Densities, Viscosities, and Refractive Indices for Binary and Ternary Mixtures of *N*,*N*-Dimethylacetamide (1) + 2-Methylbutan-2-ol (2) + Ethyl Acetate (3) at 298.15 K for the Liquid Region and at Ambient Pressure

H. Iloukhani* and K. Khanlarzadeh

Department of Chemistry, Faculty of Science, University of Bu-Ali Sina, Hamadan, Iran

Densities, viscosities, and refractive indices of the ternary system *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2) + ethyl acetate (3) at $T = 298.15$ K and the binary systems *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2), *N*,*N*-dimethylacetamide (1) + ethyl acetate (3), and 2-methylbutan-2-ol (2) + ethyl acetate (3) were measured at $T = 298.15$ K for the liquid region and at ambient pressure for the whole composition range. Excess molar volumes (V^E), deviations in the viscosity ($\Delta\eta$) from the mole fraction average, and deviations in the refractive index (Δn_D) from the volume fraction average for the mixtures were derived from the experimental data. The binary and ternary data of V^E, $\Delta\eta$, and Δn_D were correlated as a function of the mole fraction by using the Redlich−Kister and the Cibulka equations, respectively. The results are consistent with the self-association of alcohol and the polar and nonpolar characters of used ester and amide. McAlister's multibody and Kalidas−Laddha interaction model are used for correlating the kinematic viscosity of binary and ternary mixtures, respectively, with mole fraction. The experimental and the constituted binary and ternary systems are analyzed to discus the nature and strength of intermolecular interactions in these mixtures.

Introduction

This paper is a continuation of our earlier work related to the study of thermodynamic properties of binary and ternary mixtures.[1−7] In recent years, measurements of thermodynamic and transport properties have been adequately employed in understanding the nature of molecular systems and physicochemical behavior in liquid mixtures. The nonrectilinear behavior of above-mentioned properties of liquid mixtures with changing mole fractions is attributed to the difference in size of the molecules and strength of the interactions. Here, we have reported densities (ρ), viscosities (η), and refractive indices (n_D) for the binary and ternary systems formed by three oxygenated compounds, such as *N*,*N*-dimethylacetamide, 2-methylbutan-2-ol, and ethyl acetate at $T = 298.15$ K for the liquid region and at ambient pressure for the whole composition range.

The derived properties (excess molar volumes, V^E; deviations in the viscosity, $\Delta\eta$; and deviations in the refractive index, Δn_D) in combination with other mixing properties provide valuable information for qualitatively analyzing the molecular interactions between molecules. The excess and deviation quantities of binary mixtures have been fitted to the Redlich−Kister equation to determine the coefficients. For correlating the ternary data, the Cibulka equation was used. As far as we know, no ternary data are available for the mixtures investigated in the open literature. This work will also provide a test of the semiempirical McAlister and Kalidas−Laddha model to correlate viscosity of above-mentioned binary and ternary mixtures, respectively.

Experimental Section

Materials. The mole fraction purity of the components from Merck were as follows: *N*,*N*-dimethylacetamide (≥ 99.5 %), 2-methylbutan-2-ol (> 99.5 %), and ethyl acetate (≥ 99 %). Compounds were purified by distillation using a 1 m fractionation column. Densities, viscosities, and refractive indices were measured after distillation, and their values were in good agreement with the values found in the literature,[8] reported in Table 1. The purified compounds were stored in brown glass bottles and fractionally distilled immediately before use.

Apparatus and Procedure. Dynamic viscosities at 298.15 K were measured with an Ubbelohde viscometer. The equation for viscosity, according to Poiseuille's law, is

$$\eta = \rho\upsilon = \rho(kt - c/t) \tag{1}$$

where k and c are the viscometer constants and t, η, and υ are the efflux time, dynamic viscosity, and kinematic viscosity, respectively. The uncertainty of the viscosity measurements was estimated to be less than $\pm 2 \times 10^{-3}$ mPa·s The viscometer was suspended in a thermostated water bath maintained to ± 0.01 K. An electronic digital stopwatch with uncertainty to ± 0.01 s was used for flow time measurements. At least three repetitions of each data point obtained were reproducible to ± 0.05 s, and the results were averaged. Refractive indices were measured using a digital Abbe-type refractometer. The uncertainty of refractive index measurement was estimated to be less than ± 0.0001 units. The density of the compounds and their binary and ternary mixtures were measured with Anton Paar DMA 4500 oscillating U-tube densitometer, operated in the static mode. The uncertaintities were estimated to be within $\pm 1 \times 10^{-5}$ g·cm^{-3}. The temperature in the cell was regulated to ± 0.01 K with solid-state thermostat. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. Airtight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle, and the total mass was recorded. Subsequently, the other component was introduced, and the mass of bottle along with the two components were determined. Ternary mixtures were prepared by mixing the three compo-

* Corresponding author. E-mail: iloukhani@basu.ac.ir.

