Thermodynamic Properties of Binary Mixtures of Cyclohexanone with *n*-Alkanols (C$_1$–C$_5$) at 293.15 K

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The excess molar volumes (V^E), excess surface tensions (σ^E), and deviations in molar refraction (R^E) and isentropic compressibility (k_s^E) of binary mixtures of cyclohexanone with methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol have been determined over the entire composition range at 293.15 K. The results were fitted by the Redlich–Kister polynomial equation and the corresponding binary coefficients A_k have been derived. The standard deviations between the calculated and the experimental excess properties have been determined. The results provide information on the interactions of the molecules in the pure liquids as well as in the binary mixtures.

1. INTRODUCTION

Studies on the thermodynamic, optical, and ultrasonic properties of binary mixtures are of considerable importance in the fundamental understanding of the nature of the interactions between unlike molecules. In recent years there has been considerable interest in theoretical and experimental investigations of the excess thermodynamic properties of binary mixtures.[1–4] In principle, the interactions between the molecules can be established from the study of the deviations from the ideal behavior of physical properties such as molar volume, compressibility, surface tension, viscosity, and molar refraction. The negative or positive deviations of a physical property from the ideal value depend on the type and extent of the interactions between the unlike molecules, as well as on the temperature.

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For example, in the case of excess molar volume, when the interactions between the molecules of the mixed components are weaker than in the pure component, the excess molar volume will be positive, whereas when the association between the mixed components predominates, the excess molar volume will be negative. According to other researchers,[5,6] the physical interactions, which involve mainly dispersion forces, lead to positive deviations of the excess molar volume from the ideal value, whereas the chemical or specific interactions, which involve hydrogen-bond formation or charge-transfer type interactions, lead to negative deviations. The variation of the compressibility is analogous of that of the excess molar volume, whereas the change of the excess surface tension or viscosity tends to become the inverse.

Cyclohexanone is expected to exhibit dipole–dipole interactions in the pure state because of its fairly high dipole moment ($\mu = 3.01$ D). However, the association between cyclohexanone molecules is weak (probably negligible) and does not compete with the high degree of association between alcohol molecules, which are strongly associated in the pure state through hydrogen bonding to form short-lived aggregates.[7,8] Alcohols represent an important class of hydrogen-bonded solvents, for which the degree of association is very sensitive to temperature and the presence of electrolytes.[9,10] The hydroxyl group of the alcohol molecule participates in two hydrogen bonds, acting once as a proton donor and once as a proton acceptor. Therefore, in linear alcohols the behavior ranges from the presence of cyclic and linear aggregates in methanol,[11] to the coexistence of linear aggregates and monomers in higher alcohols.[12] For the branched alcohols the size of the aggregates is smaller than for the linear alcohols. The last observation has been attributed to the unfavorable steric effect of the alkyl group on the hydrogen bonding.[13]

As a continuation of our research program of determining the thermodynamic properties of binary mixtures,[14–17] we report here experimental values of density (ρ), refractive index (n_D), speed of sound (u), isentropic compressibility (k_s), and surface tension (σ) for the binary mixtures of cyclohexanone with methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol at 293.15 K. From these experimental data, the excess molar volume (V^E), excess surface tension (σ^E) and the deviations in molar refraction (R^E), and isentropic compressibility (k_s^E) have been calculated. These results are fitted by the Redlich–Kister polynomial equation to derive the A_k coefficients for the estimation of the standard deviations between the experimental and calculated values. The purpose of this work is to gain some understanding about the type and magnitude of the molecular interactions in the binary liquid mixtures of cyclohexanone with n-alkanols and their effect on the excess thermodynamic properties. Such studies would have considerable interest in chemical engineering areas because both cyclohexanone and n-alkanols have numerous applications in synthetic chemistry and industry. To the best of our knowledge, extensive data of excess thermodynamic properties of binary mixtures

of cyclohexanone with *n*-alkanols at the experimental conditions of this study are not available in the literature.

2. EXPERIMENTAL SECTION

2.1. Materials

Methanol (Merck > 99.8%), ethanol (Merck > 99.5%), 1-propanol (Merck > 99.5%), 1-butanol (Merck > 99.5%), 1-pentanol (Fluka > 99.5 %), and cyclo-hexanone (Riedel-de Häen > 99.8%) were used without purification. The water content as indicated by chromatographic analysis was less than 0.08%. The purity of the pure components was assessed by comparing the experimental densities, refractive indices, and speeds of sound with literature values (Table I). The agreement was satisfactory. The binary mixtures were prepared by mass (Mettler balance of accuracy 0.01 mg) and the mole fractions were known to ±0.0001. All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC.

