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Densities, Viscosities, and Refractive Indices of Binary Mixtures of Acetophenone and 2-Alkanols

Mohammad Almasi and Hossein Iloukhani*

Department of Physical Chemistry, Faculty of Chemistry, University of Bu-Ali Sina, Hamedan 65174, Iran

Densities, viscosities, and refractive indices of mixing of acetophenone 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 K and ambient pressure. Excess molar volumes V_m^E, viscosity deviations $\Delta\eta$, and refractive index deviations Δn_D were calculated and correlated by the Redlich−Kister type function to derive the coefficients and estimate the standard error. For mixtures of acetophenone with used 2-alkanols, V_m^E is positive, except with 2-propanol over the entire range of the composition. $\Delta\eta$ is negative, and Δn_D is positive over the entire range of mole fraction. The effect of chain length of the 2-alkanols on the excess molar volumes, viscosity, and refractive index deviations of its mixtures with acetophenone is discussed. The experimental results have been used to test the applicability of the Prigogine−Flory−Patterson (PFP) theory. The agreement between theoretical and experimental results is satisfactory for acetophenone + 2-alkanol systems.

Introduction

The thermodynamic and transport properties of liquids and liquid mixtures have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, and fluid flow.[1] Excess and deviation properties of binary mixtures are complex properties because they depend not only on solute−solute, solvent−solvent, and solute−solvent interactions but also on the structural effects arising from interstitial accommodation. Knowledge of several properties at different temperatures is required for engineering design and for subsequent operations.[2] Acetophenone, as an important industrial chemical, is widely used as an ingredient of flavor and fragrance in soaps, detergents, cosmetics, and perfumes. It has also been used as an important intermediate for pharmaceuticals and agrochemicals. The thermodynamic properties of systems containing acetophenone are helpful to better understand molecular interaction and to design and simulate the different processes of separation.[3]

This paper is a part of an ongoing research effort to measure and characterize the properties of mixtures containing 2-alkanols.[4,5] It reports the densities, viscosities, refractive indices, excess molar volumes, and viscosity and refractive index deviations of mixing for the binary mixtures of {acetophenone + 2-alkanols} at T = 298.15 K. The influence of chain length on the thermodynamic properties has been investigated. No reported mixing properties of these studied systems at these temperatures have been found.

Experimental Section

Chemicals. Acetophenone, 2-propanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol were purchased from Merck with purity higher than 99 % (all) and used without further purifications. The purity of reagents was checked by comparing the measured densities, viscosities, and refractive indices at 298.15

Table 1. Experimental and Literature Values of Densities ρ, Viscosities η, and Refractive Indices n_D of Acetophenone, 2-Propanol, 2-Butanol, 2-Pentanol, 2-Hexanol, and 2-Heptanol at T = 298.15 K

| | ρ | | η | | n_D | |
| | g·cm⁻³ | | mPa·s | | | |
compd.	exptl.	lit.	exptl.	lit.	exptl.	lit.
acetophenone	1.02330	1.02381[a]	1.678	1.6720[b]	1.5308	1.5342[a]
2-propanol	0.78098	0.78126[a]	2.044	2.0436[c]	1.3745	1.3752[a]
2-butanol	0.80256	0.80260[a]	3.132	3.1150[d]	1.3948	1.3950[a]
2-pentanol	0.80524	0.80540[a]	3.478	3.47[b]	1.4045	1.4044[a]
2-hexanol	0.81014	0.81025[e]	4.100	4.204[e]	1.4116	
2-heptanol	0.81333	0.8134[a]	5.331	5.346[e]	1.4188	

[a] From ref 7. [b] From ref 8. [c] From ref 2. [d] From ref 6. [e] From ref 4.

K with those reported in the literature;[2,4,6−8] the resultant values are in good agreement with values found in the literature and reported in Table 1.

Apparatus and Procedure. 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 ± 1·10⁻⁵ g·cm⁻³. The apparatus was calibrated once a day with dry air and bidistillated water. The temperature in the cell was regulated to ± 0.01 K with a solid state thermostat. Viscosities were measured with an Ubbleohde viscometer with an uncertainty of ± 2·10⁻³ mPa·s. The temperature in the cell was regulated to ± 0.01 K.

