Densities and Viscosities of Butyl Acrylate + 1-Butanol and Ethyl Laurate + 1-Butanol at 293.15, 303.15, and 313.15 K

Wen-Rong Liau, Muoi Tang,† and Yan-Ping Chen*

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Densities and viscosities of binary liquid mixtures of butyl acrylate + 1-butanol and ethyl laurate + 1-butanol are presented over the complete concentration range at (293.15, 303.15, and 313.15) K. The densities were measured using a vibrating tube digital densimeter, and the viscosities were measured by a capillary viscometer. Excess molar volumes and viscosity deviations were then calculated at various temperatures. All excess molar volumes are positive, indicating the effect of disruption of the hydrogen bonding between 1-butanol molecules. Excess molar volumes and viscosity deviations were correlated by the Redlich−Kister type equations. Optimally fitted parameters are presented, and the correlation results are in satisfactory agreement with the experimental data.

Introduction

Experimental data of the densities and viscosities of binary mixtures containing esters are useful in pharmaceuticals, and specialty and agricultural chemistry. Thermodynamic properties of the liquid mixtures containing esters are not yet sufficient in the literature (Rathnam, 1988). Recently, density and viscosity data have been reported for binary mixtures of esters with alkanols (e.g., Francesconi and Comelli, 1997; Gonzalez and Ortega, 1996; Gonzalez et al., 1996). Butyl acrylate ($CH_2CHCOOC_4H_9$) and ethyl laurate ($CH_3(CH_2)_{10}COOC_2H_5$) are unsaturated and saturated esters, respectively. Butyl acrylate is used as adhesives, paints, binders, and emulsifiers, while esters of fatty acids are used in the manufacture of cosmetics, food, and pharmaceutical industries. In this study, densities and viscosities for the binary liquid mixtures of butyl acrylate + 1-butanol and ethyl laurate + 1-butanol were measured at (293.15, 303.15, 313.15) K and atmospheric pressure. To our knowledge, these data are not reported previously. Excess molar volumes and deviations of viscosity were then calculated and correlated by polynomial expressions.

Experimental Section

Materials. All chemicals were purchased from Merck Co. The purities of all liquids are better than 99.5 mass % on the GC analyses, and no further purification was made. The densities and refractive indices of all pure chemicals were measured in this study. A comparison of pure fluid properties with literature data is shown in Table 1.

Measurements. Liquid mixtures of various compositions were prepared by weight, in a 50 cm^3 flask, using a precision Mettler balance (AE 2000, Switzerland) with an accuracy of ±0.1 mg. Density and viscosity measurements were carried out using a Neslab RTE220 thermostat. Temperatures were measured with a Hart 1506 thermometer with an accuracy of ±0.01 °C. A proportional integral control model was used to maintain the temperature in the thermostat to be within ±0.01 °C of the desired value. The refractive indices of pure liquids were measured at 293.15 K with an Abbe refractometer Atago 3T. The accuracy of the refractive index measurement is ±0.0001.

Table 1. Properties of Pure Liquids Used in This Study

compound	$\rho/(g\cdot cm^{-3})$ (293.15 K) exptl	$\rho/(g\cdot cm^{-3})$ (293.15 K) lit.	$n_D^{293.15\ K}$ exptl	$n_D^{293.15\ K}$ lit.	GC purity/mass %
1-butanol	0.8096	0.8097[c]	1.3992	1.3993[a]	>99.5
butyl acrylate	0.8991	0.8986[a]	1.4198	1.4190[a]	>99.5
ethyl laurate	0.8623	0.8628[b]	1.4308	1.4310[b]	>99.5

[a] Budavari et al., 1989. [b] Boit, 1975. [c] TRC Thermodynamic Tables.

