Densities, Viscosities, and Refractive Indices of the Binary Systems Methyl *tert*-Butyl Ether + 2-Methylpentane, + 3-Methylpentane, + 2,3-Dimethylpentane, and + 2,2,4-Trimethylpentane at 298.15 K

Alberto Bouzas, M. Cruz Burguet, Juan B. Montón, and Rosa Muñoz*

Departamento de Ingeniería Química, Facultad de Química, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

This paper reports experimental densities, viscosities, and refractive indices of the binary systems methyl *tert*-butyl ether (MTBE) + 2-methylpentane, + 3-methylpentane, + 2,3-dimethylpentane, and + 2,2,4-trimethylpentane over the entire range of composition, at 298.15 K and atmospheric pressure. Excess molar volumes and viscosity deviations were evaluated from the experimental data. These excess or derived properties were fitted to the Redlich−Kister equation to estimate the binary interaction parameters. The experimental values of viscosity have been compared to values predicted by means of the GC−UNIMOD model.

Introduction

The composition of reformulated gasoline includes a large amount of oxygenated additives (methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), ...), because of their octane-enhancing and pollution-reducing capabilities. Presently, there is an increasing interest in the thermodynamic behavior of liquid mixtures of these compounds, and a considerable amount of work has been carried out to determine the mixing properties of these compounds with components of gasoline.

As a part of our research on thermodynamic and transport properties, this paper reports measurements of densities, viscosities, and refractive indices of the binary systems of MTBE with 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, and 2,2,4-trimethylpentane over the entire range of composition, at 298.15 K and atmospheric pressure. From the experimental results, the excess molar volume, V^E, and the viscosity deviation, $\Delta\eta$, have been calculated, and these are then fitted to the Redlich−Kister equation to obtain the binary parameters.

A literature survey showed that no measurements have been previously reported for the mixtures studied in this paper. Only for MTBE + 2,2,4-trimethylpentane are there measurements on excess volumes (Blanco et al., 1994; Domanska, 1997).

Furthermore, we have predicted the dynamic viscosity of these mixtures using the "group contribution thermodynamic-viscosity model" (GC−UNIMOD) proposed by Cao et al. (1993a,b). All the parameters needed in GC−UNIMOD are taken directly from UNIFAC−VLE.

Experimental Section

Chemicals. 2-Methylpentane (99.8+ mass %, HPLC grade), 3-methylpentane (99+ mass %, GC grade), 2,3-dimethylpentane (99.8+ mass %, HPLC grade), 2,2,4-trimethylpentane (99.8+ mass %, HPLC grade), and methyl *tert*-butyl ether (MTBE) (99+ mass %, GC grade) were supplied by Aldrich. No further purification was carried out. The liquids were stored over freshly activated molecular sieves 4A and filtered before use. The purity of all chemicals was checked by gas chromatography (GC), and the results of these analyses showed that the impurities did not exceed 0.2 mass %. Further verification of the purity was obtained from the density and refractive index values at 298.15 K, which were found in good agreement with values published in the literature (Awwad and Pethrick, 1983; Daubert and Danner, 1989; TRC Tables, a-6040; Domanska, 1997).

Density and Refractive Index Measurements. Binary mixtures were prepared on a mass basis, using a Mettler AE 200 balance with an accuracy of $\pm 10^{-4}$ g covering the whole composition range of the mixtures. Precautions were taken such as using samples recently prepared and reducing to a minimum the vapor space into the vessels, to avoid preferential evaporation during manipulation and the subsequent composition errors. The accuracy in the determination of the mole fraction of the measured samples was $\pm 10^{-4}$. The imprecision in the determination of V^E is estimated to be $< 1.5 \times 10^{-3}$ $cm^3 \cdot mol^{-1}$.

The densities of pure liquids and their binary mixtures were measured with an Anton Paar digital densimeter (DMA 55), and the refractive indices with an Abbe refractometer (Type 3T), with accuracies of $\pm 10^{-5}$ $g \cdot cm^{-3}$ and $\pm 2 \times 10^{-4}$, respectively. Each apparatus was connected to a Julabo circulator with proportional temperature control and an automatic drift correction system that kept the samples at the desired temperature (298.15 K) with an accuracy of $\pm 10^{-2}$ K. The densimeter was calibrated periodically with distilled water and dry air.

