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Densities and Viscosities of 2-Methoxy-2-methylpropane + 2-Methyl-2-propanol at 303.15 and 313.15 K

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This paper reports the experimental data on densities and viscosities for binary mixtures of 2-methoxy-2-methylpropane and 2-methyl-2-propanol at 303.15 and 313.15 K over the entire range of composition. Excess volumes derived from experimental density data and values of the deviation of the viscosity of mixtures from the ideal mole fraction rule are negative at both the temperatures.

Introduction

2-Methoxy-2-methylpropane is an oxygenated petrochemical which has a high octane number and is less polar than alcohols. It also decreases the volatility of gasolines compared to alcohols. Accordingly, this ether and its mixtures with C_4 alcohols have been widely used as an octane booster for low-lead or even lead-free gasolines. The stringent environmental requirements will result in increased production and consumption of 2-methoxy-2-methylpropane. Besides the excellent antiknock properties, 2-methoxy-2-methylpropane is also increasingly used as a solvent and as a chemical intermediate. A literature search did not reveal any measurements on densities and viscosities of 2-methoxy-2-methylpropane + 2-methyl-2-propanol. This paper reports the measurements of density and viscosity, and calculated values of excess volume and $\Delta\eta$, the deviation of the viscosity of mixtures from the ideal mole fraction rule, as a function of composition at 303.15 and 313.15 K for the binary system of 2-methoxy-2-methylpropane + 2-methyl-2-propanol.

Experimental Section

Materials. The standard procedures (*1*) for chemical purification were used in this study. 2-Methoxy-2-methylpropane (Aldrich, 99%) was dried over anhydrous calcium sulfate, and then fractionally distilled in an all-glass 0.8-m distillation column. 2-Methyl-2-propanol (Aldrich, 99.5%) was refluxed with calcium hydride, and fractionally distilled in the same column. The middle 50% of the fraction was collected and used in density and viscosity measurements. The purity of the chemicals was verified by the measurements and comparison of densities, refractive indices, and boiling points with literature data. The measured values are given in Table I, along with the literature data. From this comparison, the purity of the chemicals is assessed to be better than 99.9 mol %.

Apparatus. Densities of the liquids and liquid mixtures were measured using a bicapillary pycnometer of volume 8.2302 cm^3 at 298.15 K, 8.2307 cm^3 at 303.15 K, and 8.2310 cm^3 at 313.15 K. The pycnometer was calibrated with deionized double-distilled water [$\rho_{298.15}$ = 0.997 047 5 g cm^{-3}, $\rho_{303.15}$ = 0.995 650 4 g cm^{-3}, $\rho_{313.15}$ = 0.992 219 1 g cm^{-3}] (*1*). The uncertainty in density measurements is ±5 × 10^{-5} g cm^{-3}.

Table I. Properties of Pure Components: 2-Methoxy-2-methylpropane (1) 2-Methyl-2-propanol (2) at 298.15 K

component	density/(g cm^{-3}) exptl	density/(g cm^{-3}) lit.	n_D exptl	n_D lit.	boiling point/K exptl	boiling point/K lit.
1	0.735 73	0.735 66[a]	1.3689[b]	1.368 92[c] 1.369 0[d]	328.20	328.211[c] 328.293[e]
2	0.775 41[f]	0.775 45[g]	1.3848	1.385 2[g] 1.385 05[h]	355.62	355.497[g] 355.65[d]

[a] Reference 3. [b] 293.15 K. [c] Reference 4. [d] Reference 2. [e] Reference 8. [f] 303.15 K. [g] Reference 1. [h] Reference 9.

Excess volumes were computed from density and composition using the relation

$$V_m^E = \frac{[x_1M_1 + (1 - x_1)M_2]}{\rho_m} - \frac{x_1M_1}{\rho_1} - \frac{(1 - x_1)M_2}{\rho_2} \quad (1)$$

where x_1 is the mole fraction of 2-methoxy-2-methylpropane, M_1 and M_2 represent molecular masses, and ρ_m, ρ_1, and ρ_2 are the respective densities of the mixture, 2-methoxy-2-methylpropane, and 2-methyl-2-propanol.

