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

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The refractive indices and densities of mixtures of water + ethanol + 2-methoxy-2-methylpropane and ethanol + 2-methoxy-2-methylpropane were determined at 298.15 K. Derived excess molar properties were correlated with the corresponding composition data using the polynomials of Redlich and Kister, Cibulka, and Singh *et al.*

Introduction

As part of our study of aqueous mixtures of alcohols and gasoline additives (Arce *et al.*, 1994, 1995), in this work we examine the systems ethanol + 2-methoxy-2-methylpropane (methyl *tert*-butyl ether or MTBE) and water + ethanol + 2-methoxy-2-methylpropane. For totally miscible mixtures, the excess molar volumes V^E and the molar refractions R were, respectively, calculated from the densities d and refractive indices n_D at 298.15 K, in the latter case employing the Lorentz–Lorenz equation. The V^E data and ΔR—the deviation of R from a mole fraction average of the molar refractions of the pure components—were then correlated with the composition data by means of the polynomials of Redlich–Kister (1948), Cibulka (1982), and Singh *et al.* (1984).

Experimental Section

Materials. Water was purified using a Milli-Q Plus system. Ethanol was supplied by Merck and had a nominal purity >99.5 mass %. 2-Methoxyl-2-methylpropane was supplied by Aldrich and was redistilled prior to use, its final purity being >99.7 mass %. Water contents in the ethanol and in the MTBE were 0.08 and 0.03 mass %, respectively (determined with a Metrohm 737 KF coulometer).

Apparatus and Procedure. The mixtures were prepared by mass using a Mettler AE 240 balance that measured to within ±0.000 01 g. Densities were measured to within ±0.000 03 g·cm^{-3} in an Anton Paar DMA 60/602 densimeter (calibrated with air and water) and refractive indices to within ±0.0001 with an ATAGO RX-1000 refractometer. In both cases, a Hetotherm thermostat was used to maintain the temperature at (298.15 ± 0.02) K.

Table 1 lists the densities and refractive indices measured for the pure components, together with published values for these parameters (Riddick *et al.*, 1986; Obama *et al.*, 1985; Mato *et al.*, 1991).

Results

The measured values of ρ and n_D for the ternary system water + ethanol + MTBE, and the V^E and ΔR values derived from them, are given in Table 2, which also includes these data for the binary system ethanol + MTBE. Figures 1 and 2 respectively, show the density and refractive index isolines for the ternary system. Figure 3 shows the dependence of V^E on the mole fractions of water and ethanol and Figure 4 the corresponding V^E isolines.

Table 1. Densities ρ and Refractive Indices n_D of the Pure Components at 298.15 K

	ρ/(g cm^{-3})		n_D	
component	exptl	lit	exptl	lit
water	0.997 04	0.997 04[a]	1.3324	1.332 50[a]
ethanol	0.785 20	0.785 04[a]	1.3592	1.359 41[a]
MTBE	0.735 58	0.735 1[b] 0.735 66[c]	1.3663	1.366 3[b]

[a] Riddick *et al.* (1986). [b] Obama *et al.* (1985). [c] Mato *et al.* (1991).

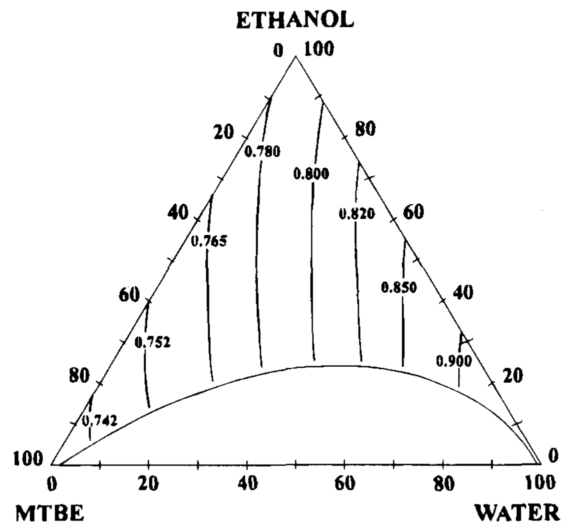

Figure 1. Density isolines for water + ethanol + MTBE at 298.15 K and atmospheric pressure.

