Density and Viscosity for Ethyl 3-Ethoxypropionate + Methacrylic Acid, + Benzyl Methacrylate, and + 2-Hydroxyethyl Methacrylate

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Densities and viscosities of binary mixtures of ethyl 3-ethoxypropionate with methacrylic acid, benzyl methacrylate, and 2-hydroxyethyl methacrylate were measured at (298.15, 308.15, and 318.15) K over the entire composition range. A pycnometer and a Cannon−Fenske routine viscometer were used to determine density and kinematic viscosity, respectively. The excess molar volumes (V^E) and viscosity deviations ($\delta\eta$) were calculated at various temperatures. A Redlich−Kister type polynomial was applied to fit the isothermal excess volumes and viscosity deviations, and McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities.

Introduction

Density and viscosity are important properties for thermodynamic model development and in the design of many types of process and transport equipment in chemical industries. Numerous experiments[1−7] have been conducted to measure the densities and viscosities for a variety of liquid mixtures in the literature; however, reliable density and viscosity data over wide ranges of composition and temperature are still needed. Methacrylic acid (MAA), benzyl methacrylate (BzMA), 2-hydroxyethyl methacrylate (2-HEMA), and a safety solvent ethyl 3-ethoxypropionate (EEP) are the key compounds in the manufacturing of the pigment-dispersed color-resistant industries. The densities and viscosities were measured for the binary mixtures composed of the methacrylates with EEP at 298.15 K, 308.15 K, and 318.15 K and over the entire composition range. No literature data were found at the comparable conditions. From the experimental results, the excess molar volumes (V^E) and viscosity deviations ($\delta\eta$) were calculated at various temperatures. A Redlich−Kister type polynomial was applied to fit the isothermal excess volumes and viscosity deviations, and McAllister's three-body and four-body interaction models were also used to correlate the kinematic viscosities.

Experimental Section

Methacrylic acid (mass fraction 99.5 %), 2-hydroxyethyl methacrylate (mass fraction 98 %), and ethyl 3-ethoxypropionate (mass fraction 99 %) were supplied by Acros Organics. Benzyl methacrylate (mass fraction 98 %) was purchased from Fisher Scientific. The purities of these substances were checked with gas chromatography. No impurity peaks were detected. All reagents were used without further purification. The densities were determined with a pycnometer having a nominal internal volume of 10 cm^3. The internal volume of the pycnometer was calibrated with pure water[8] at each temperature of interest. The sample mixture was prepared by mass using an Ohaus AR2140 balance with uncertainties of ± 0.1 mg and ± 0.0001 in mole fraction. To minimize evaporation during sample preparation, the heavier component was charged first. Three loaded pycnometers were immersed in a thermostatic bath (Neslab GP-500), which was controlled to within ± 0.03 K. A precision digital thermometer (model 1560, Hart Scientific) with a thermistor probe was used to read the temperature with an uncertainty of ± 0.015 K. The mixture densities were obtained by averaging the results from these three replications. The uncertainty of reported densities was estimated to be less than ± 0.1 %. The sample compositions were frequently checked with gas chromatography at the end of measurements indicating that the variations were minimal. The kinematic viscosities ν were measured using Cannon−Fenske routine viscometers (size 75, supplied by Cannon Instrument Co.). The

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Table 1. Densities (ρ) and Viscosities (η) of 1-Butanol at Different Temperatures

	ρ/g·cm^{-3}		η/mPa·s	
T/K	exptl	lit	exptl	lit
298.15	0.8056	0.80575[a]	2.566	2.571[a].b.c
		0.8060[b]		
		0.80576[c]		
303.15	0.8021	0.8022[b]	2.265	2.271[a,c]
		0.80201[c]		2.263[b]
308.15	0.7980	0.79821[c]	1.998	2.000[b]
				1.981[c]
313.15	0.7945	0.7946[b]	1.778	1.7734[b]
		0.79432[c]		1.692[c]

[a] Ref 9. [b] Ref 10. [c] Ref 11.

Table 2. Density (ρ) and Viscosity (η) for EEP (1) + MAA (2)

	T/K					
	298.15	308.15	318.15	298.15	308.15	318.15
x_1	ρ/(g·cm^{-3})			η/(mPa·s)		
0.0	1.0095	0.9994	0.9892	1.267	1.078	0.945
0.1000	1.0005	0.9907	0.9806	1.349	1.139	0.986
0.1999	0.9924	0.9827	0.9728	1.425	1.198	1.028
0.3000	0.9849	0.9751	0.9652	1.504	1.257	1.075
0.4000	0.9781	0.9683	0.9584	1.551	1.293	1.103
0.5000	0.9715	0.9617	0.9519	1.516	1.262	1.080
0.6000	0.9653	0.9556	0.9457	1.439	1.211	1.029
0.7000	0.9595	0.9498	0.9398	1.369	1.156	0.982
0.8000	0.9541	0.9444	0.9344	1.313	1.108	0.944
0.8999	0.9485	0.9389	0.9291	1.243	1.049	0.899
1.0	0.9432	0.9334	0.9233	1.176	0.996	0.859