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Table 1. Comparison of Measured Densities, Viscosities, and Refractive Indices of the Pure Components with Literature Values at 298.15 K

	ρ/(g·cm^{-3})		η/(mPa·s)		n_D	
component	this work	lit.	this work	lit.	this work	lit.
N,*N*-dimethylacetamide	0.93670	0.93665	0.945	0.9437[14]	1.4357	1.4356
2-methylbutan-2-ol	0.80500	0.80498	2.810[a]	2.810[a]	1.4025	1.4024
ethyl acetate	0.89460	0.89455	0. 426	0.426	1.3699	1.3698

[a] At $T = 303.15$ K.

Table 2. Experimental Densities ρ, Viscosities η, Refractive Indices n_D, Excess Molar Volumes V^E, Deviation in the Viscosity $\Delta\eta$, and Deviations in the Refractive Index Δn_D for the Binary Systems at 298.15 K

x_1	ρ/(g·cm^{-3})	η/(mPa·s)	n_D	V^E/(cm^3·mol^{-1})	$\Delta\eta$/(mPa·s)	Δn_D
			N,*N*-Dimethylacetamide (1) + 2-Methylbutan-2-ol (2)			
0.0000	0.80498	3.645	1.4025	0.000	0.000	0.0000
0.0112	0.80665	3.600	1.4031	−0.056	−0.014	0.0003
0.0284	0.80910	3.533	1.4040	−0.125	−0.035	0.0007
0.0423	0.81093	3.480	1.4046	−0.159	−0.051	0.0009
0.0681	0.81429	3.381	1.4058	−0.215	−0.080	0.0014
0.1023	0.81847	3.254	1.4072	−0.246	−0.114	0.0018
0.1613	0.82531	3.041	1.4095	−0.238	−0.168	0.0023
0.2112	0.83081	2.870	1.4113	−0.182	−0.205	0.0026
0.2530	0.83539	2.731	1.4128	−0.124	−0.231	0.0029
0.2912	0.83958	2.608	1.4141	−0.066	−0.250	0.0030
0.3366	0.84460	2.467	1.4156	0.006	−0.269	0.0031
0.3844	0.85011	2.325	1.4171	0.063	−0.282	0.0031
0.4203	0.85429	2.221	1.4182	0.107	−0.289	0.0030
0.4743	0.86087	2.071	1.4198	0.148	−0.293	0.0029
0.5864	0.87518	1.780	1.4230	0.201	−0.281	0.0024
0.6721	0.88670	1.578	1.4254	0.216	−0.252	0.0018
0.7474	0.89747	1.413	1.4276	0.188	−0.214	0.0014
0.8321	0.91006	1.242	1.4302	0.143	−0.156	0.0009
0.9168	0.92322	1.086	1.4329	0.078	−0.084	0.0004
0.9540	0.92918	1.021	1.4341	0.045	−0.048	0.0002
1.0000	0.93670	0.945	1.4357	0.000	0.000	0.0000
			N,*N*-Dimethylacetamide (1) + Ethyl Acetate (3)			
0.0000	0.89460	0.426	1.3699	0.000	0.000	0.0000
0.0392	0.89684	0.442	1.3731	−0.074	−0.004	0.0008
0.0791	0.89895	0.458	1.3763	−0.129	−0.009	0.0015
0.1560	0.90275	0.490	1.3824	−0.205	−0.017	0.0027
0.2331	0.90643	0.523	1.3883	−0.262	−0.024	0.0037
0.3109	0.90997	0.558	1.3942	−0.297	−0.029	0.0046
0.3875	0.91334	0.595	1.3999	−0.316	−0.032	0.0054
0.4646	0.91663	0.634	1.4054	−0.321	−0.033	0.0059
0.5410	0.91980	0.674	1.4106	−0.314	−0.033	0.0060
0.6137	0.92268	0.713	1.4153	−0.290	−0.032	0.0059
0.6931	0.92571	0.757	1.4201	−0.250	−0.029	0.0054
0.7718	0.92862	0.803	1.4246	−0.199	−0.024	0.0046
0.8145	0.93015	0.828	1.4269	−0.165	−0.021	0.0040
0.8896	0.93281	0.874	1.4307	−0.100	−0.014	0.0026
0.9558	0.93514	0.916	1.4338	−0.040	−0.006	0.0012
1.0000	0.93670	0.945	1.4357	0.000	0.000	0.0000
			2-Methylbutan-2-ol (2) + Ethyl Acetate (3)			
0.0000	0.89460	0.426	1.3699	0.000	0.000	0.0000
0.0279	0.89115	0.464	1.3711	0.075	−0.052	0.0002
0.0573	0.88759	0.508	1.3723	0.149	−0.102	0.0003
0.0960	0.88306	0.567	1.3739	0.234	−0.168	0.0006
0.1672	0.87497	0.691	1.3767	0.376	−0.273	0.0009
0.2475	0.86639	0.850	1.3798	0.492	−0.373	0.0012
0.3322	0.85783	1.041	1.3830	0.578	−0.454	0.0015
0.4168	0.84981	1.261	1.3861	0.620	−0.507	0.0018
0.4994	0.84259	1.503	1.3891	0.602	−0.530	0.0021
0.5831	0.83567	1.776	1.3919	0.550	−0.527	0.0022
0.6658	0.82916	2.078	1.3946	0.472	−0.491	0.0022
0.7486	0.82286	2.412	1.3970	0.377	−0.423	0.0021
0.8336	0.81662	2.791	1.3993	0.264	−0.318	0.0018
0.9149	0.81081	3.188	1.4011	0.146	−0.182	0.0011
0.9445	0.80873	3.344	1.4017	0.101	−0.122	0.0008
0.9712	0.80691	3.486	1.4021	0.054	−0.066	0.0004
1.0000	0.80498	3.645	1.4025	0.000	0.000	0.0000