Refractive indices were measured using a high accuracy Abbe refractometer. The uncertainty of refractive index measurement was estimated to be ± 0.0004 units. The measurement method relies on an optical detection of the critical angle at the wavelength of the sodium D line (589.6 nm). 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 ± 1·10⁻⁴.

* To whom correspondence should be addressed. E-mail: iloukhani@basu.ac.ir. Tel./Fax: +98 0811 8271061.
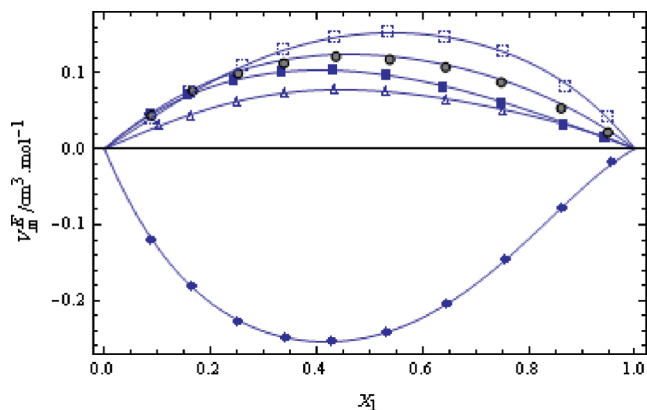
Figure 1. Excess molar volumes V_m^E vs mole fraction of acetophenone for binary mixtures of acetophenone with: ♦, 2-propanol; △, 2-butanol; ■, 2-pentanol; ●, 2-hexanol; □, 2-heptanol; at $T = 298.15$ K. The solid curves were calculated from coefficients of eq 2 given in Table 3.

Results and Discussion

Densities and Excess Molar Volumes. The excess molar volumes of the solutions of molar composition x were calculated at $T = 298.15$ K from the densities of the pure liquids and their mixtures according to the following equation

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

where ρ is the density of the mixture, ρ_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 [acetophenone (1) + 2-alkanols (2)] are measured and plotted against mole fraction of acetophenone at $T = 298.15$ K in Figure 1. The uncertainty for excess molar volume is $\pm 1 \cdot 10^{-3}$ cm$^3 \cdot$mol^{-1}. The values of density and V_m^E for the binary mixtures are in Table 2. Each set of results were fitted using a Redlich−Kister polynomial,[9] which for binary mixtures is

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

where $Y^E \equiv V_m^E$, $\Delta\eta$, or Δn_D and x_1 is the mole fraction of acetophenone. 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 σ with

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

where Y and Y_{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 σ.

The excess molar volume of acetophenone with 2-propanol is negative, but for the other binary mixtures containing 2-butanol, 2-pentanol, 2-hexanol, and 2-heptanol it is positive over the whole range of mole fraction.

Roux and Desnoyers[10] suggested that V_m^E is the resultant contribution from several opposing effects. These may be divided arbitrarily into three types, namely, chemical, physical, and structural. Physical contributions, that is, nonspecific

Table 2. Densities ρ, Viscosities η, Refractive Indices n_D, Excess Molar Volumes V_m^E, Viscosity Deviations $\Delta\eta$, and Refractive Index Deviations Δn_D of Acetophenone and 2-Alkanols at $T = 298.15$ K