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Table 3. Density (ρ) and Viscosity (η) for EEP (1) + BzMA (2)

	T/K					
	298.15	308.15	318.15	298.15	308.15	318.15
x_1	ρ/(g·cm^{-3})			η/(mPa·s)		
0.0	1.0347	1.0258	1.0170	2.302	1.885	1.580
0.1000	1.0270	1.0179	1.0089	2.160	1.767	1.479
0.2000	1.0191	1.0099	1.0007	2.027	1.664	1.398
0.3000	1.0109	1.0015	0.9921	1.910	1.571	1.323
0.4000	1.0023	0.9927	0.9832	1.795	1.480	1.247
0.4999	0.9934	0.9837	0.9740	1.681	1.391	1.173
0.6000	0.9842	0.9744	0.9645	1.569	1.303	1.101
0.7000	0.9747	0.9648	0.9547	1.457	1.215	1.029
0.8000	0.9649	0.9549	0.9446	1.347	1.129	0.961
0.9000	0.9543	0.9443	0.9341	1.242	1.047	0.899
1.0	0.9432	0.9334	0.9233	1.176	0.996	0.859

Table 4. Density (ρ) and Viscosity (η) for EEP (1) + 2-HEMA (2)

	T/K					
	298.15	308.15	318.15	298.15	308.15	318.15
x_1	ρ/(g·cm^{-3})			η/(mPa·s)		
0.0	1.0671	1.0577	1.0486	5.784	4.194	3.181
0.1000	1.0530	1.0436	1.0344	4.507	3.352	2.598
0.2000	1.0391	1.0296	1.0203	3.696	2.821	2.239
0.3000	1.0256	1.0161	1.0066	3.072	2.379	1.918
0.4000	1.0127	1.0031	0.9935	2.503	1.980	1.611
0.5000	1.0002	0.9905	0.9808	2.156	1.731	1.425
0.6000	0.9881	0.9784	0.9686	1.833	1.495	1.243
0.6999	0.9765	0.9668	0.9569	1.627	1.340	1.127
0.8000	0.9652	0.9555	0.9456	1.417	1.181	1.007
0.9000	0.9543	0.9446	0.9346	1.269	1.065	0.911
1.0	0.9432	0.9334	0.9233	1.176	0.996	0.859

viscometer was placed in a thermostatic water bath (TV-4000, TAMSON), in which the temperature was regulated to within ± 0.01 K. An electronic stop watch was used to measure the flow times. Triplicates or more measurements of flow times were reproducible within ± 0.2 % or less. The kinematic viscosities (ν, in m^2·s^{-1}) were obtained from the relation

$$\nu = kt \tag{1}$$

where k/m^2·s^{-2} is the capillary constant of viscometer and t/s is the flow time. The viscometer was calibrated with double-distilled water at each working temperature, and the capillary constant at each specific temperature was determined by averaging 10 calibration runs. The uncertainty of viscosity measurements was estimated to within ± 1.0 %, and the values of absolute viscosities (η, in mPa·s) were calculated by using the equation of $\eta = \rho\nu$. Since there are no available data for the methacrylates and EEP, the measurements of 1-butanol were conducted to test the validity of the experimental procedure. Table 1 compares the experimental results with the literature values. It shows that our measurements agree with literature values within the experimental uncertainties.

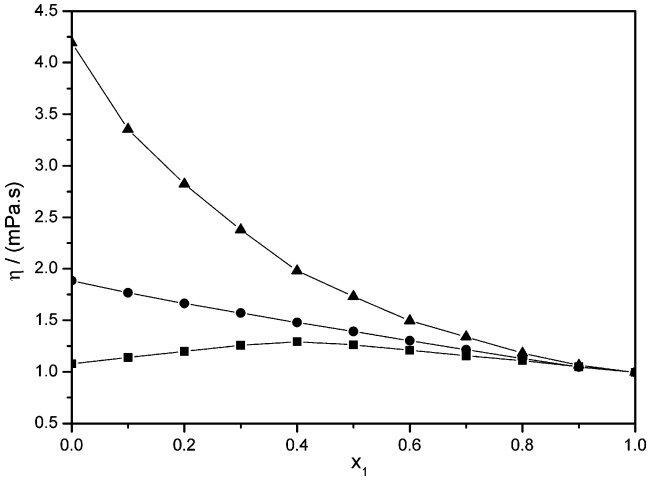

Figure 1. Viscosity (η) at 308.15 K: ■, EEP (1) + MAA (2); ●, EEP (1) + BzMA (2); ▲, EEP (1) + 2-HEMA (2).

