

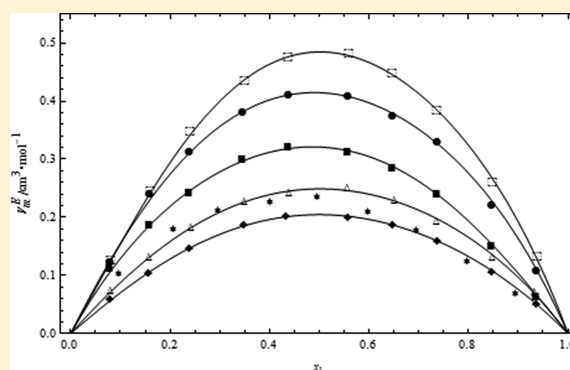
## Densities and Viscosities of Binary Mixtures of Cyclohexanone and 2-Alkanols

Mohammad Almasi\* and Bahman Sarkoohaki

Department of Chemistry, Science and Research Branch, Islamic Azad University, Khuzestan, Iran

**S** Supporting Information

**ABSTRACT:** Densities and viscosities of mixtures of cyclohexanone with 2-alkanols, namely, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-heptanol, have been measured as a function of composition range at  $T = (298.15, 303.15, 308.15, \text{ and } 313.15)$  K and ambient pressure. Excess molar volumes  $V_m^E$  and viscosity deviations  $\Delta\eta$  were calculated and correlated by the Redlich–Kister type function to derive the coefficients and estimate the standard error. For mixtures of cyclohexanone with used 2-alkanols,  $V_m^E$  is positive, and  $\Delta\eta$  is negative over the entire range of mole fraction. The effect of temperature and chain length of the 2-alkanols on the excess molar volumes and viscosity deviations of its mixtures with cyclohexanone is discussed.



### INTRODUCTION

Densities and viscosities of fluids and fluid mixtures are essential for many engineering and industrial applications. The mixture functions such as the excess molar volume,  $V_m^E$ , and the viscosity deviation,  $\Delta\eta$ , are often used to describe the intermolecular forces in mixtures to help us understand their real behavior and to develop models for their description as well as the simulation processes. Therefore, over the years, studies on multi-component liquid systems have attracted the attention of many researchers.<sup>1–4</sup>

Thermodynamic properties of cyclohexanone with alkanols are important in the fundamental understanding of the mixing processes. Knowledge of the thermophysical properties of these liquids is of high interest on account of their wide usage in science and industrial processes. Those properties are crucial for the design of chemical processes as well as for progress in the thermodynamic theories of the liquid state. The densities and viscosities as functions of temperature and pressure, and their derivatives render some insight in the molecular structure of liquids and provide information on intermolecular interactions. This paper is a part of an ongoing research effort to measure and characterize the properties of mixtures containing alkanols.<sup>5,6</sup> It reports the densities, viscosities, excess molar volumes, and viscosity deviations of mixing for the binary mixtures of cyclohexanone + 2-alkanols at the temperatures of (298.15, 303.15, 308.15, and 313.15) K. The influences of temperature and chain length on the thermodynamic properties were investigated. No reported mixing properties of these studied systems at these temperatures were found.

### EXPERIMENTAL SECTION

Cyclohexanone, 2-propanol, 2-butanol, 2-pentanol, and 2-heptanol were obtained from Merck with a mass purity of > 99 %, and

2-hexanol was supplied from Aldrich with a mass purity of > 99 %. All of the materials were used as purchased without further purification. The purity of reagents was checked by comparing the measured densities and viscosities at various temperatures with those reported in the literature;<sup>7–10</sup> the resultant values are in good agreement with values found in the literature and reported in Table 1.

The density of the pure compounds and mixtures was measured by means of an Anton Parr DMA 4500 oscillating U-tube densimeter, provided with automatic viscosity correction. The uncertainty of the density measurements was estimated to be  $\pm 5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ . The apparatus was calibrated once a day with dry air and bidistilled water. The temperature in the cell was regulated to  $\pm 0.01$  K with a solid state thermostat. Viscosities were measured with an Ubbelohde viscometer with an uncertainty of  $\pm 1 \cdot 10^{-2} \text{ mPa} \cdot \text{s}$ . The temperature in the cell was regulated to  $\pm 0.01$  K. The mixtures were prepared by weighing known masses of pure liquids in airtight, narrow-mouth ground stoppered bottles taking due precautions to minimize evaporation losses. All of the mass measurements were performed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The uncertainty in the mole fraction was estimated to be  $\pm 1 \cdot 10^{-4}$ .

