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Viscosity and Density of Water + Ethyl Acetate + Ethanol Mixtures at 298.15 and 318.15 K and Atmospheric Pressure

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The viscosities and densities of the ternary mixtures water + ethyl acetate + ethanol and their constituent binaries have been measured at 298.15 and 318.15 K and atmospheric pressure. The excess molar volumes, V_m^E , and viscosity deviations, $\Delta\eta$, were calculated from density and viscosity, respectively. A rational function due to Myers and Scott was used to describe the composition dependence of these properties. To describe the ternary system, binary pair additivity and the Pando et al. rational functions for the ternary contributions ($\Delta\eta_T$ and V_T^E) were considered.

Introduction

The extensive information on the thermodynamic and transport properties of liquid mixtures is needed in multiple industrial process areas such as fluid flow and heat and mass transfer and also for the development of theoretical research on molecular interactions in solutions. The systems alkanol + alkanoate are of great interest from a theoretical point of view because in mixing processes the breaking of H-bonded structures of the alcohol occurs and the formation of new H-bonded molecular species between the alcohol and the ester takes place.¹ Ternary mixtures are the easiest multicomponent systems to treat experimentally and represent the appropriate ground for the application of correlation and prediction models.

The present work is part of a research program which has been developed in our laboratory that aims to provide density, viscosity, and surface tension data for ternary and binary subsystems of the type water + alkanoate + alkanol at different temperatures.^{2,3} These data are particularly important in the pharmaceutical, food, and flavor industries.

We report in this paper the density, ρ , and the dynamic viscosity, η , for the ternary mixtures of water + ethyl acetate + ethanol and its binary constituents at 298.15 and 318.15 K and atmospheric pressure.

The performance of different analytical V_m^E models for the correlation and for the prediction have been studied in the literature.⁴ The conclusion is that the models including polynomial rational functions give low standard deviations. These kind of functions found a wide acceptance and have been applied to the excess enthalpy, H^E ,⁵ and excess Gibbs energy, G^E .⁶ The polynomial rational functions were first proposed by Myers and Scott.⁷ They have been used in this study together with the rational functions of Pando et al.⁸ to correlate excess molar volume and viscosity deviation.

Experimental Techniques

Materials. Tridistilled water was used. Ethanol (Cromasolv, HPLC grade) was supplied with a mass fraction purity better than 0.998. Ethyl acetate was supplied by Riedel de Hën with a stated purity better than 0.997. The measured viscosities and

Table 1. Densities, ρ , and Viscosities, η , of the Pure Components at 298.15 and 318.15 K

substance	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
	exptl	literature	exptl	literature
<i>T</i> = 298.15 K				
water	—	0.99704 ^a	—	0.8902 ^b
ethyl acetate	0.89444	0.89445 ^c	0.427	0.4260 ^d
ethanol	0.78510	0.78510 ^e	1.102	
		0.78513 ^g		1.105 ^f
air		1.169·10 ^h		
<i>T</i> = 318.15 K				
water	—	0.99017 ^a	—	0.5961 ^b
ethyl acetate	0.86997	0.86990 ^c	0.356	0.346 ⁱ
ethanol	0.76842	0.76811 ^j	0.749	0.7461 ^j
air		1.095·10 ^h		

^a Ref 9. ^b Ref 10. ^c Ref 1. ^d Ref 11. ^e Ref 12. ^f Ref 13. ^g Ref 14. ^h Ref 15. ⁱ Ref 16. ^j Ref 17.

densities of the three components together with values found in the literature are presented in Table 1.

Measurements. Viscosities were measured by the Haake Falling Ball viscosimeter (Hoppler design), calibrated with tridistilled water. An electronic digital stopwatch, with an uncertainty of $\pm 1\cdot 10^{-2}$ s, was used to measure the falling time of the ball. A borosilicate ball with a 15.81 mm diameter and with a density of $2.2186\text{ g}\cdot\text{cm}^{-3}$ was used.

Densities were measured in an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 602 measuring cell. Air and pure water were used for the calibration of the densimeter. The temperature maintenance and control were performed using an Ultratherm P Selecta thermostatic water bath, which has a temperature uncertainty of $\pm 1\cdot 10^{-2}$ K. In the case of density measurements, the Pt resistance thermometer (calibrated against a standard mercury thermometer, graduated in 0.01 K, certified by NPL, U.K.) was placed inside the vibrating tube densimeter to find the actual temperature of the measurements.

Mixtures were prepared by mass using a Mettler AT 200 balance with a precision of $\pm 1\cdot 10^{-5}$ g. The uncertainty of the mole fraction is estimated to be of the order $\pm 1\cdot 10^{-4}$. The measurement of both properties was accomplished using the following methodology. A binary mixture was used as a starting point of measurements in the water (1) + ethanol (3) or ethyl acetate (2) + ethanol (3) systems. The ternary data were