nents. A total of 44 compositions was measured at 298.15 K for the ternary system *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2) + ethyl acetate (3). Each mixtures was immediately used after it was well-mixed by shaking. All the weightings were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

Results and Discussion

Table 2 lists the experimental densities, viscosities, refractive indices, excess molar volumes, deviations in viscosity from mole fraction average, and deviations in refractive index from volume fraction average for three binary systems *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2), *N*,*N*-dimethylacetamide (1) +

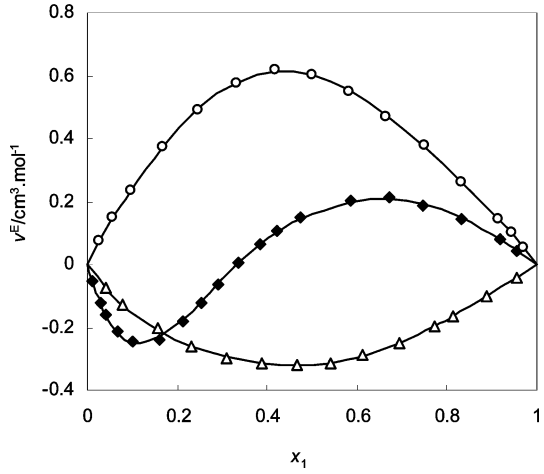

Figure 1. Variation of excess molar volume V^E with mole fraction x_1 for the binary systems at $T = 298.15$ K: ◆, *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2); △, *N*,*N*-dimethylacetamide (1) + ethyl acetate (3); ○, 2-methylbutan-2-ol (2) + ethyl acetate (3). Solid curves were calculated from the Redlich−Kister equation.

ethyl acetate (3), and 2-methylbutan-2-ol (2) + ethyl acetate (3) at 298.15 K. The excess molar volumes (V^E) were calculated from density data according to

$$V^E = \sum_{i=1}^{N} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{2}$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of the pure component *i*, respectively. ρ is the density of mixture, and *N* is the number of components. In the system studied, excess molar volumes are positive for the system 2-methylbutan-2-ol (2) + ethyl acetate (3) and are negative for the system *N*,*N*-dimethylacetamide (1) + ethyl acetate (3) over the whole composition range. For the system *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2), an inversion of sign of V^E is observed over part of the concentration range as expected steric effect. In this system V^E values are negative at lower concentrations of *N*,*N*-dimethylacetamide and positive at higher concentrations of it.. The excess molar volume V^E ($x = 0.5$) decreases in the sequence: 2-methylbutan-2-ol + ethyl acetate > *N*,*N*-dimethylacetamide + 2-methylbutan-2-ol > *N*,*N*-dimethylacetamide + ethyl acetate. The values of V^E ($x = 0.5$) vary from -0.321 cm^3·mol^{-1} to 0.603 cm^3·mol^{-1}. Figure 1 shows the excess molar volumes for the three binary systems at $T = 298.15$ K.