### RESULTS AND DISCUSSION

**Densities and Excess Molar Volumes.** The excess molar volumes of the solutions of molar composition,  $x$ , were calculated at the temperatures of (298.15, 303.15, 308.15, and 313.15) K from the densities of the pure liquids and their

Received: July 31, 2011

Accepted: December 8, 2011

Published: December 27, 2011

Table 1. Sources, Purity Grades, Densities,  $\rho$ , and Viscosities,  $\eta$ , of Pure Components at Various Temperatures

chemical name	source	initial mass purity	T/K	$\rho/(\text{g}\cdot\text{cm}^{-3})$		$\eta/(\text{mPa}\cdot\text{s})$	
				exptl	lit.	exptl	lit.
cyclohexanone	Merck	0.995	298.15	0.94191	0.9418 <sup>a</sup>	2.057	2.0205 <sup>a</sup>
			303.15	0.93724	0.9374 <sup>b</sup>	1.847	1.799 <sup>b</sup>
			308.15	0.93267	0.9328 <sup>b</sup>	1.694	1.635 <sup>b</sup>
			313.15	0.92772		1.546	
2-propanol	Merck	0.995	298.15	0.78109	0.78098 <sup>c</sup>	2.055	2.044 <sup>c</sup>
			303.15	0.77657	0.77660 <sup>d</sup>	1.788	1.763 <sup>d</sup>
			308.15	0.77187	0.7725 <sup>a</sup>	1.563	1.560 <sup>a</sup>
			313.15	0.76736		1.387	
2-butanol	Merck	0.995	298.15	0.80301	0.80256 <sup>c</sup>	3.104	3.132 <sup>c</sup>
			303.15	0.79820	0.79851 <sup>d</sup>	2.597	2.493 <sup>d</sup>
			308.15	0.79357	0.7939 <sup>a</sup>	2.152	2.125 <sup>a</sup>
			313.15	0.78915		1.733	
2-pentanol	Merck	>0.99	298.15	0.80541	0.80524 <sup>c</sup>	3.499	3.478 <sup>c</sup>
			303.15	0.80121	0.80090 <sup>d</sup>	2.801	2.774 <sup>d</sup>
			308.15	0.79666	0.7966 <sup>a</sup>	2.334	
			313.15	0.79251		1.993	
2-hexanol	Aldrich	>0.99	298.15	0.81014	0.81014 <sup>c</sup>	4.101	4.100 <sup>c</sup>
			303.15	0.80613	0.8064 <sup>a</sup>	3.411	3.33 <sup>a</sup>
			308.15	0.80206	0.80175 <sup>c</sup>	2.819	2.920 <sup>c</sup>
			313.15	0.79796	0.7984 <sup>a</sup>	2.219	2.29 <sup>a</sup>
2-heptanol	Merck	0.995	298.15	0.81318	0.81333 <sup>c</sup>	5.023	5.088 <sup>c</sup>
			303.15	0.80926		4.151	
			308.15	0.80501	0.80488 <sup>c</sup>	3.748	3.683 <sup>c</sup>
			313.15	0.80114		2.852	

<sup>a</sup>Reference 7. <sup>b</sup>Reference 8. <sup>c</sup>Reference 6. <sup>d</sup>Reference 9. <sup>e</sup>Reference 10.

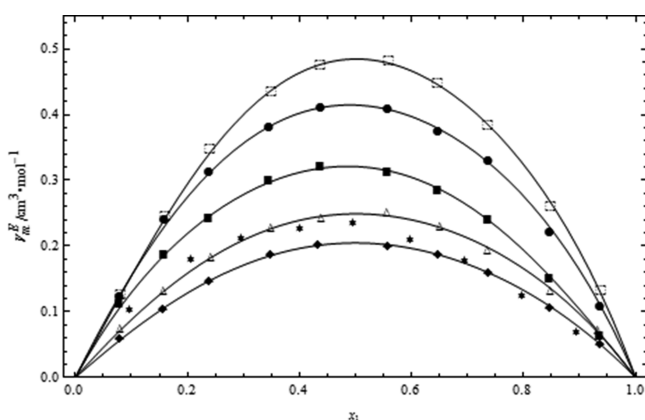


Figure 1. Excess molar volumes  $V_m^E$  vs mole fraction of cyclohexanone for binary mixtures of cyclohexanone with  $\blacklozenge$ , 2-propanol;  $\triangle$ , 2-butanol;  $\star$ , ref 19 for 2-butanol;  $\blacksquare$ , 2-pentanol;  $\bullet$ , 2-hexanol;  $\square$ , 2-heptanol; at 298.15 K. The solid curves were calculated from coefficients of eq 2 given in Table 3.

mixtures according to the following equation

$$V_m^E = \sum_{i=1}^N x_i M_i (\rho_i^{-1} - \rho^{-1}) \quad (1)$$

where  $\rho$  is the density of the mixture,  $\rho_i$  is the density of pure component  $i$ ,  $x_i$  is the mole fraction,  $M_i$  is the molar mass of component  $i$ , and  $N$  stands for the number of components in the mixture.