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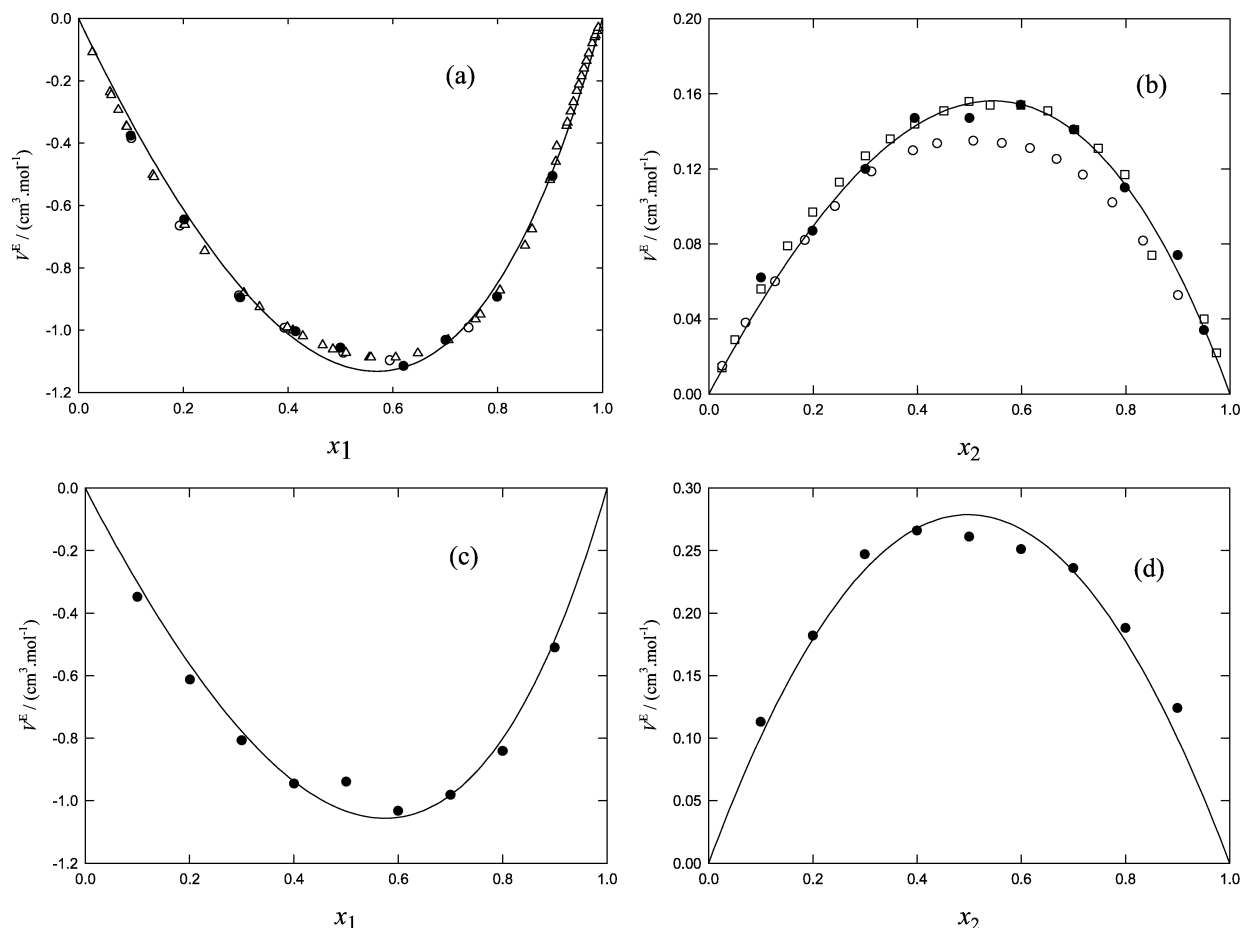


Figure 1. Excess molar volume, V_m^E , of the binary systems at 298.15 K as a function of the mole fractions: (a) water (1) + ethanol (3) and (b) ethyl acetate (2) + ethanol (3). (a) Experimental data: \bullet , this work; \circ , Arce et al.;^{14,18} Δ , Benson et al.¹⁹ (b) Experimental data: \bullet , this work; \circ , Ortega et al.;²⁰ \square , Hu et al.²¹ At 318.15 K: (c) water (1) + ethanol (3) and (d) ethyl acetate (2) + ethanol (3). (c) Experimental data: \bullet , this work. (d) Experimental data: \bullet , this work. The curves were calculated with eq 4.

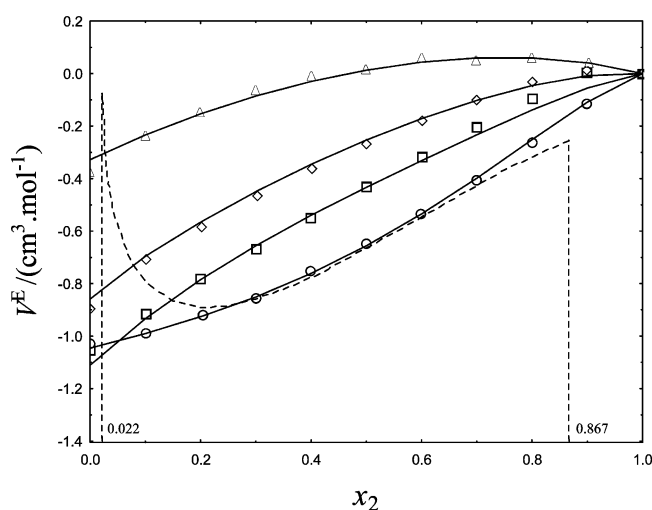


Figure 2. Excess molar volume, V_m^E , of the system water (1) + ethyl acetate (2) + ethanol (3) at 298.15 K following lines of constant $z = x_3/x_1$. The symbols represent experimental data, and the lines represent the calculated values: \circ , $z = 0.43$; \square , $z = 1.00$; \diamond , $z = 2.33$; Δ , $z = 9.00$; —, eqs 5 and 6; - - -, binodal curve.^{22,23}

obtained following lines of constant molar fraction ratio of $z = x_3/x_1$ and $z = x_3/x_2$, respectively.