The dependence of V^E on composition for the present mixtures may be explained as a balance between positive contributions (hydrogen bond rupture, dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions and geometrical fitting between components). In the present investigation, alcohols are strongly self-associated through hydrogen bonding with degrees of association depending on such variables as chain length, position of the -OH group, and dilution by other substances. The interactions of 2-methylbutan-2-ol against ethyl acetate molecules involve mainly dispersion force giving a positive contribution to V^E, because of steric effect around OH in *tert*-alcohol. The new hydrogen bonding between alcohol and ester is weaker than dipolar force in pure ester and hydrogen bonding in alcohol. The interactions between *N*,*N*-dimethylacetamide and ethyl acetate give a negative contribution to V^E. The large, more negative values of V^E for this system suggest a strong chemical or specific interaction between components due to the existence

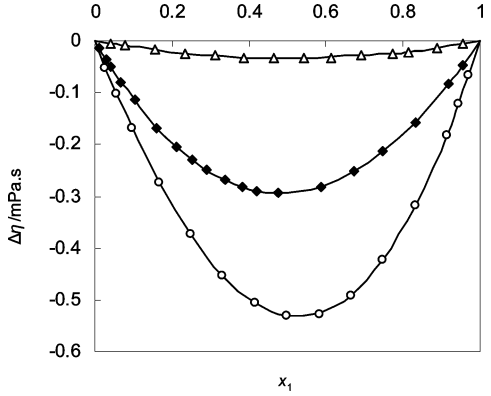

Figure 2. Variation of deviation in the viscosity $\Delta\eta$ with mole fraction x_1 for the binary systems at $T = 298.15$ K: ◆, *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2); △, *N*,*N*-dimethylacetamide (1) + ethyl acetate (3); ○, 2-methylbutan-2-ol (2) + ethyl acetate (3)**.** Solid curves were calculated from the Redlich−Kister equation.

of London and dipolar forces between amide and ester. For the system of *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2), negative values of V^E were observed in the region of x_1 below 0.33 while positive values of V^E were found for the other composition ranges. A sigmoid shape observed may be attributed to the hydrogen bond effect that occurred between amide and alcohol. At low concentration of amide, hydrogen bonding is dominant resulting in negative values of V^E whereas at higher mole fraction of amide, dispersive forces are dominant resulting in positive values of V^E. The other reason for this observation is steric hindrance of the two methyl groups of *N*,*N*-dimethylacetamide.

The deviation of the viscosity from the mole fraction average ($\Delta\eta$) is given by

$$\Delta\eta = \eta - \sum_{i=1}^{N} x_i \eta_i \tag{3}$$

where η is the absolute viscosity of the mixtures and η_i is the absolute viscosity of pure component *i*. The $\Delta\eta$ values are also graphically represented as a function of mole fraction at 298.15 K in Figure 2. It is observed that the $\Delta\eta$ values are negative for all the studied systems over the whole composition range. This reveals that the strength of specific interaction is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular size and shape of the components also play an equally important role. The values of $\Delta\eta$ ($x = 0.5$) show the order as *N*,*N*-dimethylacetamide + ethyl acetate > *N*,*N*-dimethylacetamide + 2-methylbutan-2-ol > 2-methylbutan-2-ol + ethyl acetate. The values of $\Delta\eta$ vary from -0.531 mPa·s to -0.033 mPa·s.

The deviation in the refractive index (Δn_D) was calculated from the volume fraction average as suggested by Brocos et al.[9] and is given by

$$\Delta n_D = n_D - \sum_{i=1}^{N} \phi_i n_{Di} \tag{4}$$

and

$$\phi_i = \frac{x_i V_i}{\sum_{i=1}^{N} x_i V_i} \tag{5}$$

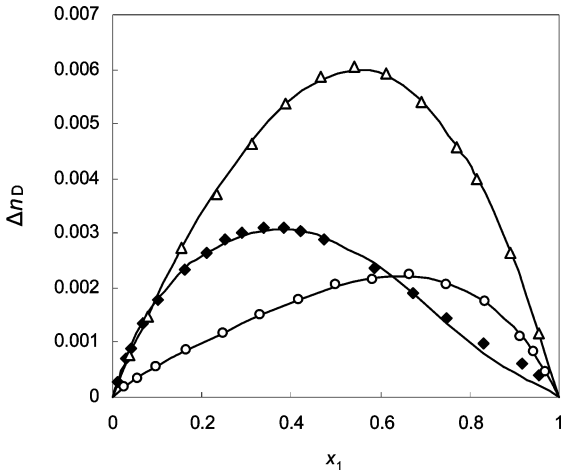

Figure 3. Variation of deviation in the refractive index Δn_D with mole fraction x_1 for the binary systems at $T = 298.15$ K: ◆, *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2); △, *N*,*N*-dimethylacetamide (1) + ethyl acetate (3); ○, 2-methylbutan-2-ol (2) + ethyl acetate (3). Solid curves were calculated from the Redlich−Kister equation.

where n_D, n_{Di}, and ϕ_i are the refractive index of the mixture, the refractive index of pure component *i*, and the volume fraction of pure component *i*, respectively. V and V_i are the molar volume of the mixture and the molar volume of pure component *i*, respectively. For the whole composition range, the Δn_D values are positive for all studied systems. The values of Δn_D ($x = 0.5$) follow the order *N*,*N*-dimethylacetamide + ethyl acetate > *N*,*N*-dimethylacetamide + 2-methylbutan-2-ol > 2-methylbutan-2-ol + ethyl acetate. The values of Δn_D ($x = 0.5$) vary from 0.0020 to 0.0059. Figure 3 shows the results of Δn_D for the three binary mixtures at $T = 298.15$.