The corresponding  $V_m^E$  values of binary mixtures of [cyclohexanone (1) + 2-alkanols (2)] are calculated and plotted against the mole fraction of cyclohexanone at 298.15 K in

Figure 1. The uncertainty for excess molar volume is  $\pm 1.10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$ . The values of density for binary mixtures are in Table 2. Each set of results was fitted using a Redlich–Kister polynomial,<sup>11</sup> which for binary mixtures is

$$Y^E = x_1(1 - x_1) \sum_{k=0}^N A_k (1 - 2x_1)^k \quad (2)$$

where  $Y^E \equiv V_m^E$  or  $\Delta\eta$  and  $x_1$  is the mole fraction of cyclohexanone.  $A_k$  is an adjustable parameter obtained by the least-squares method, and  $k$  is the degree of the polynomials. In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviation  $\sigma$  with

$$\sigma = \left[ \sum (Y - Y_{\text{cal}})^2 / (n - p) \right]^{1/2} \quad (3)$$

where  $Y$  and  $Y_{\text{cal}}$  are the experimental and calculated values of the property  $Y$ , respectively, and  $n$  and  $p$  are the number of experimental points and number of parameters retained in the respective equations. Table 3 presents the values of the parameters  $A_k$  together with the standard deviation  $\sigma$ .

Cyclohexanone is expected to exhibit dipole–dipole interactions in the pure state because of its fairly high dipole moment ( $\mu = 3.01 \text{ D}$ ). 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.<sup>12,13</sup> 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.<sup>14,15</sup> Excess molar volumes of all binary mixtures are positive and increase slightly with increasing the temperature.

Table 2. Densities,  $\rho$ , and Viscosities,  $\eta$ , for the Binary Mixtures as a Function of the Mole Fraction  $x_1$  of Cyclohexanone<sup>a</sup>

$x_1$	$\rho$		$\eta$		$x_1$	$\rho$		$\eta$	
	g·cm <sup>-3</sup>		mPa·s			g·cm <sup>-3</sup>		mPa·s	
Cyclohexanone (1) + 2-Propanol (2), T/K = 298.15					Cyclohexanone (1) + 2-Butanol (2), T/K = 298.15				
0.0000	0.7810		2.055		0.5596	0.8826		1.332	
0.0812	0.7976		1.689		0.6523	0.8953		1.400	
0.1576	0.8125		1.436		0.738	0.9069		1.501	
0.2398	0.8277		1.236		0.8494	0.9218		1.704	
0.3495	0.8469		1.067		0.9361	0.9333		1.889	
0.4363	0.8614		1.023		1.0000	0.9419		2.057	
0.5601	0.8809		1.076		T/K = 303.15				
0.6502	0.8944		1.177		0.0000	0.7982		2.597	
0.7403	0.9073		1.331		0.0814	0.8110		2.163	
0.8481	0.9221		1.581		0.1598	0.8222		1.820	
0.9384	0.934		1.845		0.2444	0.8341		1.535	
1.0000	0.9419		2.057		0.3514	0.8490		1.305	
T/K = 303.15					0.4404	0.8613		1.206	
0.0000	0.7765		1.788		0.5596	0.8777		1.183	
0.0812	0.7929		1.489		0.6523	0.8903		1.249	
0.1576	0.8076		1.268		0.738	0.9019		1.354	
0.2398	0.8228		1.081		0.8494	0.9169		1.558	
0.3495	0.8419		0.934		0.9361	0.9285		1.716	
0.4363	0.8562		0.899		1.0000	0.9372		1.847	
0.5601	0.8757		0.951		T/K = 308.15				
0.6502	0.8892		1.056		0.0000	0.7935		2.152	
0.7403	0.9021		1.202		0.0814	0.8051		1.828	
0.8481	0.917		1.437		0.1598	0.8163		1.561	
0.9384	0.929		1.675		0.2444	0.8281		1.330	
1.0000	0.9372		1.847		0.3514	0.8431		1.128	
T/K = 308.15					0.4404	0.8556		1.039	
0.0000	0.7718		1.563		0.5596	0.8721		1.036	
0.0812	0.7881		1.301		0.6523	0.8849		1.108	
0.1576	0.8027		1.098		0.738	0.8968		1.224	
0.2398	0.8176		0.934		0.8494	0.9120		1.410	
0.3495	0.8365		0.809		0.9361	0.9240		1.572	
0.4363	0.8510		0.779		1.0000	0.9326		1.694	
0.5601	0.8705		0.845		T/K = 313.15				
0.6502	0.8840		0.949		0.0000	0.7891		1.733	
0.7403	0.8972		1.087		0.0814	0.8005		1.441	
0.8481	0.9122		1.301		0.1598	0.8114		1.186	
0.9384	0.9244		1.537		0.2444	0.8231		0.982	
1.0000	0.9326		1.694		0.3514	0.8380		0.841	
T/K = 313.15					0.4404	0.8503		0.794	
0.0000	0.7673		1.378		0.5596	0.8669		0.825	
0.0812	0.7832		1.142		0.6523	0.8796		0.914	
0.1576	0.7977		0.961		0.7380	0.8915		1.051	
0.2398	0.8127		0.817		0.8494	0.9070		1.248	
0.3495	0.8317		0.715		0.9361	0.9189		1.430	
0.4363	0.8462		0.689		1.0000	0.9277		1.546	
0.5601	0.8653		0.751		Cyclohexanone (1) + 2-Pentanol (2), T/K = 298.15				
0.6502	0.8789		0.854		0.0000	0.8054		3.499	
0.7403	0.8921		0.995		0.0824	0.8153		2.631	
0.8481	0.9070		1.211		0.1615	0.8251		2.178	
0.9384	0.9193		1.412		0.2401	0.8350		1.822	
1.0000	0.9277		1.546		0.3492	0.8491		1.465	
Cyclohexanone (1) + 2-Butanol (2), T/K = 298.15					0.4397	0.8611		1.277	
0.0000	0.8030		3.104		0.5607	0.8777		1.191	
0.0814	0.8149		2.511		0.6496	0.8901		1.230	
0.1598	0.8263		2.067		0.7399	0.9030		1.354	
0.2444	0.8385		1.737		0.8498	0.9192		1.597	
0.3514	0.8537		1.472		0.9396	0.9327		1.855	
0.4404	0.8661		1.361		1.0000	0.9419		2.057	