Uncertainties. Densities were measured with an uncertainty of $\pm 1 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. Having in mind that the error in the excess molar volume, V_m^E , is determined by the uncertainties in mole

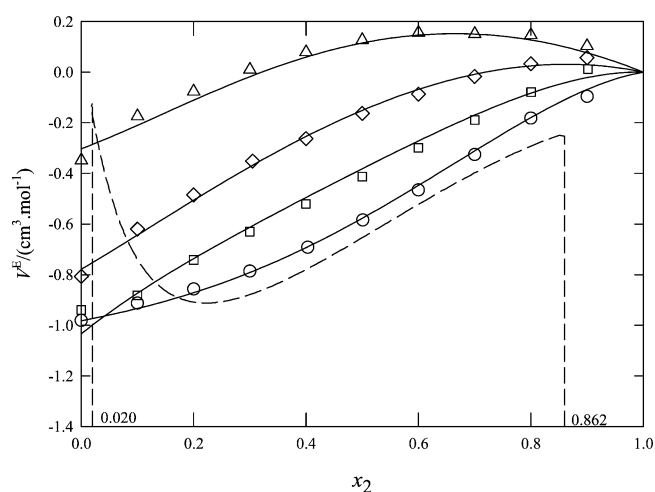


Figure 3. Excess molar volume, V_m^E , of the system water (1) + ethyl acetate (2) + ethanol (3) at 318.15 K following lines of constant $z = x_3/x_1$. The symbols represent experimental data, and the lines represent calculated values: \circ , $z = 0.43$; \square , $z = 1.00$; \diamond , $z = 2.33$; Δ , $z = 9.00$; —, eqs 5 and 6; - - -, binodal curve.^{22,23}

fraction and density, the maximum error in V_m^E resulting from the propagation law of errors is $\pm 1 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$. Taking into consideration the uncertainties in the measured time and in the density, the experimental uncertainty in the viscosity is $\pm 1 \cdot 10^{-3} \text{ mPa} \cdot \text{s}$.

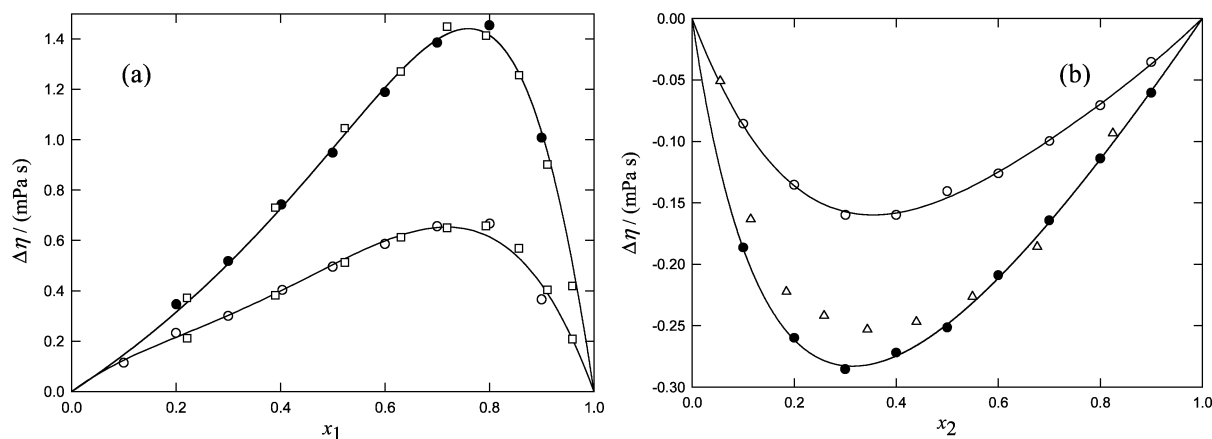


Figure 4. Viscosity deviations, $\Delta\eta$, of the binary systems at 298.15 K and 318.15 K as a function of the mole fractions: (a) water (1) + ethanol (3) and (b) ethyl acetate (2) + ethanol (3). The symbols refer to experimental data: ●, this work at 298.15 K; ○, this work at 318.15 K; □, Vargaftik;¹⁵ △, Nikam et al.¹¹ at 298.15 K. The curves are calculated with eq 4.

