Densities, Refractive Indices, and Excess Molar Volumes of Water + Methanol + 2-Methoxy-2-methylpropane at 298.15 K

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The densities and refractive indices of water + methanol + 2-methoxy-2-methylpropane mixtures were determined in the miscible region at 298.15 K and atmospheric pressure. The densities were used to calculate excess molar volumes for the ternary mixtures and for methanol + 2-methoxy-2-methylpropane mixtures. Redlich–Kister polynomials were fitted to the excess molar volume results.

Introduction

Oxygenated compounds such as ethers and alcohols are increasingly added to gasolines to increase their octane number and decrease carbon monoxide emission. The most widely used fuel additive is 2-methoxy-2-methylpropane (methyl *tert*-butyl ether or MTBE). We have accordingly undertaken a study of the thermodynamics of water + methanol + MTBE mixtures, knowledge of which is relevant to the design of MTBE production plants. As a preliminary to this work we measured the densities and refractive indices of homogeneous water + methanol + MTBE mixtures, used the densities to calculate excess molar volumes, and fitted Redlich–Kister polynomials to the latter. In this paper we report these data. Although the recent literature features data on the physical and excess properties of mixtures of MTBE with other compounds (Mato *et al.*, 1991; Mato and Berro, 1991; Jangkamolkulchal *et al.*, 1991; Kumaran *et al.*, 1993), there appears to have been no previous report concerning the systems discussed here.

Experimental Section

Materials. High-purity water was obtained with a Milli-Q Plus system. Methanol was supplied by Merck with a nominal purity >99.0%. MTBE supplied by Repsol (La Coruña, Spain) was repeatedly distilled to a purity >99.4 mass %. The purity of all compounds was verified chromatographically. Table 1 lists their measured densities and refractive indices, together with values previously published by Daubert and Danner (1989) or Riddick *et al.* (1986).

Table 1. Densities (d) and Refractive Indices (n_D) of Pure Components at 298.15 K

	d/(g·cm^{-3})		n_D	
compound	exptl	lit.	exptl	lit.
water	0.99704	0.99704[a]	1.3324	1.33250[a]
methanol	0.78659	0.78664[a]	1.3264	1.32652[a]
MTBE	0.73558	0.73528[b]	1.3663	1.3663[b]

[a] Riddick et al. (1986). [b] Daubert and Danner (1989).

Apparatus. Mixtures were made up by mass on a Mettler AE 240 balance with a precision of ±0.00001 g. Densities were measured to a nominal precision of ±0.00001 g·cm^{-3} in an Anton Paar DMA 60 digital vibrating tube densimeter with a DMA 602 measuring cell, and refractive indices to within ±0.0001 in an Atago RX-1000 refractometer. Temperature was maintained at (25.00 ± 0.02) °C with a HetoTherm Ultrathermostat.

