1478 *J. Chem. Eng. Data* **2005,** *50,* 1478−1483

Densities and Viscosities of Binary Mixtures of 1-Bromobutane with Butanol Isomers at Several Temperatures

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Densities and viscosities of 1-bromobutane + 1-butanol, + 2-methyl-1-propanol, + 2-butanol, or + 2-methyl-2-propanol were measured at several temperatures between 288.15 K and 318.15 K. At each temperature, the experimental viscosity data were correlated by means of the McAllister biparametric equation. By using our previous thermodynamic measurements (VLE, H^E), we have tested the Wei and Rowley nonparametric model at $T = 298.15$ K, obtaining average absolute deviations that are comparable to those calculated for the biparametric model.

Introduction

Although considerable progress has been achieved in the description of alkanol + alkane mixtures, the corresponding progress in mixtures of alkanol + a second polar component whose molecules may compete with alcohol molecules for hydrogen bond formation is rather limited. In recent publications, we presented thermodynamic properties[1−9] for mixtures of (1-chlorobutane or 1-bromobutane + alkanols). In this article, we report viscosity data for (1-bromobutane + butanol isomers) at four temperatures between 288.15 K and 318.15 K as well as density data at three temperatures. Earlier publications[6,7] presented the excess molar enthalpies and volumes at 298.15 K. Excess molar volumes are in agreement with other authors' measurements found in the literature[10] at 298.15 K and 313.15 K.

Experimental Section

1-Bromobutane (mole fraction >0.990), 1-butanol (mole fraction >0.998), 2-methyl-1-propanol (mole fraction >0.995), 2-butanol (mole fraction >0.990), and 2-methyl-2-propanol (mole fraction >0.995) were Aldrich products. All of the chemicals, supplied with analysis certificates, had negligible water contents and were used without further purification.

Table 1. Density ρ and Dynamic Viscosity η of the Pure Compounds

		ρ/g·cm^{-3}		η/mPa·s	
compound	T/K	exptl	lit	exptl	lit
1-bromobutane	288.15	1.28169	1.28284[a]	0.677	0.666[a]
	298.15	1.26683	1.2687[b]	0.607	0.597[b]
	303.15	1.25990	1.26120[a]	0.575	0.567[a]
	308.15	1.25271		0.546	
	313.15	1.24531		0.519	
	318.15	1.23805		0.494	
1-butanol	288.15	0.81342	0.8134[c]	3.346	3.3600[d]
	298.15	0.80540	0.8060[e]	2.560	2.5710[d]
	308.15	0.79814	0.7983[c]	1.991	2.000[d]
	318.15	0.79019	0.7907[c]	1.569	1.5786[d]
2-methyl-1-propanol	288.15	0.80547	0.8055[c]	4.805	4.6556[d]
	298.15	0.79737	0.7978[e]	3.435	3.3330[d]
	308.15	0.79010	0.7897[c]	2.508	2.445[d]
	318.15	0.78199	0.7818[c]	1.870	1.834[d]
2-butanol	288.15	0.81072	0.8111[c]	4.509	4.444[d]
	298.15	0.80182	0.8026[e]	3.035	2.998[d]
	308.15	0.79407	0.7939[c]	2.111	2.1019[d]
	318.15	0.78515	0.7854[c]	1.523	1.525[d]
2-methyl-2-propanol	298.15	0.77996	0.7812[e]	4.433	4.438[d]
	303.15	0.77530	0.7757[e]	3.355	3.390[d]
	308.15	0.77019	0.7703[c]	2.611	2.644[d]
	313.15	0.76483	0.7649[e]	2.074	2.1037[d]
	318.15	0.75952	0.7594[c]	1.685	1.705[d]

[a] From ref 12. [b] From ref 13. [c] From ref 14. [d] From ref 15. [e] Interpolated from ref 14.

Ubbelohde viscometers (Schott) of relatively long flow times (60 s to 600 s, with water) were used to minimize the kinetic energy corrections. At least three readings of the flow time with variations not exceeding ±0.1 s were taken for each solution. The viscosities were calculated from the average flow time, t, by means of the equation

$$\nu = At - \left(\frac{B}{t}\right) \tag{1}$$

where ν is the kinematic viscosity. A and B are viscometer constants that were determined by using values from Marsh[11] for the water viscosity together with the corresponding flow times measured in this study. The viscometer was held in a water bath whose temperature was controlled to within ±10 mK. Three different viscometers were used during the course of this investigation. The masses of both components were determined by weighing, and the uncertainties in the mole fractions are estimated to be less than 0.0003. Flow time measurements were performed with an electric stopwatch to ±0.01 s. The uncertainty in the kinematic viscosity measurements is not worse than $\pm 2 \times 10^{-9}$ m^2·s^{-1}.

Excess molar volumes were calculated from density measurements made with a density meter (Anton Paar DMA 60/DMA 602). The uncertainty in V^E is 0.002 cm^3·mol^{-1}.