2.2. Apparatus and Procedures

Densities of pure liquids and binary mixtures were measured with an Anton Paar (model DMA 58) microcomputer-controlled precision densimeter with a built-in solid-state thermostat. The precision in density was $\pm 0.00001 \, \text{g-cm}^{-3}$. The DMA cell was calibrated with dry air and conductivity water at 293.15 K. The sample size was $0.7 \, \text{cm}^3$. The precision in temperature of the internal thermostat was ±0.005 K and that of the sample thermostat ±0.01 K.

The speeds of sound were measured with an Anton Paar (model DSA 48) sound analyzer. The temperature was maintained constant within ±0.01 K. The sound analyzer was calibrated with dry air and conductivity water at 293.15 K. The uncertainty of the measured speeds of sound was $\pm 1 \, \text{m-s}^{-1}$. The isentropic compressibility (k_s) was determined from density (ρ) and speed of sound (u) data using the Laplace[18] equation, $k_s = 1/(u^2 \rho)$. The isentropic compressibility determined in this way is accurate to within $\pm 1 \, \text{TPa}^{-1}$.

The refractive indices at the sodium D-line were measured with a thermostat-ted Abbe refractometer (Model A. Krüss) with a built-in light source for the prism with an accuracy of ±0.0001. The thermostat temperature was constant to ±0.01 K.

The surface tension was measured by a Du Nouy Tensiometer (A. Krüss, model K8600) equipped with a platinum–iridium ring of wire diameter 0.37 mm. The platinum–iridium ring was brought to red heat and afterwards the ring was cleaned with chromosulfuric acid and boiling distilled water. The sample was introduced into a double-walled glass cell connected to a thermostat, where the temperature was constant within ±0.01 K. The tensiometer was calibrated with

Table I.   Comparison of Experimental Densities (ρ), Refractive Indices (n_D), Speeds of Sound (u), and Surface Tensions (σ) of Pure Components with the Literature Values at 293.15 K

Component	ρ (g-cm^3)		n_D		u (m-s^{-1})		σ (mN-m^{-1})	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Methanol	0.79144	0.79150[a]	1.3296	1.3284[b]	1118.4	1121[d]	22.9	22.6[c]
		0.79125[b]		1.3288[c]		1121[e]		22.95[f]
Ethanol	0.78957	0.78940[g]	1.3668	1.3610[c]	1159.6	1162[d]	22.2	22.3[c]
		0.78922[h]		1.3615[g]		1162[e]		22.31[f]
1-Propanol	0.80364	0.80375[g]	1.3847	1.3854[c]	1222.1	1223[e]	23.7	23.8[c]
		0.80360[i]		1.3850[g]		1223[j]		23.69[f]
1-Butanol	0.80992	0.80980[g]	1.3993	1.3991[c]	1256.8	1258[e]	24.6	24.6[c]
		0.80950[i]		1.3988[g]		1256[j]		25.3[k]
		0.80960[l]		1.3992[l]				
1-Pentanol	0.81472	0.81440[g]	1.4099	1.4101[c]	1292.2	1293[j]	25.3	25.8[k]
		0.81460[i]		1.4090[g]				
Cyclohexanone	0.94975	0.95100[m]	1.4518	1.4503[c]	1430.5	1430.2[°]	34.5	35.2[k]
		0.94930[n]		1.4507[e]				
		0.94911[o]		1.4510[m]				

[a] Ref. (36).
[b] Ref. (37).
[c] Ref. (38).
[d] Ref. (39).
[e] Ref. (40).
[f] Ref. (41).
[g] Ref. (42).
[h] Ref. (43).
[i] Ref. (44).
[j] Values from interpolation, Ref. (45).
[k] Values from interpolation, Ref. (40).
[l] Ref. (46).
[m] Ref. (47).
[n] Ref. (15).
[o] Ref. (17).

distilled water at 293.15 K and a correction factor was employed. The accuracy of the surface tension measurement was ± 0.1 mN-m^{-1}.

3. RESULTS AND DISCUSSION

The experimental values of density (ρ), refractive index (n_D), speed of sound (u), isentropic compressibility (k_s), and surface tension (σ) for the investigated binary mixtures are given in Table II.