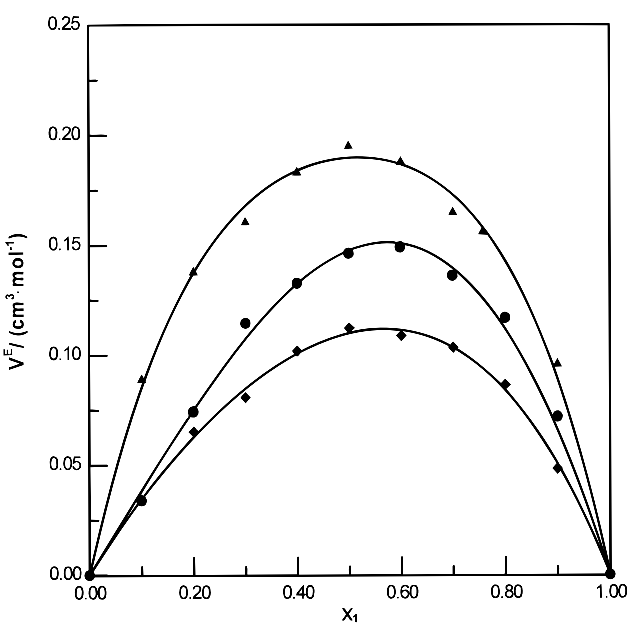

Figure 1. Excess molar volumes of butyl acrylate (1) + 1-butanol (2) binary mixture at various temperatures: ◆, 293.15 K; ●, 303.15 K; ▲, 313.15 K; −, calculated.

* Corresponding author (E-mail address: ypchen@ccms.ntu.edu.tw).
† Present address: Department of Chemical Engineering, Chinese Culture University, Taipei, Taiwan, Republic of China.

S0021-9568(98)00061-2 CCC: $15.00
Published on Web 08/19/1998

Table 2. Density, Excess Molar Volume, and Viscosity of Butyl Acrylate (1) + 1-Butanol (2)

x_1	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
	T = 293.15 K		
0.0000	0.809 56	0.0000	2.9679
0.0999	0.822 45	0.0343	2.1731
0.2001	0.834 11	0.0652	1.7250
0.2999	0.844 73	0.0806	1.4476
0.3998	0.854 35	0.1018	1.2447
0.5002	0.863 25	0.1122	1.1168
0.6002	0.871 47	0.1087	1.0254
0.7002	0.879 04	0.1033	0.9619
0.8000	0.886 10	0.0862	0.9168
0.9000	0.892 79	0.0481	0.8882
1.0000	0.899 06	0.0000	0.8763
	T = 303.15 K		
0.0000	0.801 95	0.0000	2.2896
0.0999	0.814 52	0.0339	1.7177
0.1998	0.825 78	0.0743	1.3851
0.3006	0.836 07	0.1185	1.1849
0.3999	0.845 36	0.1327	1.0354
0.4992	0.853 93	0.1463	0.9378
0.5983	0.861 82	0.1490	0.8682
0.6991	0.869 32	0.1361	0.8213
0.8002	0.876 29	0.1168	0.7840
0.9003	0.882 85	0.0718	0.7678
1.0000	0.899 08	0.0000	0.7568
	T = 313.15 K		
0.0000	0.794 10	0.0000	1.7955
0.1004	0.805 98	0.0888	1.2907
0.2001	0.816 88	0.1378	1.0177
0.3002	0.826 98	0.1580	0.8796
0.3999	0.836 08	0.1829	0.7948
0.4994	0.844 55	0.2001	0.7351
0.5998	0.852 34	0.1877	0.7091
0.6999	0.859 65	0.1648	0.6745
0.7578	0.863 60	0.1560	0.6676
0.8999	0.872 80	0.0956	0.6659
1.0000	0.879 04	0.0000	0.6609