Viscosity Measurements. The viscosities were determined using a suspended Ubbelohde viscometer in a bath controlled to ±0.01 K at 298.15 K. The flow time was determined with an electronic timer (Schott-Gerate Model AVS 350) with a precision of ±0.01 s. The estimated accuracy of the experimental viscosities is ±0.0005 mPa·s.

* To whom correspondence should be addressed. E-mail: Rosa.Munoz@uv.es.

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Table 1. Densities, ρ, Viscosities, η, Refractive Indices, n_D, Excess Molar Volumes, V^E, and Viscosity Deviations, $\Delta\eta$, for the Binary Systems MTBE (1) + Hydrocarbons at 298.15 K

x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	$\Delta\eta$
MTB (1) + 2-Methylpentane (2)					
0.0000	0.64843	0.2767	1.3689	0.000	1.0000
0.0969	0.65548	0.2794	1.3684	0.124	0.9911
0.2016	0.66331	0.2825	1.3676	0.243	0.9821
0.3021	0.67105	0.2858	1.3672	0.340	0.9745
0.4006	0.67908	0.2902	1.3668	0.379	0.9712
0.5007	0.68752	0.2956	1.3665	0.398	0.9702
0.5985	0.69613	0.3014	1.3663	0.381	0.9708
0.6965	0.70507	0.3079	1.3663	0.339	0.9734
0.7978	0.71466	0.3154	1.3662	0.271	0.9778
0.8845	0.72326	0.3228	1.3662	0.175	0.9843
1.0000	0.73529	0.3353	1.3662	0.000	1.0000
MTBE (1) + 3-Methylpentane (2)					
0.0000	0.65954	0.2909	1.3738	0.000	1.0000
0.0876	0.66517	0.2925	1.3729	0.098	0.9933
0.1993	0.67248	0.2945	1.3718	0.219	0.9842
0.2983	0.67919	0.2972	1.3708	0.301	0.9794
0.3943	0.68591	0.3008	1.3700	0.360	0.9777
0.5016	0.69379	0.3049	1.3692	0.382	0.9760
0.5934	0.70086	0.3089	1.3685	0.362	0.9760
0.6935	0.70887	0.3139	1.3678	0.312	0.9779
0.7963	0.71737	0.3199	1.3672	0.239	0.9823
0.8984	0.72614	0.3268	1.3668	0.139	0.9887
1.0000	0.73529	0.3353	1.3662	0.000	1.0000
MTBE (1) + 2,3-Dimethylpentane (2)					
0.0000	0.69080	0.3898	1.3894	0.000	1.0000
0.0983	0.69393	0.3824	1.3872	0.112	0.9957
0.1999	0.69739	0.3758	1.3850	0.205	0.9934
0.2986	0.70095	0.3693	1.3828	0.281	0.9910
0.3972	0.70479	0.3630	1.3806	0.325	0.9887
0.4975	0.70893	0.3572	1.3783	0.354	0.9877
0.5979	0.71346	0.3519	1.3759	0.341	0.9880
0.7006	0.71845	0.3469	1.3734	0.297	0.9889
0.7970	0.72347	0.3423	1.3711	0.231	0.9903
0.8949	0.72894	0.3387	1.3687	0.137	0.9942
1.0000	0.73529	0.3353	1.3662	0.000	1.0000
MTBE (1) + 2,2,4-Trimethylpentane (2)					
0.0000	0.68762	0.4804	1.3889	0.000	1.0000
0.0993	0.69080	0.4633	1.3868	0.078	0.9993
0.1996	0.69403	0.4465	1.3850	0.195	0.9985
0.3038	0.69781	0.4301	1.3830	0.267	0.9985
0.3986	0.70152	0.4159	1.3810	0.321	0.9990
0.4994	0.70593	0.4012	1.3788	0.333	0.9993
0.5974	0.71062	0.3878	1.3764	0.321	1.0006
0.7021	0.71614	0.3739	1.3738	0.280	1.0018
0.7991	0.72169	0.3611	1.3713	0.230	1.0018
0.8965	0.72800	0.3483	1.3687	0.123	1.0008
1.0000	0.73529	0.3353	1.3662	0.000	1.0000

Results and Discussion

Densities, ρ, viscosities, η, refractive indices, n_D, excess molar volumes, V^E, and viscosity deviations, $\Delta\eta$, of the binary mixtures are listed in Table 1. In all cases, x_1 is the molar fraction of MTBE in the mixture.