The excess molar volumes (V^E) were calculated from the difference between the real (V_m) and the ideal molar volume (V_m^{id}) using the density values according

Table II.   Experimental Densities (ρ), Speeds of Sound (u), Isentropic Compressibilities (k_s), Refractive Indices (n_D), and Surface Tensions (σ) of Binary Mixtures of Cyclohexanone with 1-Alkanols at 293.15 K

x_1	ρ (g-cm^3)	u (m-s^{-1})	k_s (TPa^{-1})	n_D	σ (mN-m^{-1})
	Cyclohexanone (1) + methanol (2)				
1.0000	0.94975	1430.5	515	1.4518	34.5
0.7058	0.93302	1391.9	553	1.4402	33.0
0.5587	0.92032	1362.5	585	1.4284	31.6
0.4314	0.91607	1330.1	624	1.4193	30.2
0.3296	0.89249	1299.7	663	1.4142	28.9
0.2465	0.87805	1268.3	708	1.3962	27.7
0.1828	0.86416	1240.1	752	1.3804	26.6
0.1338	0.85174	1215.7	794	1.3704	25.7
0.0739	0.82912	1177.1	870	1.3546	24.7
0.0343	0.81069	1147.4	937	1.3416	23.9
0.0000	0.79144	1118.4	1010	1.3296	22.9
	Cyclohexanone (1) + ethanol (2)				
1.0000	0.94975	1430.5	515	1.4518	34.5
0.8067	0.93158	1400.2	548	1.4419	33.3
0.6464	0.91372	1369.3	584	1.4328	31.9
0.5218	0.89764	1341.7	619	1.4265	30.6
0.4143	0.88138	1314.4	657	1.4166	29.3
0.3204	0.86529	1287.2	697	1.4048	28.0
0.2370	0.84911	1260.4	741	1.3948	26.7
0.1681	0.83434	1235.5	785	1.3862	25.6
0.1049	0.81896	1209.9	834	1.3783	24.5
0.0497	0.80396	1184.4	887	1.3712	23.3
0.0000	0.78957	1159.6	942	1.3668	22.2
	Cyclohexanone (1) + 1-propanol (2)				
1.0000	0.94975	1430.5	515	1.4518	34.5
0.8445	0.93323	1408.8	540	1.4440	33.9
0.7108	0.91771	1387.5	566	1.4366	33.0
0.5877	0.90205	1365.6	595	1.4295	32.0
0.4696	0.88576	1342.7	626	1.4221	30.8
0.3793	0.87240	1324.3	654	1.4163	29.8
0.2868	0.85767	1303.2	687	1.4093	28.6
0.2079	0.84428	1283.8	719	1.4033	27.4
0.1331	0.83056	1263.7	754	1.3968	26.2
0.0655	0.81721	1243.5	791	1.3911	25.0
0.0000	0.80364	1222.1	833	1.3847	23.7
	Cyclohexanone (1) + 1-butanol (2)				
1.0000	0.94975	1430.5	515	1.4518	34.5
0.8704	0.93385	1411.5	538	1.4458	33.7
0.7507	0.91871	1393.0	561	1.4399	32.7
0.6381	0.90404	1374.9	585	1.4340	31.7
0.5312	0.88964	1357.2	610	1.4286	30.7
0.4302	0.87564	1340.1	636	1.4236	29.7
0.3342	0.86185	1323.2	663	1.4186	28.7

Table II.   Continued

x_1	ρ (g-cm^3)	u (m-s^{-1})	k_s (TPa^{-1})	n_D	σ (mN-m^{-1})
0.2457	0.84876	1307.1	690	1.4137	27.7
0.1615	0.83583	1290.9	718	1.4089	26.7
0.0773	0.82248	1273.8	749	1.4038	25.6
0.0000	0.80992	1256.8	782	1.3993	24.6
Cyclohexanone (1) + 1-pentanol (2)					
1.0000	0.94975	1430.5	515	1.4518	34.5
0.8714	0.93179	1412.0	538	1.4459	33.6
0.7824	0.91956	1399.2	555	1.4419	33.0
0.6760	0.90500	1384.2	577	1.4372	32.1
0.5746	0.89129	1370.3	598	1.4329	31.2
0.4727	0.87758	1356.4	619	1.4287	30.3
0.3751	0.86453	1343.4	641	1.4248	29.3
0.2791	0.85174	1330.6	663	1.4210	28.3
0.1830	0.83900	1317.7	686	1.4172	27.3
0.0908	0.82673	1305.1	710	1.4135	26.3
0.0000	0.81472	1292.2	735	1.4099	25.3

to the equation:

$$V^{E} = V_m - V_m^{id} = V_m - \sum_{i=1}^{2} V_i x_i \qquad (1)$$

where V_i and x_i represent the molar volume and the mole fraction of the ith component, respectively. The real molar volume (V_m) of the binary mixtures was calculated as, $V_m = (x_1 M_1 + x_2 M_2)/\rho_m$, where ρ_m is the density of the solution and M_1 and M_2 are the molar masses of each constituent. The derived excess molar volumes were accurate to ± 0.001 cm^3-mol^{-1}.

