Densities and Viscosities for the Ternary Systems of Methyl *tert*-Butyl Ether + Methanol + Benzene and Methyl *tert*-Butyl Ether + Methanol + Toluene and Their Sub-binary Systems at 298.15 K

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Excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) at 298.15 K are reported for the five binary systems of methyl *tert*-butyl ether (MTBE) + methanol, methanol + benzene, MTBE + benzene, methanol + toluene, and MTBE + toluene and also for the ternary systems of MTBE + methanol + benzene and MTBE + methanol + toluene. The experimental V^E and $\Delta\eta$ data were correlated with Redlich−Kister and Cibulka equation for the binary systems and the ternary system, respectively. The measured binary V^E and $\Delta\eta$ data were compared with the literature values, and the ternary data were compared with the calculated values using the binary contribution models of Tsao−Smith, Kohler, Rastogi, and Radojkovič.

Introduction

Studies on the phase equilibria and excess properties of liquid mixtures are of considerable importance for the design of separation processes and theoretical understanding of the nature of molecular interaction.[1] Many investigations have already been carried out for binary mixtures, while that of ternary mixtures are not easily available in the literature. It is therefore interesting to estimate excess properties of ternary mixtures from their sub-binary data.[2−4]

Oxygenated compounds such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME) have been used as gasoline additives because of their good anti-knocking properties. The phase equilibrium and excess properties for systems containing MTBE, alcohols, and hydrocarbons have been the subject of numerous investigations in the recent years. Nevertheless, more data are required to develop solution models and to design separation processes.[5]

In our previous paper,[6] experimental results of isothermal vapor−liquid equilibria (VLE) were reported for the five binary systems of MTBE (1) + methanol (2), methanol (1) + benzene (2), MTBE (1) + benzene (2), methanol (1) + toluene (2), and MTBE (1) + toluene (2), and the ternary systems of MTBE (1) + methanol (2) + benzene (3) and MTBE (1) + methanol (2) + toluene (3) at 313.15 K. Continuously in present work, as a part of systematic study for the MTBE mixtures, the excess molar volumes (V^E) at 298.15 K for the same binary and ternary systems of MTBE (1) + methanol (2) + benzene (3) and MTBE (1) + methanol (2) + toluene (3) are determined from measured densities by using a digital vibrating tube densimeter. Besides the viscosities at the same temperature for the same mixtures are measured by using an Ubbelhode viscometer, then viscosity deviations ($\Delta\eta$) are determined from the viscosities of each pure component and the mixture. The experimental excess molar volumes and viscosity deviations were correlated using the Redlich−Kister polynomial equation[7] and the Cibulka equation[8] for the binary and ternary systems, respectively. For the binary V^E and $\Delta\eta$, the experimental data were compared with the values in the literature.[9−13] And additionally for the ternary system, the measured excess molar volumes and viscosity deviations were compared with the predicted values using several estimation methods of binary contribution with constituent binary Redlich−Kister fitting parameters.

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Table 1. Purities, Densities, and Viscosities of the Pure Components

		ρ/g·cm^{-3} at 298.15 K		η/mPa·s at 298.15 K	
chemicals	GC analysis	this work	lit. value	this work	lit. value
MTBE	99.8	0.7367	0.7359[a]	0.361	0.340[a]
			0.7374[b]		0.3687[b]
methanol	99.9	0.7867	0.7864[a]	0.550	0.550[a]
			0.7866[c]		0.5482[d]
			0.7881[d]		
benzene	99.9	0.8739	0.8738[b]	0.604	0.6489[b]
			0.8736[c]		0.6080[d]
			0.8697[d]		
toluene	99.9	0.8623	0.8605[d]	0.556	0.5641[d]
			0.8622[e]		
			0.86233[f]		

[a] Ref 9. [b] Ref 11. [c] Ref 10. [d] Ref 14. [e] Ref 12. [f] Ref 13.

Experimental Section

Materials. MTBE, benzene, toluene were from Aldrich Chemical Co., and methanol was supplied from Merck Co. MTBE had a declared purity of better than $w = 99.8$ %, was used without further purification. Others were used after the water content had been reduced using molecular sieves with a pore diameter of 0.4 nm. The purity of chemicals was checked by gas chromatography and by comparing the measured density and viscosity with the values reported in the literature.[9−14] The water content determined by Karl-Fisher titration (Metrohm 684 KF coulometer) was less than 50 ppm. The purities, densities, and viscosities of pure substances are summarized in Table 1.

Apparatus and Procedure. Densities were measured using a digital vibrating glass tube densimeter (Anton Paar, model DMA 48, Graz, Austria). Excess molar volumes (V^E) were calculated from directly measured densities of the pure and mixture samples. The uncertainty of the density is less than $\pm 1 \times 10^{-4}$ g·cm^3. Before each set of measurements, the apparatus was calibrated with doubly distilled water and dried air. Mixture

