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Densities and Viscosities of Ternary Mixtures of Cyclohexane + Cyclohexanone + Some Alkyl Acetates at 298.15 K

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The excess molar volumes, V_m^E, and viscosity deviations, $\Delta\eta$, were calculated from the measured density and viscosity data over the whole composition range for the ternary systems of cyclohexane (CHX) + cyclohexanone (CHXN) + methyl acetate (MA), ethyl acetate (EA), and propyl acetate (PA) and the constituent binary mixtures of cyclohexane or cyclohexanone + methyl acetate, ethyl acetate, propyl acetate, and cyclohexane or cyclohexanone at 298.15 K under atmospheric pressure. The excess or deviation properties of the binary and ternary systems were fitted to Redlich−Kister and Cibulka equations, respectively. The excess or deviation properties were found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

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 simulation processes. Therefore, over the years, studies on multicomponent liquid systems have attracted the attention of many researchers.[1−10] As far as our knowledge is concerned, there is a lack of thermodynamic data for the ternary and binary systems studied in this Article. In this Article, we have reported densities, viscosities, and the derived parameters for the ternary systems consisting of cyclohexane (CHX) + cyclohexanone (CHXN) + methyl acetate (MA), ethyl acetate (EA), and propyl acetate (PA) and the constituent binary mixtures of cyclohexane or cyclohexanone + methyl acetate, ethyl acetate, propyl acetate, and cyclohexane or cyclohexanone at 298.15 K under atmospheric pressure.

Experimental Section

Materials. Cyclohexane and cyclohexanone (S. D. Fine Chemicals, AR, Purity 99 %, India) were purified by distillation and stored over activated 4 Å molecular sieves to reduce water content. Methyl, ethyl, and propyl acetates (S. D. Fine Chemicals, AR, purity 99 %) were used. Methyl acetate was washed with a saturated solution of NaCl, dried with anhydrous $MgCl_2$, and then distilled. Ethyl acetate was dried over K_2CO_3, filtered, and distilled, and the first and last portions of the distillate were discarded. The entire middle fraction was then distilled over P_2O_5. Propyl acetate was purified by drying over $CaCO_3$ overnight and was then filtered and freshly distilled. The chemicals after purification were 99.7 % to 99.8 % pure, and their purity was ascertained by GLC and also by a comparison of experimental values of densities and viscosities with those reported in the open literature,[2,6,8,11−14] as presented in Table 1.

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Table 1. Physical Properties of Pure Liquids at 298.15 K

	$\rho(10^{-3})$ / kg·m^{-3}		η / mPa·s	
pure liquid	exptl	lit.	exptl	lit.
cyclohexane	0.7738	0.7739[6]	0.892	0.8945[6]
		0.7737[2]		0.8859[2]
		0.7738[11]		0.8980[11]
cyclohexanone	0.9416	0.9418[11]	2.020	2.0205[11]
		0.9410[6]		2.0215[6]
methyl acetate	0.9268	0.9261[8]	0.380	0.3798[8]
		0.9268[12]		0.384[12,14]
ethyl acetate	0.8945	0.9841[8]	0.426	0.4233[8]
		0.894[12]		0.428[12]
		0.8946[13]		0.426[13]
propyl acetate	0.8830	0.8831[14]	0.551	0.551[14]

Apparatus and Procedure. The densities (ρ) were measured with an Ostwald−Sprengel-type pycnometer with a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostatted bath controlled to ± 0.01 K. The viscosities (η) were measured by means of a suspended Ubbelohde-type viscometer calibrated at 298.15 K with triple-distilled water and purified methanol using density and viscosity values from the literature.[15−17] The flow times were accurate to ± 0.1 s, and the uncertainty in the viscosity values was ± 0.003 mPa·s. We prepared the mixtures by mixing the requisite volume of the pure liquids in airtight stoppered glass bottles (to avoid evaporation). We previously converted the required masses of the respective liquids to volumes by using their experimental densities. The reproducibility in mole fraction was within ± 0.0002 units. The mass measurements were done on a Mettler AG-285 electronic balance with a precision of ± 0.01 mg. The uncertainty of density values was ± 3·10^{-4} g·cm^{-3}. The details of the methods and techniques are described in earlier works.[7,18]

Results and Discussion

The experimental densities (ρ), the viscosities (η), and the calculated excess molar volumes (V_m^E) and deviations in viscosity ($\Delta\eta$) for the binary and ternary mixtures studied at 298.15 K

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Table 2. Experimental Values of the Density, the Viscosity, and the Calculated Excess Molar Volume and Viscosity Deviations for the Binary Mixtures at 298.15 K