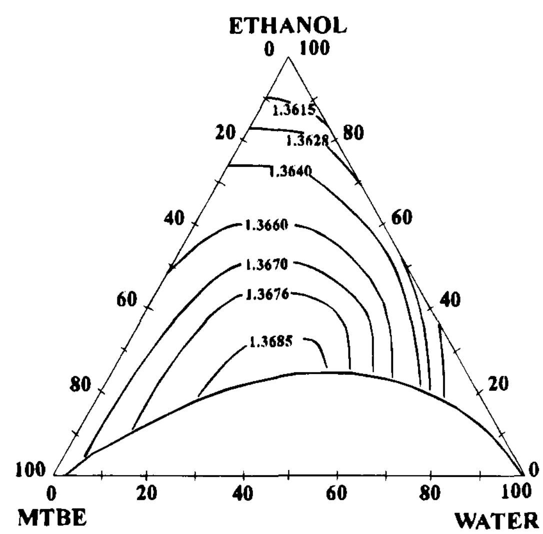

Figure 2. Refractive index isolines for water + ethanol + MTBE at 298.15 K and atmospheric pressure.

For the binary system, the V^E and ΔR data were correlated with the composition data using the Redlich–

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

x_1	x_2	ρ/(g·cm^{-3})	n_D	V^E/(cm^3·mol^{-1})	ΔR/(cm^3·mol^{-1})
0.0000	0.0414	0.737 24	1.3664	−0.100	−0.004
0.0000	0.1057	0.739 80	1.3666	−0.230	−0.010
0.0000	0.1532	0.741 68	1.3666	−0.308	−0.014
0.0000	0.2005	0.743 57	1.3667	−0.371	−0.016
0.0000	0.2550	0.745 77	1.3666	−0.429	−0.019
0.0000	0.3593	0.750 09	1.3665	−0.499	−0.021
0.0000	0.4082	0.752 20	1.3663	−0.516	−0.021
0.0000	0.4475	0.753 93	1.3662	−0.522	−0.021
0.0000	0.4560	0.754 31	1.3661	−0.523	−0.021
0.0000	0.5057	0.756 58	1.3659	−0.522	−0.020
0.0000	0.5516	0.758 75	1.3656	−0.513	−0.019
0.0000	0.5936	0.760 81	1.3654	−0.499	−0.018
0.0000	0.6522	0.763 80	1.3649	−0.468	−0.016
0.0000	0.6972	0.766 20	1.3645	−0.436	−0.015
0.0000	0.7502	0.769 16	1.3639	−0.389	−0.012
0.0000	0.7943	0.771 73	1.3633	−0.342	−0.010
0.0000	0.8460	0.774 88	1.3625	−0.275	−0.008
0.0000	0.8848	0.777 35	1.3619	−0.218	−0.006
0.0000	0.9471	0.781 50	1.3606	−0.109	−0.003
0.0078	0.0693	0.738 88	1.3665	−0.188	−0.008
0.0216	0.1915	0.745 04	1.3668	−0.454	−0.020
0.0327	0.2901	0.750 40	1.3669	−0.612	−0.027
0.0410	0.3645	0.754 74	1.3669	−0.697	−0.030
0.0527	0.4679	0.761 27	1.3667	−0.768	−0.033
0.0565	0.5019	0.763 56	1.3665	−0.779	−0.033
0.0635	0.5640	0.767 97	1.3662	−0.782	−0.033
0.0727	0.6453	0.774 21	1.3655	−0.753	−0.031
0.0813	0.7221	0.780 68	1.3646	−0.688	−0.027
0.0905	0.8041	0.788 33	1.3632	−0.575	−0.022
0.1012	0.8988	0.798 31	1.3608	−0.385	−0.014
0.0208	0.0868	0.740 54	1.3667	−0.280	−0.013
0.0388	0.1617	0.745 13	1.3669	−0.481	−0.022
0.0594	0.2478	0.750 84	1.3671	−0.671	−0.029
0.0774	0.3227	0.756 28	1.3672	−0.800	−0.034
0.0974	0.4059	0.762 96	1.3671	−0.903	−0.038
0.1073	0.4472	0.766 56	1.3670	−0.938	−0.038
0.1160	0.4833	0.769 90	1.3669	−0.960	−0.039
0.1345	0.5604	0.777 63	1.3664	−0.973	−0.037