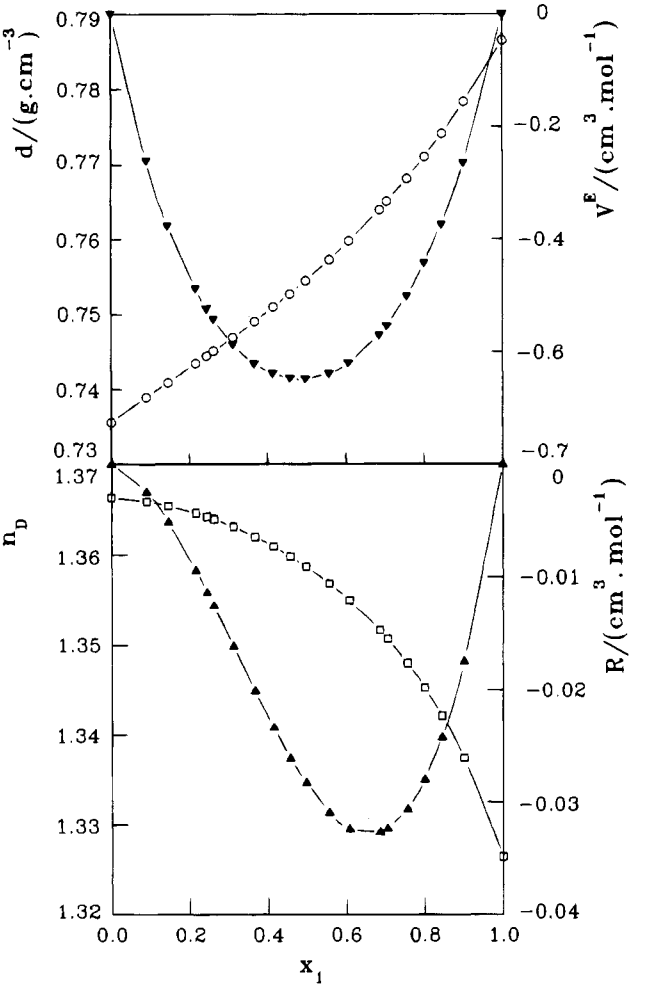

Figure 1. Density d (○), refractive index n_D (□), excess molar volume V^E (▼), and ΔR (▲) of methanol (1) + MTBE (2) as functions of mole fraction of methanol at 298.15 K and atmospheric pressure.

Precision. With the above-mentioned variation in temperature, the precision of the density measurements is estimated as ±0.00003 g·cm^{-3} and that of the refractive indices as ±0.0001. Measured densities and refractive indices are listed below to, respectively, five and four significant figures, but the imprecision of the least significant should be borne in mind and entails an imprecision of ±0.001 cm^3·mol^{-1} in the V^E and ΔR results.

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Table 2. Densities d, Refractive Indices n_D, Excess Molar Volumes V^E, and ΔR Values for Water (1) + Methanol (2) + MTBE (3) at 298.15 K