Table 2. continued

$x_1$	$\rho$		$\eta$		$x_1$	$\rho$		$\eta$	
	g·cm <sup>-3</sup>		mPa·s			g·cm <sup>-3</sup>		mPa·s	
	T/K = 303.15					T/K = 303.15			
0.0000	0.8012		2.801		0.5600	0.8699		1.080	
0.0824	0.8109		2.307		0.6490	0.8820		1.082	
0.1615	0.8206		1.893		0.7391	0.8951		1.173	
0.2401	0.8305		1.580		0.8492	0.9120		1.400	
0.3492	0.8446		1.241		0.9395	0.9266		1.662	
0.4397	0.8565		1.081		1.0000	0.9372		1.847	
0.5607	0.8729		1.016			T/K = 308.15			
0.6496	0.8854		1.072		0.0000	0.8020		2.819	
0.7399	0.8982		1.205		0.0821	0.8098		2.278	
0.8498	0.9144		1.417		0.1612	0.8180		1.823	
0.9396	0.9281		1.685		0.2409	0.8264		1.453	
1.0000	0.9372		1.847		0.3496	0.8388		1.122	
	T/K = 308.15				0.4391	0.8497		0.949	
0.0000	0.7966		2.334		0.5600	0.8652		0.873	
0.0824	0.8063		1.891		0.6490	0.8773		0.907	
0.1615	0.8159		1.541		0.7391	0.8904		1.026	
0.2401	0.8256		1.265		0.8492	0.9071		1.249	
0.3492	0.8395		1.007		0.9395	0.9219		1.505	
0.4397	0.8514		0.881		1.0000	0.9326		1.694	
0.5607	0.8677		0.865			T/K = 313.15			
0.6496	0.8801		0.935		0.0000	0.7979		2.219	
0.7399	0.8931		1.062		0.0821	0.8059		1.686	
0.8498	0.9094		1.294		0.1612	0.8140		1.307	
0.9396	0.9233		1.523		0.2409	0.8224		1.024	
1.0000	0.9326		1.694		0.3496	0.8347		0.781	
	T/K = 313.15				0.4391	0.8454		0.679	
0.0000	0.7925		1.993		0.5600	0.8608		0.655	
0.0824	0.8019		1.596		0.6490	0.8729		0.727	
0.1615	0.8115		1.285		0.7391	0.8859		0.850	
0.2401	0.8210		1.056		0.8492	0.9027		1.068	
0.3492	0.8347		0.838		0.9395	0.9172		1.326	
0.4397	0.8464		0.750		1.0000	0.9277		1.546	
0.5607	0.8626		0.771			Cyclohexanone (1) + 2-Heptanol (2), T/K = 298.15			
0.6496	0.8750		0.848		0.0000	0.8131		5.023	
0.7399	0.8880		0.982		0.0826	0.8203		4.282	
0.8498	0.9043		1.194		0.1625	0.8276		3.640	
0.9396	0.9179		1.388		0.2415	0.8352		3.081	
1.0000	0.9277		1.546		0.3506	0.8466		2.401	
	Cyclohexanone (1) + 2-Hexanol (2), T/K = 298.15				0.4400	0.8568		1.954	
0.0000	0.8101		4.101		0.5603	0.8717		1.513	
0.0821	0.8184		3.432		0.6494	0.8837		1.308	
0.1612	0.8266		2.879		0.7394	0.8969		1.243	
0.2409	0.8352		2.406		0.8500	0.9146		1.391	
0.3496	0.8478		1.896		0.9392	0.9302		1.727	
0.4391	0.8589		1.591		1.0000	0.9419		2.057	
0.5600	0.8746		1.359			T/K = 303.15			
0.6490	0.8868		1.325		0.0000	0.8092		4.151	
0.7391	0.8998		1.388		0.0826	0.8162		3.546	
0.8492	0.9167		1.576		0.1625	0.8233		2.986	
0.9395	0.9314		1.842		0.2415	0.8309		2.473	
1.0000	0.9419		2.057		0.3506	0.8421		1.874	
	T/K = 303.15				0.4400	0.8522		1.468	
0.0000	0.8061		3.411		0.5603	0.8669		1.107	
0.0821	0.8141		2.834		0.6494	0.8789		0.971	
0.1612	0.8222		2.346		0.7394	0.8921		0.976	
0.2409	0.8308		1.932		0.8500	0.9099		1.193	
0.3496	0.8433		1.477		0.9392	0.9255		1.535	
0.4391	0.8543		1.230		1.0000	0.9372		1.847	