x_1	$\rho(10^{-3})$ / kg·m^{-3}	η / mPa·s	$V_m^E(10^6)$ / m^3·mol^{-1}	$\Delta\eta$ / mPa·s
Cyclohexane (1) + Methyl Acetate (2)				
0	0.9268	0.380	0	0
0.0891	0.9037	0.381	0.4699	−0.044
0.1804	0.8833	0.383	0.7960	−0.089
0.2739	0.8647	0.388	1.0383	−0.132
0.3698	0.8485	0.407	1.1100	−0.162
0.4681	0.8331	0.437	1.1543	−0.183
0.5690	0.8194	0.477	1.0660	−0.194
0.6725	0.8064	0.535	0.9466	−0.190
0.7788	0.7949	0.603	0.6880	−0.176
0.8879	0.7842	0.708	0.3530	−0.127
1	0.7738	0.892	0	0
Cyclohexane (1) + Ethyl Acetate (2)				
0	0.8945	0.426	0	0
0.1042	0.8770	0.432	0.4220	−0.042
0.2074	0.8612	0.436	0.7260	−0.087
0.3097	0.8470	0.441	0.9052	−0.129
0.4111	0.8339	0.462	0.9940	−0.155
0.5115	0.8221	0.493	0.9729	−0.171
0.6110	0.8112	0.533	0.8730	−0.177
0.7095	0.8012	0.585	0.6860	−0.171
0.8072	0.7918	0.653	0.4710	−0.149
0.9040	0.7827	0.749	0.2340	−0.099
1	0.7738	0.892	0	0
Cyclohexane (1) + Propyl Acetate (2)				
0	0.8830	0.551	0	0
0.1188	0.8685	0.540	0.2980	−0.037
0.2328	0.8547	0.548	0.5450	−0.073
0.3421	0.8418	0.554	0.7170	−0.107
0.4472	0.8299	0.572	0.7970	−0.131
0.5482	0.8193	0.587	0.7570	−0.144
0.6454	0.8093	0.625	0.6550	−0.146
0.7390	0.8000	0.663	0.5030	−0.139
0.8292	0.7911	0.715	0.3240	−0.118
0.9161	0.7823	0.786	0.1650	−0.072
1	0.7738	0.892	0	0
Cyclohexanone (1) + Methyl Acetate (2)				
0	0.9268	0.380	0	0
0.0774	0.9274	0.407	0.0738	−0.100
0.1587	0.9285	0.445	0.1085	−0.195
0.2444	0.9299	0.504	0.1214	−0.276
0.3347	0.9313	0.577	0.1258	−0.352
0.4301	0.9329	0.666	0.1165	−0.419
0.5310	0.9346	0.779	0.1005	−0.472
0.6378	0.9364	0.936	0.0769	−0.490
0.7512	0.9382	1.163	0.0392	−0.449
0.8717	0.9402	1.488	−0.0112	−0.322
1	0.9416	2.020	0	0
Cyclohexanone (1) + Ethyl Acetate (2)				
0	0.8945	0.426	0	0
0.0907	0.8983	0.470	0.0739	−0.101
0.1833	0.9026	0.521	0.0990	−0.197
0.2778	0.9073	0.585	0.0923	−0.284
0.3744	0.9123	0.667	0.0513	−0.356
0.4730	0.9175	0.764	−0.0050	−0.416
0.5738	0.9226	0.892	−0.0460	−0.449
0.6769	0.9276	1.058	−0.0750	−0.447
0.7822	0.9326	1.289	−0.0875	−0.384
0.8899	0.9373	1.604	−0.0682	−0.241
1	0.9416	2.020	0	0
Cyclohexanone (1) + Propyl Acetate (2)				
0	0.8830	0.551	0	0
0.1036	0.8882	0.609	0.0417	−0.094
0.2064	0.8942	0.666	−0.0094	−0.188
0.3084	0.9004	0.731	−0.0731	−0.274
0.4096	0.9065	0.821	−0.1140	−0.332
0.5099	0.9124	0.926	−0.1313	−0.374
0.6095	0.9184	1.049	−0.1355	−0.398
0.7083	0.9243	1.199	−0.1251	−0.392
0.8063	0.9302	1.407	−0.1084	−0.329
0.9035	0.9361	1.685	−0.0765	−0.194
1	0.9416	2.020	0	0
Cyclohexane (1) + Cyclohexanone (2)				
0	0.9416	2.020	0	0
0.1147	0.9218	1.813	−0.0271	−0.078
0.2257	0.9030	1.638	−0.0642	−0.127
0.3332	0.8848	1.475	−0.0841	−0.169
0.4374	0.8671	1.335	−0.0822	−0.191
0.5384	0.8496	1.225	−0.0141	−0.188
0.6363	0.8325	1.126	0.0830	−0.176
0.7313	0.8160	1.038	0.2032	−0.158
0.8235	0.8000	0.965	0.3206	−0.127
0.9130	0.7859	0.921	0.2660	−0.069
1	0.7738	0.892	0	0

under atmospheric pressure are reported in Tables 2 and 3, respectively.

The excess molar volumes (V_m^E) were calculated from density data according to the following equation[7]

$$V_m^E = \sum_{i=1}^{n} x_i M_i \left[\frac{1}{\rho} - \frac{1}{\rho_i}\right] \quad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of ith component in the mixture, respectively; ρ is the density of the mixture and n is the number of components in the mixture. The estimated uncertainty for V_m^E was ± 0.005 cm^3·mol^{-1}. Whereas the negative V_m^E values may be attributed to specific interactions[7,18] between the mixing components in the mixtures, the positive values often suggest dominance of dispersion forces[7,18] between them. For the studied binary systems of cyclohexane + alkyl acetates, the V_m^E values were positive over the whole composition range, but for binary systems of cyclohexanone + alkyl acetates, the V_m^E values shifted from positive to negative as the length of the alkyl chain of the acetates increased. Therefore, specific interactions for the alkyl acetates in studied binary systems with cyclohexane and cyclohexanone follow the order PA > EA > MA. However, the mode of interaction is found to be somewhat more intense for the binaries of the alkyl acetates with cyclohexanone. Interestingly, for the binary system of cyclohexane + cyclohexanone, the V_m^E value shifts from positive to negative as the amount of cyclohexane increases in the mixture, which indicates weak unlike molecular interactions in this system, as found earlier by S. Singh et al.[6] For the ternary systems, in general, the V_m^E values were found to be positive over the whole composition range under study at 298.15 K and are depicted in Figures 1, 2, and 3 as a function of the mole fraction of cyclohexane (x_1) and cyclohexanone (x_2).

The deviation in the viscosity ($\Delta\eta$) from the mole fraction average is given by eq 2

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i \eta_i \qquad (2)$$

where η is the absolute viscosity of the mixture and η_i is the absolute viscosity of the ith pure component in the mixture.