x_1	ρ g·m^{-3}	V_m^E cm^3·mol^{-1}	η mPa·s	$\Delta\eta$ mPa·s	n_D	Δn_D
		Acetophenone (1) + 2-Propanol (2)				
0.0000	0.78098		2.044		1.3745	
0.0892	0.81369	−0.120	1.678	−0.333	1.3971	0.0023
0.1658	0.83920	−0.181	1.503	−0.480	1.4181	0.0072
0.2517	0.86544	−0.227	1.399	−0.553	1.4393	0.0118
0.3432	0.89091	−0.248	1.354	−0.564	1.4601	0.0163
0.4297	0.91304	−0.254	1.352	−0.534	1.4775	0.0194
0.5345	0.93756	−0.241	1.367	−0.481	1.4953	0.0213
0.6466	0.96131	−0.204	1.421	−0.386	1.5099	0.0203
0.7561	0.98235	−0.145	1.484	−0.283	1.5195	0.0160
0.8635	1.00126	−0.079	1.556	−0.172	1.5255	0.0094
0.9568	1.0165	−0.017	1.626	−0.067	1.5276	0.0013
1.0000	1.02330		1.678		1.5308	
		Acetophenone (1) + 2-Butanol (2)				
0.0000	0.80256		3.132		1.3946	
0.1031	0.83043	0.032	2.345	−0.637	1.4255	0.0135
0.1635	0.84612	0.044	2.009	−0.885	1.4443	0.0226
0.2517	0.86813	0.062	1.705	−1.060	1.4669	0.0315
0.3422	0.88980	0.073	1.544	−1.090	1.4877	0.0388
0.4361	0.91131	0.079	1.461	−1.037	1.5044	0.0422
0.5330	0.93256	0.076	1.460	−0.897	1.5189	0.0436
0.6461	0.95627	0.065	1.506	−0.687	1.5314	0.0416
0.7517	0.97734	0.051	1.561	−0.477	1.5367	0.0340
0.8675	0.99934	0.032	1.617	−0.254	1.5351	0.0189
0.9462	1.01372	0.016	1.650	−0.106	1.5336	0.0087
1.0000	1.02330		1.678		1.5308	
		Acetophenone (1) + 2-Pentanol (2)				
0.0000	0.80524		3.478		1.4045	
0.0917	0.82619	0.047	2.767	−0.546	1.4440	0.0279
0.1629	0.84236	0.072	2.314	−0.871	1.4676	0.0425
0.2502	0.86204	0.090	1.875	−1.152	1.4920	0.0559
0.3416	0.88241	0.101	1.626	−1.237	1.5111	0.0635
0.4371	0.90349	0.104	1.502	−1.189	1.5250	0.0653
0.5387	0.92571	0.097	1.489	−1.019	1.5333	0.0608
0.6442	0.94851	0.081	1.534	−0.784	1.5353	0.0495
0.7547	0.97208	0.061	1.605	−0.515	1.5348	0.0350
0.8716	0.9967	0.032	1.658	−0.251	1.5321	0.0175
0.949	1.01277	0.015	1.669	−0.101	1.5300	0.0057
1.0000	1.02330		1.678		1.5308	
		Acetophenone (1) + 2-Hexanol (2)				
0.0000	0.81014		4.100		1.4116	
0.0902	0.82784	0.047	3.193	−0.688	1.4485	0.0268
0.1678	0.84327	0.080	2.658	−1.035	1.4782	0.0477
0.2536	0.86063	0.103	2.160	−1.326	1.5037	0.0635
0.3400	0.87839	0.116	1.802	−1.474	1.5247	0.0745
0.4382	0.89886	0.125	1.506	−1.532	1.5425	0.0808
0.5395	0.92038	0.121	1.343	−1.450	1.5556	0.0818
0.6451	0.94323	0.111	1.273	−1.264	1.5615	0.0749
0.7500	0.96634	0.091	1.313	−0.970	1.5593	0.0599
0.8628	0.99172	0.057	1.399	−0.610	1.5505	0.0371
0.9511	1.01193	0.025	1.556	−0.234	1.5394	0.0149
1.0000	1.02330		1.678		1.5308	
		Acetophenone (1) + 2-Heptanol (2)				
0.0000	0.81333		5.330		1.4188	
0.0913	0.82912	0.040	4.282	−0.715	1.4489	0.0215
0.1631	0.84187	0.075	3.572	−1.162	1.4748	0.0406
0.2637	0.86039	0.110	2.763	−1.603	1.5079	0.0636
0.3425	0.87543	0.129	2.296	−1.783	1.5298	0.0774
0.4374	0.8942	0.146	1.908	−1.824	1.5535	0.0911
0.5387	0.91507	0.154	1.662	−1.701	1.5708	0.0971
0.6446	0.93792	0.147	1.550	−1.425	1.5820	0.0961
0.7571	0.96335	0.127	1.548	−1.017	1.5816	0.0822
0.8733	0.99114	0.081	1.606	−0.535	1.5669	0.0529
0.9542	1.01138	0.041	1.651	−0.194	1.5486	0.0240
1.0000	1.02330		1.678		1.5308	

interactions between the real species present in the mixture, contribute a positive term to V_m^E. The chemical or specific intermolecular interactions result in a volume decrease, and these