Table 2. continued

$x_1$	$\rho$		$\eta$		$x_1$	$\rho$		$\eta$	
	g·cm <sup>-3</sup>		mPa·s			g·cm <sup>-3</sup>		mPa·s	
	T/K = 308.15					T/K = 313.15			
0.0000	0.8050		3.478		0.0000	0.8011		2.852	
0.0826	0.8116		2.940		0.0826	0.8076		2.412	
0.1625	0.8188		2.449		0.1625	0.8145		1.989	
0.2415	0.8262		1.999		0.2415	0.8218		1.604	
0.3506	0.8374		1.482		0.3506	0.8329		1.151	
0.4400	0.8474		1.141		0.4400	0.8427		0.862	
0.5603	0.8621		0.849		0.5603	0.8573		0.627	
0.6494	0.8741		0.773		0.6494	0.8692		0.576	
0.7394	0.8872		0.816		0.7394	0.8823		0.647	
0.8500	0.9050		1.054		0.8500	0.9000		0.910	
0.9392	0.9207		1.411		0.9392	0.9158		1.256	
1.0000	0.9326		1.694		1.0000	0.9277		1.546	

<sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.01$  K,  $u(x) = 0.0001$ ; the combined expanded uncertainty  $U_c$  is  $U_c(\rho) = 2 \cdot 10^{-2}$  kg·m<sup>-3</sup> and for viscosity  $U_c$  is  $U_c(\eta)$  is  $2 \cdot 10^{-3}$  mPa·s (0.95 level of confidence).

Table 3. Parameters  $A_k$  and Standard Deviations,  $\sigma$ , for Cyclohexanone + 2-Alkanols at Different Temperatures

		T/K	$A_0$	$A_1$	$A_2$	$\sigma$
cyclohexanone + 2-propanol	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	298.15	0.820	0.027	0.080	0.002
		303.15	1.068	0.096	0.016	0.007
		308.15	1.328	0.051	0.045	0.008
		313.15	1.496	0.069	0.161	0.005
	$\Delta\eta$ (mPa·s)	298.15	4.080	0.737	0.224	0.005
		303.15	3.629	0.683	0.151	0.004
		308.15	3.314	0.635	0.134	0.007
		313.15	3.014	0.671	0.299	0.002
cyclohexanone + 2-butanol	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	298.15	0.996	0.036	0.043	0.004
		303.15	1.302	0.071	0.027	0.003
		308.15	1.524	0.053	0.132	0.005
		313.15	1.845	0.139	0.141	0.004
	$\Delta\eta$ (mPa·s)	298.15	4.991	1.745	0.541	0.005
		303.15	4.178	1.216	0.264	0.005
		308.15	3.591	0.802	0.595	0.003
		313.15	3.385	0.957	0.438	0.008
cyclohexanone + 2-pentanol	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	298.15	1.283	0.128	0.019	0.005
		303.15	1.432	0.140	0.006	0.009
		308.15	1.740	0.014	0.013	0.008
		313.15	1.988	0.050	0.048	0.009
	$\Delta\eta$ (mPa·s)	298.15	5.654	0.861	0.180	0.003
		303.15	5.175	0.828	0.474	0.009
		308.15	4.628	0.887	0.300	0.004
		313.15	4.087	1.022	0.188	0.007
cyclohexanone + 2-hexanol	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	298.15	1.656	0.005	0.176	0.006
		303.15	1.859	0.014	0.348	0.005
		308.15	2.033	0.042	0.476	0.008
		313.15	2.404	0.034	0.424	0.008
	$\Delta\eta$ (mPa·s)	298.15	6.494	0.333	0.285	0.005
		303.15	5.994	0.494	0.715	0.005
		308.15	5.475	0.921	0.153	0.009
		313.15	4.899	1.055	0.683	0.005
cyclohexanone + 2-heptanol	$V_m^E$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	298.15	1.939	0.150	0.022	0.008
		303.15	2.212	0.114	0.039	0.004
		308.15	2.470	0.099	0.279	0.007
		313.15	2.739	0.042	0.383	0.005
	$\Delta\eta$ (mPa·s)	298.15	7.334	1.516	0.628	0.006
		303.15	6.957	1.503	0.316	0.005
		308.15	6.463	1.224	0.480	0.008
		313.15	5.918	1.312	0.61	0.005

