	0.919	0.5088	0.907 71	2.592	1438.1	533	6.7	0.781
0.6271	0.930 42	3.156	1469.0	498	9.5	0.939	0.6731	0.921 80	2.686	1444.7	520	8.8	0.790
0.7252	0.936 61	3.089	1468.1	495	11.0	0.932	0.6779	0.922 25	2.689	1444.9	519	9.3	0.843
0.8051	0.942 12	3.050	1468.3	492	12.3	0.925	0.7761	0.932 00	2.769	1452.1	509	10.8	0.842
0.8571	0.946 02	3.033	1469.0	490	13.5	0.944	0.8609	0.941 14	2.852	1458.7	499	12.6	0.873
0.9322	0.952 11	3.019	1470.7	486	15.0	0.945	0.9315	0.949 50	2.932	1466.3	490	13.5	0.843
1.0000	0.957 99	3.018	1473.1	481	16.5		1.0000	0.957 99	3.018	1473.3	481	16.5	
			293.15 K							293.15 K			
0.0000	0.896 71	3.361	1456.1	526	2.5		0.0000	0.870 01	2.118	1397.1	589	2.4	
0.0500	0.898 08	3.262	1452.3	528	2.7	0.544	0.0500	0.872 29	2.114	1396.1	588	2.6	0.561
0.1446	0.900 51	3.118	1445.3	532	3.4	0.763	0.1500	0.876 76	2.103	1393.3	588	3.2	0.681
0.2281	0.903 33	3.006	1440.4	534	4.0	0.759	0.2415	0.881 85	2.105	1392.8	585	4.0	0.777
0.3500	0.907 98	2.863	1433.8	536	5.0	0.761	0.3447	0.888 12	2.119	1393.0	580	4.9	0.789
0.4482	0.912 49	2.767	1430.6	536	6.2	0.820	0.4511	0.895 32	2.147	1394.4	574	5.9	0.787
0.5559	0.917 90	2.680	1427.3	535	8.1	0.926	0.5088	0.899 60	2.168	1395.7	571	6.5	0.787
0.6271	0.921 90	2.634	1425.9	534	9.3	0.955	0.6731	0.913 42	2.253	1402.0	557	8.5	0.797
0.7252	0.927 92	2.586	1424.9	531	10.5	0.923	0.6779	0.913 78	2.256	1402.5	556	9.1	0.864
0.8051	0.933 33	2.560	1425.2	528	12.2	0.961	0.7761	0.923 40	2.326	1408.4	546	10.5	0.858
0.8571	0.937 20	2.549	1425.9	525	13.3	0.975	0.8609	0.932 39	2.397	1415.6	535	12.1	0.878
0.9322	0.943 12	2.543	1427.7	520	14.8	0.979	0.9315	0.940 61	2.466	1422.7	525	13.0	0.851
1.0000	0.949 11	2.546	1430.2	515	16.3		1.0000	0.949 11	2.546	1430.6	515	16.3	
			303.15 K							303.15 K			
0.0000	0.889 11	2.641	1412.8	563	2.5		0.0000	0.862 51	1.767	1356.6	630	2.4	
0.0500	0.890 32	2.558	1409.1	566	2.7	0.572	0.0500	0.864 63	1.758	1355.3	630	2.6	0.590
0.1446	0.892 69	2.471	1402.1	570	3.4	0.801	0.1500	0.868 96	1.744	1352.5	629	3.2	0.716
0.2281	0.895 41	2.399	1397.2	572	3.9	0.751	0.2415	0.873 92	1.737	1351.8	626	3.9	0.771
0.3500	0.899 88	2.302	1390.5	575	4.9	0.772	0.3447	0.880 13	1.737	1351.9	622	4.8	0.800
0.4482	0.904 31	2.231	1387.4	574	6.1	0.841	0.4511	0.887 21	1.744	1353.2	616	5.8	0.806
0.5559	0.909 59	2.159	1384.2	574	7.9	0.943	0.5088	0.891 42	1.750	1354.5	611	6.4	0.810
0.6271	0.913 50	2.115	1382.8	573	9.0	0.964	0.6731	0.904 90	1.784	1360.4	597	8.3	0.814
0.7252	0.919 41	2.060	1381.9	570	10.4	0.961	0.6779	0.905 33	1.785	1360.7	597	8.9	0.885
0.8051	0.924 70	2.019	1382.0	566	12.0	0.993	0.7761	0.914 70	1.815	1366.7	585	10.2	0.873
0.8571	0.928 50	1.995	1383.8	562	13.0	1.000	0.8609	0.923 59	1.848	1373.4	574	11.6	0.881
0.9322	0.934 26	1.964	1385.6	557	14.4	1.000	0.9315	0.931 71	1.880	1380.3	563	12.7	0.873
1.0000	0.940 20	1.915	1388.1	552	16.0		1.0000	0.940 20	1.915	1388.3	552	16.0	

was carried out by capacitors of standard values (0 S, 0 Ω, and 50 Ω) supplied by the manufacturer.