Viscosities were measured with an Ubbelohde viscometer calibrated using deionized double-distilled water [$\eta_{303.15}$ = 0.797 26 mPa s, and $\eta_{313.15}$ = 0.652 63 mPa s] (*1*). The viscometer constant, k, was calculated by $k = \eta_w/\rho_w t_w$ where η_w is the viscosity, ρ_w the density, and t_w the flow time of water. The k values are 3.9690 × 10^{-3} cm^2 s^{-2} at 303.15 K and 3.9614 × 10^{-3} cm^2 s^{-2} at 313.15 K. These are the averages of 10 calculated k values which did not differ by more than ±0.0005. An electronic stopwatch capable of reading time within ±0.01 s was used for the time measurement. Kinetic energy corrections were negligible. The estimated error in the viscosity measurement was ±5 × 10^{-4} mPa s. Experimental viscosity values were used to compute $\Delta\eta$ using the following equation:

$$\Delta\eta = \eta_m - x_1\eta_1 - (1 - x_1)\eta_2 \quad (2)$$

where η_m, η_1, and η_2 are viscosities of the mixture, 2-methoxy-2-methylpropane and 2-methyl-2-propanol, respectively.

A thermostatically controlled, well-stirred water bath with temperature control within ±0.02 K was used for all the measurements. Temperatures were read using a Hewlett-Packard 2804 digital quartz thermometer with a resolution of better than ±0.01 K. Mixtures were prepared on a mass basis by using a Sartorius analytical balance series R with an RS 232-C port. The accuracy of this balance is up to ±0.1

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Table II. Data on the Density (ρ), Excess Volume (V^E), Viscosity (η), and $\Delta\eta$ for 2-Methoxy-2-methylpropane (1) + 2-Methyl-2-propanol (2)

x_1	$\rho/(\mathrm{g\ cm^{-3}})$	$V^E/(\mathrm{cm^3\ mol^{-1}})$	$\eta/(\mathrm{mPa\ s})$	$\Delta\eta/(\mathrm{mPa\ s})$
303.15 K				
0.0000	0.775 41	0.0000	3.3653	0.0000
0.0443	0.773 21	−0.0379	2.7257	−0.5045
0.0877	0.771 01	−0.0634	2.2362	−0.8617
0.1262	0.769 09	−0.0850	1.8939	−1.0866
0.1702	0.766 91	−0.1058	1.5871	−1.2593
0.2519	0.762 92	−0.1355	1.1922	−1.4051
0.2645	0.762 31	−0.1389	1.1463	−1.4125
0.3232	0.759 49	−0.1512	0.9699	−1.4100
0.3619	0.757 65	−0.1560	0.8794	−1.3825
0.4504	0.753 53	−0.1616	0.7203	−1.2717
0.5434	0.749 29	−0.1543	0.5955	−1.1130
0.5686	0.748 16	−0.1505	0.5668	−1.0648
0.6631	0.744 00	−0.1307	0.4759	−0.8676
0.7872	0.738 72	−0.0922	0.3997	−0.5654
0.8887	0.734 56	−0.0525	0.3669	−0.2888
0.9442	0.732 35	−0.0288	0.3487	−0.1377
1.0000	0.730 15	0.0000	0.3163	0.0000
313.15 K				
0.0000	0.764 81	0.0000	2.0807	0.0000
0.0480	0.762 66	−0.0709	1.7419	−0.2527
0.0499	0.762 56	−0.0717	1.7300	−0.2612
0.0796	0.761 10	−0.0952	1.5564	−0.3816
0.0920	0.760 48	−0.1029	1.4908	−0.4249
0.1717	0.756 57	−0.1500	1.1493	−0.6235
0.2531	0.752 60	−0.1799	0.9105	−0.7164
0.2670	0.751 93	−0.1840	0.8780	−0.7239
0.3697	0.747 01	−0.1986	0.6901	−0.7277
0.4552	0.742 98	−0.1940	0.5827	−0.6818
0.5678	0.737 81	−0.1722	0.4803	−0.5823
0.6723	0.733 17	−0.1400	0.4109	−0.4643
0.7686	0.729 04	−0.1031	0.3634	−0.3391
0.8802	0.724 45	−0.0570	0.3241	−0.1783
0.9456	0.721 88	−0.0330	0.3050	−0.0801
1.0000	0.719 72	0.0000	0.2876	0.0000

mg. Precautions were taken to minimize evaporation losses during the preparation of mixtures and property measurements.