The mixing functions V^E, $\Delta\eta$, and Δn_D were represented mathematically by the Redlich−Kister equation for correlating the experimental data:[10]

$$\Delta Q_{ij} = x_i x_j \sum_{k=0}^{m} A_k (x_j - x_i)^k \tag{6}$$

where ΔQ_{ij} refers to V^E/cm^3·mol^{-1}, $\Delta\eta$/mPa·s, or Δn_D for each $i-j$ binary pair; x_i is the mole fraction of component *i*; and A_k values are the coefficients. The values of coefficients A_k were determined by a multiple regression analysis based on the least-squares method and are summarized along with the standard deviations between the experimental and the fitted values of the respective functions in Table 3. The standard deviation is defined by

$$\sigma = \left[\sum_{i=1}^{n} \frac{(\Delta Q_i^{\text{exptl}} - \Delta Q_i^{\text{calcd}})^2}{n - p} \right]^{1/2} \tag{7}$$

where n is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.0024 cm^3·mol^{-1} and 0.0043 cm^3·mol^{-1}, between 0.00025 mPa·s and 0.00085 mPa·s, and between 0.000023 and 0.000047 for V^E, $\Delta\eta$, and Δn_D, respectively.

The experimental densities, viscosities, excess molar volumes, deviations in the viscosity from mole fraction average, and deviations in the refractive index from volume fraction average of ternary mixtures system *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2) + ethyl acetate (3) at $T = 298.15$ K are listed in Table 4. The derived data (V^E, $\Delta\eta$, and Δn_D) as defined in eqs 2 to 4 for the ternary system were correlated respectively using the equation

$$\Delta Q_{123} = \Delta Q_{\text{bin}} + x_1 x_2 x_3 \Delta_{123} \tag{8}$$

and

$$\Delta Q_{\text{bin}} = \sum_{i=1}^{3} \sum_{j>i}^{3} \Delta Q_{ij} \tag{9}$$

where ΔQ_{123} refers to V^E, $\Delta\eta$, and Δn_D for the ternary system *N*,*N*-dimethylacetamide (1) + 2-methylbutan-2-ol (2) + ethyl acetate (3) and $x_3 = 1 - x_1 - x_2$. ΔQ_{ij} in eq 9 is the binary contribution of each $i-j$ pair to the V^E, $\Delta\eta$, or Δn_D given by eq 6 with the parameters shown in Table 3. The ternary contribution term Δ_{123} was correlated using the expression suggested by Cibulka:[11]

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \tag{10}$$

The ternary parameters B_0, B_1, and B_2 were determined with the optimization algorithm similar to that for the binary parameters. The fitting parameters and the corresponding standard deviations are given in Table 3. The σ values are 0.057 cm^3·mol^{-1}, 0.029 mPa·s, and 0.00053 for V^E, $\Delta\eta$, and Δn_D respectively. As can be expected, the ternary system shows positive values of V^E at almost all compositions (Table 4), except at compositions close to the binary system *N*,*N*-dimethylacetamide (1) + ethyl acetate (3) where a change in

Table 3. Binary Coefficients of the Redlich−Kister Equation at 298.15 K and Ternary Coefficients of the Cibulka Equation for V^E, $\Delta\eta$, and Δn_D at 298.15 K

ΔQ_{ij}	A_0	A_1	A_2	A_3	A_4	σ
			N,*N*-Dimethylacetamide (1) + 2-Methylbutan-2-ol (2)			
V^E/(cm^3·mol^{-1})	0.6655	−1.2082	−1.6949	−1.8400	−1.0857	4.3×10^{-3}
$\Delta\eta$/(mPa·s)	−1.1720	−0.0881	−0.0212	0.0048	0.0185	4.9×10^{-4}
Δn_D	0.0115	0.0066	−0.0040	0.0043	0.0088	6.2×10^{-5}
			N,*N*-Dimethylacetamide (1) + Ethyl Acetate (3)			
V^E/(cm^3·mol^{-1})	−1.2830	−0.1828	0.0724	−0.4193	−0.3117	2.4×10^{-3}
$\Delta\eta$/(mPa·s)	−0.1330	−0.0047	−0.0226	0.0262	0.0369	2.5×10^{-4}
Δn_D	0.0235	−0.0052	0.0008	0.0017		7.9×10^{-5}
			2-Methylbutan-2-ol (2) + Ethyl acetate (3)			
V^E/(cm^3·mol^{-1})	2.4128	0.7510	−0.4707	−0.3548	0.4558	2.9×10^{-3}
$\Delta\eta$/(mPa·s)	−2.1260	0.2505	0.0050	−0.0110	−0.0083	8.5×10^{-4}
Δn_D	0.0081	−0.0052	0.0037	0.0009	−0.0006	4.6×10^{-5}