Table 3. Experimental Values of the Density, the Viscosity, and the Calculated Excess Molar Volume and Viscosity Deviations for the Ternary Mixtures at 298.15 K

x_1	x_2	$\rho(10^{-3})$ / kg·m^{-3}	η / mPa·s	$V_m^E(10^6)$ / m^3·mol^{-1}	$\Delta\eta$ / mPa·s
Cyclohexane (1) + Cyclohexanone (2) + Methyl Acetate (3)					
0.0454	0.0778	0.9175	0.397	0.1494	−0.134
0.0786	0.8191	0.9259	1.461	0.0528	−0.303
0.0999	0.7614	0.9209	1.329	0.1195	−0.351
0.0942	0.1777	0.9087	0.471	0.3089	−0.249
0.1297	0.6490	0.9135	1.084	0.1796	−0.427
0.1213	0.1361	0.9014	0.441	0.4317	−0.224
0.1415	0.1618	0.8983	0.470	0.4469	−0.247
0.1767	0.7103	0.9083	1.299	0.0533	−0.336
0.1924	0.2062	0.8893	0.515	0.5769	−0.301
0.2454	0.2525	0.8813	0.579	0.6111	−0.341
0.3008	0.5527	0.8841	1.078	0.2274	−0.363
0.3582	0.3510	0.8676	0.772	0.4931	−0.367
0.4182	0.4035	0.8614	0.918	0.3706	−0.338
0.4810	0.4582	0.8558	1.116	0.1735	−0.262
0.5050	0.2425	0.8408	0.721	0.7220	−0.315
0.5609	0.2536	0.8341	0.794	0.6458	−0.289
0.6462	0.1278	0.8156	0.682	0.9123	−0.239
0.6967	0.1109	0.8089	0.704	0.8487	−0.215
0.7495	0.1028	0.8026	0.744	0.7518	−0.188
0.8067	0.0854	0.7929	0.801	1.0151	−0.482
Cyclohexane (1) + Cyclohexanone (2) + Ethyl Acetate (3)					
0.0528	0.0905	0.8897	0.466	0.2544	−0.129
0.0799	0.8327	0.9239	1.529	−0.0239	−0.261
0.1021	0.7786	0.9188	1.383	−0.0495	−0.332
0.1066	0.2011	0.8889	0.549	0.1684	−0.247
0.1345	0.6727	0.9094	1.166	−0.0047	−0.395
0.1377	0.1543	0.8813	0.516	0.3217	−0.221
0.1592	0.1819	0.8799	0.536	0.3179	−0.254
0.1799	0.7233	0.9064	1.353	−0.0572	−0.310
0.2128	0.2281	0.8751	0.585	0.3493	−0.304
0.2668	0.2745	0.8710	0.647	0.2983	−0.341
0.3080	0.5659	0.8827	1.131	−0.0358	−0.341
0.3756	0.3681	0.8636	0.824	0.1218	−0.364
0.4305	0.4153	0.8601	0.958	0.0064	−0.331
0.4857	0.4627	0.8576	1.137	−0.2240	−0.253
0.5262	0.2527	0.8398	0.771	0.1150	−0.303
0.5780	0.2613	0.8351	0.830	−0.0114	−0.282
0.6703	0.1326	0.8169	0.716	0.1101	−0.234
0.7188	0.1145	0.8109	0.729	0.0401	−0.214
0.7676	0.1053	0.8061	0.760	−0.1293	−0.192
0.8599	0.0434	0.7858	0.757	0.7803	−0.363
Cyclohexane (1) + Cyclohexanone (2) + Propyl Acetate (3)					
0.0598	0.1025	0.8800	0.597	0.2881	−0.125
0.0809	0.8428	0.9227	1.592	−0.0023	−0.225
0.1038	0.7915	0.9167	1.479	0.0369	−0.270
0.1178	0.2222	0.8805	0.678	0.2748	−0.239
0.1382	0.6911	0.9065	1.279	0.0749	−0.335
0.1525	0.1710	0.8731	0.648	0.3970	−0.206
0.1750	0.2001	0.8722	0.667	0.4045	−0.238
0.1824	0.7331	0.9039	1.411	0.0973	−0.279
0.2305	0.2471	0.8688	0.712	0.4070	−0.281
0.2847	0.2929	0.8650	0.767	0.4561	−0.311
0.3134	0.5759	0.8793	1.202	0.2135	−0.302
0.3893	0.3815	0.8582	0.919	0.4620	−0.326
0.4398	0.4243	0.8558	1.029	0.3521	−0.296
0.4892	0.4660	0.8534	1.176	0.2321	−0.227
0.5427	0.2606	0.8341	0.856	0.5633	−0.263
0.5911	0.2672	0.8298	0.895	0.4654	−0.250
0.6889	0.1363	0.8112	0.783	0.6114	−0.203
0.7356	0.1171	0.8047	0.794	0.6613	−0.180
0.7812	0.1072	0.7995	0.810	0.6038	−0.165
0.8715	0.0439	0.7865	0.796	0.5783	−0.326

Table 4. Redlich−Kister Coefficients and Standard Deviations (σ) for Excess or Deviation Properties of the Binary Mixtures at 298.15 K

mixture property	a_0	a_1	a_2	a_3	σ
Cyclohexane (1) + Methyl Acetate (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	4.517	−0.939	0.888	−0.731	0.017
$\Delta\eta$/(mPa·s)	−0.751	−0.221	−0.187	−0.403	0.001
Cyclohexane (1) + Ethyl Acetate (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	3.917	−1.123	−0.509		0.005
$\Delta\eta$/(mPa·s)	−0.682	−0.237	−0.164	−0.302	0.001
Cyclohexane (1) + Propyl Acetate (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	3.154	−0.613	−1.532	0.321	0.005
$\Delta\eta$/(mPa·s)	−0.554	−0.267	−0.105	−0.165	0.001
Cyclohexanone (1) + Methyl Acetate (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	0.427	−0.509			0.010
$\Delta\eta$/(mPa·s)	−1.835	−0.950	−0.363	0.416	0.001
Cyclohexanone (1) + Ethyl Acetate (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	−0.047	−0.978	0.246		0.004
$\Delta\eta$/(mPa·s)	−1.709	−0.829	−0.368	0.085	0.001
Cyclohexanone (1) + Propyl Acetate (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	−0.524	−0.211	0.259	−0.840	0.001
$\Delta\eta$/(mPa·s)	−1.504	−0.768	−0.268		0.006
Cyclohexane (1) + Cyclohexanone (2)					
$V_m^E(10^6)$/(m^3·mol^{-1})	−0.200	1.270	2.611	1.442	0.009
$\Delta\eta$/(mPa·s)	−0.761	−0.018	−0.876	−0.128	0.004