Table 3. Parameters and Standard Deviations of Equations 2 and 3 for Acetophenone + 2-Alkanols at $T = 298.15$ K

system			A_0	A_1	A_2	A_3	σ
acetophenone + 2-propanol	V_m^E	$cm^3 \cdot mol^{-1}$	−0.9898	−0.3139	−0.0398	−0.3456	0.001
	$\Delta\eta$	mPa·s	−1.9836	−1.2760	−1.1210	−0.4625	0.005
	Δn_D		0.0849	−0.0284	−0.0470	0.0138	0.0006
acetophenone + 2-butanol	V_m^E	$cm^3 \cdot mol^{-1}$	0.3071	0.0744	−0.0070	−0.0760	0.001
	$\Delta\eta$	mPa·s	−3.7934	−3.0669	−1.2225	0.03376	0.006
	Δn_D		0.1768	−0.0164	−0.0205	0.0136	0.0008
acetophenone + 2-pentanol	V_m^E	$cm^3 \cdot mol^{-1}$	0.3990	0.1515	0.0340	0.0233	0.001
	$\Delta\eta$		−4.4058	−3.6164	−0.0149	1.3604	0.009
	Δn_D		0.2514	0.1049	−0.0265	0.0152	0.0004
acetophenone + 2-hexanol	V_m^E	$cm^3 \cdot mol^{-1}$	0.4949	0.0646	0.0721	−0.0199	0.001
	$\Delta\eta$	mPa·s	−5.9465	−1.7103	−0.8655	−0.2655	0.016
	Δn_D		0.3292	0.0128	−0.0059	0.0022	0.0006
acetophenone + 2-heptanol	V_m^E	$cm^3 \cdot mol^{-1}$	0.6066	−0.0913	0.0617	−0.1276	0.002
	$\Delta\eta$	mPa·s	−7.0810	−2.8936	0.6376	0.6982	0.003
	Δn_D		0.3833	−0.1133	−0.0001	−0.0482	0.0008

Table 4. Parameters of Pure Components Used in Flory Theory at $T = 298.15$ K

component	P*	V*	T*
	$J \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$	K
acetophenone	249.652	95.9907	5614.68
2-propanol	479.031	62.9024	5163.6
2-butanol	347.579	75.5056	5947.78
2-pentanol	190.82	89.4952	5396.01
2-hexanol	210.706	103.181	5269.12
2-heptanol	231.155	116.803	5279.53

include charge-transfer type forces and other complex-forming interactions. This effect contributes negative values to V_m^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume. In other words, structural contributions arising from geometrical fitting (interstitially accommodated) of one component into the other due to the differences in the free volume and molar volume between components lead to a negative contribution to V_m^E.

The negative V_m^E values for 2-propanol + acetophenone systems indicate strong specific interactions through dipolar association between 2-propanol and acetophenone molecules over the entire composition range, revealing that the physical forces between the dissimilar molecules are dominant in these investigated mixtures.

The positive V_m^E values for mixtures of acetophenone with other 2-alkanols can be ascribed to the dominance of the disruption of H-bonds between alkanols over dipole−dipole interactions between the 2-alkanol and the acetophenone molecule.

Figure 1 shows that V_m^E, at equimolar concentrations of acetophenone, increases with the increasing of carbon number of 2-alkanols. It may be due to the increasing difficulty to form crossed associations between acetophenone and 2-alkanols with increasing steric hindrance and aliphatic chain of 2-alkanols.

Theoretical Analysis. The Prigogine−Flory−Patterson (PFP) theory[11−13] has been commonly employed to analyze excess thermodynamic function. This theory has been used to interpret the results of measurements of the excess properties of a number of binary systems formed by molecular species which differ in size and shape. Although in the development of the theory hydrogen bonds and interactions of strong electrostatic nature are specifically excluded, a purely empirical application of the Flory formalism can still provide an interesting correlation between the excess volumes of more complex mixtures. In fact, and despite the ionic character of the IL (ionic liquid) systems, the use of Flory-type theories has proven successful in predicting and modeling both the excess properties and the fluid-phase behavior of IL-containing mixtures.[14−17] The PFP theory considered a molecule to be made of up of equal segments (isometric portions), the effective number. Each segment has intermolecular contact sites capable of interacting with neighboring sites.