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Table 2. Densities, Viscosities, Excess Molar Volumes, and Viscosity Deviations for the Five Binary Systems of MTBE, Methanol, Benzene, and Toluene at 298.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s
MTBE (1) + Methanol (2)				
0.0512	0.7825	0.547	−0.153	0.0068
0.0994	0.7790	0.536	−0.282	0.0046
0.1991	0.7714	0.488	−0.427	−0.025
0.3011	0.7654	0.455	−0.556	−0.038
0.4015	0.7602	0.436	−0.635	−0.039
0.4993	0.7557	0.420	−0.669	−0.035
0.6001	0.7516	0.402	−0.669	−0.035
0.7001	0.7477	0.387	−0.591	−0.031
0.8007	0.7441	0.376	−0.485	−0.023
0.8998	0.7403	0.366	−0.266	−0.014
0.9494	0.7385	0.360	−0.142	−0.010
Methanol (1) + Benzene (2)				
0.0504	0.8717	0.581	0.0150	−0.020
0.1000	0.8695	0.563	0.0207	−0.035
0.1998	0.8647	0.553	0.0301	−0.040
0.2982	0.8591	0.560	0.0534	−0.028
0.4000	0.8530	0.561	0.0458	−0.021
0.5000	0.8462	0.566	0.0315	−0.011
0.6000	0.8385	0.565	0.0024	−0.0067
0.7000	0.8290	0.560	−0.0045	−0.0060
0.8009	0.8176	0.557	−0.0071	−0.0034
0.9013	0.8037	0.553	−0.0030	−0.0025
0.9500	0.7957	0.551	0.0031	−0.0022
MTBE (1) + Benzene (2)				
0.0502	0.8651	0.566	−0.0276	−0.026
0.0999	0.8567	0.551	−0.0590	−0.029
0.1994	0.8403	0.499	−0.0805	−0.056
0.3005	0.8249	0.473	−0.130	−0.058
0.4006	0.8104	0.457	−0.160	−0.050
0.5003	0.7967	0.437	−0.181	−0.045
0.6000	0.7838	0.422	−0.203	−0.037
0.7003	0.7712	0.397	−0.182	−0.036
0.8000	0.7592	0.395	−0.137	−0.014
0.8997	0.7479	0.376	−0.102	−0.0095
0.9497	0.7420	0.372	−0.0126	−0.0014
Methanol (1) + Toluene (2)				
0.0499	0.8607	0.551	0.0146	−0.0049
0.0998	0.8591	0.547	0.0168	−0.0084
0.1993	0.8559	0.540	−0.0143	−0.015
0.2998	0.8521	0.541	−0.0382	−0.014
0.4007	0.8475	0.550	−0.0482	−0.0038
0.4998	0.8421	0.557	−0.0608	0.0044
0.6002	0.8356	0.562	−0.0675	0.0097
0.7000	0.8277	0.572	−0.0722	0.020
0.8000	0.8177	0.569	−0.0679	0.018
0.9000	0.8044	0.561	−0.0399	0.010
0.9501	0.7963	0.555	−0.0256	0.0052
MTBE (1) + Toluene (2)				
0.0500	0.8558	0.541	−0.0623	−0.0048
0.1000	0.8493	0.528	−0.116	−0.0085
0.2001	0.8365	0.505	−0.223	−0.012
0.3002	0.8237	0.479	−0.295	−0.018
0.4001	0.8112	0.458	−0.365	−0.020
0.5001	0.7987	0.438	−0.385	−0.021
0.6001	0.7857	0.419	−0.306	−0.020
0.6998	0.7734	0.398	−0.283	−0.022
0.8000	0.7609	0.383	−0.193	−0.017
0.8999	0.7486	0.372	−0.0862	−0.0086
0.9502	0.7425	0.365	−0.0295	−0.0053

samples were prepared in a 20 mL vial by mass using a microbalance (A&D, HA202) with a uncertainty of $\pm 1 \times 10^{-5}$ g, charging the heavier component first to minimize vaporization effects. The operating procedure has been described elsewhere.[15,16]

Viscosity deviation ($\Delta\eta$) values of the mixture samples were calculated from the viscosities (η) that are experimentally measured. η of the pure components and mixtures were determined from the kinematic viscosities (ν) measured using an Ubbelhode viscometer with automatic measuring unit (LAUDA, model PVS1, Germany). The uncertainty of the flowing time measurement is ± 0.01 s. The mole fractions of the mixture samples were the same as the samples used in the density measurements. Further detailed description for the measuring procedure can be found in our previous paper.[17]

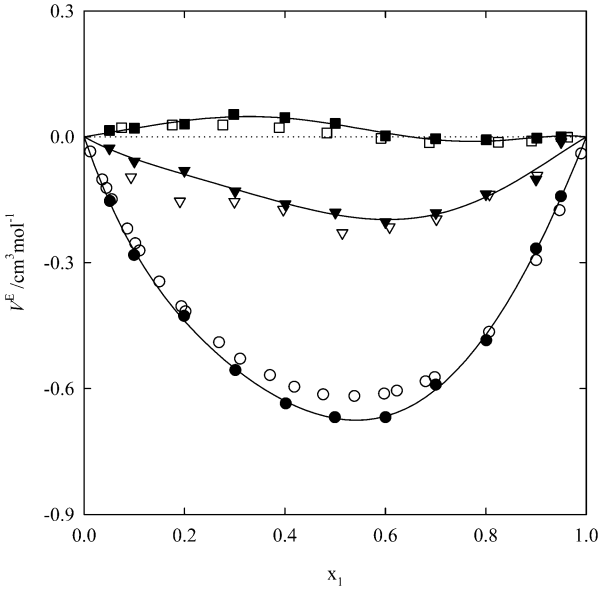

Figure 1. Excess molar volumes (V^E) for the three binary systems of MTBE, methanol, and benzene at 298.15 K: ●, MTBE (1) + methanol (2); ○, MTBE (1) + methanol (2) from Pal and Dass;[9] ■, methanol (1) + benzene (2); □, methanol (1) + benzene (2) from Rodríguez et al.;[10] ▼, MTBE (1) + benzene (2); ▽, MTBE (1) + benzene (2) from Viswanathan et al.[11] Solid curves were calculated from the Redlich−Kister equation.