Table 5. C_i Coefficients of Equation 6 Fitted to the Excess or Deviation Properties for the Ternary Mixtures at 298.15 K

mixture property	C_0	C_1	C_2	σ
Cyclohexane (1) + Cyclohexanone (2) + Methyl Acetate (3)				
$V_m^E(10^6)$/(m^3·mol^{-1})	130.021	−182.233	−232.652	0.006
$\Delta\eta$/(mPa·s)	−102.135	147.015	165.882	0.004
Cyclohexane (1) + Cyclohexanone (2) + Ethyl Acetate (3)				
$V_m^E(10^6)$/(m^3·mol^{-1})	321.906	−460.437	−459.373	0.001
$\Delta\eta$/(mPa·s)	−83.503	119.090	138.765	0.003
Cyclohexane (1) + Cyclohexanone (2) + Propyl Acetate (3)				
$V_m^E(10^6)$/(m^3·mol^{-1})	0.947	−6.908	−17.619	0.004
$\Delta\eta$/(mPa·s)	−68.904	98.445	118.327	0.003

Table 6. Maxima and Minima of the Ternary Contributions to the Excess Molar Volumes and Viscosity Deviations for the Ternary Mixtures at 298.15 K

x_1	x_2	$(V_m^E - V_{m,BIN}^E)(10^6)$ / m^3·mol^{-1}			$\Delta\eta - \Delta\eta_{BIN}$ / mPa·s
Cyclohexane (1) + Cyclohexanone (2) + Methyl Acetate (3)					
0.8067	0.0854	maximum	0.0404	minimum	−0.029
0.4810	0.4583	minimum	−1.1089	maximum	0.550
Cyclohexane (1) + Cyclohexanone (2) + Ethyl Acetate (3)					
0.8599	0.0434	maximum	0.049	minimum	−0.012
0.4857	0.4627	minimum	−1.156	maximum	0.515
Cyclohexane (1) + Cyclohexanone (2) + Propyl Acetate (3)					
0.0598	0.1025	maximum	0.104	minimum	−0.009
0.4892	0.4660	minimum	−0.372	maximum	0.462[a]

[a] Value found at $x_1 = 0.8715$, $x_2 = 0.0439$.

The estimated uncertainty for viscosity deviation, $\Delta\eta$, is ± 0.004 mPa·s. Table 2 shows that $\Delta\eta$ values are negative for all of the studied binaries over the entire composition range at the experimental temperature. A perusal of Table 2 shows that the $\Delta\eta$ values become more negative as the chain length of the alkyl acetates increases. Also, the $\Delta\eta$ values for all ternaries studied were found to be negative over the whole composition range at 298.15 K and are depicted in Figures 4, 5, and 6 as a function of the mole fraction of cyclohexane (x_1) and cyclohexanone (x_2).

The excess or deviation properties of the binaries were fitted to the Redlich−Kister equation[19]

$$Y_{ij}^{E} = x_i x_j \sum_{k=1}^{n} a_k (x_i - x_j)^k \quad (3)$$

where Y_{ij}^{E} refers to an excess or deviation property for each $i-j$ binary pair, x_i is the mole fraction of the ith component, and a_k represents the coefficients. The values of coefficients (a_k) were determined by a multiple-regression analysis based on the least-squares method and were reported along with the corresponding standard deviations between the experimental and calculated values of the respective functions in Table 4.

The standard deviation (σ) was calculated using the relation

$$\sigma = \left[\sum_{i=1}^{n} \frac{(Y_{i,\mathrm{exptl}}^{E} - Y_{i,\mathrm{calcd}}^{E})^2}{n-p} \right] \quad (4)$$

where n is the number of experimental points and p is the number of adjustable parameters.

The partial excess molar volumes, $V_{m,1}^{0,E}$ in these binaries over the entire composition range at 298.15 K were calculated by the use of the relation[21]