ΔQ_{123}	B_o	B_1	B_2	σ
V^E/(cm^3·mol^{-1})	−5.11445	71.56964	−48.1376	5.7×10^{-2}
$\Delta\eta$/(mPa·s)	5.207243	−6.46465	−15.9427	2.9×10^{-2}
Δn_D	−0.42269	0.468529	0.633803	5.3×10^{-4}

Table 4. Experimental Densities ρ, Viscosities η, Refractive Indices n_D, Excess Molar Volumes V^E, Deviations in the Viscosity $\Delta\eta$, and Deviations in the Refractive Index Δn_D for the Ternary System *N*,*N*-Dimethylacetamide (1) + 2-Methylbutan-2-ol (2) + Ethyl Acetate (3) at 298.15 K

x_1	x_2	ρ/(g·cm^{-3})	η/(mPa·s)	n_D	V^E/(cm^3·mol^{-1})	$\Delta\eta$(mPa·s)	Δn_D
0.0506	0.0513	0.89116	0.512	1.3762	0.039	−0.105	0.0013
0.0505	0.2484	0.87050	0.835	1.3821	0.221	−0.417	0.0004
0.0492	0.4412	0.85205	1.306	1.3892	0.292	−0.566	0.0011
0.0552	0.6475	0.83486	2.012	1.3970	0.184	−0.527	0.0019
0.0501	0.8473	0.81844	2.928	1.4025	0.087	−0.251	0.0016
0.0501	0.8998	0.81427	3.206	1.4040	0.063	−0.142	0.0016
0.0513	0.6973	0.83051	2.218	1.3977	0.174	−0.479	0.0013
0.0509	0.5027	0.84673	1.493	1.3915	0.274	−0.577	0.0013
0.0503	0.3000	0.86543	0.943	1.3836	0.248	−0.475	0.0001
0.0499	0.1000	0.88571	0.579	1.3774	0.110	−0.195	0.0008
0.0997	0.0505	0.89356	0.545	1.3796	−0.003	−0.095	0.0017
0.0998	0.2494	0.87291	0.868	1.3851	0.146	−0.412	0.0003
0.0993	0.4488	0.85470	1.327	1.3918	0.105	−0.595	0.0004
0.0992	0.6460	0.83789	2.010	1.3992	0.008	−0.547	0.0016
0.0999	0.8497	0.82054	3.021	1.4060	−0.001	−0.192	0.0021
0.2017	0.0525	0.89756	0.614	1.3876	−0.017	−0.086	0.0032
0.2004	0.2524	0.87635	0.942	1.3914	0.155	−0.400	0.0003
0.1991	0.4738	0.85663	1.446	1.4005	0.030	−0.608	0.0022
0.2001	0.6503	0.84104	2.124	1.4073	0.002	−0.499	0.0035
0.1983	0.7391	0.83328	2.601	1.4085	−0.006	−0.307	0.0021
0.1992	0.5524	0.84971	1.712	1.4039	0.005	−0.595	0.0032
0.2000	0.3504	0.86721	1.133	1.3950	0.136	−0.524	0.0007
0.2010	0.1503	0.88621	0.773	1.3882	0.161	−0.241	0.0005
0.3005	0.0505	0.90188	0.672	1.3942	−0.031	−0.072	0.0036
0.2874	0.2775	0.87619	1.043	1.3988	0.277	−0.425	0.0014
0.2983	0.4480	0.86156	1.459	1.4069	0.157	−0.564	0.0034
0.3003	0.6482	0.84386	2.334	1.4132	0.107	−0.334	0.0034
0.3990	0.0504	0.90595	0.737	1.4007	−0.034	−0.058	0.0037
0.3980	0.2505	0.88115	1.085	1.4054	0.491	−0.354	0.0019
0.4001	0.4498	0.86406	1.593	1.4140	0.283	−0.488	0.0041
0.3995	0.5499	0.85556	2.032	1.4164	0.192	−0.371	0.0034
0.3998	0.3499	0.87227	1.289	1.4102	0.422	−0.471	0.0034
0.3999	0.1507	0.89189	0.915	1.4024	0.395	−0.204	0.0020
0.4996	0.0515	0.91043	0.799	1.4073	−0.082	−0.052	0.0037
0.5002	0.2487	0.88422	1.155	1.4137	0.611	−0.331	0.0037
0.4989	0.4492	0.86795	1.749	1.4201	0.260	−0.382	0.0040
0.6001	0.0501	0.91432	0.849	1.4138	−0.033	−0.050	0.0037
0.5917	0.2458	0.88848	1.215	1.4202	0.568	−0.309	0.0044
0.6004	0.3497	0.88122	1.510	1.4237	0.277	−0.354	0.0041
0.7008	0.0499	0.91849	0.896	1.4203	−0.022	−0.055	0.0035
0.7010	0.2488	0.89585	1.288	1.4268	0.202	−0.303	0.0037
0.8495	0.0504	0.92463	0.957	1.4300	−0.002	−0.072	0.0031
0.8497	0.1000	0.91923	1.036	1.4317	0.008	−0.153	0.0033
0.9006	0.0500	0.92763	0.974	1.4323	−0.078	−0.081	0.0019