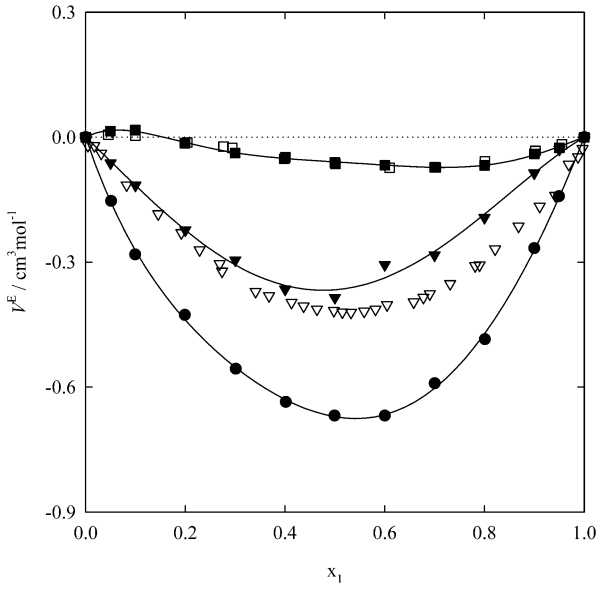

Figure 2. Excess molar volumes (V^E) for the three binary systems of MTBE, methanol, and toluene at 298.15 K: ●, MTBE (1) + methanol (2); ■, methanol (1) + toluene (2); □, methanol (1) + toluene (2) from Rodríguez et al.;[12] ▼, MTBE (1) + toluene (2); ▽, MTBE (1) + toluene (2) from Domanska.[13] Solid curves were calculated from the Redlich−Kister equation.

Results and Discussions

Binary Systems. The excess molar volumes for the multicomponent mixtures are calculated from the measured densities of pure substances and mixtures from eq 1:

$$V^{\mathrm{E}} = \frac{\sum_i x_i M_i}{\rho_{\mathrm{m}}} - \sum_i \left(\frac{x_i M_i}{\rho_i}\right) \quad (1)$$

where x_i, M_i, ρ_i, and ρ_{m} are the mole fraction, molar mass, pure component density, and mixture density, respectively.

The viscosity (η) is determined from the experimental density (ρ) and kinematic viscosity (ν) as shown in eq 2. The viscosity deviations ($\Delta\eta$) for the multicomponent system are calculated from the viscosity of pure substances and mixtures from eq 3:

$$\eta = \rho\nu \quad (2)$$

$$\Delta\eta = \eta_{\mathrm{m}} - \sum_{i=1}^{n} x_i \eta_i \quad (3)$$

The experimental densities, viscosities, excess molar volumes, and viscosity deviations at 298.15 K for the binary systems of MTBE (1) + methanol (2), methanol (1) + benzene (2), MTBE (1) + benzene (2), methanol (1) + toluene (2), and MTBE (1) + toluene (2) are listed and plotted in Table 2 and Figures 1 to 4. The V^{E} of the MTBE (1) + methanol (2) system show negative values in the whole composition range, and the $\Delta\eta$ of this mixture also has negative values in the whole range with the exception of low MTBE concentration. The V^{E} values of methanol (1) + benzene (2) and methanol (1) + toluene (2) systems are very close to ideal behavior. In case of MTBE (1) + benzene (2) and MTBE (1) + toluene (2), all measured V^{E} and $\Delta\eta$ showed negative values, and similar results were obtained for the two binary systems. It can be said that the interactions between these compounds in the mixtures are not so strong.

These binary V^{E} and $\Delta\eta$ data were correlated with the five-parameter Redlich−Kister polynomial equation:

$$V_{12}^{\mathrm{E}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} \text{ or } \Delta\eta_{12}/\mathrm{mPa\cdot s} = x_1 x_2 \sum_{i=1}^{5} A_i (x_1 - x_2)^{i-1} \quad (4)$$

where A_i is the adjustable parameter and n is the number of fitted parameters, A_i. The standard deviation of the fits σ_{st} is defined as

$$\sigma_{\mathrm{st}} = \left[\frac{\sum_i (V_{\mathrm{cal}}^{\mathrm{E}} - V_{\mathrm{exp}}{}^{\mathrm{E}})_i^2}{(N-n)}\right]^{1/2} \quad (5)$$

where N is the number of experimental data points.

In Figures 1 to 4, the continuous solid lines represent the calculated values according to Redlich−Kister polynomial. The calculated values agree well with the experimental data as shown in the figures.

The experimental binary V^{E} data were compared with the literature values[9−13] and matched well, as shown in Figures 1 and 2. For binary $\Delta\eta$, the measured data were compared with the published values[9,11] for the systems MTBE (1) + methanol (2) and MTBE (1) + benzene (2) and showed good agreements as shown in Figure 3.

Ternary Systems. The densities, viscosities, excess molar volumes, and viscosity deviations at 298.15 K for the ternary systems of MTBE (1) + methanol (2) + benzene (3) and MTBE (1) + methanol (2) + toluene (3) are determined and listed in Tables 3 and 4. The measured ternary V^{E} and $\Delta\eta$ data have negative deviations from ideal behaviors over almost whole composition range. The ternary $\Delta\eta$ show very small deviations from the ideality such as the results of their sub-binary mixtures.