The excess molar volumes and viscosity deviations for binary mixtures were calculated from eqs 1 and 2, respectively,

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \quad (1)$$

$$\ln \Delta\eta = \ln \eta/\text{mPa·s} - \sum_{i=1}^{N} x_i \ln \eta_i/\text{mPa·s} \quad (2)$$

where M_i is the molecular weight of component i in the mixture, ρ_i and η_i are the properties of the pure components, ρ and η are the properties of the mixture, and N is the number of components in the mixture.

Table 2. Parameters of the Redlich−Kister Equation, A_p, and Standard Deviations, σ, at 298.15 K

function	A_0	A_1	A_2	A_3	σ
MTBE (1) + 2-Methylpentane (2)					
V^E/cm^3·mol^{-1}	1.5915	−0.0353	0.0020	0.3961	0.004
$\Delta\eta$	−0.1202	−0.0001	−0.0146	−0.0556	0.0003
MTBE (1) + 3-Methylpentane (2)					
V^E/cm^3·mol^{-1}	1.5116	−0.0181	−0.2418	0.2966	0.004
$\Delta\eta$	−0.0968	−0.0047	−0.0181	−0.0235	0.0006
MTBE (1) + 2,3-Dimethylpentane (2)					
V^E/cm^3·mol^{-1}	1.3978	0.1126	−0.0917	0.0099	0.003
$\Delta\eta$	−0.0480	−0.0135	−0.0082	0.0033	0.0004
MTBE (1) + 2,2,4-Trimethylpentane (2)					
V^E/cm^3·mol^{-1}	1.3462	0.0129	−0.2326	0.4398	0.009
$\Delta\eta$	−0.0010	0.0214	0.0045	−0.0153	0.0003

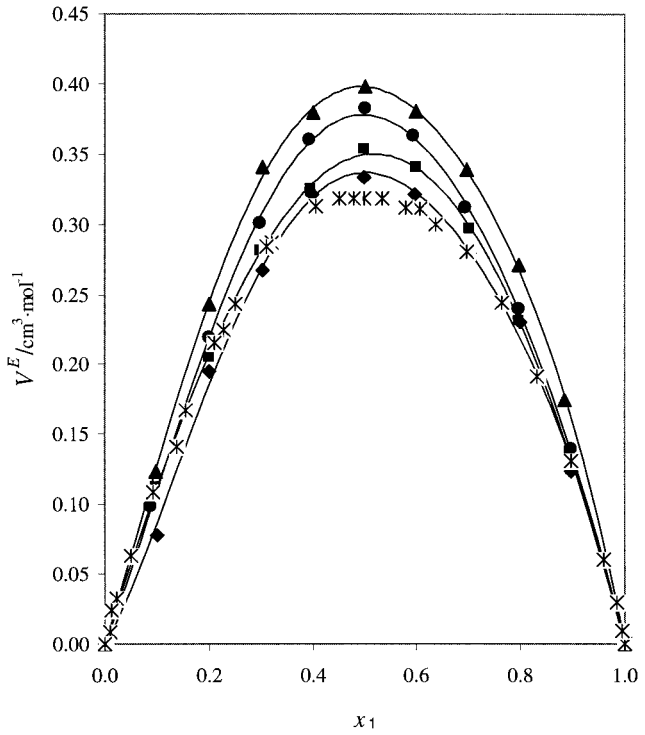

Figure 1. Excess molar volumes, V^E, at 298.15 K of MTBE (1) + alkane (2): ▲, 2-methylpentane; ●, 3-methylpentane; ■, 2,3-dimethylpentane; ◆, 2,2,4-trimethylpentane; ∗, 2,2,4-trimethylpentane (Domanska, 1997); —, calculated from eq 3 and the parameters of Table 2.

The derived binary excess properties were correlated with the Redlich−Kister equation, according to the expression

$$\Delta Q_{ij} = x_i x_j \sum_{p=1}^{m} A_p (x_j - x_i)^p \quad (3)$$

In this equation ΔQ_{ij} denotes V^E and $\Delta\eta$, respectively. A_p is a parameter and m is the degree of the polynomial expansion.