x_1	x_2	d/(g·cm^{-3})	n_D	V^E/(cm^3·mol^{-1})	ΔR/(cm^3·mol^{-1})	x_1	x_2	d/(g·cm^{-3})	n_D	V^E/(cm^3·mol^{-1})	ΔR/(cm^3·mol^{-1})
0.0000	0.0000	0.73558	1.3663	0.000	0.000	0.0368	0.0840	0.74162	1.3661	−0.421	−0.016
0.0000	0.0906	0.73895	1.3659	−0.260	−0.002	0.0653	0.1492	0.74670	1.3658	−0.682	−0.026
0.0000	0.1453	0.74093	1.3654	−0.375	−0.005	0.0942	0.2151	0.75240	1.3651	−0.898	−0.035
0.0000	0.2160	0.74348	1.3646	−0.488	−0.009	0.1238	0.2826	0.75902	1.3642	−1.077	−0.043
0.0000	0.2445	0.74451	1.3642	−0.523	−0.011	0.1590	0.3629	0.76829	1.3625	−1.232	−0.048
0.0000	0.2613	0.74512	1.3640	−0.541	−0.013	0.1727	0.3943	0.77244	1.3617	−1.275	−0.049
0.0000	0.3117	0.74699	1.3631	−0.586	−0.016	0.1848	0.4220	0.77640	1.3608	−1.302	−0.050
0.0000	0.3669	0.74909	1.3620	−0.621	−0.020	0.2162	0.4935	0.78817	1.3578	−1.327	−0.048
0.0000	0.4143	0.75098	1.3609	−0.639	−0.023	0.2450	0.5593	0.80154	1.3537	−1.275	−0.043
0.0000	0.4576	0.75277	1.3598	−0.647	−0.026	0.2767	0.6318	0.82027	1.3464	−1.112	−0.033
0.0000	0.4967	0.75447	1.3587	−0.648	−0.028	0.3046	0.6954	0.84200	1.3358	−0.852	−0.020
0.0000	0.5574	0.75725	1.3568	−0.639	−0.031	0.0529	0.0807	0.74267	1.3663	−0.470	−0.012
0.0000	0.6086	0.75978	1.3550	−0.620	−0.032	0.0889	0.1356	0.74845	1.3656	−0.783	−0.060
0.0000	0.6861	0.76397	1.3517	−0.570	−0.033	0.1223	0.1867	0.75434	1.3649	−1.024	−0.093
0.0000	0.7057	0.76510	1.3507	−0.553	−0.032	0.1658	0.2531	0.76284	1.3639	−1.249	−0.103
0.0000	0.7564	0.76818	1.3480	−0.501	−0.031	0.1950	0.2977	0.76930	1.3633	−1.350	−0.092
0.0000	0.8005	0.77106	1.3453	−0.443	−0.028	0.2187	0.3339	0.77517	1.3627	−1.409	−0.078
0.0000	0.8448	0.77414	1.3421	−0.373	−0.024	0.2374	0.3624	0.78034	1.3622	−1.443	−0.065
0.0000	0.9011	0.77835	1.3374	−0.263	−0.017	0.2828	0.4316	0.79553	1.3599	−1.484	−0.044
0.0103	0.0974	0.73983	1.3657	−0.299	−0.013	0.3206	0.4895	0.81218	1.3561	−1.457	−0.043
0.0212	0.2005	0.74455	1.3647	−0.533	−0.023	0.3568	0.5447	0.83259	1.3496	−1.329	−0.047
0.0283	0.2677	0.74802	1.3639	−0.671	−0.028	0.3958	0.6042	0.86026	1.3380	−0.973	−0.023
0.0355	0.3357	0.75175	1.3628	−0.778	−0.031	0.0599	0.0583	0.74280	1.3667	−0.518	−0.019
0.0492	0.4645	0.75927	1.3598	−0.860	−0.035	0.1150	0.1120	0.74993	1.3667	−0.865	−0.031
0.0575	0.5437	0.76453	1.3572	−0.854	−0.034	0.1599	0.1558	0.75643	1.3665	−1.088	−0.040
0.0752	0.7108	0.77891	1.3492	−0.761	−0.027	0.2027	0.1974	0.76350	1.3661	−1.266	−0.047
0.0859	0.8114	0.79001	1.3411	−0.585	−0.018	0.2582	0.2515	0.77451	1.3652	−1.452	−0.056
0.0957	0.9043	0.80324	1.3297	−0.347	−0.008	0.2883	0.2808	0.78160	1.3645	−1.531	−0.059
0.0193	0.0770	0.73991	1.3662	−0.315	−0.003	0.3602	0.3509	0.80303	1.3616	−1.628	−0.063
0.0417	0.1665	0.74516	1.3656	−0.589	−0.010	0.4132	0.4025	0.82451	1.3577	−1.574	−0.059
0.0616	0.2457	0.75023	1.3646	−0.771	−0.019	0.4601	0.4481	0.84965	1.3514	−1.389	−0.047
0.0773	0.3087	0.75469	1.3635	−0.884	−0.026	0.5066	0.4934	0.88352	1.3400	−1.029	−0.024
0.1033	0.4122	0.76320	1.3611	−1.017	−0.037	0.5859	0.3677	0.88263	1.3484	−1.243	−0.043
0.1084	0.4326	0.76510	1.3605	−1.036	−0.039	0.5549	0.3482	0.86201	1.3538	−1.434	−0.055
0.1397	0.5577	0.77882	1.3557	−1.082	−0.045	0.5236	0.3286	0.84402	1.3575	−1.528	−0.058
0.1602	0.6396	0.79035	1.3509	−1.032	−0.042	0.5014	0.3147	0.83256	1.3593	−1.543	−0.054
0.1807	0.7213	0.80465	1.3437	−0.891	−0.032	0.6144	0.3856	0.90455	1.3410	−0.974	−0.023
0.1900	0.7585	0.81237	1.3392	−0.788	−0.025	0.6543	0.2897	0.89521	1.3494	−1.313	−0.081
0.1961	0.7830	0.81798	1.3357	−0.704	−0.019	0.6199	0.2745	0.87137	1.3550	−1.472	−0.080
0.2003	0.7997	0.82207	1.3329	−0.639	−0.015	0.6931	0.3069	0.92251	1.3409	−0.862	−0.020

Table 3. Coefficients and Standard Deviations of Eq 6 for Excess Volumes V^E and Refractive Index Deviations ΔR

property	A_0	A_1	A_2	σ
V^E	−2.5924	0.1127	−0.6951	0.001
ΔR	−0.1137	−0.1024		0.001

Results and Discussion

The molar volume V of each mixture was calculated from the expression

$$V = \sum x_i M_i / d \qquad (1)$$

where x_i is the mole fraction of component i, M_i its molecular weight, and d the measured density of the mixture. Excess molar volumes V^E were calculated from

$$V^E = V - \sum x_i V_i \qquad (2)$$

where V_i is the molar volume of component i.