The deviations in molar refraction (R^{E}) were calculated from the equation

$$R^{E} = R_m - \sum_{i=1}^{2} R_i y_i \qquad (2)$$

where R_i and R_m are the molar refractions of the pure components and the mixture, respectively, and y_i is the volume fraction of the ith component given as:

$$y_i = \frac{x_i V_i}{\sum_{i=1}^{2} x_i V_i} \qquad (3)$$

The molar refraction of the ith component (R_i) was obtained from the Lorentz–Lorenz equation, which is based on the electromagnetic theory and expresses the relationship between the molar refraction, the refractive index, and the

molar volume of the liquid

$$R_i = \frac{n_{D(i)}^2 - 1}{n_{D(i)}^2 + 2} V_i \tag{4}$$

where $n_{D(i)}$ is the refractive index of the ith component. The equation for the binary mixture becomes

$$R_m = \frac{n_{D(m)}^2 - 1}{n_{D(m)}^2 + 2} V_m \tag{5}$$

where $n_{D(m)}$ is the refractive index of the mixture. The obtained deviations in molar refraction were accurate to within $\pm 0.005 \, \text{cm}^3\text{-mol}^{-1}$.

In a similar manner, the deviation in isentropic compressibility (k_s^{E}) was calculated from the equation

$$k_s^{\text{E}} = k_{s(m)} - \sum_{i=1}^{2} y_i k_{s(i)} \tag{6}$$

where $k_{s(m)}$ and $k_{s(i)}$ refer to the isentropic compressibility of the mixture and the ith pure component, respectively. The derived values of the deviations in isentropic compressibility were accurate to $\pm 4 \, \text{TPa}^{-1}$.

The deviation of binary mixtures from the ideal behavior can be also quantified by the excess surface tension (σ^{E}) given by

$$\sigma^{\text{E}} = \sigma_m - \sum_{i=1}^{2} x_i \sigma_i \tag{7}$$

where σ_m and σ_i refer to the surface tension of the mixture and the ith pure component, respectively. The derived excess surface tensions were accurate to $\pm 0.1 \, \text{mN-m}^{-1}$. The derived excess molar volumes (V^{E}), excess surface tensions (σ^{E}), deviations in molar refraction (R^{E}), and deviations in isentropic compressibility (k_s^{E}) at 293.15 K are given in Table III.

Each set of the calculated values ΔY (V^{E}, k_s^{E}, R^{E}, or σ^{E}) was fitted by the Redlich–Kister[19] polynomial equation to derive the binary coefficients A_k

$$\Delta Y = x_1 x_2 \sum_{k=0}^{n} A_k (2x_1 - 1)^k \tag{8}$$

In each case, the optimum number m of the A_k coefficients ($m = n + 1$) was determined through an examination of the variation of standard deviation (d) according to the equation:

$$d = \left[\frac{\sum (\Delta Y_{\text{calc}} - \Delta Y_{\text{exp}})^2}{(p - m)} \right]^{1/2} \tag{9}$$

Table III. Excess Molar Volumes (V^E), Excess Surface Tensions (σ^E), Deviations in Molar Refraction (R^E), and Deviations in Isentropic Compressibility (k_s^E) of Binary Mixtures of Cyclohexanone with 1-Alkanols at 293.15 K