Table 2. Experimental Densities, ρ , and Excess Molar Volumes, V_m^E , for the System Water (1) + Ethyl Acetate (2) + Ethanol (3) and Its Binary Constituents at 298.15 K and Atmospheric Pressure

		ρ		V_m^E				ρ		V_m^E	
x_1	x_2	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$	x_1	x_2	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$	x_1	x_2	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$
0.0269	0.9731	0.89532	-0.039	0.2091	0.3036	0.85688	-0.466				
0.0469	0.9531	0.89613	-0.081	0.1798	0.4012	0.86415	-0.364				
0.0722	0.9278	0.89709	-0.124	0.1500	0.5005	0.87056	-0.267				
0.0892	0.9108	0.89790	-0.168	0.1200	0.6004	0.87623	-0.178				
0.1045	0.8955	0.89848	-0.189	0.0899	0.7006	0.88129	-0.099				
0.1249	0.8751	0.89950	-0.240	0.0600	0.8002	0.88585	-0.032				
0.9051	0	0.96551	-0.506	0.0300	0.9001	0.89010	0.014				
0.7992	0	0.93360	-0.893	0.0894	0.1001	0.81245	-0.239				
0.7005	0	0.90469	-1.031	0.0795	0.2002	0.82585	-0.149				
0.6205	0	0.88556	-1.115	0.0696	0.3004	0.83760	-0.069				
0.5001	0	0.85865	-1.056	0.0596	0.4006	0.84814	-0.011				
0.4145	0	0.84326	-1.004	0.0497	0.5002	0.85782	0.010				
0.3085	0	0.82673	-0.895	0.0397	0.6003	0.86624	0.055				
0.2018	0	0.81078	-0.645	0.0298	0.7001	0.87430	0.048				
0.0998	0	0.79760	-0.376	0.0199	0.8002	0.88143	0.057				
0	0.1000	0.80150	0.062	0.0095	0.9047	0.88844	0.038				
0	0.1992	0.81625	0.087	0.0980	0.0902	0.81203	-0.274				
0	0.3006	0.82952	0.120	0.1999	0.0800	0.82398	-0.561				
0	0.3949	0.84061	0.147	0.2989	0.0701	0.83694	-0.785				
0	0.5001	0.85204	0.147	0.4009	0.0599	0.85192	-0.953				
0	0.5987	0.86164	0.154	0.4989	0.0501	0.86726	-1.003				
0	0.7000	0.87079	0.141	0.5999	0.0400	0.88645	-1.027				
0	0.7981	0.87906	0.110	0.6970	0.0303	0.90890	-1.006				
0	0.9000	0.88696	0.074	0.8000	0.0200	0.93352	-0.778				
0	0.9501	0.89081	0.034	0.9000	0.0100	0.96227	-0.454				
0.6303	0.1000	0.90340	-0.990	0.1000	0.2700	0.83804	-0.203				
0.5573	0.2042	0.90200	-0.921	0.2003	0.2401	0.84760	-0.476				
0.4902	0.2999	0.90104	-0.857	0.3006	0.2100	0.85816	-0.691				
0.4202	0.4000	0.89974	-0.755	0.3972	0.1810	0.86948	-0.837				
0.3501	0.5000	0.89862	-0.647	0.5004	0.1500	0.88297	-0.914				
0.2802	0.5999	0.89768	-0.536	0.6003	0.1200	0.89927	-0.967				
0.2100	0.7001	0.89670	-0.405	0.6996	0.0902	0.91701	-0.890				
0.1401	0.8000	0.89577	-0.265	0.8002	0.0600	0.93809	-0.704				
0.0700	0.9000	0.89489	-0.116	0.9001	0.0300	0.96529	-0.448				
0.4503	0.1001	0.86609	-0.914	0.1000	0.4500	0.85899	-0.151				
0.4003	0.2000	0.87181	-0.783	0.2004	0.3998	0.86677	-0.409				
0.3503	0.2999	0.87656	-0.669	0.3000	0.3500	0.87539	-0.614				
0.3002	0.3999	0.88033	-0.552	0.4000	0.3000	0.88549	-0.786				
0.2500	0.5004	0.88341	-0.434	0.4998	0.2501	0.89653	-0.869				
0.2001	0.6000	0.88598	-0.318	0.6000	0.2000	0.91013	-0.916				
0.1500	0.7001	0.88823	-0.206	0.1000	0.6300	0.87643	-0.127				
0.1000	0.8001	0.89016	-0.095	0.1999	0.5601	0.88273	-0.358				
0.0500	0.9001	0.89198	0.001	0.3059	0.4859	0.89062	-0.582				
0.2700	0.1008	0.83752	-0.707	0.4000	0.4200	0.89852	-0.728				
0.2400	0.2007	0.84791	-0.583								

Table 3. Experimental Densities, ρ , and Excess Molar Volumes, V_m^E , for the System Water (1) + Ethyl Acetate (2) + Ethanol (3) and Its Binary Constituents at 318.15 K and Atmospheric Pressure