Table 5. Binary Coefficients of McAlister's Multibody−Interaction Equations and Standard Deviations, σ, for Kinematic Viscosities at 298.15 K

three-body			four-body			
υ_{12}/(mm^2·s^{-1})	υ_{21}/(mm^2·s^{-1})	σ/(mm^2·s^{-1})	υ_{1112}/(mm^2·s^{-1})	υ_{1122}/(mm^2·s^{-1})	υ_{2221}/(mm^2·s^{-1})	σ/(mm^2·s^{-1})
N,*N*-Dimethylacetamide (1) + 2-Methylbutan-2-ol (2)						
1.89387	2.99169	2.8×10^{-3}	1.61031	2.39496	3.30311	8.2×10^{-4}
N,*N*-Dimethylacetamide (1) + Ethyl Acetate (3)						
0.80963	0.63236	3.7×10^{-4}	0.85527	0.71576	0.58887	4.0×10^{-4}
2-Methylbutan-2-ol (2) + Ethyl Acetate (3)						
2.60048	1.39398	5.1×10^{-3}	3.02111	1.876741	1.07753	8.7×10^{-4}

sign occurs. The maximum V^E value and the minimum $\Delta\eta$ value were found in the binary system 2-methylbutan-2-ol (2) + ethyl acetate (3), and the maximum Δn_D value was found in the binary system *N*,*N*-dimethylacetamide (1) + ethyl acetate (3). Table 4 shows the values for V^E, $\Delta\eta$, and Δn_D at all compositions of ternary system.

McAllister's multibody−interaction model[12] is widely used for correlating the kinematic viscosity of binary mixtures with mole fraction. The three-body model is defined as

$$\ln \upsilon = x_1^3 \ln \upsilon_1 + 3x_1^2 x_2 \ln \upsilon_{12} + 3x_1 x_2^2 \ln \upsilon_{21} + x_2^3 \ln \upsilon_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left(\frac{2 + M_2/M_1}{3}\right) + 3x_1 x_2^2 \ln\left(\frac{1 + 2M_2/M_1}{3}\right) + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad (11)$$

and the four-body model is given by

$$\ln \upsilon = x_1^4 \ln \upsilon_1 + 4x_1^3 x_2 \ln \upsilon_{1112} + 6x_1^2 x_2^2 \ln \upsilon_{1122} + 4x_1 x_2^3 \ln \upsilon_{2221} + x_2^4 \ln \upsilon_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 4x_1^3 x_2 \ln\left(\frac{3 + M_2/M_1}{4}\right) + 6x_1^2 x_2^2 \ln\left(\frac{1 + M_2/M_1}{2}\right) + 4x_1 x_2^3 \ln\left(\frac{1 + 3M_2/M_1}{4}\right) + x_2^4 \ln\left(\frac{M_2}{M_1}\right) \quad (12)$$

where υ, υ_1, and υ_2 are the kinematic viscosities of the mixture and the viscosities of pure components 1 and 2, respectively. υ_{12}, υ_{21}, υ_{1112}, υ_{1122}, and υ_{2221} are the model parameters. Table 5 records the calculated results with the standard deviation defined as eq 7. It is shown that McAllister's four-body equation

gave a better result for those three systems. The $\sigma/(mm^2 \cdot s^{-1})$ values for this model lie between 0.0004 and 0.00087, and the largest value corresponds to the 2-methylbutan-2-ol (2) + ethyl acetate (3) system.