Molar refractions R were calculated from the Lorentz–Lorenz equation

$$R = V(n_D^2 - 1)/(n_D^2 + 2) \qquad (3)$$

where n_D is the refractive index of the mixture. The deviation of R from ideal linear dependence on the components of the mixture, ΔR, was calculated from

$$\Delta R = R - \sum x_i R_i \qquad (4)$$

where R_i is the molar refraction of component i.

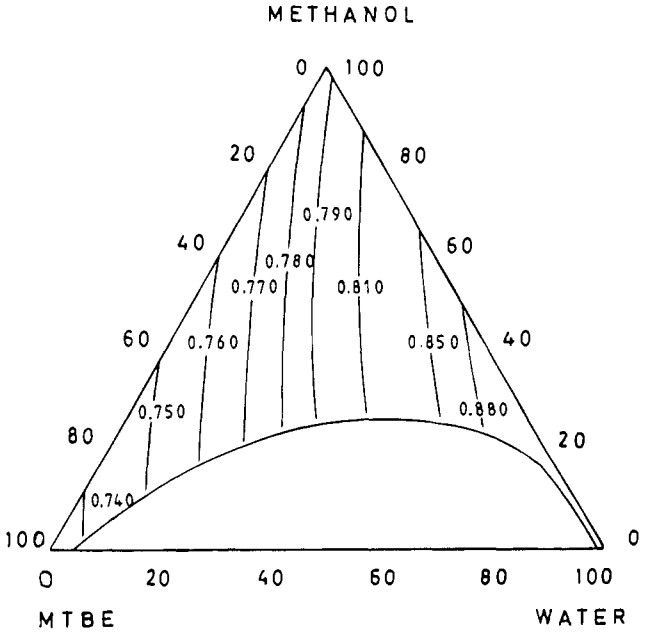

Figure 2. Density isolines for the mixture water (1) + methanol (2) + MTBE (3) at 298.15 K and atmospheric pressure.

Table 2 lists the measured densities and refractive indices of the water + methanol + MTBE mixtures studied, together with the calculated values of V^E and ΔR. This table includes data for mixtures with zero water content, i.e. for the binary system methanol + MTBE, for which the

Table 4. Coefficients and Standard Deviations of Eq 5 for Excess Volumes V^E and Refractive Index Deviations ΔR

property	A	B_1	B_2	B_3	C_1	C_2	C_3	D_1	D_2	D_3	σ
V^E	−23.1088	−22.3915	15.5244	6.8671	−55.7344	−38.2626	14.6006	−66.1288	37.0155	0.1025	0.027
ΔR	−1.4742	−1.7493	1.6024	0.1469							0.010

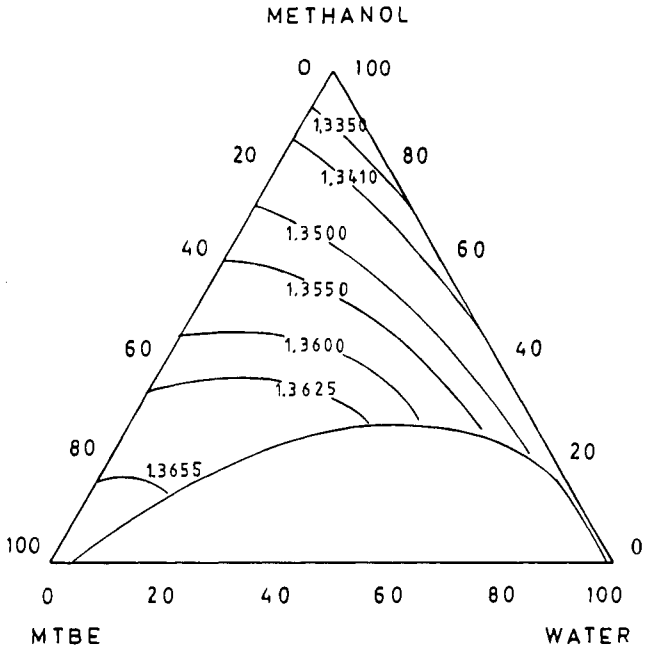

Figure 3. Refractive index isolines for water (1) + methanol (2) + MTBE (3) at 298.15 K and atmospheric pressure.