		ρ		V_m^E				ρ		V_m^E	
x_1	x_2	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$	x_1	x_2	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$	x_1	x_2	$\text{g}\cdot\text{cm}^{-3}$	$\text{cm}^3\cdot\text{mol}^{-1}$
0.0249	0.9751	0.87081	-0.033	0.1802	0.4000	0.84183	-0.262				
0.0524	0.9476	0.87180	-0.072	0.1501	0.5000	0.84759	-0.163				
0.0766	0.9234	0.87273	-0.108	0.1201	0.5999	0.85282	-0.087				
0.1003	0.8997	0.87394	-0.171	0.0901	0.7000	0.85744	-0.017				
0.1255	0.8745	0.87508	-0.216	0.0601	0.8000	0.86169	0.033				
0.9000	0	0.95247	-0.510	0.0300	0.9000	0.86570	0.057				
0.8001	0	0.91919	-0.841	0.0902	0.1000	0.79380	-0.174				
0.7001	0	0.88876	-0.981	0.0802	0.2000	0.80606	-0.076				
0.5998	0	0.86331	-1.033	0.0702	0.3000	0.81683	0.010				
0.5003	0	0.84031	-0.939	0.0601	0.4000	0.82643	0.079				
0.4004	0	0.82381	-0.945	0.0501	0.5000	0.83514	0.127				
0.3001	0	0.80771	-0.807	0.0401	0.6000	0.84307	0.156				
0.2010	0	0.79360	-0.613	0.0301	0.7001	0.85051	0.151				
0.1000	0	0.78053	-0.348	0.0200	0.8000	0.85721	0.146				
0	0.1000	0.78309	0.113	0.0100	0.9000	0.86362	0.103				
0	0.2001	0.79645	0.182	0.1000	0.0900	0.79301	-0.168				
0	0.3000	0.80831	0.247	0.2010	0.0799	0.80552	-0.499				
0	0.4001	0.81937	0.266	0.3000	0.0700	0.81823	-0.704				
0	0.5000	0.82953	0.261	0.4000	0.0600	0.83274	-0.853				
0	0.6000	0.83875	0.251	0.5004	0.0500	0.84959	-0.947				
0	0.7000	0.84718	0.236	0.6001	0.0400	0.86909	-0.973				
0	0.8001	0.85516	0.188	0.7004	0.0300	0.89358	-0.966				
0	0.8999	0.86260	0.124	0.8000	0.0200	0.92159	-0.823				
0.6300	0.1001	0.88433	-0.913	0.8997	0.0100	0.95419	-0.525				
0.5600	0.2000	0.88156	-0.857	0.1005	0.2698	0.81719	-0.101				
0.4901	0.3000	0.87932	-0.786	0.2001	0.2402	0.82677	-0.378				
0.4179	0.4031	0.87726	-0.692	0.2998	0.2102	0.83743	-0.598				
0.3493	0.5010	0.87549	-0.584	0.3955	0.1815	0.84893	-0.752				
0.2801	0.5999	0.87393	-0.466	0.5004	0.1500	0.86358	-0.862				
0.2100	0.7000	0.87242	-0.326	0.5999	0.1201	0.88016	-0.907				
0.1401	0.7999	0.87112	-0.182	0.6999	0.0901	0.90041	-0.884				
0.0699	0.9001	0.87054	-0.096	0.8000	0.0601	0.92541	-0.769				
0.4504	0.0999	0.84779	-0.882	0.9000	0.0300	0.95755	-0.548				
0.4004	0.2000	0.85200	-0.742	0.1000	0.4500	0.83669	-0.054				
0.3504	0.2999	0.85569	-0.630	0.2028	0.3986	0.84485	-0.326				
0.3003	0.3999	0.85868	-0.520	0.3009	0.3496	0.85359	-0.535				
0.2501	0.5002	0.86118	-0.413	0.4018	0.2991	0.86405	-0.710				
0.2002	0.6000	0.86315	-0.299	0.4996	0.2502	0.87574	-0.817				
0.1501	0.7003	0.86490	-0.189	0.5998	0.2001	0.88990	-0.861				
0.0998	0.8005	0.86638	-0.079	0.0993	0.6305	0.85379	-0.121				
0.0500	0.9018	0.86793	0.012	0.2002	0.5599	0.85964	-0.292				
0.2702	0.1000	0.81816	-0.620	0.3081	0.4844	0.86800	-0.527				
0.2402	0.2000	0.82732	-0.485	0.4011	0.4193	0.87610	-0.671				
0.2087	0.3050	0.83533	-0.351								

the excess molar volumes, V_m^E , of the mixture were obtained from the measured density by

$$V_m^E = \rho^{-1}(\sum x_i M_i) - \sum x_i M_i \rho_i^{-1} \quad (1)$$

Experimental Results and Discussion

In Tables 2 and 3, the densities, ρ , are listed as a function of the composition at the two temperatures. In the same tables,

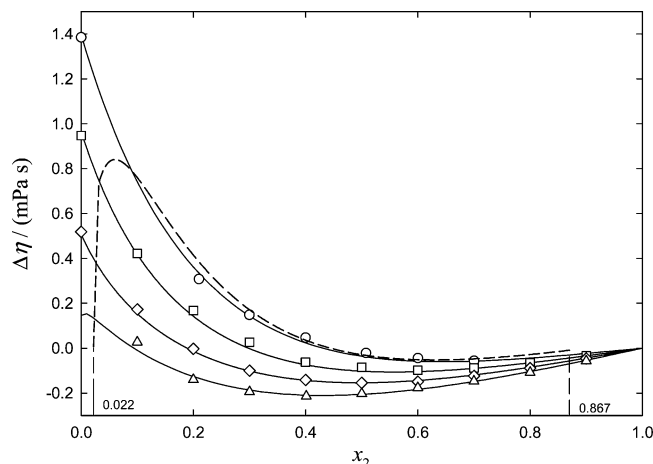


Figure 5. Viscosity, $\Delta\eta$, of the system water (1) + ethyl acetate (2) + ethanol (3) at 298.15 K following lines of constant $z = x_3/x_1$. The symbols represent experimental data, and the lines are calculated: \circ , $z = 0.43$; \square , $z = 1.00$; \diamond , $z = 2.33$; \triangle , $z = 9.00$; —, eqs 5 and 6; - - -, binodal curve.^{22,23}