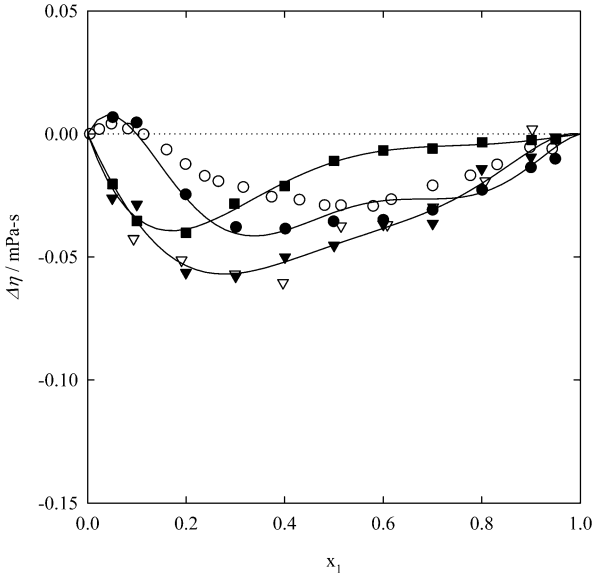

Figure 3. Viscosity deviations ($\Delta\eta$) for the three binary systems of MTBE, methanol, and benzene at 298.15 K: ●, MTBE (1) + methanol (2); ○, MTBE (1) + methanol (2) from Pal and Dass;[9] ■, methanol (1) + benzene (2); ▼, MTBE (1) + benzene (2); ▽, MTBE (1) + benzene (2) from Viswanathan et al.[11] Solid curves were calculated from the Redlich−Kister equation.

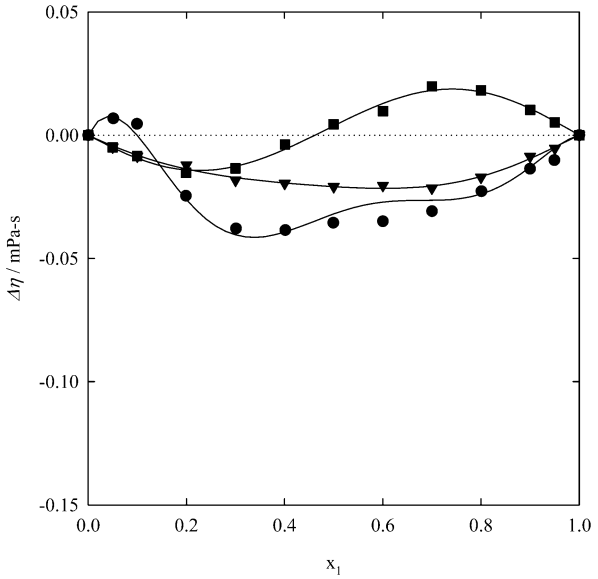

Figure 4. Viscosity deviations ($\Delta\eta$) for the three binary systems of MTBE, methanol, and toluene at 298.15 K: ●, MTBE (1) + methanol (2); ■, methanol (1) + toluene (2); ▼, MTBE (1) + toluene (2). Solid curves were calculated from the Redlich−Kister equation.

For the ternary system, excess volume and viscosity deviation data were correlated with following Cibulka equation[8] as a modification of the Radojkovič equation[18] (eq 10):

$$M_{123}^{\mathrm{E}} = M_{12^*}^{\mathrm{E}} + M_{23^*}^{\mathrm{E}} + M_{13^*}^{\mathrm{E}} + x_1 x_2 x_3 (A_1 + A_2 x_1 + A_3 x_2) \quad (6)$$

where $M_{12^*}{}^{\mathrm{E}}$, $M_{23^*}{}^{\mathrm{E}}$, and $M_{13^*}{}^{\mathrm{E}}$ represent the excess properties calculated from binary Redlich−Kister parameters and x_1, x_2 and x_3 are mole fractions in the ternary mixture.

The correlated values are in good agreement with the experimental data with standard deviations of 0.0907 $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$ and 0.018 mPa·s for the MTBE (1) + methanol (2) + benzene (3). The correlation results were represented in Figure 5 for V^{E}

Table 3. Densities, Viscosities, Excess Molar Volumes, and Viscosity Deviations for the Ternary System of MTBE (1) + Methanol (2) + Benzene (3) at 298.15 K