Results and Discussion

Experimental results for the three binary systems of EEP with MAA, BzMA, and 2-HEMA are listed in Tables 2 to 4, respectively. Figure 1 shows the variations of the absolute viscosities with the mole fraction of EEP for these three investigated systems at 308.15 K. In the MAA system, the viscosity increases with the mole fraction of

Table 5. Correlated Results of Excess Molar Volume (V^E)

mixture	T/K	A_0	A_1	A_2	A_3	σ^a/(cm^3·mol^{-1})
EEP + MAA	298.15	−2.3692	−0.2264	−0.0642	−0.0528	0.012
	308.15	−2.4679	−0.1800	−0.4672	−0.2271	0.008
	318.15	−2.6243	0.0639	−0.7597	−1.0314	0.014
EEP + BzMA	298.15	−1.5346	−0.3552	−0.2963	−0.2598	0.010
	308.15	−1.3600	−0.2285	−0.0944	−0.1369	0.013
	318.15	−1.2070	0.0266	0.0948	−0.2359	0.006
EEP + 2-HEMA	298.15	−1.3017	−0.0289	−0.7468	−0.3150	0.010
	308.15	−1.3253	−0.0030	−0.9432	−0.4262	0.010
	318.15	−1.3601	0.0047	−1.0782	−0.4551	0.010

[a] $\sigma = [\sum(V^E_{exp} - V^E_{cal})^2/N - n]^{1/2}$, where N is the number of data points and n is the number of coefficients.

Table 6. Correlated Results of Viscosity Deviation ($\delta\eta$)

mixture	T/K	B_0	B_1	B_2	B_3	σ^a/(mPa·s)
EEP + MAA	298.15	1.1406	−0.6695	−0.5256	0.7332	0.013
	308.15	0.8940	−0.4630	−0.4263	0.4915	0.009
	318.15	0.6866	−0.4000	−0.3940	0.4571	0.008
EEP + BzMA	298.15	−0.2222	0.0409	−0.3044	−0.2412	0.002
	308.15	−0.1881	0.0296	−0.2753	−0.1372	0.002
	318.15	−0.1748	−0.0292	−0.2434	0.0115	0.002
EEP + 2-HEMA	298.15	−5.2299	2.1075	−1.9275	1.5164	0.036
	308.15	−3.4050	1.2206	−1.2399	0.9841	0.028
	318.15	−2.3274	0.6620	−0.8232	0.7723	0.026

[a] $\sigma = [\sum(\delta\eta_{exp} - \delta\eta_{cal})^2/N - n]^{1/2}$, where N is the number of data points and n is the number of coefficients.

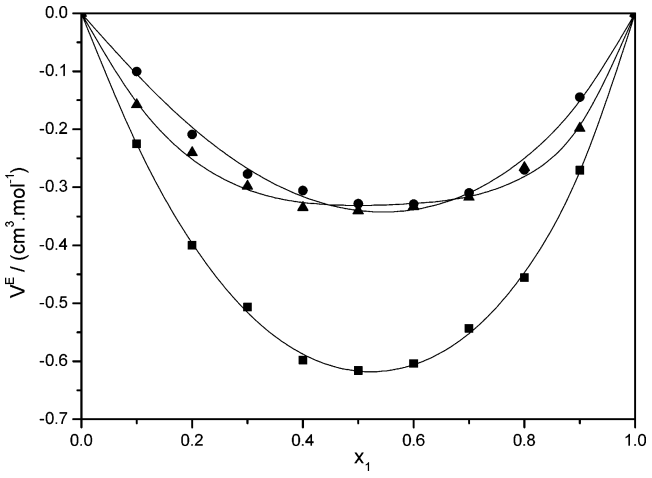

Figure 2. Excess volumes (V^E) at 308.15 K: ■, EEP (1) + MAA (2); ●, EEP (1) + BzMA (2); ▲, EEP (1) + 2-HEMA (2); −, calculated from eq 4.

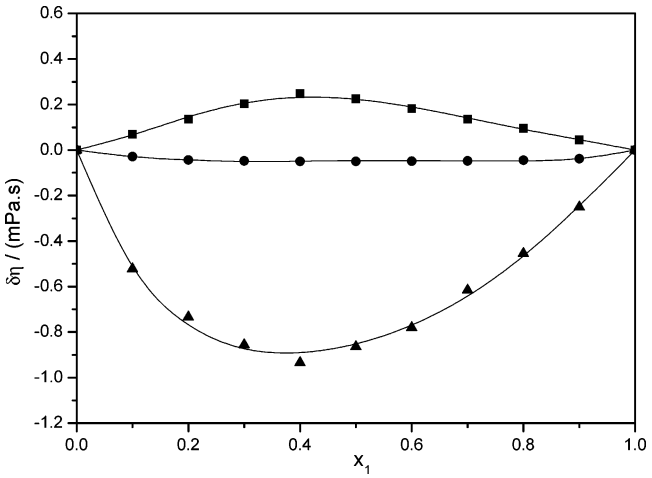

Figure 3. Viscosity deviations ($\delta\eta$) at 308.15 K: ■, EEP (1) + MAA (2); ●, EEP (1) + BzMA (2); ▲, EEP (1) + 2-HEMA (2); −, calculated from eq 5.