0.1544	0.6433	0.787 09	1.3656	−0.935	−0.034
0.1728	0.7201	0.797 14	1.3642	−0.844	−0.029
0.1935	0.8065	0.810 35	1.3618	−0.665	−0.021
0.0329	0.0745	0.741 21	1.3669	−0.350	−0.009
0.0660	0.1494	0.747 23	1.3674	−0.626	−0.015
0.0871	0.1970	0.751 33	1.3677	−0.769	−0.018
0.1317	0.2979	0.761 00	1.3680	−0.999	−0.022
0.1587	0.3590	0.767 71	1.3680	−1.094	−0.023
0.1772	0.4010	0.772 80	1.3679	−1.140	−0.023
0.1901	0.4302	0.776 59	1.3678	−1.162	−0.024
0.2158	0.4883	0.784 92	1.3674	−1.181	−0.024
0.2437	0.5514	0.795 31	1.3666	−1.157	−0.024
0.2739	0.6197	0.808 60	1.3649	−1.070	−0.025
0.3065	0.6935	0.826 07	1.3618	−0.889	−0.027
0.0386	0.0595	0.741 01	1.3669	−0.347	−0.016
0.0813	0.1254	0.747 40	1.3674	−0.649	−0.027
0.1201	0.1852	0.753 76	1.3678	−0.866	−0.033
0.1698	0.2619	0.763 06	1.3681	−1.082	−0.040
0.2069	0.3192	0.771 15	1.3682	−1.202	−0.044
0.2233	0.3445	0.775 09	1.3682	−1.243	−0.045
0.2396	0.3696	0.779 29	1.3682	−1.275	−0.047
0.2814	0.4340	0.791 49	1.3678	−1.317	−0.049
0.3126	0.4822	0.802 24	1.3672	−1.302	−0.048
0.3517	0.5425	0.818 20	1.3658	−1.209	−0.043
0.3933	0.6067	0.839 24	1.3629	−0.993	−0.029
0.0518	0.0506	0.741 84	1.3670	−0.412	−0.018
0.0966	0.0943	0.747 56	1.3675	−0.692	−0.031
0.1467	0.1433	0.754 53	1.3680	−0.941	−0.043
0.1928	0.1883	0.761 69	1.3683	−1.122	−0.050
0.2562	0.2503	0.773 22	1.3685	−1.308	−0.056
0.2786	0.2721	0.777 88	1.3686	−1.356	−0.057
0.3120	0.3047	0.785 57	1.3686	−1.410	−0.057
0.3569	0.3486	0.797 59	1.3684	−1.443	−0.055
0.4016	0.3922	0.811 94	1.3678	−1.423	−0.051
0.4512	0.4407	0.831 74	1.3664	−1.318	−0.043
0.5059	0.4941	0.860 34	1.3628	−1.073	−0.030
0.5942	0.4058	0.878 95	1.3620	−1.097	−0.029
0.5317	0.3632	0.844 15	1.3659	−1.368	−0.050
0.4910	0.3354	0.826 86	1.3673	−1.462	−0.057
0.4543	0.3103	0.813 65	1.3680	−1.493	−0.060
0.4197	0.2867	0.803 36	1.3686	−1.520	−0.060
0.3954	0.2701	0.796 65	1.3687	−1.503	−0.059
0.7447	0.2553	0.917 40	1.3585	−0.992	−0.025
0.7135	0.2446	0.894 56	1.3615	−1.171	−0.043
0.6795	0.2329	0.873 75	1.3637	−1.314	−0.057
0.6559	0.2248	0.860 86	1.3647	−1.367	−0.063