x_1	x_2	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s
0.0599	0.5405	0.8313	0.537	−0.165	−0.024
0.0501	0.4496	0.8400	0.557	−0.094	−0.010
0.0410	0.3596	0.8477	0.549	−0.0441	−0.026
0.0295	0.2824	0.8544	0.549	0.0101	−0.032
0.0212	0.1786	0.8614	0.562	0.0429	−0.027
0.1798	0.4202	0.8178	0.508	−0.334	−0.030
0.1541	0.3479	0.8279	0.514	−0.266	−0.034
0.1198	0.2800	0.8384	0.531	−0.167	−0.029
0.0899	0.2101	0.8477	0.537	−0.0867	−0.034
0.0303	0.0694	0.8648	0.555	0.0564	−0.038
0.3000	0.2996	0.8069	0.471	−0.452	−0.044
0.2505	0.2498	0.8184	0.481	−0.352	−0.049
0.2000	0.1995	0.8298	0.498	−0.252	−0.047
0.1503	0.1498	0.8408	0.509	−0.154	−0.051
0.1001	0.0999	0.8519	0.524	−0.0820	−0.051
0.3502	0.1498	0.8092	0.461	−0.349	−0.050
0.2802	0.1196	0.8217	0.472	−0.265	−0.058
0.2099	0.0896	0.8342	0.496	−0.162	−0.052
0.0699	0.0305	0.8597	0.550	0.0273	−0.035
0.3599	0.0404	0.8090	0.554	0.407	0.039
0.0402	0.5997	0.8292	0.540	−0.0505	−0.022
0.0301	0.6999	0.8212	0.551	−0.0215	−0.0080
0.0201	0.7998	0.8125	0.559	−0.0419	0.0032
0.1503	0.4997	0.8164	0.532	−0.293	−0.0089
0.1199	0.5999	0.8132	0.526	−0.274	−0.016
0.0901	0.6999	0.8086	0.535	−0.217	−0.0096
0.0299	0.9002	0.7960	0.542	−0.0809	−0.0065
0.3001	0.3999	0.7983	0.471	−0.471	−0.038
0.2488	0.5023	0.7975	0.491	−0.417	−0.025
0.2001	0.6001	0.7971	0.507	−0.411	−0.016
0.1500	0.7000	0.7956	0.533	−0.332	0.0031
0.0999	0.8001	0.7940	0.526	−0.264	−0.011
0.4204	0.3997	0.7783	0.437	−0.542	−0.044
0.3500	0.5000	0.7800	0.459	−0.539	−0.033
0.2803	0.5998	0.7820	0.476	−0.536	−0.027
0.2101	0.6999	0.7834	0.496	−0.446	−0.019
0.0701	0.8999	0.7858	0.532	−0.180	−0.0060
0.5400	0.4003	0.7601	0.418	−0.624	−0.033
0.4501	0.4999	0.7637	0.440	−0.649	−0.028
0.3602	0.5999	0.7673	0.452	−0.604	−0.032
0.2699	0.7001	0.7713	0.478	−0.519	−0.023
0.1799	0.8001	0.7756	0.501	−0.388	−0.016
0.3999	0.0598	0.8071	0.460	−0.237	−0.044
0.5002	0.0493	0.7942	0.437	−0.311	−0.042
0.6001	0.0397	0.7767	0.415	0.353	−0.041
0.6994	0.0308	0.7692	0.400	−0.224	−0.033
0.8008	0.0191	0.7578	0.393	−0.172	−0.015
0.4001	0.1801	0.8002	0.448	−0.464	−0.049
0.5002	0.1494	0.7878	0.427	−0.464	−0.048
0.6006	0.1204	0.7749	0.409	−0.280	−0.043
0.7003	0.0895	0.7654	0.400	−0.375	−0.029
0.8998	0.0301	0.7464	0.378	−0.262	−0.0059
0.4002	0.2995	0.7907	0.446	−0.502	−0.045
0.4998	0.2503	0.7798	0.419	−0.516	−0.050
0.6001	0.1999	0.7699	0.401	−0.500	−0.046
0.7003	0.1498	0.7607	0.389	−0.438	−0.037
0.8001	0.0998	0.7520	0.377	−0.309	−0.028
0.5000	0.3501	0.7714	0.414	−0.623	−0.049
0.6003	0.2796	0.7650	0.401	−0.802	−0.042
0.7002	0.2097	0.7557	0.390	−0.494	−0.033
0.9003	0.0698	0.7427	0.375	−0.228	−0.0067
0.6000	0.3600	0.7550	0.395	−0.567	−0.043
0.7000	0.2698	0.7498	0.381	−0.472	−0.039
0.8000	0.1801	0.7450	0.371	−0.345	−0.028

Table 4. Densities, Viscosities, Excess Molar Volumes, and Viscosity Deviations for the Ternary System of MTBE (1) + Methanol (2) + Toluene (3) at 298.15 K