Experimental details of measurements of density, viscosity, and relative permittivity are the same as those described previously.[1,2,7]

The speeds of sound were measured with an Anton Paar (DSA 48) sound analyzer. The temperature was maintained constant within ±0.01 K. The sound analyzer was calibrated with distilled water and air at the experimental temperatures. The uncertainty of the measured speeds of sound was ±1 m·s⁻¹. The isentropic compressibility (k_s) was calculated from density (ρ) and speed of sound (u) data, as $k_s = 1/(u^2\rho)$.

Results and Discussion

The values of density (ρ), viscosity (η), speed of sound (u), isentropic compressibility (k_s), and relative permittivity (ϵ) are given in Table 2. The calculations of excess molar volumes (V^E) and the deviations in viscosity ($\Delta\eta$), speeds of sound (Δu), isentropic compressibilities (Δk_s), and molar polarizations (ΔP) were carried out from the general equation

$$\Delta Y = Y_m - \sum c_i Y_i \qquad (1)$$

where ΔY refers to V^E/cm³·mol⁻¹, $\Delta\eta$/mPa·s, Δk_s/TPa⁻¹, Δu/m·s⁻¹, and ΔP/cm³·mol⁻¹; Y_m and Y_i refer to the mixture property and to the respective property of the ith pure component; and the term c_i is the mixture composition expressed in mole fraction (x_i) for the calculation of V^E, $\Delta\eta$, Δu, and ΔP and in volume fraction (φ_i) for the calculation of Δk_s.

The molar polarizations of the mixture (P_m) and of the ith pure component (P_i) were calculated using the Clausius–Mossotti equation:[8]

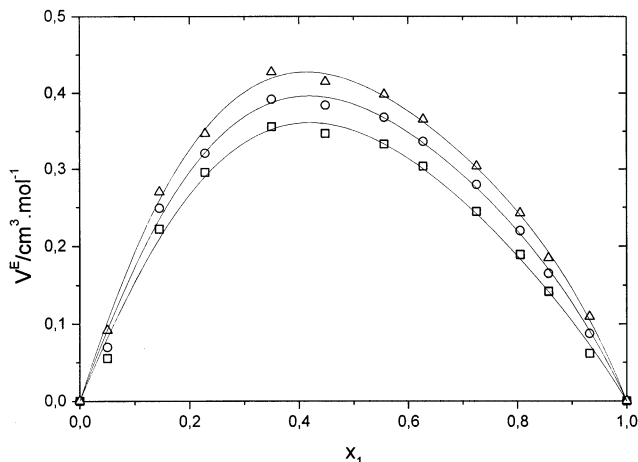$$P_m = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{\sum x_i M_i}{\rho} \qquad (2)$$

$$P_i = \frac{(\epsilon_i - 1)}{(\epsilon_i + 2)} \frac{M_i}{\rho_i} \qquad (3)$$

where M_i is the molar mass of the ith pure component.

The values of V^E, $\Delta\eta$, Δu, ΔP, and Δk_s were fitted to the Redlich–Kister[9] equation:

$$\Delta Y = c_1 c_2 \sum_{k=0}^{n} A_k (2c_1 - 1)^k \qquad (4)$$
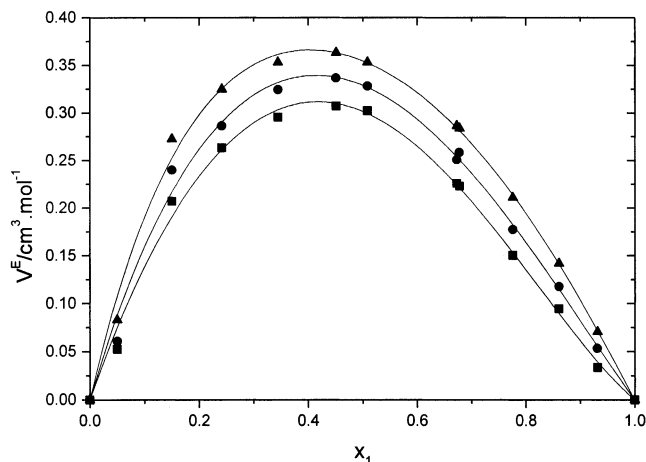
where A_k represent the parameters.