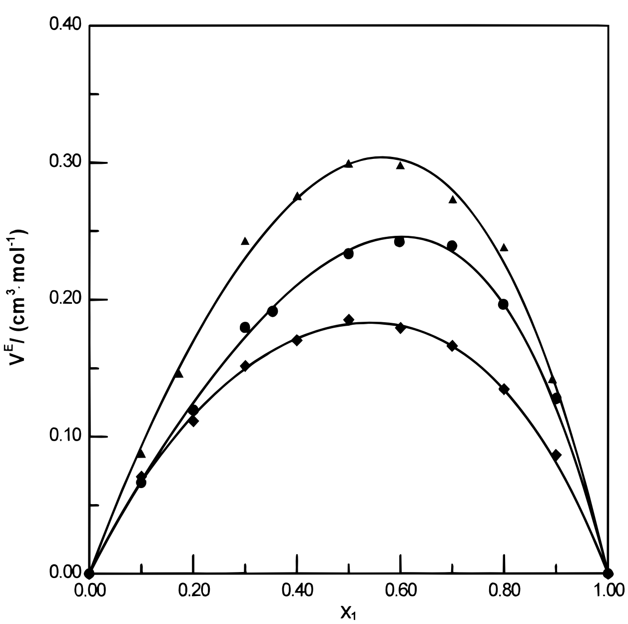

Figure 2. Excess molar volumes of ethyl laurate (1) + 1-butanol (2) binary mixture at various temperatures: ◆, 293.15 K; ●, 303.15 K; ▲, 313.15 K; —, calculated.

Densities of pure liquids and binary liquid mixtures were measured at various temperatures with an Anton Parr digital vibrating tube densimeter (model 60/602, Anton Parr, Austria). The densimeter was calibrated with degassed water and dehumidized air at atmospheric pressure.

Table 3. Density, Excess Molar Volume, and Viscosity of Ethyl Laurate (1) + 1-Butanol (2)

x_1	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
	T = 293.15 K		
0.0000	0.809 56	0.0000	2.9679
0.1001	0.821 88	0.0708	2.7032
0.2001	0.830 98	0.1113	2.6434
0.3002	0.837 90	0.1515	2.6536
0.4000	0.843 42	0.1702	2.7184
0.5001	0.847 90	0.1852	2.8001
0.6002	0.851 68	0.1791	2.8907
0.6997	0.854 85	0.1660	3.0078
0.8000	0.857 64	0.1345	3.1113
0.9001	0.860 09	0.0867	3.2250
1.0000	0.862 34	0.0000	3.3803
	T = 303.15 K		
0.0000	0.801 95	0.0000	2.2896
0.0997	0.814 21	0.0664	2.1289
0.2001	0.823 24	0.1194	2.0927
0.2998	0.830 00	0.1794	2.1176
0.3532	0.833 10	0.1913	2.1423
0.4999	0.839 92	0.2334	2.2327
0.5982	0.843 58	0.2421	2.3133
0.6997	0.846 78	0.2391	2.3861
0.7986	0.849 59	0.1962	2.4740
0.9006	0.852 15	0.1278	2.5820
1.0000	0.854 22	0.0000	2.6951
	T = 313.15 K		
0.0000	0.794 10	0.0000	1.7955
0.1000	0.806 28	0.0868	1.7442
0.1724	0.812 94	0.1452	1.7243
0.2999	0.821 88	0.2418	1.7197
0.4004	0.827 41	0.2748	1.7419
0.4998	0.821 85	0.2983	1.7813
0.5998	0.838 64	0.2971	1.8180
0.7011	0.838 94	0.2722	1.8623
0.7997	0.841 72	0.2372	1.9266
0.8926	0.844 19	0.1409	1.9787
1.0000	0.846 77	0.0000	2.0454

Table 4. Regression Results for the Excess Volumes of Two Binary Mixtures at Various Temperatures

system	θ_0	θ_1	θ_2	σ/(cm^3·mol^{-1})
	T = 293.15 K			
butyl acrylate + 1-butanol	0.439 51	0.110 41	0.049 68	0.0028
ethyl laurate + 1-butanol	0.725 98	0.105 97	0.174 51	0.0035
	T = 303.15 K			
butyl acrylate + 1-butanol	0.590 56	0.191 36	0.018 84	0.0058
ethyl laurate + 1-butanol	0.937 44	0.388 03	0.203 13	0.0050
	T = 313.15 K			
butyl acrylate + 1-butanol	0.759 02	0.029 49	0.324 51	0.0069
ethyl laurate + 1-butanol	1.196 89	0.292 15	0.105 61	0.0082

More than eight readings were taken for each density measurement. The precision in the density measurement is estimated to be better than 1.0×10^{-5} g cm^{-3}. The corresponding uncertainty in excess molar volume calculation is ± 0.002 cm^3 mol^{-1}.