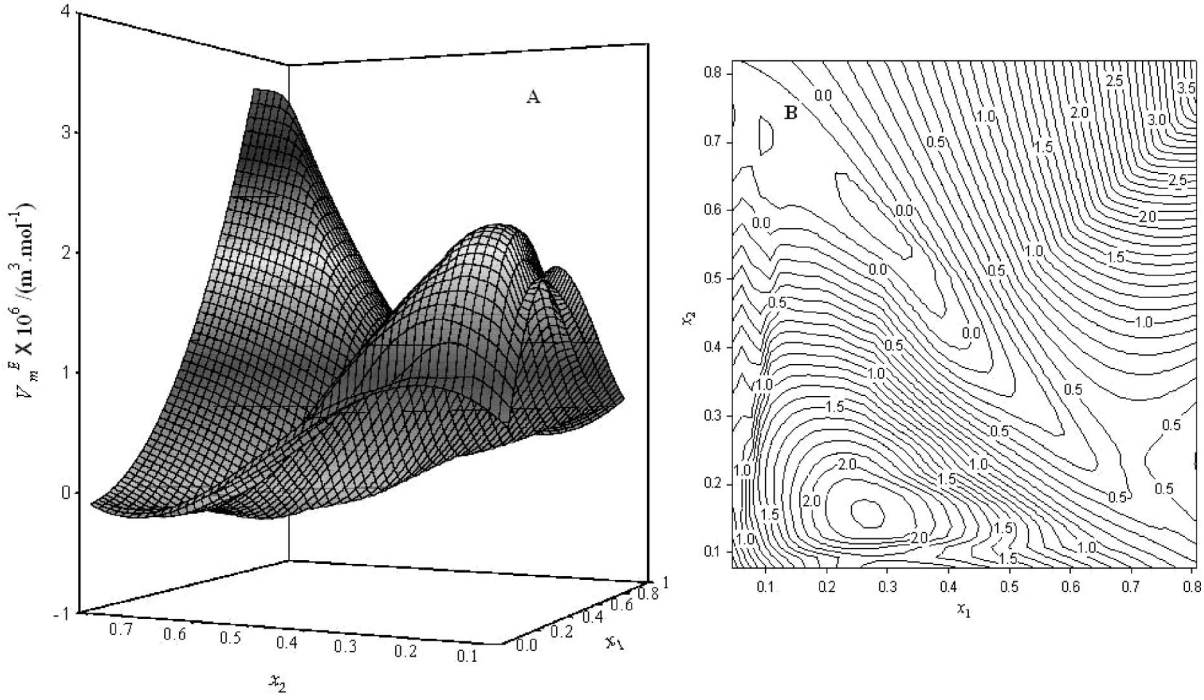

Figure 1. (A) 3D mesh plots of excess molar volumes, V_m^E, for the CHX (1) + CHXN (2) + MA (3) system calculated using eqs 6 and 7 and (B) the corresponding pseudo-2D contour plot of constant values of V_m^E for the same system.

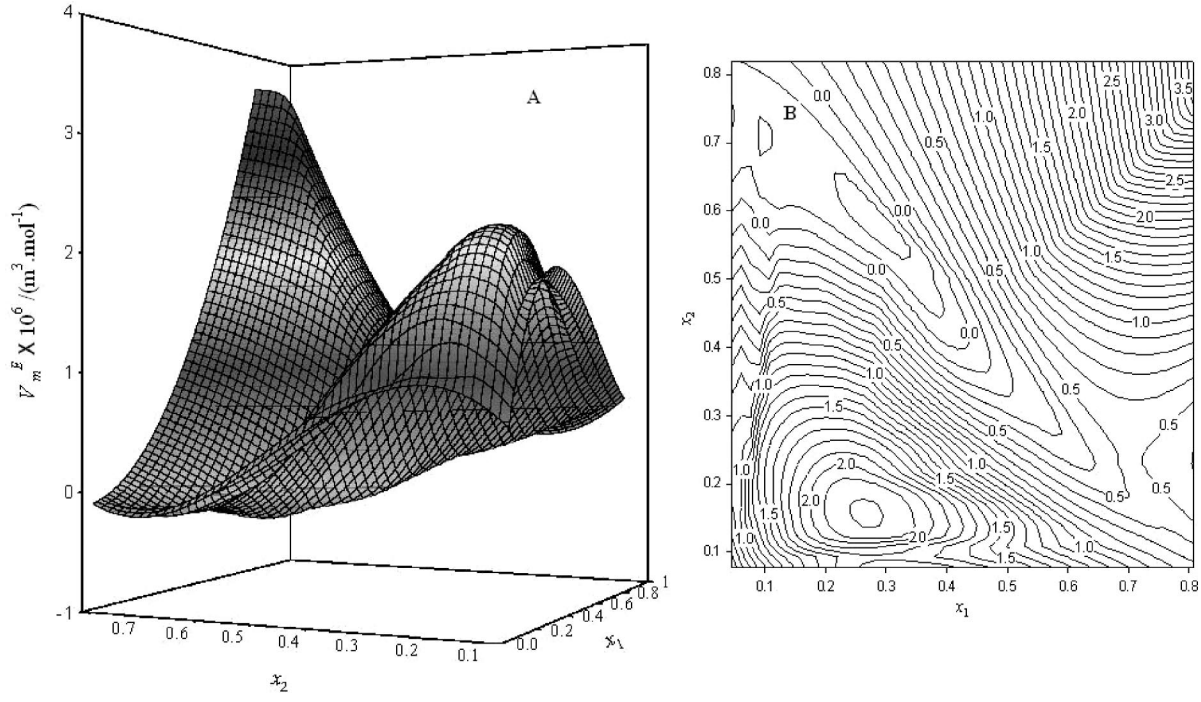

Figure 2. (A) 3D mesh plots of excess molar volumes, V_m^E, for the CHX (1) + CHXN (2) + EA (3) system calculated using eqs 6 and 7 and (B) the corresponding pseudo-2D contour plot of constant values of V_m^E for the same system.

$$V^{0,E}_{m,1} = V^{E}_{m} + x_2(\partial V^{E}_{m}/\partial x_1)_{T,P} \quad (5)$$

The $(\partial V^{E}_{m}/\partial x_1)_{T,P}$ values were calculated using eq 3. The $V^{0,E}_{m,1}$ values are depicted as a function of $x_1$in Figure 7, which shows that the $V^{0,E}_{m,1}$ value gradually decreases as the alkyl chain length of the acetate molecules increases in the binaries studied. A similar trend in $V^{0,E}_{m,1}$ values was also reported by V. Mollica et al.[20] while studying volumetric properties of the binaries of isomeric butanols in C8 solvents at 298.15 K.