X_1	V^E (cm^3-mol^{-1})	k_s^E (TPa^{-1})	R^E (cm^3-mol^{-1})	σ^E (mN-m^{-1})
Cyclohexanone (1) + methanol (2)				
0.7058	−0.499	−310	−2.875	1.91
0.5587	−0.655	−460	−3.935	2.22
0.4314	−0.763	−590	−4.299	2.30
0.3296	−0.888	−710	−4.090	2.18
0.2465	−0.929	−770	−3.945	1.94
0.1828	−0.913	−780	−3.542	1.58
0.1338	−0.891	−760	−2.930	1.25
0.0739	−0.593	−560	−1.874	0.94
0.0343	−0.320	−320	−0.973	0.60
Cyclohexanone (1) + ethanol (2)				
0.8067	−0.093	−180	−1.095	1.18
0.6464	−0.169	−320	−1.712	1.75
0.5218	−0.229	−410	−1.902	1.98
0.4143	−0.239	−460	−2.026	2.00
0.3204	−0.238	−500	−2.049	1.86
0.2370	−0.219	−460	−1.853	1.58
0.1681	−0.202	−440	−1.547	1.33
0.1049	−0.143	−340	−1.117	1.01
0.0497	−0.061	−190	−0.618	0.49
Cyclohexanone (1) + 1-propanol (2)				
0.8445	−0.070	−120	−0.398	1.08
0.7108	−0.124	−210	−0.655	1.62
0.5877	−0.152	−270	−0.790	1.95
0.4696	−0.172	−310	−0.838	2.03
0.3793	−0.183	−340	−0.801	2.00
0.2868	−0.178	−330	−0.729	1.80
0.2079	−0.167	−300	−0.599	1.46
0.1331	−0.127	−230	−0.440	1.06
0.0655	−0.063	−140	−0.226	0.59
Cyclohexanone (1) + 1-butanol (2)				
0.8704	−0.042	−81	−0.075	0.48
0.7507	−0.080	−140	−0.137	0.67
0.6381	−0.114	−190	−0.189	0.78
0.5312	−0.135	−220	−0.203	0.84
0.4302	−0.151	−230	−0.191	0.84
0.3342	−0.149	−220	−0.168	0.79
0.2457	−0.138	−200	−0.143	0.67
0.1615	−0.104	−160	−0.106	0.50
0.0773	−0.053	−92	−0.063	0.24
Cyclohexanone (1) + 1-pentanol (2)				
0.8714	−0.012	−58	−0.010	0.28
0.7824	−0.030	−88	−0.018	0.50

Table III. Continued

X_1	V^E (cm^3·mol^{-1})	k_s^E (TPa^{-1})	R^E (cm^3·mol^{-1})	σ^E (mN·m^{-1})
0.6760	-0.043	-120	-0.026	0.58
0.5746	-0.059	-130	-0.028	0.61
0.4727	-0.069	-140	-0.026	0.65
0.3751	-0.074	-140	-0.020	0.55
0.2791	-0.071	-120	-0.013	0.43
0.1830	-0.062	-98	-0.008	0.32
0.0908	-0.033	-58	-0.004	0.16

where p represents the number of measurements and m the number of coefficients used for fitting the experimental data in Eq. (8). The estimated values of A_k and d for V^E, σ^E, R^E, and k_s^E are presented in Table IV. In all the cases, the best fit in Eq. (8) was found by using four adjustable fitting coefficients ($m = 4, n = 3$). The agreement between the measured excess quantities and those calculated from the Redlich–Kister relation is satisfactory. A comparison of our A_k coefficients for the excess volume with those of Venkatesu and Prabhakara Rao[20] for mixtures of cyclohexanone with 1-propanol and 1-butanol at 303.15 K is shown in Table IV.

The excess molar volumes (V^E) for the mixtures of cyclohexanone with the n-alkanols are presented graphically in Fig. 1. It is observed that the V^E values are negative (there is a reduction in volume) for all the investigated systems and tend systematically to smaller negative values with an increase in size of the n-alkanol; the algebraic values of V^E fall in the order: 1-pentanol > 1-butanol > 1-propanol > ethanol > methanol. Large negative V^E values are observed for mixtures containing methanol, while the V^E values become less negative on going from ethanol to 1-butanol and finally have slightly negative values for the mixtures containing 1-pentanol (the mixture of cyclohexanone with 1-pentanol shows almost ideal behavior). The negative V^E values prove that the specific interactions through hydrogen-bond formation between the mixed components are stronger than the interactions between the molecules of the pure components. Anyhow, the hydrophobic character of the n-alkanol is amplified by an increase in chain length and, consequently, the hydrogen bonds between n-alkanol and cyclohexanone molecules weaken, resulting in a positive contribution to the excess molar volume.[21] The dependence of the excess molar volume of the equimolar mixtures ($x_1 = x_2 = 0.5$) on the chain length of the n-alkanol molecule is shown in Fig. 2. The estimated chain-length values for the n-alkanols were taken from the literature.[18] This curve gives a unique examination of the influence of the chain length of the alcohol molecule on the excess molar volumes of the binary mixtures. Similar conclusions have already been reported for the binary mixtures of n-alkanols with dimethyl sulfoxide,[22] acrylonitrile,[23,24] acetonitrile,[25] benzene,[26] 1,4-dioxane,[27] diethyl carbonate,[28] p-chlorotoluene[29], and nitromethane.[30]