x_1	x_2	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s
0.0598	0.5400	0.8295	0.544	−0.240	0.0027
0.0499	0.4502	0.8368	0.550	−0.181	0.0061
0.0412	0.3596	0.8429	0.536	−0.121	−0.0094
0.0303	0.2700	0.8489	0.532	−0.103	−0.016
0.0208	0.1809	0.8537	0.533	−0.058	−0.018
0.1801	0.4197	0.8181	0.501	−0.489	−0.018
0.1507	0.3497	0.8273	0.504	−0.414	−0.020
0.1199	0.2797	0.8357	0.515	−0.325	−0.016
0.0898	0.2097	0.8431	0.523	−0.223	−0.014
0.0294	0.0711	0.8562	0.533	−0.042	−0.017
0.3005	0.2994	0.8075	0.467	−0.568	−0.029
0.2502	0.2495	0.8181	0.498	−0.482	−0.0080
0.2000	0.2000	0.8282	0.494	−0.414	−0.022
0.1500	0.1495	0.8365	0.503	−0.197	−0.023
0.0996	0.0989	0.8461	0.518	−0.184	−0.018
0.3563	0.1341	0.8097	0.459	−0.466	−0.027
0.2802	0.1191	0.8210	0.472	−0.420	−0.028
0.2107	0.0889	0.8319	0.492	−0.350	−0.023
0.0695	0.0331	0.8525	0.529	−0.133	−0.014
0.3602	0.0396	0.8149	0.462	−0.466	−0.023
0.2702	0.0294	0.8265	0.486	−0.332	−0.017
0.1805	0.0193	0.8384	0.499	−0.233	−0.022
0.0400	0.5996	0.8284	0.553	−0.187	0.0081
0.0377	0.8730	0.8213	0.557	−1.488	0.014
0.0201	0.7998	0.8131	0.559	−0.118	0.012
0.1499	0.5000	0.8170	0.520	−0.441	−0.0036
0.1200	0.6000	0.8137	0.535	−0.387	0.0059
0.0899	0.6999	0.8097	0.534	−0.323	0.0000
0.0301	0.8999	0.7966	0.538	−0.112	−0.0065
0.3002	0.3998	0.7999	0.495	−0.607	0.0002
0.2500	0.4996	0.7996	0.481	−0.583	−0.024
0.2000	0.6001	0.7986	0.516	−0.511	0.0027
0.1500	0.6999	0.7969	0.513	−0.406	−0.0097
0.1000	0.8001	0.7947	0.526	−0.293	−0.0052
0.4207	0.4008	0.7804	0.442	−0.687	−0.030
0.3500	0.4999	0.7812	0.450	−0.577	−0.035
0.2801	0.6000	0.7831	0.467	−0.576	−0.031
0.2100	0.7000	0.7842	0.494	−0.477	−0.017
0.0699	0.9001	0.7862	0.530	−0.191	−0.0066
0.5401	0.3999	0.7605	0.388	−0.608	−0.060
0.4500	0.4999	0.7639	0.422	−0.621	−0.043
0.3601	0.5998	0.7673	0.443	−0.570	−0.039
0.2699	0.7000	0.7714	0.461	−0.506	−0.038
0.1801	0.7999	0.7756	0.489	−0.378	−0.027
0.3999	0.0608	0.8082	0.460	−0.448	−0.018
0.5003	0.0497	0.7957	0.436	−0.430	−0.023
0.6002	0.0400	0.7838	0.417	−0.454	−0.022
0.7005	0.0294	0.7715	0.402	−0.357	−0.017
0.8006	0.0193	0.7597	0.390	−0.271	−0.0095
0.4006	0.1796	0.8010	0.449	−0.550	−0.028
0.5003	0.1496	0.7893	0.429	−0.555	−0.029
0.6004	0.1195	0.7781	0.411	−0.525	−0.027
0.7001	0.0901	0.7670	0.394	−0.427	−0.025
0.9004	0.0294	0.7461	0.369	−0.122	−0.011
0.4000	0.3000	0.7924	0.446	−0.628	−0.030
0.4999	0.2504	0.7816	0.428	−0.620	−0.029
0.6005	0.1994	0.7719	0.406	−0.612	−0.032
0.7003	0.1494	0.7620	0.392	−0.467	−0.026
0.7999	0.1000	0.7531	0.382	−0.349	−0.018
0.5000	0.3500	0.7724	0.420	−0.640	−0.037
0.6000	0.2800	0.7643	0.402	−0.608	−0.036
0.7000	0.2099	0.7564	0.386	−0.487	−0.032
0.8990	0.0711	0.7425	0.363	−0.152	−0.017
0.6005	0.3596	0.7555	0.396	−0.575	−0.041
0.7006	0.2693	0.7502	0.383	−0.490	−0.035
0.7997	0.1802	0.7453	0.374	−0.356	−0.025

and in Figure 6 for $\Delta\eta$. The solid lines in figures represent constant excess molar volumes of the ternary systems calculated by the Cibulka equation. For the system MTBE (1) + methanol (2) + toluene (3), the standard deviations of fits are 0.0362 cm^3·mol^{-1} and 0.078 mPa·s for V^E and $\Delta\eta$, respectively. These were plotted in Figures 7 and 8. In Table 5, the parameters of the Redlich−Kister and Cibulka equations are listed together with standard deviations of the binary and ternary systems studied in this work.

Prediction of Ternary Data from Binary Fitting Parameters. Excess molar volumes and viscosity deviations for the ternary

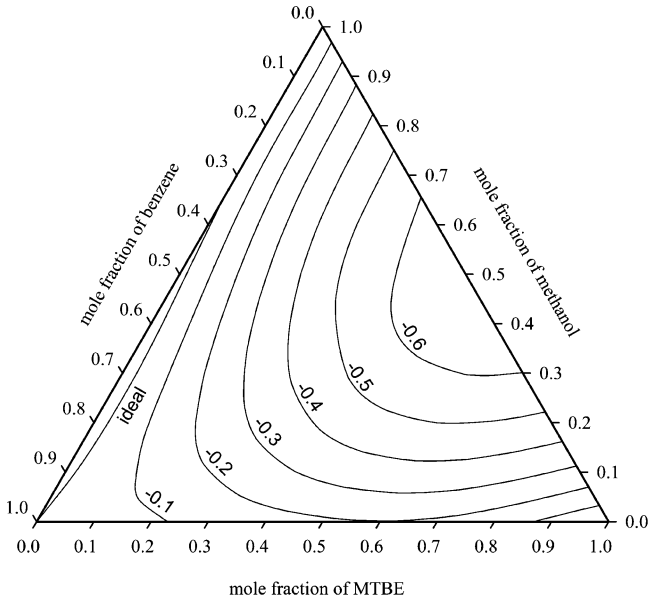

Figure 5. Constant lines of the excess molar volumes (cm^3·mol^{-1}) for the ternary system of MTBE (1) + methanol (2) + benzene (3) at 298.15 K.