Table 4. Experimental Viscosities, η , for the System Water (1) + Ethyl Acetate (2) + Ethanol (3) and Its Binary Constituents at 298.15 K and Atmospheric Pressure

x_1		η	x_1		η
x_2	mPa·s		x_2	mPa·s	
0.0258	0.9742	0.436	0.1798	0.4001	0.653
0.0450	0.9550	0.444	0.1499	0.5001	0.579
0.0748	0.9252	0.456	0.1199	0.6000	0.523
0.0853	0.9147	0.460	0.0899	0.7001	0.487
0.1053	0.8947	0.468	0.0599	0.8001	0.460
0.1258	0.8742	0.476	0.0300	0.9000	0.442
0.2009	0	1.407	0.0902	0.1000	1.042
0.3001	0	1.558	0.0802	0.2000	0.810
0.4016	0	1.761	0.0701	0.3000	0.691
0.5001	0	1.946	0.0600	0.4012	0.605
0.6000	0	2.166	0.0501	0.5000	0.551
0.7000	0	2.342	0.0401	0.6000	0.512
0.8000	0	2.390	0.0301	0.7000	0.476
0.9000	0	1.923	0.0200	0.8000	0.450
0	0.1000	0.848	0.0100	0.9000	0.435
0	0.2000	0.707	0.2000	0.0800	1.132
0	0.3000	0.614	0.3008	0.0699	1.283
0	0.4000	0.560	0.4000	0.0600	1.461
0	0.5000	0.513	0.5003	0.0500	1.654
0	0.6000	0.488	0.6000	0.0400	1.868
0	0.7000	0.465	0.7001	0.0300	2.069
0	0.8000	0.448	0.8000	0.0200	2.119
0	0.9000	0.434	0.9000	0.0100	1.834
0.5529	0.2101	1.153	0.1002	0.2700	0.713
0.4900	0.3000	0.946	0.2000	0.2400	0.821
0.4200	0.4000	0.791	0.3000	0.2100	0.948
0.3446	0.5078	0.666	0.4002	0.1800	1.107
0.2800	0.6001	0.594	0.5000	0.1500	1.268
0.2098	0.7002	0.529	0.6000	0.1200	1.464
0.1401	0.7999	0.480	0.7000	0.0900	1.679
0.4499	0.1001	1.363	0.8000	0.0600	1.844
0.3999	0.2000	1.052	0.9000	0.0300	1.681
0.3500	0.3000	0.854	0.1001	0.4500	0.579
0.3002	0.3999	0.708	0.2003	0.3999	0.661
0.2502	0.4999	0.628	0.3002	0.3499	0.762
0.2001	0.6000	0.557	0.4001	0.3000	0.887
0.1501	0.7000	0.510	0.5002	0.2499	1.027
0.1000	0.8000	0.477	0.6002	0.1999	1.226
0.0500	0.9001	0.450	0.1003	0.6297	0.506
0.2697	0.1002	1.151	0.3002	0.4898	0.646
0.2398	0.2001	0.914	0.4000	0.4200	0.745
0.2098	0.3000	0.756			

where x_i , M_i , and ρ_i are the mole fraction, the molecular weight, and the measured density of the pure component i , respectively.

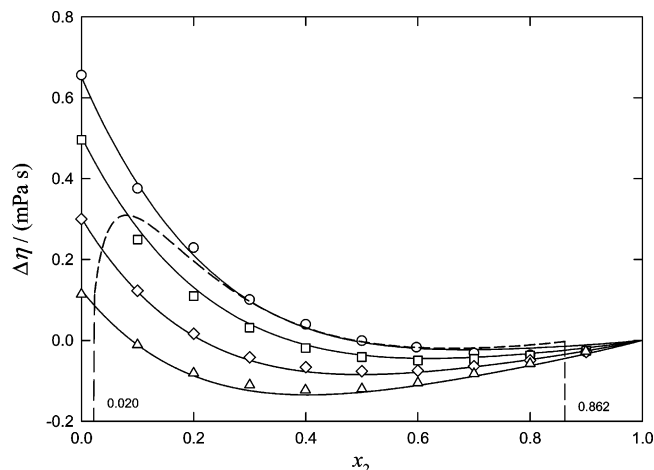


Figure 6. Viscosity, $\Delta\eta$, of the system water (1) + ethyl acetate (2) + ethanol (3) at 318.15 K following lines of constant $z = x_3/x_1$. The symbols represent experimental data, and the lines are calculated: \circ , $z = 0.43$; \square , $z = 1.00$; \diamond , $z = 2.33$; \triangle , $z = 9.00$; —, eqs 5 and 6; - - -, binodal curve.^{22,23}