Table 4. Partial Molar Volumes at Infinite Dilution,  $\bar{V}_{m,i}^0$  for Cyclohexanone + 2-Alkanols at Different Temperatures

system	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
Cyclohexanone + 2-Propanol				
$\bar{V}_{m,1}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	105.00	105.68	106.55	107.28
$\bar{V}_{m,2}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	77.77	78.53	79.20	79.93
Cyclohexanone + 2-Butanol				
$\bar{V}_{m,1}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	105.18	105.98	106.76	107.70
$\bar{V}_{m,2}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	93.34	94.21	94.83	95.60
Cyclohexanone + 2-Pentanol				
$\bar{V}_{m,1}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	105.55	106.19	106.92	107.72
$\bar{V}_{m,2}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	110.64	111.34	112.39	113.28
Cyclohexanone + 2-Hexanol				
$\bar{V}_{m,1}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	105.91	106.66	107.36	108.30
$\bar{V}_{m,2}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	127.84	128.72	129.63	130.64
Cyclohexanone + 2-Heptanol				
$\bar{V}_{m,1}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	106.07	106.86	107.69	108.57
$\bar{V}_{m,2}^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )	144.93	145.90	147.01	147.96

It has been pointed out that excess molar volumes are the consequence and the sum of some different contributions deriving from a structural modification (stabilization of particular rotamers and conformers) of the mixed species, changes in the free volumes, and interstitial accommodation of unlike molecules. Furthermore, the specific intermolecular interactions that take place during the mixing process can be classified as follows: (i) favorable interactions (attractive and charge transfer) between polar groups ( $-\text{C}=\text{O}$  and  $-\text{OH}$ ), responsible for a negative contribution to  $V_m^E$ , (ii) unfavorable interactions involving polar substituents and apolar groups ( $-\text{CH}_2-$  and alkyl chains). In this light, we can assert that the positive deviations of  $V_m^E$  for the cyclohexanone and 2-alkanols system should be dominated by steric hindrances of molecule components which overcome each effect due to specific interactions between different species.

Figure 1 shows that  $V_m^E$ , at equimolar concentrations of cyclohexanone, increases with the increase in carbon number of 2-alkanols. This fact can be described by considering the steric-hindrance effects of the heterocyclic ring of the cyclohexanone and of the alkyl chain of the 2-alkanols, because the hydrophobic character of the 2-alkanol is amplified by an increase in chain length and, consequently, the molecular interactions between 2-alkanol and cyclohexanone molecules weaken.

The partial molar volumes  $\bar{V}_{m,i}$  in these mixtures were calculated over the whole composition range using eqs 4 and 5.<sup>16,17</sup>

$$\bar{V}_{m,1} = V_m^E + V_{m,1}^* + (1 - x_1)(\partial V_m^E / \partial x_1)_{T,P} \quad (4)$$

$$\bar{V}_{m,2} = V_m^E + V_{m,2}^* - x_1(\partial V_m^E / \partial x_1)_{T,P} \quad (5)$$

where  $V_{m,1}^*$  and  $V_{m,2}^*$  are pure molar volumes of components 1 and 2, respectively. The partial properties at infinite dilution are of interest since at the limit of infinite dilution the solute–solvent interactions disappear and only interactions present are solute–solvent interactions. Values of partial molar volumes at infinite dilution  $\bar{V}_{m,i}^0$  are in Table 4.

Partial molar volumes at infinite dilution of each component are not very different from the corresponding molar volumes  $V_{m,i}^*$ . Partial molar volumes close to pure component molar volumes indicate ideal behavior. As a matter of fact, in ideal solutions, partial molar volumes are equal to the pure component molar volume over the whole composition range.  $\bar{V}_{m,i}^0$  increase slightly with increasing temperature.

**Dynamic Viscosities.** The viscosity deviation can be calculated as

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (6)$$

where  $\eta$  is the viscosity of the mixture and  $\eta_1$  and  $\eta_2$  are pure component viscosities. The values of  $\eta$  for binary systems are listed in Table 2. The uncertainty for viscosity deviation is  $\pm 4 \cdot 10^{-3}$  mPa·s. The  $\Delta\eta$  values were fitted to Redlich–Kister eq 2, and the adjustable parameters and standard deviations are given in Table 3.

The viscosity deviations for the mixtures of cyclohexanone with the 2-alkanols at 298.15 K are presented graphically in Figure 2. It is observed that the  $\Delta\eta$  values are negative for all of