Table IV. Parameters A_k of the Redlich–Kister Equation, Eq. (8), and Standard Deviations (d) of Excess Functions of Binary Mixtures of Cyclohexanone with 1-Alkanols at 293.15 K

| Function	A_o	A_1	A_2	A_3	D
Cyclohexanone + methanol					
V^E (cm^3-mol^{-1})	−2.8113	1.8484	−3.4811	3.2510	0.0212
σ^E (mN-m^{-1})	9.2132	−0.2724	1.6366	−3.6748	0.0818
k_s^E (TPa^{-1})	−2996.66	1405.18	−654.47	−693.69	7.9178
R^E (cm^3-mol^{-1})	−16.3740	−5.9383	−4.8114	−3.4944	0.0738
Cyclohexanone + ethanol					
V^E (cm^3-mol^{-1})	−0.9045	0.5133	−0.1243	0.1874	0.0150
σ^E (mN-m^{-1})	7.9556	−0.9268	1.2205	−1.5386	0.0304
k_s^E (TPa^{-1})	−1930.37	442.36	−288.69	67.60	9.4488
R^E (cm^3-mol^{-1})	−8.1698	−0.6339	−1.7551	−2.0139	0.1078
Cyclohexanone + 1-propanol					
V^E (cm^3-mol^{-1})	−0.6814	0.3521	−0.2555	0.0053	0.0052
V^E (cm^3-mol^{-1})	−0.2372[a]	0.1238[a]	−0.0118[a]		
σ^E (mN-m^{-1})	8.1484	−1.0584	1.0906	0.7342	0.0172
k_s^E (TPa^{-1})	−1313.90	395.99	−193.54	−120.15	3.8598
R^E (cm^3-mol^{-1})	−3.3164	−0.6078	−0.1699	−0.0049	0.0067
Cyclohexanone + 1-butanol					
V^E (cm^3-mol^{-1})	−0.5713	0.3264	−0.0162	−0.1188	0.0023
V^E (cm^3-mol^{-1})	−0.1470[a]	−0.0794[a]	−0.1077[a]		
σ^E (mN-m^{-1})	3.379	−0.4185	0.9530	1.6148	0.0082
k_s^E (TPa^{-1})	−907.06	177.13	−76.44	113.13	1.9760
R^E (cm^3-mol^{-1})	−0.7929	−0.2126	0.1032	0.4384	0.0030
Cyclohexanone + 1-pentanol					
V^E (cm^3-mol^{-1})	−0.2694	0.1980	−0.0019	−0.0085	0.0021
σ^E (mN-m^{-1})	2.5276	0.6627	−0.2928	−0.3649	0.0226
k_s^E (TPa^{-1})	−554.19	105.82	−78.80	53.24	2.4980
R^E (cm^3-mol^{-1})	−0.1081	−0.0608	0.0816	0.0776	0.0005

[a] Literature values at 303.15 K (Ref. (20)).

      The deviations in isentropic compressibility (k_s^E) are presented graphically in Fig. 3. The k_s^E values are negative for all the investigated binary mixtures and the algebraic values fall in the order: 1-pentanol > 1-butanol > 1-propanol > ethanol > methanol. The results point out that the compressibility of the mixed solutions diminishes from 1-pentanol to methanol, which suggests that the extent of the interactions between unlike molecules increases in the same order as indicated by the V^E results. Similar conclusions have been reported for the binary mixtures of the n-alkanols (C$_1$–C$_5$) with diethyleneglycol dimethylether.[31]

      The excess surface tensions (σ^E) are plotted as function of composition in Fig. 4. The values of σ^E are positive and tend to decrease as the chain length of the alcohol increases. This behavior is explained by the difference in the distribution
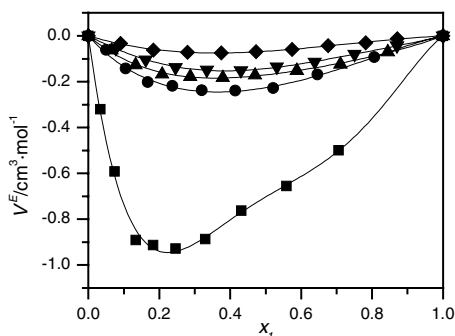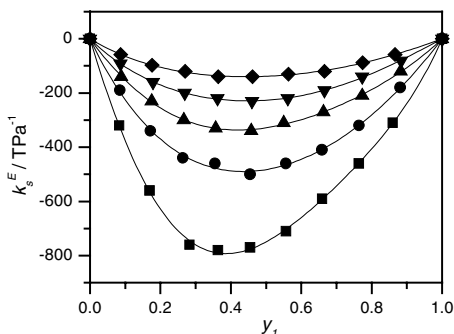
Fig. 1. Excess molar volume (V^E) *versus* the mole fraction of cyclohexanone (x_1) for binary mixtures of cyclohexanone with methanol (■), ethanol (●), 1-propanol (▲), 1-butanol (▼), and 1-pentanol (◆) at 293.15 K.