The values for the X^{E}_{123} properties (V^{E}_{m} and $\Delta\eta$) of the ternaries were fitted to the Cibulka equation[21]

$$X^{E}_{123} = X^{E}_{BIN} + x_1x_2x_3(C_0 + C_1x_1 + C_2x_2) \quad (6)$$

where X^{E}_{BIN} represents the sum of the corresponding binary properties

$$X^{E}_{BIN} = X^{E}_{12} + X^{E}_{13} + X^{E}_{23} \quad (7)$$

We calculated the values X^{E}_{12}, X^{E}_{13}, and X^{E}_{23} by substituting the values of the coefficients a_k and the corresponding mole fractions of the components in eq 3. The C_i coefficients were calculated by least-squares fitting and are listed in Table 5. Although the second term in the right-hand side of eq 6 is asymmetric, the correlations provided for the ternaries do

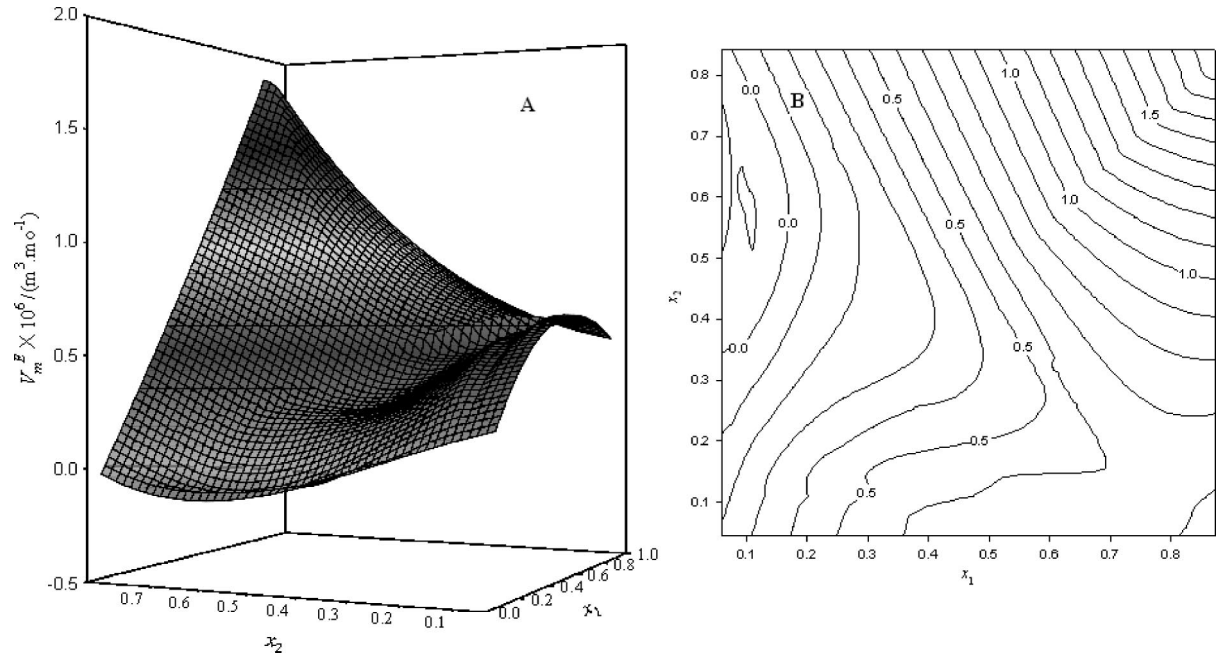

Figure 3. (A) 3D mesh plots of excess molar volumes, V^{E}_{m}, for the CHX (1) + CHXN (2) + PA (3) system calculated using eqs 6 and 7 and (B) the corresponding pseudo-2D contour plot of constant values of V^{E}_{m} for the same system.

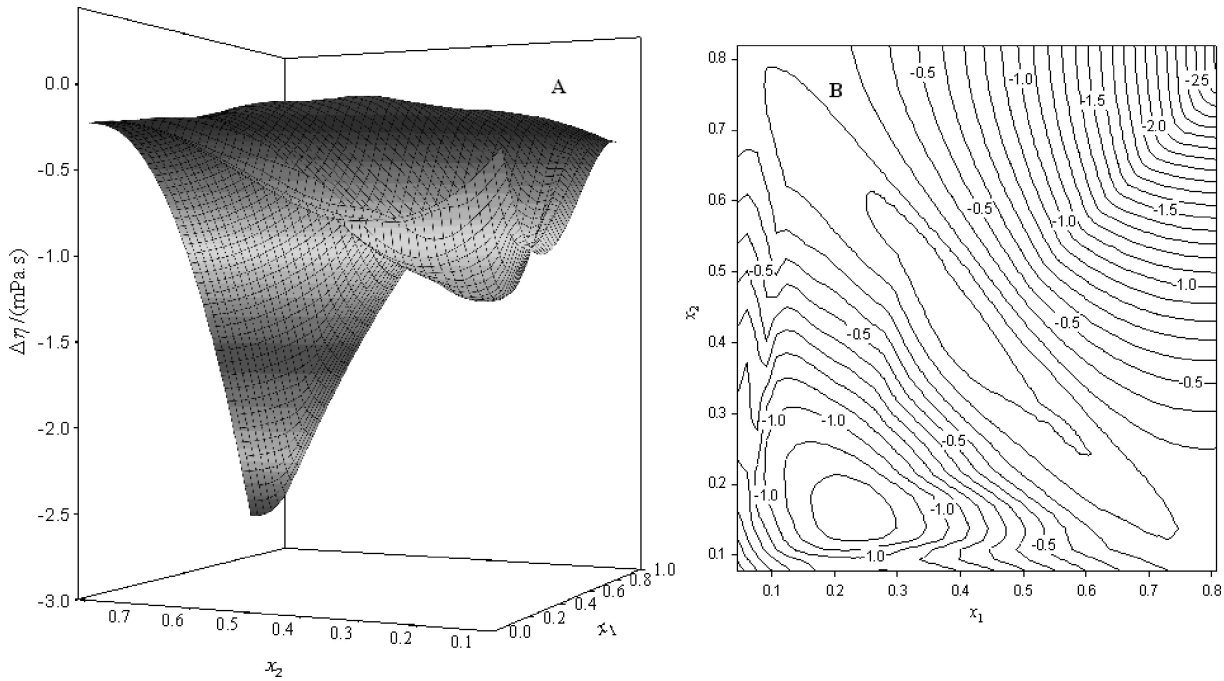

Figure 4. (A) 3D mesh plots of viscosity deviation, $\Delta\eta$, for the CHX (1) + CHXN (2) + MA (3) system calculated using eqs 6 and 7 and (B) the corresponding pseudo-2D contour plot of constant values of $\Delta\eta$ for the same system.