Theoretical Correlations

On the basis of the corresponding state treatment, the viscosities of mixtures have been well correlated using the relation (*5*)

$$\ln(\eta_m \xi_m) = x_1 \ln(\eta_1 \xi_1) + (1 - x_1) \ln(\eta_2 \xi_2) \tag{3}$$

where $\xi = (V^c)^{2/3}/(T^c M)^{1/2}$; T^c and V^c are the critical temperature and critical volume, respectively. The values of the critical temperature, critical volume, and molecular mass of the mixture at each composition were evaluated using the following equations (*6*):

$$V_m^{\ c} = x_1^{\,2} V_1^{\ c} + (1 - x_1)^2 V_2^{\ c} + 2x_1(1 - x_1) V_{12}^{\ c} \tag{4}$$

$$T_m^{\ c} = \frac{[x_1^{\,2} T_1^{\ c} V_1^{\ c} + (1 - x_1)^2 T_2^{\ c} V_2^{\ c} + 2x_1(1 - x_1) T_{12}^{\ c} V_{12}^{\ c}]}{V_m^{\ c}} \tag{5}$$

$$M_m = x_1 M_1 + (1 - x_1) M_2 \tag{6}$$

$$V_{12}^{\ c} = \left[\frac{(V_1^{\ c})^{1/3} + (V_2^{\ c})^{1/3}}{2}\right]^3 \tag{7}$$

$$T_{12}^{\ c} V_{12}^{\ c} = \epsilon_{12} (T_1^{\ c} T_2^{\ c} V_1^{\ c} V_2^{\ c})^{1/2} \tag{8}$$

where ϵ_{12}, the interaction parameter, was evaluated from the viscosity value at $x_1 = 0.5$.

Table III. Values of the Parameters of Equation 10 and the Standard Deviation, σ

T/K	a_0	a_1	a_2	a_3	a_4	a_5	σ
$V^E/(\mathrm{cm^3\ mol^{-1}})$							
303.15	−0.6404	−0.1872	0.0844	0.1737	−0.2050	−0.2091	0.0567
313.15	−0.7722	−0.4351	0.2846	0.4260	−0.7971	−0.6018	0.0673
$\Delta\eta/(\mathrm{mPa\ s})$							
303.15	−4.7641	−3.4511	−2.9688	−2.0345			0.5126
313.15	−2.5857	−1.7175	−1.1640	−0.5965			0.2577

Table IV. Experimental and Calculated Values of the Viscosity for 2-Methoxy-2-methylpropane (1) + 2-Methyl-2-propanol (2)

x_1	η(exptl)/(mPa s)	η(eq3)/(mPa s)	η(eq9)/(mPa s)
303.15 K			
0.0000	3.3653	3.3653	3.3653
0.0443	2.7257	2.8599	2.8081
0.0877	2.2362	2.4380	2.3679
0.1262	1.8939	2.1169	2.0472
0.1702	1.5871	1.8036	1.7448
0.2519	1.1922	1.3496	1.3210
0.2645	1.1463	1.2923	1.2683
0.3232	0.9699	1.0630	1.0568
0.3619	0.8794	0.9417	0.9434
0.4504	0.7203	0.7351	0.7427
0.5434	0.5955	0.5955	0.5955
0.5686	0.5668	0.5672	0.5639
0.6631	0.4759	0.4850	0.4691
0.7872	0.3997	0.4106	0.3869
0.8887	0.3669	0.3627	0.3444
0.9442	0.3487	0.3390	0.3282
1.0000	0.3163	0.3163	0.3163
ϵ_{12}		−0.2004	
d_{12}			−1.8014
AAD[a]		0.0755	0.0597
313.15 K			
0.0000	2.0807	2.0807	2.0807
0.0480	1.7419	1.7916	1.7668
0.0499	1.7300	1.7811	1.7557
0.0796	1.5564	1.6242	1.5925
0.0920	1.4908	1.5631	1.5301
0.1717	1.1493	1.2257	1.1967
0.2531	0.9105	0.9657	0.9496
0.2670	0.8780	0.9285	0.9146
0.3697	0.6901	0.7079	0.7058
0.4552	0.5827	0.5827	0.5827
0.5678	0.4803	0.4735	0.4681
0.6723	0.4109	0.4078	0.3953
0.7686	0.3634	0.3642	0.3482
0.8802	0.3241	0.3243	0.3112
0.9456	0.3050	0.3037	0.2965
1.0000	0.2876	0.2876	0.2876
ϵ_{12}		−0.0513	
d_{12}			−1.5000
AAD[a]		0.0283	0.0206

[a] Average absolute deviation, $|\eta_{\mathrm{exptl}} - \eta_{\mathrm{calcd}}|/n$, where n is the number of measurements.