Figure 1. Excess molar volume (V^E) versus the mole fraction (x_1) for cyclohexanone (1) + *cis*-decalin (2) mixtures at the following temperatures: □, 283.15 K; ○, 293.15 K; △, 303.15 K.

Figure 2. Excess molar volume (V^E) versus the mole fraction (x_1) for cyclohexanone (1) + *trans*-decalin (2) mixtures at the following temperatures: ■, 283.15 K; ●, 293.15 K; ▲, 303.15 K.

Table 3. Parameters of the Redlich–Kister Equation and Standard Deviations (d) of Excess Functions of Cyclohexanone + *cis*-Decalin and Cyclohexanone + *trans*-Decalin Mixtures at 283.15, 293.15, and 303.15 K

function	A_0	A_1	A_2	A_3	d
Cyclohexanone + *cis*-Decalin					
283.15 K					
V^E/cm³·mol⁻¹	1.4035	−0.4908	0.0442	0.2209	0.0133
$\Delta\eta$/mPa·s	−1.1192	−0.0071	−0.1116	0.1510	0.0026
Δu/m·s⁻¹	−57.488	−4.849	−4.672	−2.551	0.1721
Δk_s/TPa⁻¹	48.520	−14.188	5.753	−2.887	0.1506
ΔP/cm³·mol⁻¹	75.911	−1.683	−10.171	−13.168	1.0301
293.15 K					
V^E/cm³·mol⁻¹	1.5420	−0.5036	0.1987	0.2916	0.0115
$\Delta\eta$/mPa·s	−0.9191	−0.0045	−0.1107	0.1459	0.0026
Δu/m·s⁻¹	−58.028	−5.043	−6.098	−3.769	0.1902
Δk_s/TPa⁻¹	54.296	−15.125	7.845	−2.750	0.1766
ΔP/cm³·mol⁻¹	69.122	3.533	−11.728	−12.194	0.8885
303.15 K					
V^E/cm³·mol⁻¹	1.6605	−0.5435	0.3393	0.3399	0.0089
$\Delta\eta$/mPa·s	−0.3275	0.0427	−0.0900	0.4702	0.0051
Δu/m·s⁻¹	−60.153	−8.158	−4.170	1.110	0.3711
Δk_s/TPa⁻¹	61.945	−14.853	6.028	−7.724	0.3122
ΔP/cm³·mol⁻¹	67.002	8.262	−10.177	−20.065	0.8435
Cyclohexanone + *trans*-Decalin					
283.15 K					
V^E/cm³·mol⁻¹	1.2063	−0.4771	−0.1508	−0.0930	0.0115
$\Delta\eta$/mPa·s	−0.8391	−0,0468	−0.0097	0.0058	0.0004
Δu/m·s⁻¹	−73.648	−16.063	1.826	14.747	0.3318
Δk_s/TPa⁻¹	39.397	−16.295	−0.733	−9.492	0.2597
ΔP/cm³·mol⁻¹	69.755	−24.954	−11.975	22.705	0.9728
293.15 K					
V^E/cm³·mol⁻¹	1.3159	−0.4716	0.0419	−0.1024	0.0144
$\Delta\eta$/mPa·s	−0.6699	−0.0508	−0.0125	−0.0951	0.0011
Δu/m·s⁻¹	−73.692	−15.883	−6.018	3.011	0.2481
Δk_s/TPa⁻¹	44.922	−15.132	5.112	−7.954	0.2378
ΔP/cm³·mol⁻¹	66.942	−18.880	−19.672	15.891	0.9482
303.15 K					
V^E/cm³·mol⁻¹	1.4185	−0.4563	0.3376	−0.2293	0.0126
$\Delta\eta$/mPa·s	−0.3669	−0.0252	−0.0012	0.0016	0.0003
Δu/m·s⁻¹	−72.862	−15.048	−8.875	2.215	0.1941
Δk_s/TPa⁻¹	50.257	−15.699	9.245	−11.144	0.2187
ΔP/cm³·mol⁻¹	65.150	−14.827	−21.701	5.364	0.8081