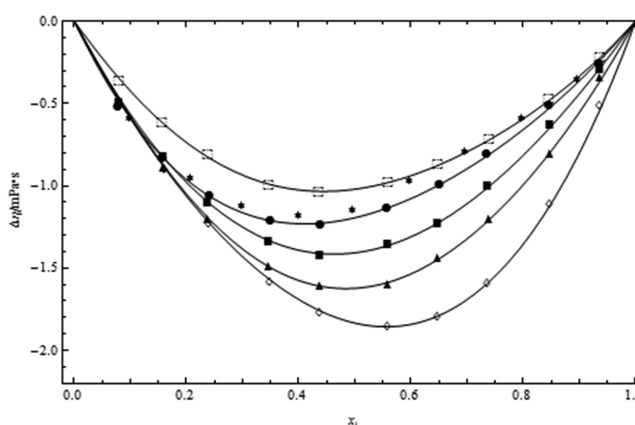


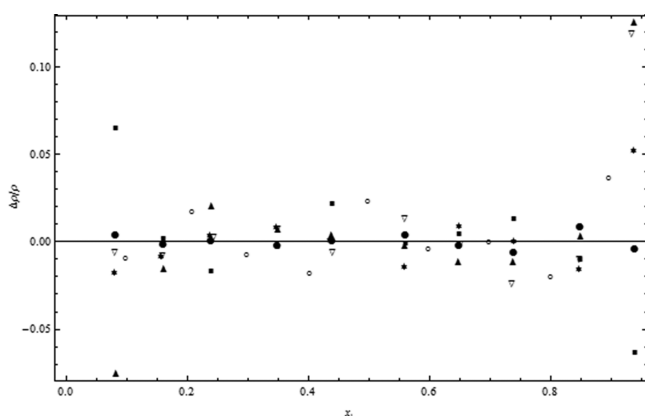
Figure 2. Viscosity deviations  $\Delta\eta$  vs mole fraction of cyclohexanone, for binary mixtures of cyclohexanone with  $\square$ , 2-propanol;  $\bullet$ , 2-butanol;  $\star$ , ref 19 for 2-butanol;  $\blacksquare$ , 2-pentanol;  $\blacktriangle$ , 2-hexanol;  $\diamond$ , 2-heptanol; at 298.15 K. The solid curves were calculated from coefficients of eq 2 given in Table 3.

the investigated systems and tend systematically to larger negative values with an increase in size of the 2-alkanol; the negative values of  $\Delta\eta$  for all of the binary systems fall in the order: 2-heptanol > 2-hexanol > 2-pentanol > 2-butanol > 2-propanol. Our results are in agreement with Vogel and Weiss<sup>18</sup> who have shown that mixtures with a positive deviation of Raoult's law and without strong specific interactions present the negative viscosity deviation.

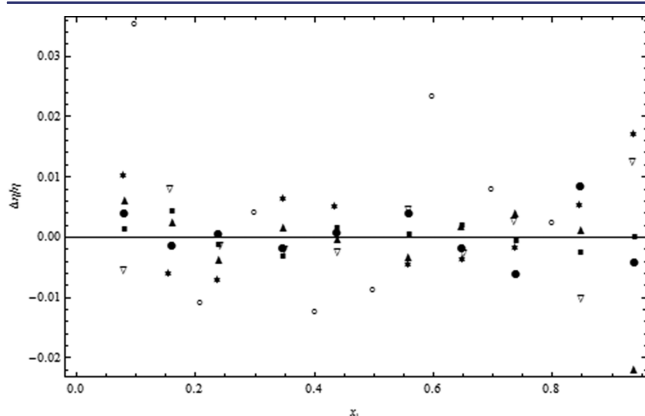
Also in Figures 1 and 2, we compare our data of excess molar volumes and viscosity deviations for binary mixtures of



cyclohexanone and 2-butanol at 298.15 K with data of ref 19. The discrepancy between experimental data and the literature value may be due to the difference between the applied apparatus. In Figures 3 and 4 the differences between experimental and literature data and the fitted equation are graphically represented.



**Figure 3.** Differences  $\Delta\rho = \rho(\text{experimental}) - \rho(\text{calculated})$  between experimental and literature data and the fitted equation for the cyclohexanone and  $\star$ , 2-propanol;  $\nabla$ , 2-butanol;  $\circ$ , ref 19 for 2-butanol;  $\blacksquare$ , 2-pentanol;  $\bullet$ , 2-hexanol;  $\blacktriangle$ , 2-heptanol; at 298.15 K.



**Figure 4.** Differences  $\Delta\eta = \eta(\text{experimental}) - \eta(\text{calculated})$  between experimental and literature data and the fitted equation for the cyclohexanone and  $\star$ , 2-propanol;  $\nabla$ , 2-butanol;  $\circ$ , ref 19 for 2-butanol;  $\blacksquare$ , 2-pentanol;  $\bullet$ , 2-hexanol;  $\blacktriangle$ , 2-heptanol; at 298.15 K.

## CONCLUSION

Excess molar volumes and viscosity deviations for mixtures of cyclohexanone and 2-alkanols were obtained from experimental results and fitted by the Redlich–Kister type equation to derive the coefficients and estimate the standard error. For mixtures of cyclohexanone with used 2-alkanols,  $V_m^E$  is positive, and  $\Delta\eta$  is negative over the entire range of mole fraction. It has been concluded that an increase in chain length of the 2-alkanol causes a greater 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.

## ASSOCIATED CONTENT

### Supporting Information

Excess molar volumes, partial molar volumes, and viscosity deviations for the mixtures of cyclohexanone and 2-alkanol.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [m.almasi@khuzestan.srbiau.ac.ir](mailto:m.almasi@khuzestan.srbiau.ac.ir). Tel.: + 98-611-4431018.