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10.1021/je0501235 CCC: $30.25

Table 2. Experimental Densites ρ and Excess Molar Volumes V^E at Several Temperatures

	ρ	V^E		ρ	V^E		ρ	V^E		ρ	V^E		ρ	V^E
x_2	g·cm^{-3}	cm^3·mol^{-1}	x_2	g·cm^{-3}	cm^3·mol^{-1}	x_2	g·cm^{-3}	cm^3·mol^{-1}	x_2	g·cm^{-3}	cm^3·mol^{-1}	x_2	g·cm^{-3}	cm^3·mol^{-1}
1-Bromobutane (1) + 1-Butanol (2)														
$T = 288.15$ K														
0.0651	1.25436	0.077	0.2243	1.18762	0.111	0.4554	1.08566	0.085	0.7017	0.96875	0.024	0.8665	0.88503	−0.021
0.0908	1.24372	0.089	0.3496	1.13318	0.103	0.5543	1.03978	0.067	0.7817	0.92875	−0.004	0.8665	0.88503	−0.021
0.1711	1.21018	0.107	0.4142	1.10435	0.093	0.6421	0.99792	0.038	0.8097	0.91445	−0.009	0.9373	0.84742	−0.022
$T = 308.15$ K														
0.1003	1.21163	0.163	0.2872	1.13422	0.244	0.5004	1.04157	0.219	0.7005	0.94899	0.145	0.8995	0.85058	0.050
0.1981	1.17151	0.221	0.3997	1.08606	0.237	0.6152	0.98922	0.178	0.7972	0.90196	0.104			
$T = 318.15$ K														
0.0985	1.19792	0.196	0.2858	1.12153	0.293	0.4965	1.03133	0.280	0.6965	0.94053	0.181	0.8967	0.84328	0.055
0.1984	1.15754	0.266	0.3937	1.07599	0.298	0.5958	0.98693	0.243	0.7954	0.89334	0.122	0.9519	0.81523	0.019
1-Bromobutane (1) + 2-Methyl-1-propanol (2)														
$T = 288.15$ K														
0.0278	1.26940	0.050	0.2862	1.15747	0.160	0.5347	1.04344	0.117	0.7389	0.94357	0.032	0.9030	0.85835	−0.023
0.0624	1.25460	0.087	0.3542	1.12698	0.159	0.5743	1.02455	0.103	0.7991	0.91289	0.006	0.9444	0.83599	−0.022
0.1314	1.22512	0.125	0.4107	1.10121	0.156	0.6930	0.96657	0.053	0.8566	0.88302	−0.020	0.9516	0.83205	−0.019
0.2047	1.19336	0.150	0.4499	1.08317	0.145									
$T = 308.15$ K														
0.0981	1.21121	0.184	0.2793	1.13398	0.309	0.4989	1.03668	0.292	0.6956	0.94428	0.224	0.9005	0.84219	0.077
0.1965	1.16947	0.280	0.3949	1.08344	0.314	0.5936	0.99285	0.265	0.7937	0.89628	0.153			
$T = 318.15$ K														
0.0581	1.21335	0.163	0.1896	1.15850	0.317	0.3863	1.07439	0.382	0.6160	0.97079	0.345	0.7860	0.88986	0.235
0.0947	1.19804	0.229	0.2827	1.11903	0.371	0.4919	1.02754	0.379	0.6927	0.93470	0.312	0.8930	0.83677	0.136
1-Bromobutane (1) + 2-Butanol (2)														
$T = 288.15$ K														
0.0491	1.25995	0.138	0.2504	1.17314	0.326	0.4675	1.07575	0.350	0.7143	0.95830	0.231	0.8880	0.87041	0.070
0.0823	1.24578	0.184	0.3943	1.10918	0.354	0.5438	1.04028	0.329	0.7675	0.93185	0.191	0.9581	0.83331	0.015
0.1594	1.21263	0.271	0.2889	1.15622	0.340	0.6796	0.97528	0.259	0.8287	0.90094	0.132			
$T = 308.15$ K														
0.0952	1.21155	0.299	0.2848	1.13078	0.519	0.3969	1.08185	0.563	0.7967	0.89646	0.342	0.5969	0.99140	0.528
0.2083	1.16356	0.460	0.4970	1.03711	0.563	0.6985	0.94371	0.460	0.8994	0.84559	0.179			
$T = 318.15$ K														
0.0933	1.19787	0.332	0.2787	1.11947	0.599	0.4931	1.02614	0.651	0.6890	0.93692	0.526	0.8967	0.83714	0.214
0.1938	1.15545	0.516	0.3912	1.07108	0.646	0.5904	0.98229	0.618	0.7866	0.89076	0.401			
1-Bromobutane (1) + 2-Methyl-2-propanol (2)														
$T = 303.15$ K														
0.1016	1.21226	0.339	0.2803	1.12995	0.592	0.4877	1.03205	0.705	0.6906	0.93291	0.640	0.8924	0.83098	0.326
0.1957	1.16889	0.509	0.3841	1.08132	0.672	0.5853	0.98472	0.704	0.7842	0.88596	0.546	0.9481	0.80235	0.165
$T = 308.15$ K														
0.1002	1.20558	0.364	0.3414	1.09454	0.672	0.5891	0.97659	0.725	0.7899	0.87735	0.544	0.0606	1.22394	0.251
0.1950	1.16233	0.515	0.4891	1.02482	0.728	0.6909	0.92667	0.668	0.9446	0.79888	0.177	0.8499	0.84704	0.440
0.2446	1.13939	0.588												
$T = 313.15$ K														
0.1012	1.19757	0.398	0.2790	1.11619	0.664	0.4858	1.01964	0.757	0.6887	0.92163	0.674	0.9031	0.81445	0.308
0.1882	1.15781	0.559	0.3873	1.06607	0.730	0.5848	0.97220	0.747	0.7888	0.87183	0.569			
$T = 318.15$ K														
0.0517	1.21346	0.238	0.2703	1.11316	0.682	0.4825	1.01456	0.780	0.6845	0.91746	0.701	0.8905	0.81519	0.350
0.1069	1.18793	0.407	0.3791	1.06303	0.752	0.5831	0.96660	0.766	0.7853	0.86782	0.570	0.9288	0.79592	0.233
0.1938	1.14816	0.583												