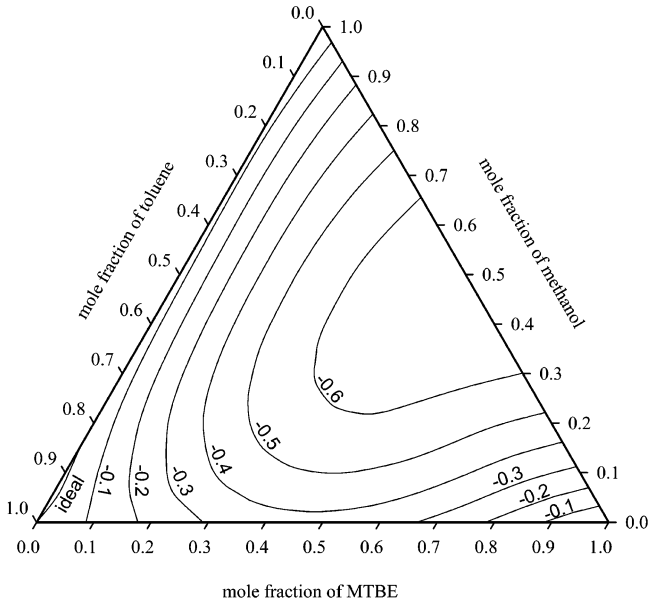

Figure 6. Constant lines of the excess molar volumes (cm^3·mol^{-1}) for the ternary system of MTBE (1) + methanol (2) + toluene (3) at 298.15 K.

system were calculated using four conventional prediction models of Tsao−Smith,[19] Kohler,[20] Rastogi,[21] and Radojkovič.[18] The expressions for these models are as follow:

Tsao-Smith equation:

$$M_{123}^{\mathrm{E}} = \frac{x_2 M_{12}^{\mathrm{E}}}{1 - x_1} + \frac{x_3 M_{13}^{\mathrm{E}}}{1 - x_1} + (1 - x_1) M_{23}^{\mathrm{E}} \qquad (7)$$

where M_{ij}^{E} is the binary contribution of the ternary property at x_i^0 and x_j^0:

$$(x_i^0 = 1 - x_j^0 = x_i/(x_i + x_j))$$

Kohler equation:

$$M_{123}^{\mathrm{E}} = (x_1 + x_2)^2 M_{12}^{\mathrm{E}} + (x_1 + x_3)^2 M_{13}^{\mathrm{E}} + (x_2 + x_3)^2 M_{23}^{\mathrm{E}} \qquad (8)$$

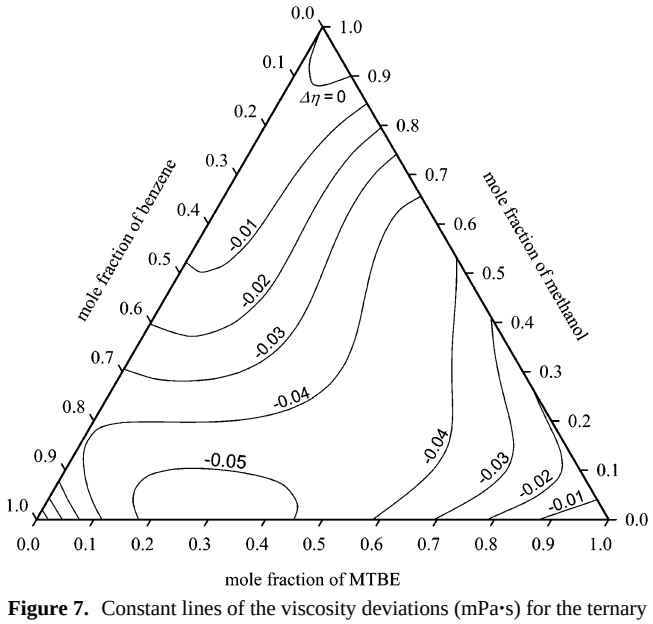

Figure 7. Constant lines of the viscosity deviations (mPa·s) for the ternary system of MTBE (1) + methanol (2) + benzene (3) at 298.15 K.

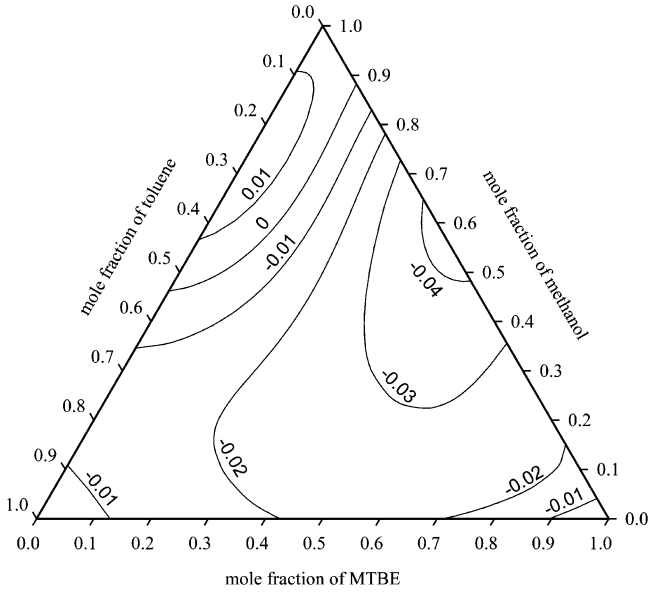

Figure 8. Constant lines of the viscosity deviations (mPa·s) for the ternary system of MTBE (1) + methanol (2) + toluene (3) at 298.15 K.