Kinematic viscosities of binary liquid mixtures were measured by factory-calibrated Ubbelohde capillary viscometers (Schott Gerate, FRG). A Lauda Viscoboy 2 timer (Lauda, FRG), which measured automatically the flow time of liquid, was used with an accuracy of time measurement of 0.01 s. The kinematic viscosities of liquids were calculated with the measured flow time and the calibration constants. Dynamic viscosities were determined from these data and the corresponding densities of the mixtures at the same compositions. The reported dynamic viscosities were the averaged values of at least five to eight runs. The accuracy of dynamic viscosity measurement was estimated to be ± 0.003 mPa s.

Table 5. Regression Results for the Deviations of Viscosity of Two Binary Mixtures at Various Temperatures

system	H_0	H_1	H_2	H_3	σ/(mPa·s)
		T = 293.15 K			
butyl acrylate + 1-butanol	−1.463 92	0.469 98	−0.261 90	0.139 97	0.0037
ethyl laurate + 1-butanol	−0.487 84	0.390 81	−0.406 11	0.168 56	0.0031
		T = 303.15 K			
butyl acrylate + 1-butanol	−1.353 07	0.424 19	−0.258 22	0.207 61	0.0037
ethyl laurate + 1-butanol	−0.419 29	0.297 70	−0.351 67	0.201 49	0.0015
		T = 313.15 K			
butyl acrylate + 1-butanol	−1.560 27	0.795 83	−0.460 23	0.249 54	0.0079
ethyl laurate + 1-butanol	−0.305 42	0.170 11	−0.053 87	0.005 53	0.0025

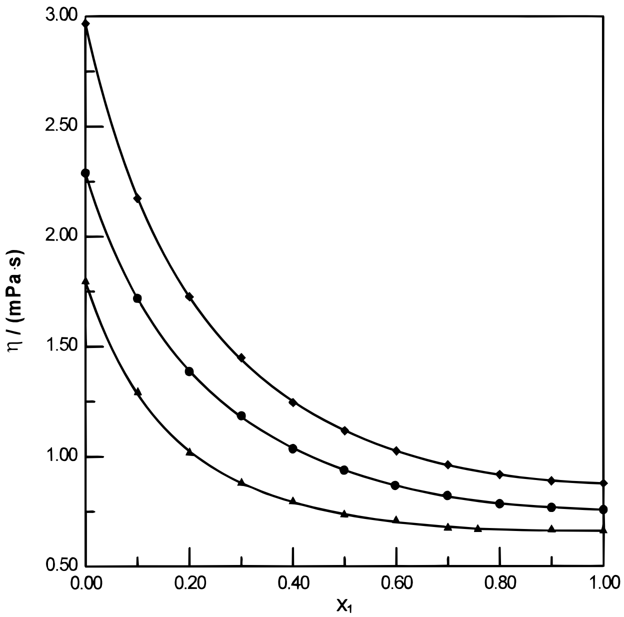

Figure 3. Experimental viscosities of butyl acrylate (1) + 1-butanol (2) binary mixture at various temperatures: ◆, 293.15 K; ●, 303.15 K; ▲, 313.15 K; —, calculated.