Results

Table 1 presents density and dynamic viscosity data of the pure compounds, which are compared with values found in the literature. Excess molar volumes, dynamic viscosities, and viscosity deviations were calculated according to the following equations

$$V^E = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{2}$$

$$\eta = \nu\rho \tag{3}$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

where ρ and η are the density and the viscosity of the mixture, respectively, x is the mole fraction, M is the molar mass, ν is the kinematic viscosity, and subscripts 1 and 2 indicate 1-bromobutane and alcohol, respectively.

Tables 2 and 3 show the density and viscosity measurements at several temperatures together with excess molar volumes and viscosity deviations, which were fitted to the polynomial

$$Q = x_1 x_2 \sum_{i=0}^{m} A_i (x_1 - x_2)^i \tag{5}$$

where Q denotes V^E or $\Delta\eta$. Table 4 lists the A_i coefficients together with the standard deviation, which is defined by

$$s(Q) = \left[\frac{\sum (Q_{\text{exptl}} - Q_{\text{calcd}})^2}{N - m}\right]^{1/2} \tag{6}$$

Table 3. Absolute Viscosities η and Viscosity Deviations $\Delta\eta$ for {1-Bromobutane (1) + Butanol Isomers (2)} at Different Temperatures

	$T = 288.15$ K		$T = 298.15$ K		$T = 308.15$ K		$T = 318.15$ K	
	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
x_2	mPa·s		mPa·s		mPa·s		mPa·s	
1-Bromobutane (1) + 1-Butanol (2)								
0.1114	0.712	−0.262	0.630	−0.194	0.554	−0.153	0.495	−0.118
0.2168	0.784	−0.472	0.685	−0.345	0.588	−0.272	0.522	−0.205
0.3241	0.883	−0.659	0.759	−0.481	0.638	−0.376	0.561	−0.282
0.4255	1.016	−0.796	0.860	−0.578	0.706	−0.455	0.613	−0.338
0.5172	1.183	−0.874	0.983	−0.635	0.793	−0.500	0.679	−0.371
0.6158	1.424	−0.896	1.158	−0.651	0.918	−0.518	0.771	−0.385
0.7127	1.750	−0.829	1.394	−0.605	1.086	−0.490	0.899	−0.361
0.7911	2.079	−0.709	1.636	−0.517	1.261	−0.427	1.029	−0.316
0.8968	2.645	−0.425	2.046	−0.313	1.581	−0.260	1.264	−0.194
1-Bromobutane (1) + 2-Methyl-1-propanol (2)								
0.1010	0.706	−0.388	0.626	−0.266	0.549	−0.195	0.492	−0.141
0.2014	0.768	−0.740	0.671	−0.504	0.576	−0.365	0.512	−0.259
0.3080	0.866	−1.083	0.743	−0.734	0.624	−0.526	0.555	−0.363
0.4025	0.984	−1.355	0.830	−0.914	0.682	−0.653	0.593	−0.454
0.5066	1.190	−1.578	0.980	−1.059	0.783	−0.757	0.664	−0.527
0.6100	1.497	−1.698	1.196	−1.135	0.934	−0.809	0.774	−0.559
0.7006	1.844	−1.725	1.436	−1.152	1.100	−0.821	0.895	−0.563
0.8004	2.436	−1.545	1.845	−1.025	1.387	−0.729	1.098	−0.497
0.8984	3.333	−1.053	2.449	−0.699	1.807	−0.502	1.389	−0.341
1-Bromobutane (1) + 2-Butanol (2)								
0.1100	0.692	−0.406	0.613	−0.261	0.538	−0.180	0.483	−0.125
0.2080	0.731	−0.743	0.642	−0.470	0.552	−0.319	0.492	−0.216
0.3145	0.796	−1.086	0.689	−0.682	0.581	−0.458	0.512	−0.306
0.3968	0.870	−1.327	0.742	−0.828	0.614	−0.553	0.537	−0.366
0.4998	1.001	−1.592	0.833	−0.987	0.675	−0.653	0.579	−0.429
0.6057	1.206	−1.792	0.975	−1.103	0.770	−0.724	0.653	−0.464
0.7046	1.508	−1.869	1.176	−1.142	0.905	−0.744	0.741	−0.478
0.7860	1.896	−1.793	1.428	−1.087	1.075	−0.701	0.855	−0.448
0.8988	2.816	−1.305	2.018	−0.771	1.461	−0.492	1.111	−0.308