of molecules between the surface and the bulk region of the liquid.[32,33] In binary mixtures containing methanol, due to the stronger interaction between unlike molecules, both components tend to prefer the bulk region of the liquid rather than the interface, where they can form hydrogen bonds. This behavior leads to large positive σ^E values for these mixtures. As the chain length of the alcohol increases, the interactions between unlike molecules weaken, resulting in a different distribution of molecules between the surface and the bulk region; the alcohol
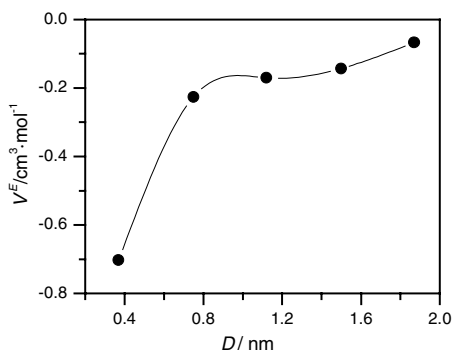

Fig. 2. Excess molar volumes (V^E) *versus* the chain-length (D) of *n*-alkanol for equimolar binary mixtures of cyclohexanone with methanol ($D = 0.37$ nm), ethanol ($D = 0.75$ nm), 1-propanol ($D = 1.12$ nm), 1-butanol ($D = 1.50$ nm), and 1-pentanol ($D = 1.87$ nm).
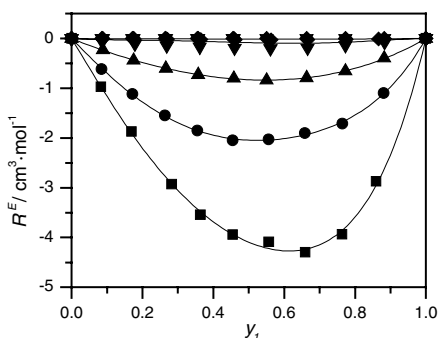
Fig. 3. Deviation in isentropic compressibility (k_s^E) *versus* the volume fraction of cyclohexanone (y_1) for binary mixtures of cyclohexanone with methanol (■), ethanol (●), 1-propanol (▲), 1-butanol (▼), and 1-pentanol (◆) at 293.15 K.

having lower surface tension tends to prefer the interface, whereas cyclohexanone prefers the bulk liquid phase. This behavior leads to slightly positive σ^E values for mixtures containing 1-pentanol.

The results for the deviations in molar refraction (R^E) *versus* the volume fraction of cyclohexanone (y_1) are displayed in Fig. 5 and exhibit almost the same dependence as the V^E and k_s^E values; the algebraic values of R^E increase systematically from methanol to 1-pentanol supporting once more the explanation given above.
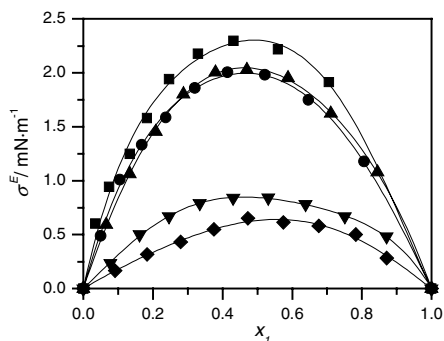
Fig. 4. Excess surface tension (σ^E) *versus* the mole fraction of cyclohexanone (x_1) for binary mixtures of cyclohexanone with methanol (■), ethanol (●), 1-propanol (▲), 1-butanol (▼), and 1-pentanol (◆) at 293.15 K.

Fig. 5. Deviation in molar refraction (R^E) *versus* the volume fraction of cyclohexanone (y_1) for binary mixtures of cyclohexanone with methanol (■), ethanol (●), 1-propanol (▲), 1-butanol (▼), and 1-pentanol (◆) at 293.15 K.

The experimental speed of sound values for the binary mixtures were compared with the ideal speed of sound (u_{calc}) values calculated from the Nomoto relation[34,35]

$$u_{calc} = \left(\sum_{i=1}^{2} y_i u_i^{1/3} \right)^3 \qquad (10)$$

The results are presented in Table V. It is recognized that the variation between the experimental and calculated values of speed of sound is related to the association between the molecules of the binary mixtures.