The unweighted least-squares method was used to fit the polynomials to the data. The parameters of eq 3 and the corresponding standard deviations obtained are given in Table 2. The standard deviations were calculate using the

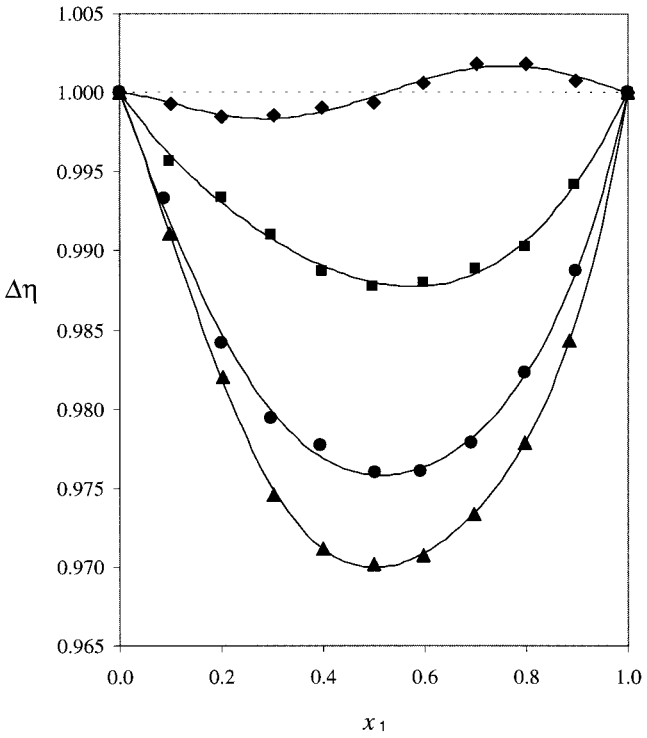

Figure 2. Viscosity deviations, $\Delta\eta$, at 298.15 K of MTBE (1) + alkane (2): ▲, 2-methylpentane; ●, 3-methylpentane; ■, 2,3-dimethylpentane; ◆, 2,2,4-trimethylpentane; —, calculated from eq 3 and the parameters of Table 2.

following expression:

$$\sigma = \left(\frac{\sum_{i}^{n} (z_{\text{exp}} - z_{\text{calc}})^2}{n - n_{\text{P}}} \right)^{1/2} \tag{4}$$

In this equation z is the value of the property, n is the number of experimental data, and n_{P} is the number of parameters.

The excess molar volumes for all the binary mixtures are plotted in Figure 1 as a function of the MTBE mole fraction. V^{E} values for the system MTBE + 2,2,4-trimethylpentane are in agreement with the values published by Domanska (1997). All the systems show positive deviations over the whole compositions range with a maximum at nearly equimolar composition. The V^{E} values increase slightly in the order 2,2,4-trimethylpentane < 2,3-dimethylpentane < 3-methylpentane < 2-methylpentane.

Viscosity deviations, $\Delta\eta$, for all the binary mixtures are plotted, as a function of MTBE mole fraction, in Figure 2. In this figure, it can be observed that the values of $\Delta\eta$ are negative for the systems MTBE + 2-methylpentane, + 3-methylpentane, and + 2,3-dimethylpentane over the whole mole fraction range with a maximum at nearly equimolar composition, while in the system MTBE + 2,2,4-trimethylpentane a significant change of sign appears at a mole fraction of $x_1 \approx 0.5$.

Table 3. Prediction of Viscosity Using the GC-UNIMOD Model

system	MRSD_η[a]
MTBE (1) + 2-methylpentane (2)	0.0250
MTBE (1) + 3-methylpentane (2)	0.0069
MTBE (1) + 2,3-dimethylpentane (2)	0.0027
MTBE (1) + 2,2,4-trimethylpentane (2)	0.0053

[a] $\text{MRSD}_\eta = \left[\frac{1}{n} \sum_{i=1}^{n} \left(\frac{\eta_{\text{calc}} - \eta_{\text{exp}}}{\eta_{\text{exp}}} \right)^2 \right]^{1/2}$.

Prediction of Dynamic Viscosities. The dynamic mixture viscosity was predicted using the GC−UNIMOD method (Cao et al., 1993a,b). UNIFAC−VLE parameters were used for the prediction of dynamic viscosities without any mixture viscosity information. The mean relative standard deviations between experimental and predicted values are presented in Table 3. The calculations confirm that VLE and viscosity predictions can be done with one parameter set with reasonable accuracy.

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