	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K	
	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
x_2	mPa·s		mPa·s		mPa·s		mPa·s		mPa·s	
1-Bromobutane (1) + 2-Methyl-2-propanol (2)										
0.0988	0.597	−0.387	0.564	−0.286	0.534	−0.216	0.508	−0.165	0.494	−0.118
0.1970	0.612	−0.748	0.576	−0.547	0.540	−0.412	0.511	−0.315	0.482	−0.246
0.3014	0.643	−1.117	0.602	−0.810	0.563	−0.605	0.529	−0.459	0.497	−0.356
0.4101	0.692	−1.485	0.642	−1.073	0.598	−0.795	0.557	−0.600	0.521	−0.462
0.5017	0.798	−1.729	0.736	−1.234	0.679	−0.903	0.632	−0.667	0.581	−0.510
0.5982	0.926	−1.970	0.839	−1.399	0.763	−1.018	0.700	−0.749	0.638	−0.569
0.7029	1.148	−2.148	1.018	−1.511	0.909	−1.088	0.817	−0.795	0.737	−0.594
0.7982	1.509	−2.153	1.302	−1.492	1.134	−1.060	0.995	−0.765	0.882	−0.563
0.8931	2.232	−1.793	1.841	−1.217	1.543	−0.846	1.311	−0.597	1.127	−0.431

where N is the number of experimental points and m is the number of parameters in the corresponding analytical equation. In Figures 1 and 2, the excess molar volume and the viscosity deviation are plotted at $T = 318.15$ K.

Discussion

At $T = 318.15$ K, Figures 1 and 2 show the experimental data for the four mixtures (1-bromobutane + butanol isomers). V^E increases with the branching around the OH group, and for $\Delta\eta$ the more negative values are observed in mixtures containing 2-methyl-2-propanol. For all systems, both V^E and $\Delta\eta$ increase with increasing temperature, and the lowest dependence on temperature in V^E and the highest one in $\Delta\eta$ are observed for mixtures containing 2-methyl-2-propanol. By comparing data in Table 5 of the four butanol isomers with the two halobutanes, it becomes apparent that the kinetic and volumetric behavior of these mixtures is related to the perturbation that the size of the halogen provokes in the alcohol structure.

Many semitheoretical and empirical equations have been used to fit the isothermal viscosity data of mixtures. These equations can be distinguished as predictive or correlative and have been reviewed and discussed extensively by Mehrotra et al.[16] We have selected the McAllister two-parameters equation,[17] based on Eyring's equation, which takes into account interactions of both like and unlike molecules by a 2D, three-body model. The McAllister equation is given by

$$\ln \nu = x_1^3 \ln \nu_1 + 2x_1^2 x_2 \ln \nu_{12} + 2x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left(x_1 + x_2 \frac{M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left(\frac{2 + (M_2/M_1)}{3}\right) + 3x_1 x_2^2 \ln\left(\frac{1 + (2M_2/M_1)}{3}\right) + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad (7)$$

$i = 1$ for 1-bromobutane and 2 for an alcohol, ν is the

Table 4. Coefficients A_i and Standard Deviations $s(V^E)$ and $s(\Delta\eta)$ for Equation 5