Table V. Experimental (u_{exp}) and Calculated (u_{calc}, Eq. (10)) Speeds of Sound of Binary Mixtures of Cyclohexanone with 1-Alkanols at 293.15 K

y_1	u_{exp} (m·s^{-1})	u_{calc} (m·s^{-1})	% variation	y_1	u_{exp} (m·s^{-1})	u_{calc} (m·s^{-1})	% variation
Cyclohexanone (1) + methanol (2)				Cyclohexanone (1) + ethanol (2)			
1.0000	1430.5	1430.5	0.000	1.0000	1430.5	1430.5	0.000
0.8596	1391.9	1383.6	−0.597	0.8808	1400.2	1396.2	−0.284
0.7637	1362.5	1352.1	−0.762	0.7640	1369.3	1363.2	−0.450
0.6595	1330.1	1318.5	−0.876	0.6590	1341.7	1333.9	−0.584
0.5566	1299.7	1285.8	−1.073	0.5561	1314.4	1305.6	−0.669
0.4551	1268.3	1254.1	−1.121	0.4550	1287.2	1278.2	−0.702
0.3635	1240.1	1226.0	−1.143	0.3549	1260.4	1251.4	−0.710
0.2828	1215.7	1201.5	−1.170	0.2636	1235.5	1227.4	−0.655
0.1692	1177.1	1167.7	−0.801	0.1719	1209.9	1203.5	−0.526
0.0831	1147.4	1142.4	−0.433	0.0848	1184.4	1181.2	−0.275
0.0000	1118.4	1118.4	0.000	0.0000	1159.6	1159.6	0.000

Table V. Continued

y_1	u_{exp} (m-s^{-1})	u_{calc} (m-s^{-1})	% variation	y_1	u_{exp} (m-s^{-1})	u_{calc} (m-s^{-1})	% variation
Cyclohexanone (1) + 1-propanol (2)				Cyclohexanone (1) + 1-butanol (2)			
1.0000	1430.5	1430.5	0.000	1.0000	1430.5	1430.5	0.000
0.8824	1408.8	1404.9	−0.281	0.8835	1411.5	1409.5	−0.139
0.7725	1387.5	1381.2	−0.459	0.7727	1393.0	1389.7	−0.235
0.6633	1365.6	1357.9	−0.562	0.6657	1374.9	1370.8	−0.300
0.5503	1342.7	1334.1	−0.641	0.5613	1357.2	1352.5	−0.351
0.4578	1324.3	1314.8	−0.720	0.4602	1340.1	1334.9	−0.388
0.3572	1303.2	1294.0	−0.701	0.3618	1323.2	1317.9	−0.401
0.2662	1283.8	1275.4	−0.651	0.2689	1307.1	1302.1	−0.385
0.1750	1263.7	1257.0	−0.527	0.1786	1290.9	1286.8	−0.323
0.0883	1243.5	1239.6	−0.309	0.0864	1273.8	1271.2	−0.199
0.0000	1222.1	1222.1	0.000	0.0000	1256.8	1256.8	0.000
Cyclohexanone (1) + 1-pentanol (2)							
1.0000	1430.5	1430.5	0.000	0.3644	1343.4	1341.5	−0.140
0.8662	1412.1	1411.4	−0.043	0.2700	1330.6	1328.6	−0.152
0.7745	1399.2	1398.5	−0.051	0.1762	1317.7	1315.9	−0.142
0.6659	1384.2	1383.2	−0.073	0.0871	1305.1	1303.8	−0.097
0.5633	1370.3	1368.9	−0.098	0.0000	1292.2	1292.1	0.000
0.4613	1356.4	1354.8	−0.114				

4. CONCLUSIONS

In this study, the excess molar volumes, the excess surface tensions, the deviations in molar refraction, and the deviations in isentropic compressibility for the binary mixtures of cyclohexanone with methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol have been determined over the entire composition range at 293.15 K. It has been concluded that an increase in chain length of the n-alkanol causes a smaller deviation of the mixtures from ideal mixing behavior. The obtained excess quantities show that the alcohol chain length is a determining factor conditioning the excess thermodynamic properties of the binary mixtures. There is a clear tendency of the n-alkanol molecules to establish interactions with cyclohexanone molecules through hydrogen-bond formation, and this propensity weakens as the alkyl chain of the n-alkanol is lengthened.

5. ACKNOWLEDGMENT

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