Figure 3. Deviations in viscosity ($\Delta\eta$) versus the mole fraction (x_1) for cyclohexanone (1) + *cis*-decalin (2) mixtures at the following temperatures: □, 283.15 K; ○, 293.15 K; △, 303.15 K.
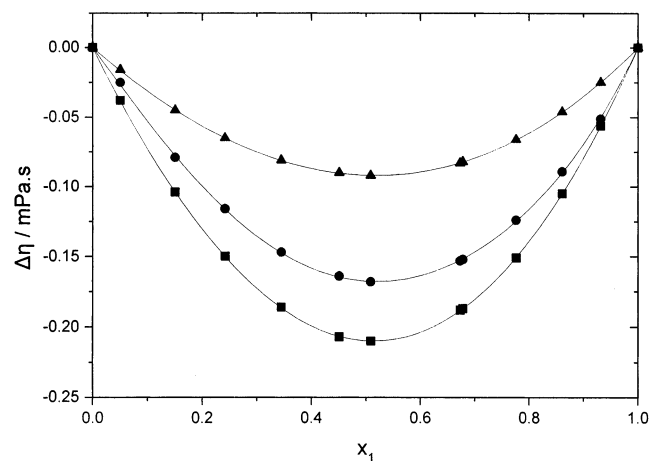
Figure 4. Deviations in viscosity ($\Delta\eta$) versus the mole fraction (x_1) for cyclohexanone (1) + *trans*-decalin (2) mixtures at the following temperatures: ■, 283.15 K; ●, 293.15 K; ▲, 303.15 K.

A nonlinear least-squares method was used to estimate the parameters A_k. The optimum number of the parameters was obtained through examination of the standard deviation (d). The values of A_k and d are presented in Table 3.

The V^E values are positive (Figures 1 and 2), the $\Delta\eta$ values are negative (Figures 3 and 4), and both increase with increasing temperature. The positive V^E values indi-

cate that the interactions between like molecules are stronger than the interactions between unlike molecules. The fact that the $\Delta\eta$ values are negative shows that dispersion forces are dominating.

The Δk_s values, presented in Figure 5, are positive and increase with increasing temperature, indicating that the elasticity of the solution is diminished.
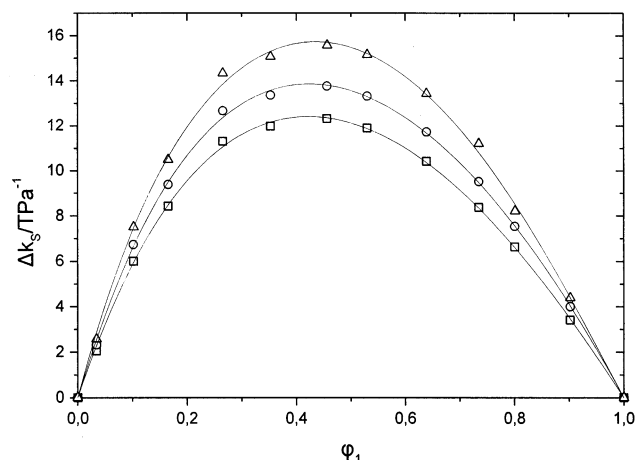
Figure 5. Deviations in isentropic compressibility (Δk_s) versus the volume fraction (φ_1) for cyclohexanone (1) + *cis*-decalin (2) mixtures at the following temperatures: □, 283.15 K; ○, 293.15 K; △, 303.15 K.
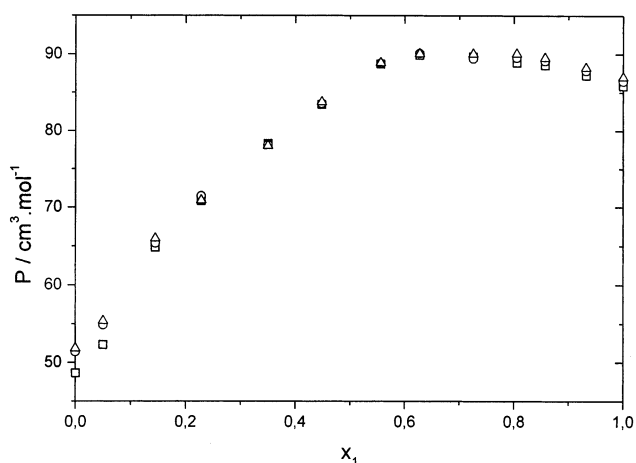
Figure 6. Molar polarization (P) versus the mole fraction (x_1) for cyclohexanone (1) + *cis*-decalin (2) mixtures at the following temperatures: □, 283.15 K; ○, 293.15 K; △, 303.15 K.

The ΔP values are positive and are approximately independent of temperature. The molecular polarization values P increase with the cyclohexanone concentration, as is expected (Figure 6). Figures 5 and 6 refer to cyclohexanone + *cis*-decalin mixtures. The corresponding figures for *trans*-decalin mixtures are not displayed, as they are very similar. It is observed that the values af all properties are lower for mixtures containing *trans*-decalin. This fact can be attributed to the different geometries of the *trans*- and *cis*-decalin molecules.