	V^E/cm^3·mol^{-1}					$\Delta\eta$/mPa·s				
T/K	A_0	A_1	A_2	A_3	$s(V^E)$	A_0	A_1	A_2	A_3	$s(\Delta\eta)$
					1-Bromobutane (1) + 1-Butanol (2)					
288.15	0.301	0.400	0.100	0.639	0.003	−3.453	1.372	−0.237	−0.220	0.002
298.15						−2.507	0.993	−0.231	−0.153	0.002
308.15	0.861	0.518	0.452	0.369	0.004	−1.975	0.865	−0.330	−0.089	0.002
318.15	1.098	0.559	0.357	0.658	0.006	−1.467	0.620	−0.271	−0.071	0.001
					1-Bromobutane (1) + 2-Methyl-1-propanol (2)					
288.15	0.517	0.571	−0.060	0.582	0.005	−6.234	3.681	−2.551	1.440	0.009
298.15						−4.188	2.386	−1.675	0.941	0.006
308.15	1.182	0.504	0.467	0.439	0.004	−2.987	1.671	−1.246	0.686	0.005
318.15	1.499	0.272	0.733	0.779	0.007	−2.071	1.142	−0.831	0.344	0.005
					1-Bromobutane (1) + 2-Butanol (2)					
288.15	1.364	0.402	0.229	1.033	0.005	−6.306	4.405	−4.239	3.081	0.020
298.15						−3.917	2.646	−2.419	1.571	0.009
308.15	2.243	0.268	0.667	0.969	0.004	−2.595	1.661	−1.501	0.896	0.006
318.15	2.587	0.417	0.702	0.898	0.006	−1.697	0.996	−0.939	0.531	0.004
					1-Bromobutane (1) + 2-Methyl-2-propanol (2)					
298.15						−6.796	5.052	−6.951	6.432	0.046
303.15	2.816	−0.268	1.117	0.726	0.006	−4.878	3.474	−4.554	4.066	0.028
308.15	2.905	−0.342	1.213	1.056	0.010	−3.590	2.418	−3.054	2.640	0.017
313.15	3.012	−0.110	1.399	0.912	0.009	−2.675	1.681	−2.088	1.789	0.010
318.15	3.118	−0.034	1.224	0.883	0.006	−2.056	1.177	−1.369	1.321	0.006

Table 5. Viscosity Deviations $\Delta\eta$ and Excess Volumes V^E for {0.5 1-Chlorobutane or 1-Bromobutane + 0.5 Butanol Isomer} at T = 298.15 K

		1-butanol	2-methyl-1-propanol	2-butanol	2-methyl-2-propanol
1-chlorobutane[a]	$\Delta\eta$/mPa·s	−0.700	−1.133	−1.039	−1.724
	V^E/cm^3·mol^{-1}	0.061	0.144	0.398	0.675
1-bromobutane	$\Delta\eta$/mPa·s	−0.627	−1.047	−0.979	−1.699
	V^E/cm^3·mol^{-1}	0.141[b]	0.207[c]	0.452[c]	0.728[b]

[a] Ansón et al.[9] [b] Garriga et al.[6] [c] Garriga et al.[7]

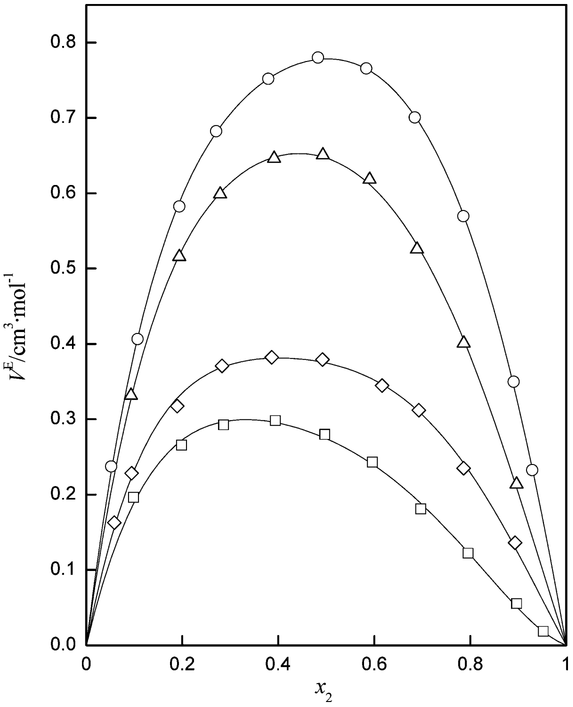

Figure 1. Excess molar volume V^E at T = 318.15 K for the following mixtures: □, $x_1$1-bromobutane + $x_2$1-butanol; ◇, $x_1$1-bromobutane + $x_2$2-methyl-1-propanol; △, $x_1$1-bromobutane + $x_2$2-butanol; ○, $x_1$1-bromobutane + $x_2$2-methyl-2-propanol. −, from analytical equations.

