Densities and Viscosities of Binary Mixtures of Butanenitrile with Butanol Isomers at Several Temperatures

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Densities and viscosities of butanenitrile + 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 which 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 equilibrium thermodynamic properties[1−3] and viscosity data[4] for mixtures of butanone + butanol isomers. In this paper we report viscosity data at four temperatures between 288.15 K and 318.15 K as well as density data at three temperatures for binary mixtures of butanol isomers with butanenitrile, a strongly polar solvent. For these mixtures, equilibrium properties have been published.[5−7] Recently we found a mistake in our V^E measurements at $T = 298.15$ K for butanenitrile + 2-methyl-1-propanol or + 2-butanol.[6,7] Therefore, the correct values for these mixtures, at $T = 298.15$ K, are collected in this work.

Experimental Section

Butanenitrile (mole fraction > 0.998) and 1-butanol (mole fraction > 0.995) were Fluka products, and 2-butanol (mole fraction > 0.995), 2-methyl-1-propanol (mole fraction > 0.995), and 2-methyl-2-propanol (mole fraction > 0.995) were from Aldrich. All of the chemicals were of low water content, were supplied with an analysis certificate, and were used without further purification.

Ubbelohde viscosimeters (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

$$\nu = At - B/t \qquad (1)$$

where ν is the kinematic viscosity. A and B are viscosimeter constants which were determined by using values from Marsh[8] for the water viscosity together with the corresponding flow times measured in this study. The viscosimeter was held in a water bath whose temperature was controlled to within ±10 mK. Three different viscosimeters 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 electrical stopwatch to ±0.01 s. The uncertainty in the kinematic viscosity measurements is estimated to be $\pm 2 \times 10^{-9}$ m^2·s^{-1}.

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

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

		ρ/cm^3·mol^{-1}		η/mPa·s	
compound	T/K	exptl	lit.	exptl	lit.
butanenitrile	288.15	0.795 38	0.7954[a]	0.628	0.6265[b]
	298.15	0.786 20	0.7861[a]	0.556	0.5529[b]
	303.15	0.781 62	0.7815[a]	0.525	0.5210[b]
	308.15	0.777 02	0.7768[a]	0.496	0.4919[b]
	313.15	0.772 16	0.7722[a]	0.470	0.4652[b]
	318.15	0.765 30	0.7676[a]	0.446	0.4408[b]
1-butanol	288.15	0.813 24	0.8134[c]	3.354	3.3790[a]
	298.15	0.805 48	0.8060[d]	2.560	2.5710[e]
	308.15	0.798 11	0.7983[c]	1.991	2.000[e]
	318.15	0.790 20	0.7907[c]	1.574	1.5786[e]
2-methyl-1-propanol	288.15	0.805 68	0.8055[c]	4.792	4.6556[e]
	298.15	0.797 42	0.7978[d]	3.410	3.3330[e]
	308.15	0.790 29	0.7897[c]	2.489	2.445[e]
	318.15	0.782 20	0.7818[c]	1.861	1.834[e]
2-butanol	288.15	0.810 44	0.8111[c]	4.564	4.444[e]
	298.15	0.802 06	0.8026[d]	3.068	2.998[e]
	308.15	0.793 98	0.7939[c]	2.128	2.1019[e]
	318.15	0.785 00	0.7854[c]	1.533	1.525[e]
2-methyl-2-propanol	298.15	0.780 49	0.7812[d]	4.444	4.438[e]
	303.15	0.775 73	0.7757[d]	3.361	3.390[e]
	308.15	0.770 20	0.7703[c]	2.609	2.644[e]
	313.15	0.764 84	0.7649[d]	2.077	2.1037[e]
	318.15	0.759 41	0.7594[c]	1.690	1.705[e]

[a] From ref 9. [b] Interpolated from ref 10. [c] Interpolated from ref 11. [d] From ref 11. [e] From ref 12.

Results

Table 1 presents density and dynamic viscosity data of the pure compounds, which are compared with values