The relative permittivity results were used for the calculation of the Kirkwood[10] correlation factor (g) according to the equation

$$g = \frac{9 k_B T}{4 \pi N \mu^2 x_1} \frac{(2\epsilon + \epsilon_\infty)^2}{(\epsilon_\infty + 2)^2 (2\epsilon + 1)} \left[V \frac{(\epsilon - 1)}{\epsilon} - \frac{3 x_2 V_2 (\epsilon_2 - 1)}{(2\epsilon + \epsilon_2)} - \frac{3 x_1 V_1 (\epsilon_\infty - 1)}{(2\epsilon + \epsilon_\infty)} \right] \quad (5)$$

where μ is the dipole moment of cyclohexanone; V, V_1, and V_2 are the molar volumes of the mixture, cyclohexanone, and decalin, respectively; ϵ and ϵ_2 are the relative permittivities of the mixture and decalin, respectively; ϵ_∞ is taken as the square of the refractive index of cyclohexanone; k_B is the Boltzmann constant; N is Avogadro's number; and T is the temperature.

The Kirkwood parameter g is a measure of short-range orientational correlations and is expresed as the ratio μ^*/μ, where μ^* is the dipole moment of a sphere where the central molecule has a steady orientation while the other molecules are oriented in the sphere by structural factors, and μ is the dipole moment of the polar molecule in the liquid. The departure of g from unity is a measure of the degree of hindered molecular orientation. Positive deviations from unity indicate parallel alignment of the dipoles of the neighboring molecules, and negative deviations, that antiparallel orientation is favored.[11,12]

In this work is observed a monotonic increase of the correlation factors with the increase of cyclohexanone molar fraction. The values tend to unity for pure cyclohexanone (Table 2), indicating that the decalin molecules exhibit a structure breaking behavior to the cyclohexanone multimers.

Literature Cited

(1) Tsierkezos, N. G.; Molinou, I. E. Thermodynamic Properties of Water + Ethylene Glycol at 283.15, 293.15, 303.15, and 313.15 K. *J. Chem. Eng. Data* **1998**, *43*, 989−993.
(2) Tsierkezos, N. G.; Palaiologou, M. M.; Molinou, I. E. Densities and Viscosities of 1-Pentanol Binary Mixtures at 293.15. *J. Chem. Eng. Data* **2000**, *45*, 272−275.
(3) Aralaguppi, M. I.; Jadar, C. V.; Aminabhavi, T. M. Density, Refractive Index, Viscosity, and Speed of Sound in Binary Mixtures of Cyclohexanone with Hexane, Octane, Nonane, Decane, Dodecane, and 2,2,4-Trimethylpentane. *J. Chem. Eng. Data* **1999**, *44*, 435−440.
(4) Aralaguppi, M. I.; Jadar, C. V.; Aminabhavi, T. M. Density, Refractive Index, Viscosity, and Speed of Sound in Binary Mixtures of Cyclohexanone with Benzene, Methylbenzene, 1,4-Dimethylbenzene, 1,3,5-Trimethylbenzene, and Methoxybenzene in the Temperature Interval (298.15 to 308.15) K. *J. Chem. Eng. Data* **1999**, *44*, 446−450.
(5) Korosi, G.; Kovats, E. Sz. Density and Surface Tension of 83 Organic Liquids. *J. Chem. Eng. Data* **1981**, *26*, 323−332.
(6) Camin, D. L.; Rossini, F. D. Physical Properties of 14 American Petroleum Institute Research Hydrocarbons, C_9 to C_{15}. *J. Phys. Chem.* **1955**, *59*, 1173−1179.
(7) Molinou, I. E.; Tsierkezos, N. G. Conductance Studies on Manganese (II), Cobalt (II), Nickel (II), and Cadmium (II) Sulfates in Water + *N,N*-Dimethylformamide Mixtures at 293.15 K. *J. Chem. Eng. Data* **2001**, *46*, 1399−1403.
(8) Sastry, N. V.; Valand, M. K. Dielectric Constants, Refractive Indexes and Polarizations for 1-Alcohol+Heptane Mixtures at 298.15 and 308.15 K. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101* (2), 243−250.
(9) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.
(10) Avraam, T.; Moumouzias, G.; Ritzoulis, G. A Study on Excess Volumes and Dielectric Properties in the γ-Butyrolactone + *p*-Xylene System at Various Temperatures. *J. Chem. Eng. Data* **1998**, *43* (1), 51−54.
(11) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973.
(12) Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill Book Company: 1955.