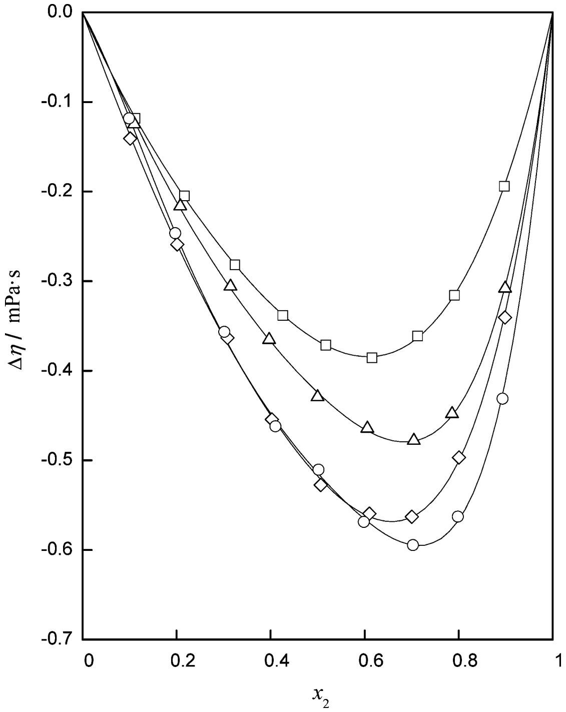

Figure 2. Viscosity deviation $\Delta\eta$ at T = 318.15 K for the following mixtures: □, $x_1$1-bromobutane + $x_2$1-butanol; ◇, $x_1$1-bromobutane + $x_2$2-methyl-1-propanol; △, $x_1$1-bromobutane + $x_2$2-butanol; ○, $x_1$1-bromobutane + $x_2$2-methyl-2-propanol. −, from analytical equations.

kinematic viscosity of the pure compounds, x is the mole fraction, M is the molar mass, ν_{12} and ν_{21} are fitting parameters that denote viscosity contributions for 112 and 221 interactions, respectively, and have been calculated for each temperature by a least-squares method. For each system at several temperatures, the mixed viscosity pa-

Table 6. Mixed Kinematic Viscosity Parameters and Average Absolute Deviations (AAD) of Experimental and Calculated Kinematic Viscosities (10^{-6} m^2·s^{-1}) at Several Temperatures

	1-bromobutane (1) +							
	1-butanol (2)		2-methyl-1-propanol (2)		2-butanol (2)		2-methyl-2-propanol (2)	
T/K	ν_{12}	ν_{21}	ν_{12}	ν_{21}	ν_{12}	ν_{21}	ν_{12}	ν_{21}
288.15	0.646	1.543	0.666	1.399	0.667	0.904		
298.15	0.574	1.234	0.591	1.114	0.590	0.761	0.646	0.577
303.15							0.594	0.577
308.15	0.520	1.001	0.529	0.914	0.525	0.660	0.545	0.573
313.15							0.508	0.565
318.15	0.468	0.842	0.480	0.767	0.468	0.584	0.478	0.544
AAD(%)	0.34		0.52		1.00		2.50	

Table 7. Standard Deviations $s(\eta)$ for Experimental and Calculated Dynamic Viscosities η (mPa·s) according to the Wei and Rowley Model, at T = 298.15 K, for σ = 0.00, σ = 0.25, and σ (fitted)

system	σ	$s(\eta)$	σ	$s(\eta)$	σ	$s(\eta)$
1-bromobutane (1) + 1-butanol (2)	0.00	0.051	0.25	0.106	−0.11	0.044
1-bromobutane (1) + 2-methyl-1-propanol (2)	0.00	0.034	0.25	0.060	0.09	0.007
1-bromobutane (1) + 2-butanol (2)	0.00	0.149	0.25	0.051	0.32	0.044
1-bromobutane (1) + 2-methyl-2-propanol (2)	0.00	0.377	0.25	0.245	0.71	0.116