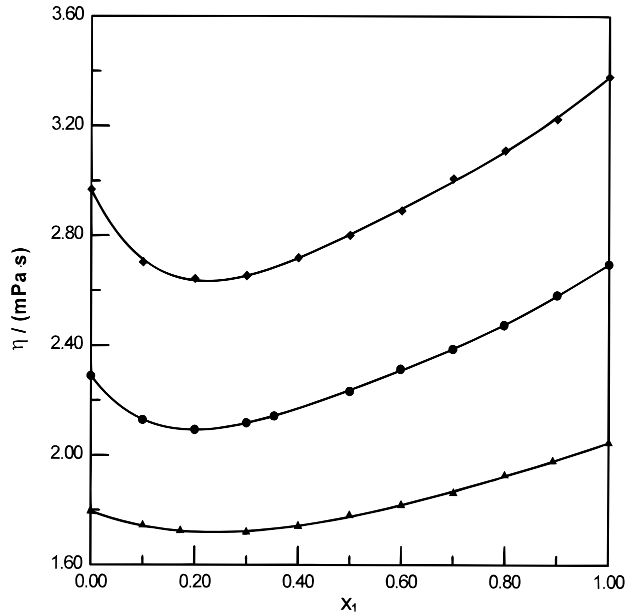

Figure 4. Experimental viscosities of ethyl laurate (1) + 1-butanol (2) binary mixture at various temperatures: ◆, 293.15 K; ●, 303.15 K; ▲, 313.15 K; —, calculated.

Results and Discussion

Excess Molar Volumes. The excess molar volumes, V^E, were calculated from the density data by the relationship

$$V^E = x_1M_1(1/\rho_m - 1/\rho_1) + x_2M_2(1/\rho_m - 1/\rho_2) \quad (1)$$

where x, M, and ρ are the mole fraction, molecular weight, and density, respectively. Subscript m represents the mixture property. The excess molar volumes of two binary mixtures of butyl acrylate (1) +1-butanol (2) and ethyl laurate (1) + 1-butanol (2) at various temperatures are listed in Tables 2 and 3, respectively. The excess molar volumes were then correlated by a Redlich−Kister type equation

$$V^E/\text{cm}^3\ \text{mol}^{-1} = x_1x_2\sum_{i=1}^{3}\theta_{i-1}(x_1 - x_2)^{i-1} \quad (2)$$

The coefficients in eq 2 were estimated by the least-squares method, where the square of the difference between the calculated and experimental excess molar volume results is minimized. The optimal values of the coefficients in eq 2 are listed in Table 4. The standard deviations were calculated by

$$\sigma(V^E) = [\sum(V^{E,\exp} - V^{E,\text{cal}})^2/(D - N)]^{0.5} \quad (3)$$

where D is the number of data points and N is the number of parameters in eq 2. It is observed that the average standard deviation for both systems at three temperatures is about 0.005 $\text{cm}^3\ \text{mol}^{-1}$.

Graphical presentations of the excess molar volumes are shown in Figures 1 and 2, respectively. Both binary mixtures show positive deviations. Maximum deviations of the excess molar volumes occur at the mole fractions of 0.5 to 0.6 of both binary mixtures. Maximum values of excess molar volume in this temperature range for the butyl acrylate (1) + 1-butanol (2) system is about 0.19 cm^3 mol^{-1}, and it is about 0.30 $\text{cm}^3\ \text{mol}^{-1}$ for the mixture of ethyl laurate (1) + 1-butanol (2). Excess molar volumes for both systems increase with temperature. According to the discussion of previous studies (e.g., Venkateswarlu and Raman, 1985; Pal and Singh, 1997), the factors that influence the excess volume include the decrease of dipolar association of the components, the dissociation of self-associated compounds, or the formation of hydrogen bonding between unlike molecules. For these two binary mixtures, 1-butanol is a polar and associating fluid and the esters are taken as polar and nonassociating. One possible explanation for the experimental results is that the strong hydrogen-bonding effect between the 1-butanol molecules is disrupted in the binary mixture with esters. This contributes positive values to the excess molar volume. When 1-butanol is mixed with an ester compound of longer alkyl groups, the depression of the hydrogen-bonding effect becomes more significant. Thus the excess molar volumes of 1-butanol with ethyl laurate have larger positive values than those with butyl acrylate. The disruption of the hydrogen-bonding effect, which involves the absorption of energy, becomes more evident as the temperature is increased. It is thus shown in Figures 1 and 2 that the excess molar volumes of both binary mixtures are larger at higher temperatures.