Table 5. Viscosities, η , for the System Water (1) + Ethyl Acetate (2) + Ethanol (3) and Its Binary Constituents at 318.15 K and Atmospheric Pressure

x_1		η	x_1		η
x_2	mPa·s		x_2	mPa·s	
0.0250	0.9750	0.362	0.2400	0.2004	0.650
0.0496	0.9504	0.368	0.2101	0.3000	0.557
0.0751	0.9250	0.373	0.1801	0.4000	0.498
0.0999	0.9001	0.379	0.1501	0.5000	0.453
0.1254	0.8746	0.385	0.1201	0.6000	0.420
0.1000	0	0.848	0.0900	0.7000	0.396
0.2000	0	0.951	0.0601	0.7999	0.376
0.3001	0	1.003	0.0300	0.9000	0.362
0.4036	0	1.090	0.0900	0.1000	0.685
0.5002	0	1.168	0.0800	0.2000	0.577
0.6000	0	1.243	0.0700	0.3001	0.510
0.7000	0	1.298	0.0600	0.3994	0.460
0.8007	0	1.293	0.0500	0.5000	0.425
0.9000	0	0.977	0.0400	0.5999	0.402
0	0.1000	0.624	0.0300	0.7000	0.387
0	0.2000	0.535	0.0200	0.8000	0.374
0	0.3007	0.471	0.0101	0.8991	0.367
0	0.4000	0.432	0.1000	0.0900	0.704
0	0.5000	0.412	0.2001	0.0800	0.781
0	0.6003	0.387	0.2895	0.0710	0.850
0	0.7006	0.374	0.4000	0.0600	0.946
0	0.8000	0.364	0.5014	0.0499	1.034
0	0.9000	0.360	0.6000	0.0400	1.128
0.6300	0.1000	0.989	0.7000	0.0300	1.200
0.5600	0.2000	0.814	0.8000	0.0200	1.204
0.4900	0.3000	0.657	0.1000	0.2700	0.534
0.4200	0.4000	0.567	0.2004	0.2399	0.593
0.3500	0.4999	0.498	0.3001	0.2100	0.670
0.2818	0.5974	0.454	0.4019	0.1794	0.761
0.2101	0.6999	0.410	0.5002	0.1500	0.861
0.1399	0.8001	0.377	0.6000	0.1200	0.987
0.0703	0.8996	0.356	0.1000	0.4500	0.442
0.4500	0.1000	0.890	0.2000	0.4000	0.493
0.4000	0.2000	0.719	0.3005	0.3497	0.558
0.3500	0.2999	0.609	0.4000	0.3000	0.630
0.3000	0.4000	0.527	0.5006	0.2497	0.718
0.2500	0.5000	0.473	0.6000	0.2000	0.827
0.2000	0.6001	0.433	0.1002	0.6298	0.398
0.1500	0.7000	0.405	0.1999	0.5601	0.439
0.1000	0.7999	0.382	0.3000	0.4900	0.487
0.0500	0.9000	0.362	0.4200	0.4000	0.551
0.2701	0.1000	0.791			

The calculation of the dynamic viscosity, η , is done using the equation

$$\eta = K(\rho_b - \rho)t \quad (2)$$

Table 6. Coefficients of Equation 4 Fitted to the Excess Molar Volumes, V_m^E , and Viscosity Deviations, $\Delta\eta$, for the Binary Systems and of Equation 6 for the Ternary Systems

system		B_0	B_1	B_2	C_1	C_2	σ	AAD %
$T = 298.15 \text{ K}$								
water + ethyl acetate	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-3.123	-2.602	—	0.617	—	0.01	3.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	-0.059	0.038	—	—	—	0.00	5.8
water + ethanol	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-4.443	—	—	-0.271	—	0.04	4.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	3.861	—	—	-1.271	0.554	0.03	2.7
ethyl acetate + ethanol	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	0.620	—	—	-0.180	—	0.01	5.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	-0.995	—	—	0.652	—	0.00	1.0
water + ethyl acetate + ethanol	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	3.910	-1170.750	—	-450.302	—	0.02	3.0
	$\Delta h/(\text{mPa}\cdot\text{s})$	-9.295	-13.476	—	—	1.088	0.03	9.9
$T = 318.15 \text{ K}$								
water + ethyl acetate	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-4.298	-3.493	—	0.210	—	0.01	4.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	-0.279	-0.604	-0.350	—	—	0.00	6.9
water + ethanol	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	-4.134	—	—	-0.290	—	0.05	5.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	2.015	2.076	1.611	—	—	0.03	5.1
ethyl acetate + ethanol	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	1.115	—	—	0.007	—	0.02	6.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	-0.584	0.346	-0.164	—	—	0.00	1.8
water + ethyl acetate + ethanol	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	6.493	10.947	—	—	0.267	0.02	4.0
	$\Delta\eta/(\text{mPa}\cdot\text{s})$	-2.925	-0.191	—	—	0.554	0.01	9.8

where t is the falling time of the ball measured with the stopwatch. K is a calibration constant, and ρ_b represents the density of the ball. The viscosity deviations, $\Delta\eta$, were obtained using the expression

$$\Delta\eta = \eta - \sum x_i \eta_i \quad (3)$$

where η is the measured mixture viscosity and η_i represents the pure component viscosity. The viscosity measurements were made for different compositions than those made for the density measurements because they were not performed simultaneously. For that reason, the density value needed to obtain the viscosity from eq 2 was calculated with eq 1 with a fitted equation for V_m^E .

In Tables 4 and 5 the viscosities, η , for the ternary system and constituent binaries at 298.15 and 318.15 K are shown.

The dependence of binary V_m^E and $\Delta\eta$ on composition, X_{ij} , can be described by a flexible equation proposed by Myers and Scott⁷

$$X_{ij} = x_i x_j \frac{\sum_{k=0}^p B_k z_{ij}^k}{1 + \sum_{l=1}^m C_l z_{ij}^l} \quad (4)$$

where $z_{ij} = x_i - x_j$. B_k and C_l are adjustable coefficients obtained from the fitting of eq 4 to V_m^E or $\Delta\eta$.