According to the PFP theory, V_m^E calculations include three contributions: (i) interactional, which is proportional to the (χ_{12}) parameters; (ii) the free volume contribution, which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components; and (iii) the (P*) contribution, which depends both on the difference of internal pressures and differences of reduced volumes of the components. The V_m^E was calculated by means of the PFP theory with the three contributions.

The values of pure parameters for the pure liquid components and the mixture are obtained by Flory theory.[13] The parameters for the pure liquid components derived using Flory theory are in Table 4.

The values of the thermal expansion coefficient and isothermal compressibility for the pure components are obtained from the literature. To obtain V_m^E, it is necessary to find the interactional parameter (χ_{12}) which was obtained by fitting the theory to experimental values of V_m^E for each one of the binary system. Table 5 presents the calculated equimolar values of the three contributions to V_m^E, together with the interactional parameter (χ_{12}). An analysis of each of the three contributions to V_m^E shows that, except for 2-propanol, the interactional contribution is always positive in all binary mixtures of acetophenone and 2-alkanols and seems to be the most important

Table 5. Calculated Values of Three Contributions of the PFP Theory to V_m^E for (2-Alkanols + Acetophenone) Mixtures at $T = 298.15$ K

system	$\chi_{1,2}$	interactional	free volume	P*
	$J \cdot cm^{-3}$			
acetophenone (1) + 2-propanol (2)	−18.7	−0.4551	−0.0258	0.3420
acetophenone (1) + 2-butanol (2)	7.8	0.2092	−0.0100	−0.1208
acetophenone (1) + 2-pentanol (2)	6.1	0.1898	−0.0059	−0.0798
acetophenone (1) + 2-hexanol (2)	7	1.8187	−0.0085	0.3766
acetophenone (1) + 2-heptanol (2)	6.07	0.2137	−0.0176	−0.0428
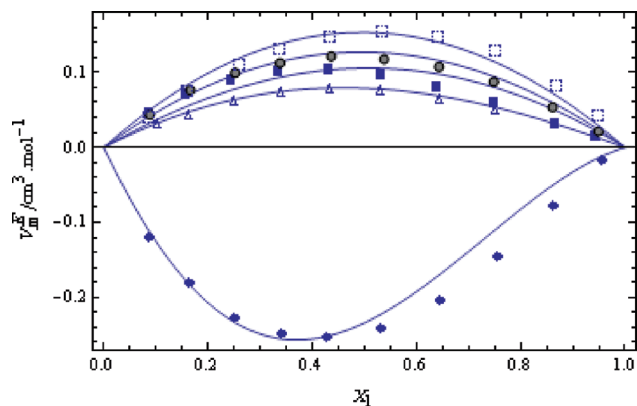
Figure 2. Plot of excess molar volume V_m^E against the mole fraction of acetophenone for the acetophenone + ◆, 2-propanol; △, 2-butanol; ■, 2-pentanol; ●, 2-hexanol; □, 2-heptanol; at $T = 298.15$ K. The solid lines were calculated by using PFP theory.
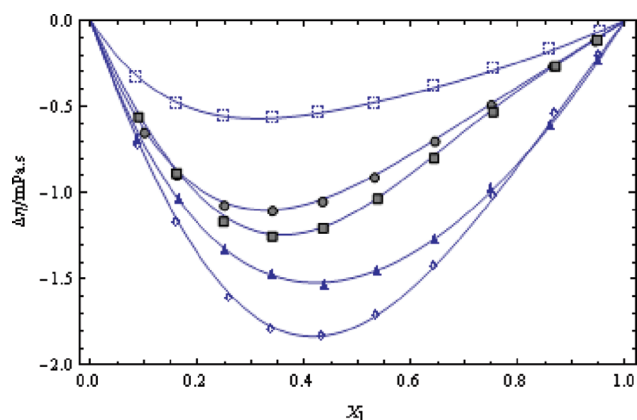
Figure 3. Viscosity deviations of binary mixtures for acetophenone with: ◆, 2-propanol; ●, 2-butanol; ■, 2-pentanol; ▲, 2-hexanol; and ◇, 2-heptanol; at $T = 298.15$ K. Solid lines represent the Redlich–Kister fit.

to explain the V_m^E behavior for system studied. The free volume effect is negative, and it seems to have little significance for the system studied. The third contribution is due to the difference in internal pressure and in reduced volume of the components for system studied. Figure 2 shows the calculated excess molar values from eq 1 and the excess molar values predicted by PFP theory for acetophenone and 2-alkanol systems.