This model is similar to the Grunberg and Nissan (*7*) model for the calculation of viscosity at low temperature:

$$\ln \eta_m = x_1 \ln \eta_1 + (1 - x_1) \ln \eta_2 + x_1(1 - x_1) d_{12} \tag{9}$$

where d_{12} is an interaction parameter which is a function of the chemical nature of the components and temperature. The value of d_{12}, obtained from a fit of eq 9 to the viscosity at $x_1 = 0.5$, was used in the computation of the viscosities over the entire composition range.

Results

The experimental densities, viscosities, derived excess volumes, and $\Delta\eta$ at 303.15 and 313.15 K are given in Table II. Figures 1 and 2 show the excess volume and $\Delta\eta$ as a function of the mole fraction of 2-methoxy-2-methylpropane.

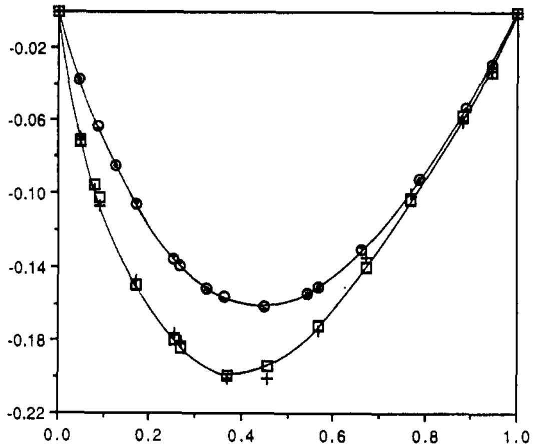

Figure 1. Excess molar volume for 2-methoxy-2-methylpropane (1) + 2-methyl-2-propanol (2): (○) 303.15 K (exptl), (●) 303.15 K (eq 10), (□) 313.15 K (exptl), (+) 313.15 K (eq 10), (x axis) x_1, (y axis) V^E/(cm^3 mol^{-1}).

The dependence of V^E and $\Delta\eta$ on the mole fraction was fitted to the Redlich–Kister equation:

$$M = x_1(1 - x_1)\sum_{i=0}^{n}[a_i(1 - 2x_1)^i] \qquad (10)$$

where M is V^E/(cm^3 mol^{-1}) or $\Delta\eta$/(mPa s) and a_i's are empirical constants. The values of the constants, obtained from the least-squares analysis, are included in Table III, along with the standard deviation, σ.

The values of V^E are negative over the entire range of composition at both temperatures and show that hydrogen-bonding interactions prevail in the system. The values of $\Delta\eta$ are also negative, and there is an order of magnitude difference in the viscosity values for pure alcohol and pure ether. The $\Delta\eta$ values are negative similar to the glycerol + water system, indicating the breaking of bonds and thus decrease of the flow times. Thus, a simple explanation may not suffice to understand the experimental results. Further, the data included in Table II indicate that the effect of temperature on excess volumes is less than that on $\Delta\eta$. Viscosity data, computed on the basis of the corresponding states principle and Grunberg and Nissan equation, are given in Table IV along with experimental results. The values of the interaction parameters and the average absolute deviation (AAD) are also included in Table IV. A comparison of the data indicates that viscosity data of this mixture can be adequately represented by the corresponding states method and the Grunberg and Nissan relation. However, the errors at the end compositions are greater, indicating that one value of the interaction parameter evaluated at x_1 = 0.5 may not be sufficient to provide an excellent agreement.

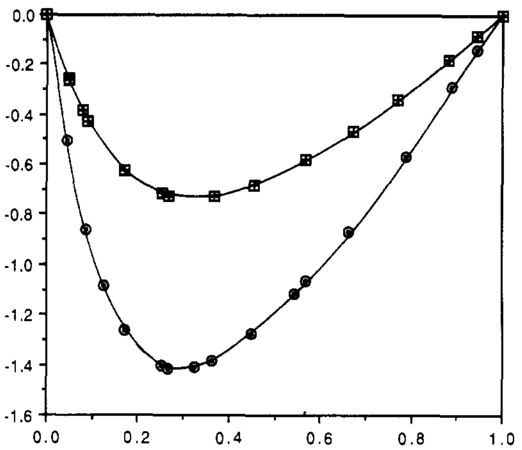

Figure 2. $\Delta\eta$ for 2-methoxy-2-methylpropane (1) + 2-methyl-2-propanol (2): (○) 303.15 K (exptl), (●) 303.15 K (eq 10), (□) 313.15 K (exptl), (+) 313.15 K (eq 10), (x axis) x_1, (y axis) $\Delta\eta$/(mPa s).

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