Rastogi equation:

$$M_{123}^{\mathrm{E}} = \frac{1}{2}[(x_1 + x_2) M_{12}^{\mathrm{E}} + (x_1 + x_3) M_{13}^{\mathrm{E}} + (x_2 + x_3) M_{23}^{\mathrm{E}}] \qquad (9)$$

Radojkovič equation:

$$M_{123}^{\mathrm{E}} = M_{12^*}^{\mathrm{E}} + M_{23^*}^{\mathrm{E}} + M_{13^*}^{\mathrm{E}} \qquad (10)$$

In the Radojkovič equation, the binary contribution $M_{ij^*}^{\mathrm{E}}$ is evaluated using directly the ternary mole fractions.

The standard deviations between our experimental ternary data and estimated values were determined from eq 5, and the results are listed in Table 6. The Kohler equation gave the closest estimation results to the experimental data with the standard deviations of (0.095 and 0.043) cm^3·mol^{-1} for the ternary V^{E} of MTBE (1) + methanol (2) + benzene (3) and MTBE (1) + methanol (2) + toluene (3). The Radojkovič equation also provides good results in the estimation of ternary V^{E}, and it gave the best results for the calculation of the ternary $\Delta\eta$ of

Table 5. Fitted Redlich−Kister Parameters and Cibulka Parameters with the Standard Deviations for V^E and $\Delta\eta$ of MTBE (1) + Methanol (2) + Benzene (3) and MTBE (1) + Methanol (2) + Toluene (3) at 298.15 K

	system	A_1	A_2	A_3	A_4	A_5	σ_{st}[a]
		MTBE (1) + Methanol (2) + Benzene (3)					
V^E	1 + 2	−2.6843	−0.4066	−0.3677	0.6542	−0.2359	0.0106[b]
	2 + 3	0.1190	−0.3845	−0.1714	0.3643	0.2276	0.0047[b]
	1 + 3	−0.7423	−0.4229	0.0318	0.3983	0.0140	0.0132[b]
	1 + 2 + 3	−3.5134	1.5113	1.1520			0.0907[b]
$\Delta\eta$	1 + 2	−0.1277	0.1409	−0.2919	−0.3590	0.5910	0.0056[c]
	2 + 3	−0.0456	0.1281	−0.2436	0.1427	−0.0088	0.0017[c]
	1 + 3	−0.1805	0.1386	−0.2044	0.0988	0.1838	0.0054[c]
	1 + 2 + 3	1.2896	−2.5870	−0.8048			0.018[c]
		MTBE (1) + Methanol (2) + Toluene (3)					
V^E	1 + 2	−2.6843	−0.4066	−0.3677	0.6542	−0.2359	0.0106 [b]
	2 + 3	−0.2375	−0.1495	−0.2377	−0.3778	0.5602	0.0023[b]
	1 + 3	−1.4659	0.1894	0.5175	0.0271	0.0362	0.0143[b]
	1 + 2 + 3	−6.5518	6.2873	4.0743			0.0362[b]
$\Delta\eta$	1 + 2	−0.1277	0.1409	−0.2919	−0.3590	0.5910	0.0056[c]
	2 + 3	0.0153	0.1982	−0.0133	−0.0910	0.0025	0.0018[c]
	1 + 3	−0.0835	−0.0240	−0.0458	0.0226	0.0368	0.0011[c]
	1 + 2 + 3	0.4524	−1.1767	−0.3326			0.0078[c]

[a] Calculated using eq 5. [b] The unit is cm^3mol^{-1}. [c] The unit is mPa·s.

Table 6. Standard Deviations for the Estimation Results of the Excess Molar Volumes and Viscosity Deviations for the Ternary Systems of MTBE (1) + Methanol (2) + Benzene (3) and MTBE (1) + Methanol (2) + Toluene (3) at 298.15 K

model eq	Tsao−Smith	Kohler	Rastogi	Radojkovič
	MTBE (1) + Methanol (2) + Benzene (3)			
V^E/cm^3mol^{-1}	0.172	0.095	0.154	0.101
$\Delta\eta$/mPa·s	0.028	0.026	0.026	0.020
	MTBE (1) + Methanol (2) + Toluene (3)			
V^E/cm^3mol^{-1}	0.170	0.043	0.103	0.066
$\Delta\eta$/mPa·s	0.013	0.0094	0.013	0.0082

MTBE (1) + methanol (2) + benzene (3) and MTBE (1) + methanol (2) + toluene (3) with the standard deviations of (0.020 and 0.0082) mPa·s, respectively.

Conclusions

Excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) at 298.15 K were experimentally determined for the five binary systems of methyl *tert*-butyl ether (MTBE) (1) + methanol (2), methanol (1) + benzene (2), MTBE (1) + benzene (2), methanol (1) + toluene (2), and MTBE (1) + toluene (2) and also for the ternary systems of MTBE (1) + methanol (2) + benzene (3) and MTBE (1) + methanol (2) + toluene (3) from the densities and kinematic viscosities measured. The binary and ternary V^E values show negative deviations from ideal behavior over the whole composition range with the small exception of the benzene-rich region. The $\Delta\eta$ data have small deviations from the ideal solution. That is because the molecular interactions between each component are not very strong in every binary and ternary system. The binary V^E and $\Delta\eta$ data agreed well with the literature[9−13] values, and they were correlated reliably with the Redlich−Kister equation, while the Cibulka equation was applied successfully for the ternary system. The experimental ternary $V^E$and $\Delta\eta$ results were compared with the predicted values using binary contribution models. The Kohler equation gave the closest values to the measured data for the ternary V^E, and the Radojkovič equation provided the best results for the ternary $\Delta\eta$.

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