## ACKNOWLEDGMENTS

The authors thank the University authorities for providing the necessary facilities to carry out the work.

## REFERENCES

- Venkatesu, P.; Prabhakar Rao, M. V. Excess volumes of *N,N*-Dimethylformamide + Cyclohexanone + Alkanols at 303.15 K. *J. Chem. Eng. Data* **1997**, *42*, 90–92.
- Gascon, I.; Mainar, A. M.; Royo, F. M.; Urieta, J. S. Experimental Viscosities and Viscosity Predictions of the Ternary Mixture (Cyclohexane + 1,3-Dioxolane + 2-Butanol) at 298.15 and 313.15 K. *J. Chem. Eng. Data* **2000**, *45*, 751–755.
- García, B.; Alcalde, R.; Aparicio, S.; Leal, J. M.; Matos, J. S. Solute–Solvent interactions in the (*N,N*-Dimethylformamide + *N*-Methylformamide + Water) Ternary System at 298.15 K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2866–2871.
- Pineiro, M. M.; Mascato, E.; Mosteiro, L.; Legido, J. L. Mixing Properties of the Ternary Mixture Methyl *tert*-Butyl Ether + 1-Butanol + Decane at 298.15 K. *J. Chem. Eng. Data* **2003**, *48*, 758–762.
- Almasi, M.; Shojabakhtiar, M. Excess molar volumes of diisopropylamine + ( $C_1$ – $C_5$ ) alkan-1-ols: Application of the ERAS model and cubic EOS. *Thermochim. Acta* **2011**, *523*, 105–110.
- Almasi, M.; Mousavi, L. Excess molar volumes of binary mixtures of aliphatic alcohols ( $C_1$ – $C_5$ ) with Nitromethane over the temperature range 293.15 to 308.15 K: Application of the ERAS model and cubic EOS. *J. Mol. Liq.* **2011**, *163*, 46–52.
- Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.
- Aralaguppi, I. M.; Jadar, V. C.; Aminabhavi, M. T. Density, Refractive Index, Viscosity, and Speed of Sound in Binary Mixtures of Cyclohexanone with Hexane, Heptane, Octane, Nonane, Decane, Dodecane, and 2,2,4-Trimethylpentane. *J. Chem. Eng. Data* **1999**, *44*, 435–440.
- González, B.; Domínguez, A.; Tojo, J. Viscosities, Densities, and Speed of Sound of the Cycloalkanes with Secondary Alcohols at  $T = (293.15, 298.15, \text{ and } 303.15)$  K: New UNIFAC-VISCO Interaction Parameters. *J. Chem. Eng. Data* **2006**, *51*, 1076–1087.
- Hasan, M.; Shirude, F. D.; Hiray, P. A.; Sawant, B. A.; Kadam, B. U. Densities, viscosities and ultrasonic velocities of binary mixtures of methylbenzene with hexan-2-ol, heptan-2-ol and octan-2-ol at  $T = 298.15$  and 308. *Fluid Phase Equilib.* **2007**, *252*, 88–95.
- Redlich, O. J.; Kister, A. T. Thermodynamic of nonelectrolyte solutions: algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
- Cheng, Y.; Page, M.; Jolicoeur, C. Comparative study of hydrophobic effects in water/alcohol and water/ethylene glycol, water/ethanolamine, water/ethylenediamine, and water/2-methoxyethanol systems. *J. Phys. Chem.* **1993**, *97*, 7359–7363.
- Tamura, K.; Saito, M.; Yamada, T. Ternary Excess Molar Enthalpies for Methanol or Ethanol + 1-Propanol + 2-Propanol at the Temperature 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 626–630.
- Lebed, V. A.; Oleg, N. O.; Vyunnik, N. I. Properties of 1–1 electrolytes solutions in ethylene glycol at temperatures from 5 to 175 °C, Part 1: Conductance measurements and experimental data treatment. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2097–2101.
- Provencal, R. A.; Casaes, R. N.; Roth, K.; Paul, J. B.; Chapo, C. N.; Saykally, R. J.; Tschumper, G. S.; Schaefer, H. F. Hydrogen Bonding in Alcohol Clusters: A Comparative Study by Infrared Cavity

Ringtown Laser Absorption Spectroscopy. *J. Phys. Chem. A* **2000**, *104*, 1423–1429.

(16) Lide, R. D. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 2000; Section 6, pp 180–184.

(17) Davis, I. M. An analytic model for the excess properties of binary liquid mixtures. *Thermochim. Acta* **1983**, *63*, 67–82.

(18) Vogel, H.; Weiss, A. Transport properties of liquids. III. Viscosity of athermal liquid mixtures. *Ber. Bunsen-Ges., Phys. Chem.* **1982**, *86*, 193–198.

(19) Riggio, R.; Martinez, H. E.; De Salas, N. Z.; de Tolgo, M. D. Excess properties for cyclohexanone + butanols at 298.15 K. *Can. J. Chem.* **1995**, *73*, 1274–1277.