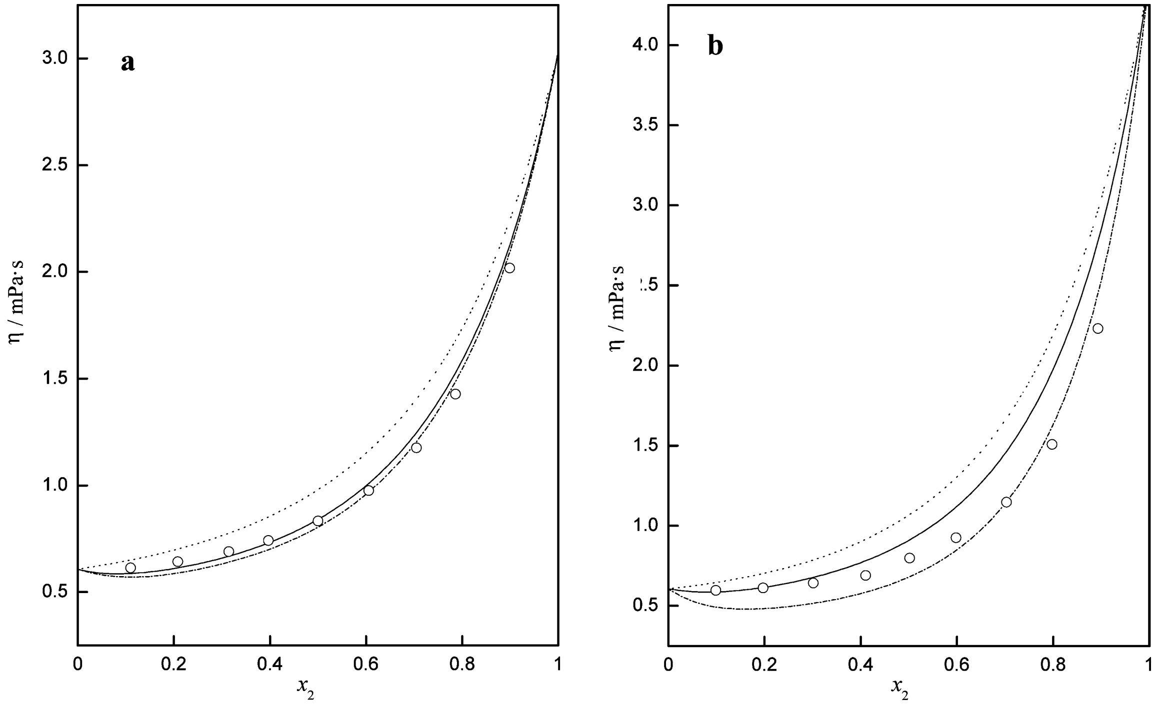

Figure 3. Dynamic viscosity η at T = 298.15 K for the following mixtures: (a) $x_1$1-bromobutane + $x_2$2-butanol and (b) $x_1$1-bromobutane + $x_2$2-methyl-2-propanol. ○, Experimental. Curves from the NRTL model: ···, with σ = 0.00; –, with σ = 0.25 (predictive); – · – · –, with σ (fitted).

rameters are collected in Table 6 together with the average absolute deviations (AAD) that are defined by

$$\mathrm{AAD} = \left[\frac{100}{N}\sum\left|\ln \nu_{\mathrm{exptl}} - \ln \nu_{\mathrm{calcd}}\right|\right] \tag{8}$$

where N is the number of experimental points.

Wei and Rowley[18,19] proposed a local composition model for the multicomponent nonelectrolyte liquid mixture viscosity, which requires only binary equilibrium thermodynamic information (H^{E}, G^{E}) in addition to pure component data. No mixture viscosities and no adjustable parameters are required. The basic equations of the model are given by

$$\eta = \frac{\exp(\xi)}{V} \tag{9}$$

$$\xi = \sum_i \phi_i \xi_i^0 + \sum_i \phi_i \left[\frac{\sum_j \phi_j G_{ji}(\xi_{ji} - \xi_j^0)}{\sum_l \phi_l G_{li}}\right] - \frac{\sigma H^{\mathrm{E}}}{RT} \tag{10}$$

$$\xi_{ji} = \xi_{ij} = \frac{\sum_i (\phi_i^* \, \phi_{ii}^* \xi_i^0)}{\sum_j (\phi_j^* \, \phi_{jj}^*)} \tag{11}$$

where for an i, j ($i \neq j$) pair of interactions

$$G_{ji} = \exp\left(\frac{-\alpha A_{ji}}{RT}\right) \tag{12}$$

$$\phi_j^* = (1 + \Gamma_{ji})^{-1} \qquad \phi_{ii}^* = \left(\frac{1 + \phi_j^* G_{ji}}{\phi_i^*}\right)^{-1} \tag{13}$$

$$\Gamma_{ji} = \left(\frac{V_i}{V_j}\right)\left(\frac{G_{ij}}{G_{ji}}\right)^{1/2} \exp\left[\frac{\xi_i^0 - \xi_j^0}{2}\right] \tag{14}$$

V is the molar volume, ϕ_j is the volume fraction, ϕ_{ij} is the local volume fraction, the * symbol refers to the particular composition where the average mixture is considered to be equivalent to a hypothetical mixture composed entirely of 1−2 type interactions, and ξ_i^0 denotes the pure component i value

$$\xi_i^0 = \ln(\eta_i V_i) \tag{15}$$

The same notation as in the original paper is used. α, A_{ij}, and A_{ji} stand for the binary NRTL parameters. In this work, these parameters have been calculated from our vapor pressure data, and H^E values have been taken from our experimental results.[6,7] If the factor σ in eq 10 is chosen as 0.25, a value identical to that used in the original paper, then the validity of the model as a nonparametric predictive method is tested. In Table 7, standard deviations $s(\eta)$, defined by eq 6 at 298.15 K for three σ values ($\sigma = 0.00$ (no H^E contribution), $\sigma = 0.25$ (predictive), and σ (fitted)), are collected, and the corresponding dynamic viscosity is plotted in Figure 3 for 2-butanol and 2-methyl-2-propanol, the best and the worst standard deviation for $\sigma = 0.25$, respectively. We can conclude that in all systems η is well described by the predictive model ($\sigma = 0.25$). The agreement with the experimental results is comparable to that obtained with σ fitted (monoparametric) or with the McAllister biparametric equation. Previous studies of mixtures of butanol isomers with butanone, butanenitrile, or 1-chlorobutane yield similar agreement between experimental and calculated results.[9,20,21] By taking into account the complicated interactions in these mixtures, we can conclude that the NRTL model (predictive) gives an adequate representation of these systems.