Viscosities. Dynamic viscosities η of both binary mixtures at various temperatures are calculated from the measured density and kinematic viscosity data. These results are listed in Tables 2 and 3, respectively. The deviation of viscosity was calculated by

$$\delta(\ln \eta) = \ln \eta_m - \sum_{i=1}^{2} x_i \ln \eta_i \quad (4)$$

The $\delta(\ln \eta)$ values were also correlated by a Redlich–Kister equation similar to eq 2 but with one more coefficient

$$\delta(\ln \eta) = x_1 x_2 \sum_{i=1}^{4} H_{i-1}(x_1 - x_2)^{i-1} \quad (5)$$

The coefficients in eq 5 are also regressed by employing the least-squares method. Standard deviations for the viscosity calculations were determined similar to eq 3.

$$\sigma[\delta(\ln \eta)] = \{\sum[\delta(\ln \eta)^{\mathrm{exp}} - \delta(\ln \eta)^{\mathrm{cal}}]^2/(D - N)\}^{0.5} \quad (6)$$

The optimal parameters in correlating the deviation of viscosity are listed in Table 5 for both binary mixtures. The results are also satisfactory. Graphical presentations of the viscosities of both systems are shown in Figures 3 and 4, respectively. The viscosities of butyl acrylate (1) + 1-butanol (2) show a smooth decreasing curve against composition. The binary system of ethyl laurate (1) + 1-butanol (2) shows a minimum viscosity at x_1 around 0.2. This minimum point becomes more evident at lower temperatures.

Literature Cited

Boit, H.-G. *Beilsteins Handbuch der Organischen Chemie*, Springer-Verlag: Berlin, 1975; E IV 2, Band 2/2, p 1092.

Budavari, S.; O'Neil, M. J.; Smith, A.; Hecklman, P. E. *The Merck Index*, 11th ed.; Merck Co., Inc.: Rahway, NJ, 1989.

Francesconi R.; Comelli, F. Excess molar enthalpies, densities and excess molar volumes of diethyl carbonate in binary mixtures with seven *n*-alkanols at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 45–48.

Gonzalez, E.; Ortega, J. Densities and isobaric vapor–liquid equilibria for the mixtures formed by four butyl esters and 1-butanol. *J. Chem. Eng. Data* **1996**, *41*, 53–58.

Gonzalez, E.; Pena, J.; Ortega, J. Excess volumes of 12 binary liquid mixtures of propyl *n*-alkanoates (C_4–C_7) + propan-2-ol, + butan-2-ol, or + 2-methylpropan-1-ol at 298.15K. *ELDATA: Int. Electron. J. Phys.-Chem. Data* **1996**, *2*, 5–12.

Pal, A.; Singh, W. Excess Molar Volumes and Viscosities of Binary Mixtures of 2-Butoxyethanol (Butyl Cellosolve) with Chloroalkanes at 298.15 K. *Fluid Phase Equilibr.* **1997**, *129*, 211–221.

Rathnam, M. V. Viscosities of Some Binary Ethyl Acetate Mixtures at 313.15 K. *J. Chem. Eng. Data* **1988**, *33*, 14–15.

TRC Thermodynamic Tables, Non-Hydrocarbons; Thermodynamic Research Center, The Texas A & M University System: College Station, TX, 1993.

Venkateswarlu, P.; Raman, G. K. Excess volumes of ethanoic, propanoic, and butanoic acids with 1,2-dichloroethane and 1,2-dibromoethane. *J. Chem. Eng. Data* **1985**, *30*, 180–181.

Received for review March 4, 1998. Accepted June 4, 1998. The authors are grateful to the National Science Council, Republic of China for supporting this research.

JE9800611