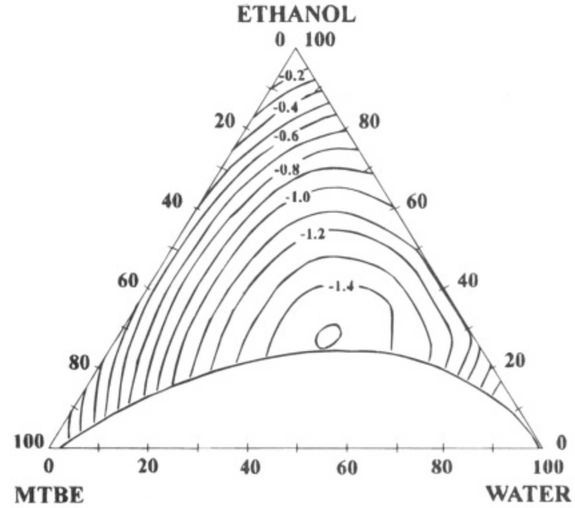

Figure 3. Composition dependence of the excess molar volume of water + ethanol + MTBE at 298.15 K and atmospheric pressure.

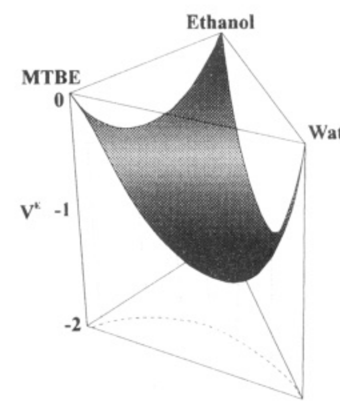

Figure 4. Excess molar volume isolines for water + ethanol + MTBE at 298.15 K and atmospheric pressure.

Table 3. Coefficients and Standard Deviations (σ) for the Excess Volume−Composition and ΔR−Composition Curves Fitted to the Data for the Ethanol (1) + MTBE (2) System

property	A_0/(cm^3·mol^{-1})	A_1/(cm^3·mol^{-1})	A_2/(cm^3·mol^{-1})	σ/(cm^3·mol^{-1})
V^E	−2.0902	0.1855	−0.3160	0.001
ΔR	−0.0820	0.0336		0.001

Kister polynomial (Redlich and Kister, 1948)

$$Q_{12} = x_1(1 - x_1)\sum_{k=0}^{N} A_k(2x_1 - 1)^k \quad k = 0, 1, 2, ..., N \qquad (1)$$

where Q_{12} is either V^E or ΔR, x_1 is the mole fraction of the first component, and N corresponds to the number of polynomial coefficients.

For the ternary system, the above properties were correlated using the polynomials of Redlich and Kister (1948)

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3(A + B(x_1 - x_2) + C(x_2 - x_3) + D(x_3 - x_1) + E(x_1 - x_2)^2 + ...) \qquad (2)$$

Cibulka (1982)

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3(A + Bx_1 + Cx_2) \qquad (3)$$

and Singh *et al.* (1984)

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3(A + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2) \qquad (4)$$

all of which include terms Q_{ij} for each binary system involved (the term Q_{31} is considered to be zero here, since

Table 4. Coefficients and Standard Deviations (σ) for the Excess Volume–Composition and ΔR–Composition Surfaces Fitted to the Data for the Water + Ethanol + MTBE System

property	polynomial	A/(cm^3·mol^{-1})	B/(cm^3·mol^{-1})	C/(cm^3·mol^{-1})	D/(cm^3·mol^{-1})	E/(cm^3·mol^{-1})	F/(cm^3·mol^{-1})	G/(cm^3·mol^{-1})	σ/(cm^3·mol^{-1})
V^E	Redlich–Kister	−19.225	−19.217	17.028	2.189	−20.809	−28.472	−1.927	0.03
	Cibulka	−34.916	−0.039	41.525					0.05
	Singh *et al.*	−18.703	85.640	−609.77					0.07
ΔR	Redlich–Kister	−0.946	−1.095	0.648	0.447				0.006
	Cibulka	−1.148	−1.340	1.945					0.006
	Singh *et al.*	−0.810	1.171						0.008

it corresponds to the immiscible binary subsystem water + MTBE). These equations were fitted to the corresponding excess molar property–composition data by least-squares regression, applying Fischer's F-test to compare fits and thus minimize the number of coefficients, except in the case of the Cibulka polynomial. The coefficients and their mean standard deviations (σ) in cm^3·mol^{-1} for both excess properties have already been published for the water + ethanol system (Arce *et al.*, 1993) and are listed in Table 3 for the binary ethanol + MTBE system and in Table 4 for the ternary water + ethanol + MTBE system.

Conclusions

For the miscible ternary mixtures water + ethanol + MTBE at 298.15 K and atmospheric pressure, excess molar volumes were negative and quite large, reaching ca. −1.52 cm^3·mol^{-1}. The V^E–composition values were best correlated using the Redlich–Kister polynomial, although it required a greater number of coefficients than the polynomials of Cibulka and Singh *et al.*

The deviations of R from the mole fraction average of the molar refractions of the pure components were also negative, but had smaller values which did not exceed ca. −0.06 cm^3·mol^{-1}. The mean standard deviations (σ) were similar for the three polynomials: it is noteworthy that the very slightly higher value of σ obtained for the polynomial of Singh *et al.* was not improved by the inclusion of the second-order term and that, of the other two correlations, the Cibulka polynomial required the fewest coefficients.

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