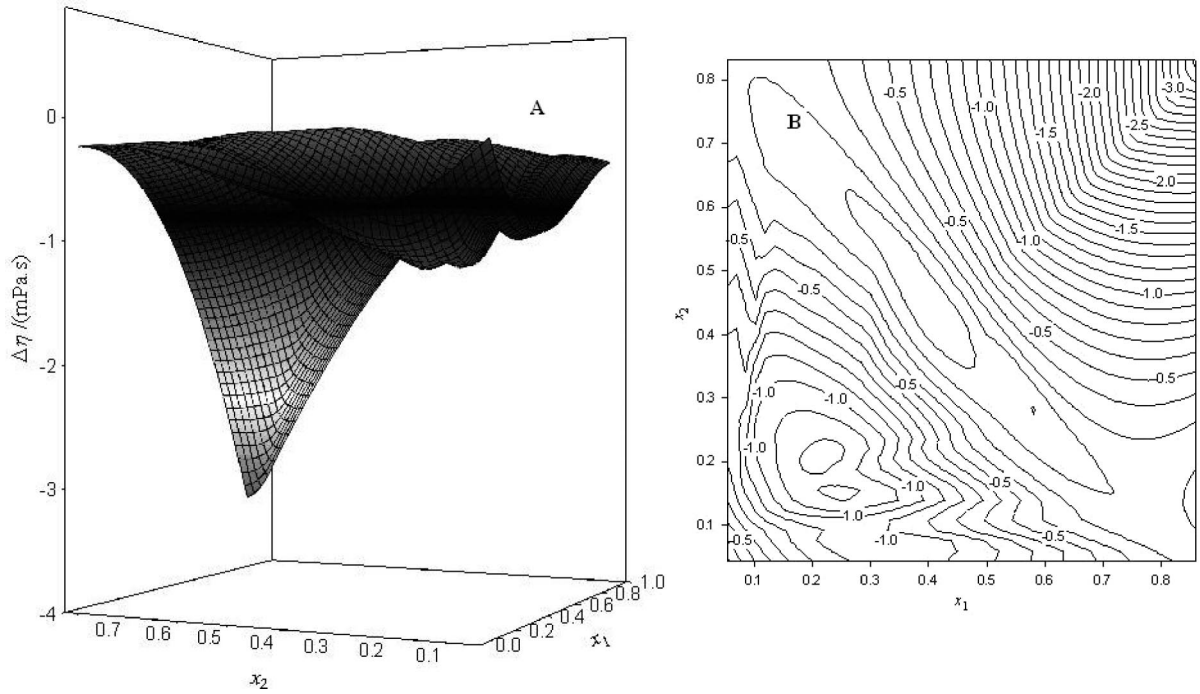

Figure 5. (A) 3D mesh plots of viscosity deviation, $\Delta\eta$, for the CHX (1) + CHXN (2) + EA (3) system calculated using eqs 6 and 7 and (B) the corresponding pseudo-2D contour plot of constant values of $\Delta\eta$ for the same system.

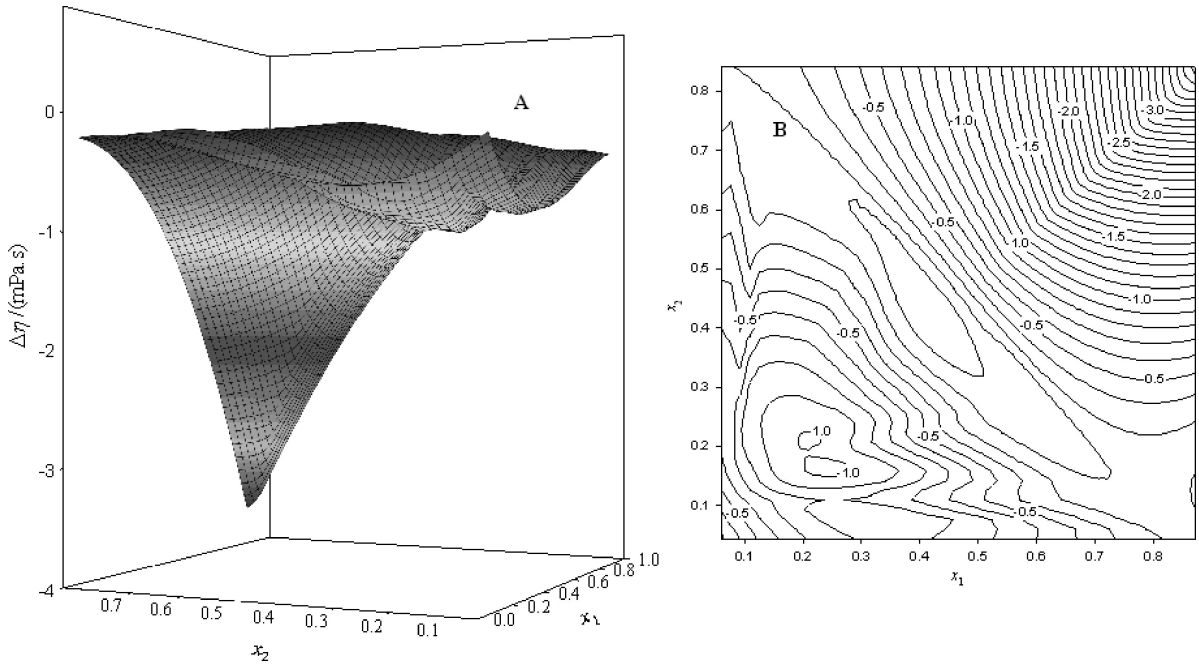

Figure 6. (A) 3D mesh plots of viscosity deviation, $\Delta\eta$, for the CHX (1) + CHXN (2) + PA (3) system calculated using eqs 6 and 7 and (B) the corresponding pseudo-2D contour plot of constant values of $\Delta\eta$ for the same system.