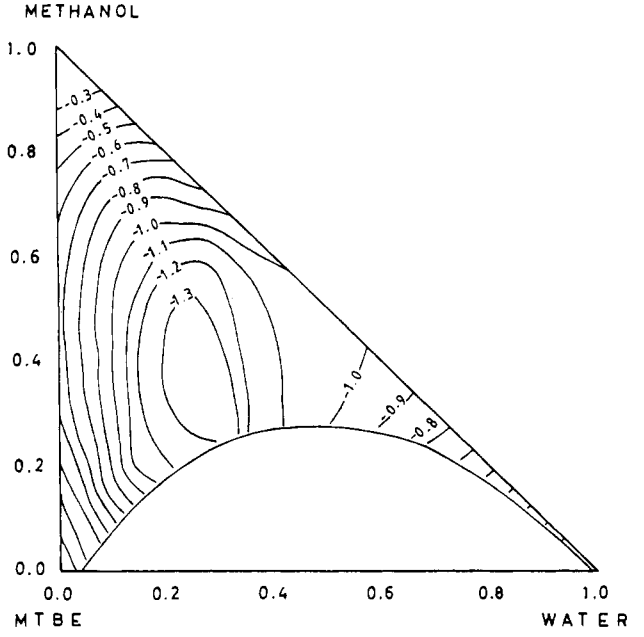

Figure 4. Excess molar volume isolines for water (1) + methanol (2) + MTBE (3) at 298.15 K and atmospheric pressure.

measured values of d, n_D, V^E and ΔR are plotted against the mole fraction of methanol in Figure 1; data for water + methanol mixtures have been published elsewhere (Arce *et al.*, 1994a). Isolines of d, n_D, and V^E for the ternary system are shown in Figures 2–4, respectively; the binodal curve shown in these figures has been reported elsewhere (Arce *et al.*, 1994b).

The V^E and ΔR data were fitted with ternary Redlich–Kister polynomials (Redlich and Kister, 1948)

$$Q_{123}/(cm^3 \cdot mol^{-1}) = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3[A + B_1(x_1 - x_2) + B_2(x_2 - x_3) + B_3(x_3 - x_1) + C_1(x_1 - x_2)^2 + C_2(x_2 - x_3)^2 + C_3(x_3 - x_1)^2 + ...] \quad (5)$$

where Q_{123} represents V^E or ΔR for the ternary mixture and Q_{ij} is the value of the Redlich–Kister polynomial for the same property fitted to the data for the binary system (i, j):

$$Q_{ij}/(cm^3.mol^{-1}) = x_ix_j\sum A_k(x_i - x_j)^k \; k = 0, 1, 2, ..., n \quad (6)$$

The A_k values used for Q_{12} (water + methanol) were those published previously (Arce *et al.*, 1994a), those for Q_{23} (methanol + MTBE) are listed in Table 3 together with the corresponding standard deviations of fit, and Q_{31} was treated as identically zero due to the almost total immiscibility of water and MTBE. The Redlich–Kister coefficients for the ternary system are listed in Table 4 together with the corresponding standard deviations of fit. Both binary and ternary polynomials were fitted by least squares, the F test being used to decide the degree of the polynomial.

Conclusions

The excess molar volumes of the ternary system water + methanol + MTBE are negative throughout the miscible region, with a minimum of about −1.6 $cm^3 \cdot mol^{-1}$, in the neighborhood of the composition 0.36:0.35:0.29 (water/methanol/MTBE). The complexity of the V^E-composition surface is witnessed to by its being necessary to use a Redlich–Kister polynomial with 10 ternary coefficients (plus the binary terms) to achieve satisfactory fit.

The values of ΔR are likewise negative throughout the miscible region, but the absolute value of the nonideality is never more than about 0.1 $cm^3 \cdot mol^{-1}$.

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