EEP, reaching a weak maximum at about $x_1 = 0.4$, and then decreasing slightly to the value of pure EEP. However, the viscosities of the other two systems decrease monotonically with the mole fraction of EEP. Excess volumes (V^E) and viscosity deviations ($\delta\eta$) were calculated from the experimental results by the following equations, respectively:

$$V^E = V_M - (x_1V_1 + x_2V_2) \quad (2)$$

$$\delta\eta = \eta_M - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where x_i, V_i, and η_i are the mole fraction, molar volume, and viscosity of the pure component i, respectively. The subscript M represents mixture properties. The isothermal excess volumes and viscosity deviations were correlated by a Redlich−Kister type polynomial:[12]

$$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}) = x_1x_2\sum_{k=0}^{3}A_k(x_1 - x_2)^k \quad (4)$$

$$\delta\eta/(\mathrm{mPa\cdot s}) = x_1x_2\sum_{k=0}^{3}B_k(x_1 - x_2)^k \quad (5)$$

The coefficients of A_k and B_k were obtained by fitting the equations to the experimental values with a least-squares method. Tables 5 and 6 give the coefficients together with the standard deviation (σ) of the calculated excess volumes and viscosity deviations, respectively.

The variations of V^E and $\delta\eta$ with the mole fraction of EEP at 308.15 K are presented in Figures 2 and 3, respectively. Figure 2 shows that the excess molar volumes are negative over the entire composition range for all the investigated binaries. It implies that volume contraction takes place when EEP mixes with the methacrylates. The volume contraction in EEP + MAA is slightly greater than those in EEP + BzMA and EEP + 2-HEMA. Figure 3 illustrates that the viscosity deviations are positive in EEP + MAA, negative in EEP + 2-HEMA, and nearly zero in EEP + BzMA over the entire composition range.

McAllister's multi-body interaction model[13] was widely used to correlate kinematic viscosity (ν) data. The three-body McAllister model was defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2x_2 \ln [(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \quad (6)$$

and the four-body McAllister model was given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (7)$$

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are model parameters. The calculated results are presented in Table 7. The values of AAD are approximately within the experimental uncertainty, regardless of whether the three-body or the four-body model was used.

Table 7. Correlated Results of McAllister's Models

		three-body model			four-body model			
mixture	T/K	ν_{12}	ν_{21}	AAD[a] × 10^2	ν_{1112}	ν_{1122}	ν_{2221}	AAD[a] × 10^2
EEP + MAA	298.15	1.4780	1.8732	1.2	1.3420	1.9335	1.5202	0.9
	308.15	1.2633	1.5506	1.0	1.1615	1.5669	1.2996	0.7
	318.15	1.0716	1.3237	1.2	0.9735	1.4095	1.0835	0.8
EEP + BzMA	298.15	1.5296	1.8738	0.5	1.3972	1.7968	1.8949	0.2
	308.15	1.2839	1.5517	0.5	1.1781	1.5003	1.5673	0.2
	318.15	1.0845	1.3264	0.5	1.0008	1.2907	1.3232	0.1
EEP + 2-HEMA	298.15	1.5638	2.5486	0.9	1.4283	2.1380	3.0038	0.7
	308.15	1.2989	2.0673	0.9	1.2066	1.7285	2.3749	0.7
	318.15	1.1066	1.7234	0.9	1.0516	1.4013	1.9740	0.9

[a] AAD = $(1/n)\sum_{k=1}^{n}|v_k^{cal} - v_k^{exp}|/v_k^{exp}$.

Conclusions

In this study, the densities and viscosities of binary mixtures of ethyl 3-ethoxypropionate (EEP) with methacrylic acid (MAA), benzyl methacrylate (BzMA), and 2-hydroxyethyl methacrylate (2-HEMA) were measured at 298.15 K, 308.15 K, and 318.15 K over the entire composition range. The excess molar volumes are negative for all the investigated binaries. However, the viscosity deviations are positive in EEP + MAA, negative in EEP + 2-HEMA, and nearly zero in EEP + BzMA over the entire composition range. All physical properties were correlated with appropriate regression equations, and the results showed good agreements with the experimental values.

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