not depend on the particular subscript. Figures 1, 2, 3, 4, 5, and 6 depict 3D mesh plots of X^{E}_{123} properties calculated by using eqs 6 and 7 as a function of the mole fraction of cyclohexane (x_1) and cyclohexanone (x_2); the contour diagrams denote a constant value of the corresponding properties as defined by the mole fractions x_1 and x_2. The so-called ternary contribution, defined as $X^{E}_{123} - X^{E}_{BIN}$, representing the difference between the experimental value for the ternary property and the value predicted by the corresponding data of the binary mixtures, has also been calculated; the maximum and minimum values are listed in Table 6. It is expected that positive contributions arise from the breakup interaction[3] of like molecules, but the maximum and minimum values of ternary contributions[3] revealed nonhomogeneous behavior of the ternary mixtures.

Several semiempirical models have been proposed for estimating the properties of ternary mixtures by utilizing the available data of the constituent binary mixtures. We used the symmetric equations proposed by Rastogi,[22] Köhler,[23] Jacob−Fitzner,[24] and Knobeloch−Schwartz[25] and the asymmetric equations of Tsao−Smith[26] and Toop.[27] The standard deviations between the experimental and the calculated values are listed in Table 7. With these equations, lower deviations are usually obtained for those ternary properties for which the

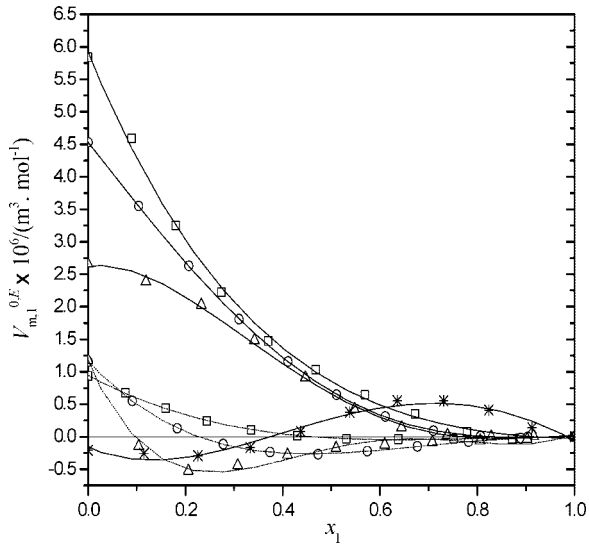

Figure 7. Excess partial molar volumes, $V_{m,1}^{0,E}$, versus x_1 at 298.15 K for the binary mixtures of CHX (1) or CHXN (1) with alkyl acetates (2). □, MA; ○, EA; △, PA; *, CHX (1) in CHXN (2); —, CHX systems; ···, CHXN systems.

Table 7. Standard Deviations between the Experimental and Calculated Ternary Property Values Derived from Different Semiempirical Equations

equation	$\sigma(V_m^E)(10^6)$ / $m^3 \cdot mol^{-1}$	$\sigma(\Delta\eta)$ / mPa·s
Cyclohexane (1) + Cyclohexanone (2) + Methyl Acetate (3)		
Rastogi	0.2364	0.1208
Köhler	0.0942	0.0777
Jacob−Fitzner	0.1207	0.0757
Knobeloch−Schwartz	0.1527	0.1033
Tsao−Smith	0.1743	0.1116
Toop	0.1790	0.0907
Cyclohexane (1) + Cyclohexanone (2) + Ethyl Acetate (3)		
Rastogi	0.2509	0.1094
Köhler	0.3416	0.0653
Jacob−Fitzner	0.2902	0.0635
Knobeloch−Schwartz	0.4088	0.0872
Tsao−Smith	0.2919	0.0951
Toop	0.2812	0.0755
Cyclohexane (1) + Cyclohexanone (2) + Propyl Acetate (3)		
Rastogi	0.2362	0.0955
Köhler	0.1555	0.0681
Jacob−Fitzner	0.1962	0.0586
Knobeloch−Schwartz	0.1068	0.0861
Tsao−Smith	0.2189	0.0932
Toop	0.2092	0.0733

ternary contribution is of little or no importance; therefore, the lower deviations in Table 7 justify our view that the ternary mixtures under study are characterized by nonhomogeneity and weak interactions.

Conclusions

In this Article, the parameters (V_m^E and $\Delta\eta$) derived from the experimental densities and viscosities for the ternary mixtures and the constituent binary mixtures at 298.15 K under atmospheric pressure were fit to Redlich−Kister and Cibulka equations, respectively. Whereas the σ values for the binary V_m^E and $\Delta\eta$ data fitted to the Redlich−Kister equation were in the range of 0.001 to 0.017 and 0.001 to 0.006, respectively, the σ values for the ternary V_m^E and $\Delta\eta$ data fitted to the Cibulka equation were in the range of 0.001 to 0.006 and 0.003 to 0.004, respectively. These results indicate that the derived V_m^E and $\Delta\eta$ data are quite systematic and are a function of the composition of the binary and ternary mixtures. It was found that the binary contribution term, X_{BIN}^E, plays a significant role in characterizing the ternary mixtures, and the maximum and minimum values of the so-called ternary contribution, $X_{123}^E - X_{BIN}^E$, revealed that nonhomogeneity prevails in the studied ternary mixtures.

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