Dynamic Viscosities. The viscosity deviation can be calculated as

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \qquad (4)$$

where η is the viscosity of the mixture and η_1 and η_2 are the viscosity of the pure components. The values η and $\Delta\eta$ for binary systems are listed in Table 2, and the values of $\Delta\eta$ are shown in Figure 3. The uncertainty for viscosity deviation is ± $4 \cdot 10^{-3}$ mPa·s. The $\Delta\eta$ values were fitted to the Redlich–Kister eq 2, and the adjustable parameters and standard deviations are given in Table 3.

The values of $\Delta\eta$ for the system containing acetophenone + 2-alkanols are asymmetrical and all negative throughout the whole concentration range and became the more negative as the length of the 2-alkanol chain increased.

From these observations, we can conclude that for these systems the structure of the alcohol is broken when the mixture is formed. It appears that alcohols with −OH groups located almost at the end of the molecular chain are more suitable to form hydrogen bonds with acetophenone. Consequently, their η values are lower than those for pure systems.
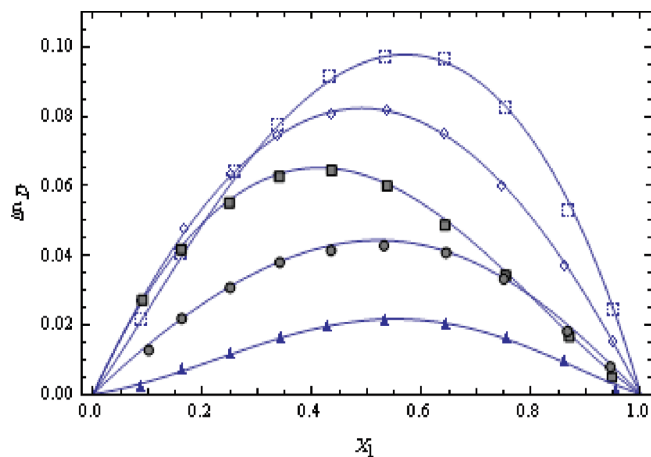
Figure 4. Refractive index deviations on mixing of acetophenone with: ▲, 2-propanol; ●, 2-butanol; ■, 2-pentanol; ◇, 2-hexanol; □, 2-heptanol; at $T = 298.15$ K. Solid lines represent the Redlich–Kister fit.

Refractive Index. Refractive index deviations were defined by

$$\Delta n_D = n_D - \phi_1 n_{D1} - \phi_2 n_{D2} \qquad (5)$$

where n_D, n_{Di}, and ϕ_i are the refractive index of the mixture, the refractive index of the pure component i, and the volume fraction of pure component i, respectively. The volume fraction of pure component i is defined as

$$\phi_i = \frac{x_i V_i}{\sum\limits_{i=1}^{N} x_i V_i} \qquad (6)$$

where V_i is the molar volume of pure component i. The experimental refractive indices of the binary mixtures, n_D and Δn_D, values are listed in Table 2, and the values of Δn_D are shown in Figure 4. The results were fitted by eq 2, and the adjustable parameters and standard deviations are given in Table 3.

It can be seen that the changes in the refractive index of all 2-alkanol mixtures with acetophenone are positive throughout the entire composition range; while the chain length of the 2-alkanol increases, the change in the refractive index becomes more positive.

Conclusions

Excess molar volumes, viscosities, and refractive index deviations for mixtures of acetophenone and 2-alkanols were obtained from experimental results and fitted by the Redlich–Kister type equation. Positive quantities show that dominant factors are physical interactions, and negative values suggested that the main factor in the interactional forces is chemical interactions. The PFP theory has shown good performance in predicting the excess molar volumes of acetophenone and 2-alkanol mixtures.

Acknowledgment

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