The ternary data were correlated by the following equation

$$X_{123} = \sum_{i < j} X_{ij} + X_T \quad (5)$$

where X_{123} represents ΔV_{123}^E and $\Delta\eta_{123}$ for the ternary mixtures; X_{ij} are functions for the same properties, obtained by fitting eq 4 to binary data; and X_T is a ternary contribution. To express X_T , the Pando et al. expression⁸

$$X_T = x_1 x_2 x_3 \left(\frac{B_0 + B_1 z_{13} + B_2 z_{23}}{1 + C_1 z_{13} + C_2 z_{23}} \right) \quad (6)$$

was used. We have realized that three adjustable parameters were enough in eq 6 to reproduce the experimental data, and the use of more parameters does not improve the fitting.

Table 6 presents the coefficients B_k and C_l of eq 4 fitted to binary V_m^E and $\Delta\eta$ data. The standard deviation, σ , and the average absolute deviation, AAD, of the corresponding fittings are also shown. The coefficients corresponding to the fitted eq 6 of the ternary data are also presented. The σ and the AAD of the fittings are defined as usual

$$\sigma = \left[\sum_{i=1}^N \frac{(X_{\text{calcd}} - X_{\text{exptl}})_i^2}{N - m} \right]^{1/2} \quad (7)$$

and

$$\text{AAD} = \frac{100}{N} \left[\sum_{i=1}^N |(X_{\text{calcd}} - X_{\text{exptl}})/X_{\text{exptl}}|_i \right] \quad (8)$$

where N and m represent the number of experimental points and parameters, respectively, and X stands for V_m^E and $\Delta\eta$. In Figure 1a and b, we have plotted the experimental and fitted values of V_m^E at 298.15 K for the binary systems water + ethanol and ethyl acetate + ethanol as a function of the composition of water and ester, respectively.

As can be seen, our data for the water + ethanol system are in good agreement with the literature values. For the ethyl acetate + ethanol system, our experimental values agree with those obtained by Hu et al.²¹ and show significant deviations from the data reported by Ortega et al.²⁰ Plots of the excess molar volume at 318.15 K for the same binary systems are shown in Figure 1c and d. As the water + ethyl acetate system shows a short miscibility range, the data were not plotted although they have been used in correlation.

We have found in the literature excess molar volumes for ethyl acetate with methanol and with 1-propanol at 298.15 and 318.15 K.¹ It is interesting to compare the relative magnitude of the V_m^E values for the equimolar mixtures. At 298.15 K, these systems have V_m^E ($x = 0.5$) values of -0.07 , $+0.14$ (this work), and $+0.24 \text{ cm}^3\cdot\text{mol}^{-1}$ for methanol, ethanol, and 1-propanol, respectively. The corresponding values at 318.15 K are -0.12 , $+0.28$ (this work), and $+0.30 \text{ cm}^3\cdot\text{mol}^{-1}$. The increasing V_m^E values with increasing chain length of the alcohol may be explained by the reduction of intermolecular association between the molecules of the pure species (hydrogen bonding in alcohols and dipolar interactions in esters) and to a more difficult accommodation of the ester and alcohol molecules.

In Figures 2 and 3, we compare experimental and calculated V_m^E values for the ternary system at 298.15 and 318.15 K as a function of x_2 for different values of $z = x_3/x_1$. The values of the excess molar volume were obtained from eq 5 with the ternary contribution, V_T^E , defined by eq 6. The experimental values of V_m^E agree quite well with the calculated ones from the correlations. We have compared our ternary density data with those due to Resa et al.²⁴ Considering $X = \rho$ in eq 8 with ρ_{calcd} calculated from our correlations and ρ_{exptl} being the experimental values of Resa et al.,²⁴ we obtained AAD values less than 0.1 % at the two temperatures.

The experimental and fitted values of the viscosity deviations at 298.15 and 318.15 K for the systems water + ethanol and ethyl acetate + ethanol as a function of the compositions of water and ester, respectively, are compared in Figure 4. In this figure, we have plotted also values taken from the literature. For the system water + ethanol, the literature values are in excellent agreement with our data. For the ethyl acetate + ethanol system, the data of Nikam et al.¹¹ at 298.15 K deviate significantly from our values. It can be observed that the absolute values of $\Delta\eta$ decrease with the temperature for a fixed composition at both temperatures. In Figures 5 and 6, we compare the experimental and fitted viscosity deviations at the two temperatures studied for the ternary system as a function of x_2 for different values of $z = x_3/x_1$. The experimental and the calculated values of $\Delta\eta$ show good agreement.

Conclusions

Experimental viscosities and densities of water + ethyl acetate + ethanol were measured at 298.15 and 318.15 K and atmospheric pressure. The excess molar volume, V_m^E , and the viscosity deviations, $\Delta\eta$, have been well correlated using rational functions. Our V_m^E binary data are in close agreement with those taken from the literature at 298.15 K. For the viscosity deviation of both binary systems, the same conclusion can be drawn. The ternary V_m^E and $\Delta\eta$ behavior is well described using additivity of binaries and a ternary term with only three coefficients.

Note Added after ASAP Publication. This paper was published ASAP on May 8, 2007. Data in Table 1 were changed. The updated paper was reposted on June 8, 2007.

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