As in the binary case, the ternary viscosities were correlated with composition through a specific equation that incorporates both parameters from the binary systems and experimental viscosities of the pure components. The extension to ternary systems of the McAllister cubic equation by Kalidas and Laddha,[13] expressed as

$$\ln \upsilon = \sum_{i=1}^{3} x_i^3 \ln \upsilon_i + \sum_{i=1}^{3} x_i^3 \ln M_i - \ln \sum_{i=1}^{3} x_i M_i + 3 \sum_{i,j=1,i\neq j}^{3} x_i^2 x_j \ln \upsilon_{ij}\left(\frac{2M_i + M_j}{3}\right) + x_1 x_2 x_3 \ln \upsilon_{123}\left(\frac{M_1 + M_2 + M_3}{3}\right) \quad (13)$$

The equation comprising six binary constants may be determined from three binary systems of components 1 and 2, 2 and 3, and 3 and 1 (Table 5). The equation contains only one undetermined constant υ_{123}, which is determined from least-squares fitting. The kinematic viscosities of binary and ternary liquid mixtures are well-correlated with $\upsilon_{123} = 0.08686$ and $\sigma = 5.6 \times 10^{-3}$ $mm^2 \cdot s^{-1}$.

Conclusions

Densities, viscosities, and refractive indices for binary and ternary mixtures consist of, *N*,*N*-dimethylacetamide, 2-methylbutan-2-ol, and ethyl acetate have been measured at $T = 298.15$ K. The corresponding excess molar volumes, viscosity deviations, and refractive index deviations have been calculated. The derived values have been discussed. We conclude that the main property responsible for volumetric behavior is the breaking of the hydrogen bonds of the alkanols. In fact results show that the positive contributions from the breaking of H bonds of alcohols and from physical interactions which usually predominate over negative contributions. The negative viscosity deviation suggests that, in these mixtures, the forces between pairs of unlike molecules is less than the forces between like molecules due to difference in shape and size of component molecules.

Literature Cited

(1) Iloukhani, H.; Rezaei-Sameti, M. Excess molar volumes of ternary system {methylcyclohexane (1) + cyclohexane (2) + *n*-alkanes (3)} at $T = 298.15$ K. *J. Chem. Thermodyn.* **2005**, *37*, 1151−1161.

(2) Iloukhani, H.; Rezaei-Sameti, M.; Zarei, H. A. Volumetric and viscometric studies of molecular interaction of the ternary system toluene (1) + cyclohexane (2) + *n*-hexane (3) at 298.15 K. *Thermochim. Acta* **2005**, *438*, 9−15.

(3) Iloukhani, H.; Rezaei-Sameti, M. Viscosities and excess molar of the ternary system toluene (1) + cyclohexane (2) + pentane (3) at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1228−1231.

(4) Iloukhani, H.; Rezaei-Sameti, M.; Basiri-Parsa, J. Excess molar volume and dynamic viscosities for binary mixtures of toluene + *n*-alkanes (C_5−C_{10}) at $T = 298.15$ K—comparison with Prigogine−Flory−Paterson theory. *J. Chem. Thermodynm*. (in press).

(5) Iloukhani, H.; Rostami, Z. Measurement of some thermodynamic and acoustic properties of binary solution of *N*,*N*-dimethylformamide with 1-alkanols at 30 °C and comparison with theories. *J. Solution Chem.* **2003**, *32*, 451−462.

(6) Iloukhani, H.; Zarei, H. A. Excess molar enthalpies of *N*,*N*-dimethylformamide + alkan-1-ols (C_1−C_6) at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 195−197.

(7) Iloukhani, H.; Zarei, H. A. Excess molar enthalpies of amides + some alkan-2-ols at 298.15 K. *Phys. Chem. Liq.* **2004**, *42*, 75−79.

(8) Riddick, J. A.; Bunger, W. B.; Sakano, T. *Organic Solvents, Physical Properties and Method of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(9) Brocos, P.; Pineiro, A.; Bravo, R.; Amigo, A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. *Phys. Chem. Chem. Phys*. **2003**, *5*, 550−557

(10) Redlich, O. J.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(11) Cibulka, I. Estimation of excess volume and density of ternary liquid mixtures of non electrolytes from binary data. *Collect. Czech, Chem. Commun.* **1982**, *47*, 1414−1419.

(12) McAllister, R. A. The viscosity of liquid mixtures. *AIChE J.* **1960**, *6*, 427−431.

(13) Chandramouli, V. V.; Laddha, G. S. Viscosity of ternary liquid mixtures. *Indian J. Technol.* **1963**, *1*, 199−203.

(14) Ali, A.; Nain, A. K. Interactions in binary *N*,*N*-dimethylacetamide + ethanol and ternary lithium nitrate + *N*,*N*-dimethylacetamide + ethanol mixtures. *Phys. Chem. Liq.* **1999**, *37*, 161−174.

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