Literature Cited

(1) Martínez, S.; Garriga, R.; Pérez, P.; Gracia, M. Isothermal Vapor−Liquid Equilibrium of 1-Chlorobutane with Ethanol or 1-Hexanol at Ten Temperatures between 278.15 K and 323.15 K. *J. Chem. Eng. Data* **2001**, *46*, 535−540.

(2) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Isothermal (vapour + liquid) equilibrium at several temperatures of (1-chlorobutane + 1-butanol, or 2-methyl-2-propanol). *J. Chem. Thermodyn.* **2001**, *33*, 523−534.

(3) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Thermodynamic excess properties for binary mixtures of 1-chlorobutane with 2-butanol or 2-methyl-1-propanol. *Fluid Phase Equilib.* **2001**, *181*, 203−214.

(4) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Isothermal (vapour + liquid) equilibrium at several temperatures of (1-chlorobutane + 1-octanol, or 1-decanol). *J. Chem. Thermodyn.* **2003**, *36*, 59−69.

(5) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Vapour pressures at 10 temperatures between 278.15 K and 323.15 K for binary mixtures of 1-bromobutane with ethanol or 1-hexanol. *Fluid Phase Equilib.* **2003**, *207*, 97−109.

(6) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Vapor Pressures at Several Temperatures between 278.15 and 323.15 K and Excess Functions at T = 298.15 K for 1-Bromobutane with 1-Butanol or 2-Methyl-2-propanol. *J. Chem. Eng. Data* **2002**, *47*, 322−328.

(7) Martínez, S.; Garriga, R.; Pérez, P.; Gracia, M. Vapor Liquid Equilibrium between (278.15 and 323.15) K and Excess Functions at T = 298.15 K for 1-Bromobutane with 2-Methyl-1-propanol or 2-Butanol. *J. Chem. Eng. Data* **2003**, *48*, 294−301.

(8) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Vapor Liquid Equilibrium between (278.15 and 323.15) K and Excess Functions at T = 298.15 K for 1-Bromobutane with 1-Octanol or 1-Decanol. *J. Chem. Eng. Data* **2004**, *49*, 224−230.

(9) Ansón, A.; Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Densities and Visicosities of Binary Mixtures of 1-Chlorobutane with Butanol Isomers at Several Temperatures. *J. Chem. Eng. Data* **2005**, *50*, 677−682.

(10) Artigas, H.; Lafuente, C.; Rodríguez, V.; Royo, F. M.; Urieta, J. S. Excess volumes of (1-bromobutane + each of several isomers of butanol) at the temperatures 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 151−154.

(11) *Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh, K. N., Ed.; Blackwell: Oxford, U.K., 1987.

(12) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1950; Vol. 1, p 265.

(13) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*; Wiley: New York, 1986; p 529.

(14) *TRC-Thermodynamic Tables-Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1966; p d-5030.

(15) *TRC-Thermodynamic Tables-Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1971; p c-5030.

(16) Mehrotra, A. K.; Monnery, W. D.; Svrcek, W. Y. A review of practical calculation methods for the viscosity of liquid hydrocarbons and their mixtures. *Fluid Phase Equilib.* **1996**, *117*, 344−355.

(17) McAllister, R. A. The Viscosity of Liquid Mixtures. *AIChE J.* **1960**, *6*, 427−431.

(18) Wei, I. C.; Rowley, R. L. Binary Liquid Mixture Viscosities and Densities. *J. Chem. Eng. Data* **1984**, *29*, 332−335.

(19) Wei, I. C.; Rowley, R. L A Local Composition Model for Multicomponent Liquid Mixture Shear Viscosity. *Chem. Eng. Sci.* **1985**, *40*, 401−408.

(20) Martínez, S.; Garriga, R.; Pérez, P.; Gracia, M. Densities and Viscosities of Binary Mixtures of Butanenitrile with Butanol Isomers at Several Temperatures. *J. Chem. Eng. Data* **2000**, *45*, 1182−1188.

(21) Martínez, S.; Garriga, R.; Pérez, P.; Gracia, M. Densities and viscosities of binary mixtures of butanone with butanol isomers at several temperatures. *Fluid Phase Equilib.* **2000**, *168*, 267−279.

Received for review March 30, 2005. Accepted April 28, 2005. We are grateful for the financial support of the Spanish Ministry of Science and Technology and FEDER (European Funds for Regional Development) (project FIS2004-02166) and also the University of Zaragoza (project INF2004-CIE-19).

JE0501235