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

x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
Butanenitrile (1) + 1-Butanol (2)								
T = 288.15 K								
0.0761	0.796 43	0.041	0.4979	0.803 95	0.059	0.8799	0.81121	−0.003
0.1332	0.797 31	0.060	0.5977	0.805 84	0.047	0.9199	0.811 92	−0.005
0.2226	0.798 82	0.075	0.7101	0.808 01	0.025	0.9548	0.812 52	−0.006
0.3211	0.800 62	0.075	0.7188	0.808 19	0.022			
0.4069	0.802 25	0.067	0.7941	0.809 60	0.011			
T = 308.15 K								
0.0649	0.777 99	0.052	0.3966	0.784 45	0.133	0.7997	0.793 55	0.056
0.1489	0.779 44	0.096	0.4927	0.786 57	0.124	0.8838	0.795 51	0.028
0.2106	0.780 61	0.116	0.5951	0.788 85	0.109	0.9417	0.796 85	0.009
0.2981	0.782 36	0.131	0.6994	0.791 23	0.085			
T = 318.15 K								
0.0657	0.768 57	0.060	0.3973	0.775 38	0.163	0.7958	0.785 06	0.078
0.1419	0.769 98	0.104	0.4964	0.776 79	0.157	0.8809	0.787 21	0.046
0.2057	0.771 20	0.135	0.5954	0.780 04	0.143	0.9398	0.788 71	0.021
0.3022	0.773 26	0.155	0.6966	0.782 55	0.114			
Butanenitrile (1) + 2-Methyl-1-propanol (2)								
T = 288.15 K								
0.0961	0.795 96	0.051	0.4474	0.799 30	0.093	0.7295	0.802 60	0.046
0.1827	0.796 61	0.082	0.5230	0.800 15	0.085	0.8202	0.803 69	0.025
0.2628	0.797 34	0.095	0.6079	0.801 14	0.072	0.9213	0.804 87	0.005
0.3633	0.798 38	0.098	0.6336	0.801 44	0.068			
T = 298.15 K								
0.0354	0.786 35	0.030	0.3943	0.789 50	0.145	0.6989	0.793 33	0.097
0.1087	0.786 76	0.081	0.5092	0.790 87	0.137	0.8231	0.795 00	0.061
0.2061	0.787 54	0.122	0.5788	0.791 76	0.124	0.8854	0.795 86	0.039
0.3388	0.788 90	0.141	0.6677	0.792 91	0.106			
T = 308.15 K								
0.0658	0.777 33	0.070	0.3964	0.780 89	0.181	0.7909	0.786 79	0.099
0.1392	0.777 93	0.118	0.4944	0.782 24	0.177	0.8854	0.788 37	0.055
0.2061	0.778 59	0.148	0.5981	0.783 75	0.161	0.9409	0.789 33	0.025
0.3010	0.779 66	0.174	0.6868	0.781 52	0.137			
T = 318.15 K								
0.1004	0.768 24	0.098	0.4006	0.771 77	0.216	0.7974	0.778 32	0.124
0.1968	0.769 16	0.163	0.4957	0.773 19	0.215	0.8805	0.779 90	0.075
0.2447	0.769 73	0.181	0.5998	0.774 83	0.201	0.9407	0.781 07	0.036
0.3023	0.770 46	0.198	0.7071	0.776 72	0.161			
Butanenitrile (1) + 2-Butanol (2)								
T = 288.15 K								
0.0904	0.795 75	0.116	0.4462	0.799 63	0.296	0.7859	0.805 57	0.199
0.1776	0.796 39	0.196	0.5295	0.800 91	0.294	0.8561	0.807 03	0.150
0.2645	0.797 27	0.248	0.6424	0.802 82	0.270	0.9368	0.808 86	0.076
0.3652	0.798 54	0.279	0.7094	0.804 04	0.244			
T = 298.15 K								
0.0285	0.786 26	0.046	0.4757	0.790 86	0.351	0.8350	0.797 76	0.206
0.0778	0.786 41	0.122	0.5205	0.791 61	0.349	0.8470	0.798 04	0.195
0.1850	0.787 14	0.239	0.5383	0.791 88	0.348	0.9626	0.800 91	0.068
0.3208	0.788 65	0.318	0.7142	0.795 18	0.288			
0.3633	0.789 20	0.334	0.7171	0.795 23	0.286			
T = 308.15 K								
0.0651	0.777 23	0.109	0.3831	0.780 47	0.377	0.7927	0.788 23	0.278
0.1567	0.777 75	0.235	0.4986	0.782 34	0.389	0.8818	0.790 38	0.197
0.2191	0.778 35	0.292	0.5930	0.784 07	0.374	0.9436	0.792 15	0.108
0.3010	0.779 31	0.346	0.6968	0.786 16	0.334			
T = 318.15 K								
0.0671	0.767 70	0.1242	0.4064	0.771 34	0.4155	0.8116	0.779 56	0.2730
0.1413	0.768 12	0.2338	0.5000	0.772 89	0.4275	0.8836	0.781 47	0.1899
0.2060	0.768 70	0.3036	0.5935	0.774 66	0.4111	0.9417	0.783 12	0.1090
0.3019	0.769 82	0.3751	0.6965	0.776 86	0.3609			
Butanenitrile (1) + 2-Methyl-2-propanol (2)								
T = 303.15 K								
0.0609	0.780 11	0.128	0.3937	0.775 69	0.412	0.7458	0.774 71	0.295
0.1347	0.778 68	0.241	0.4763	0.775 20	0.415	0.8750	0.775 04	0.168
0.2616	0.776 89	0.360	0.5866	0.774 83	0.386	0.9375	0.775 36	0.087
0.2948	0.776 55	0.377	0.6564	0.774 70	0.355			

Table 2 (Continued)

x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	x_2	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
				T = 308.15 K				
0.0695	0.775 24	0.147	0.3967	0.770 78	0.406	0.7878	0.769 60	0.241
0.1219	0.774 12	0.233	0.4831	0.770 20	0.407	0.8789	0.769 80	0.145
0.1979	0.772 89	0.315	0.5858	0.769 72	0.385	0.9388	0.770 00	0.073
0.3129	0.771 51	0.385	0.6934	0.769 52	0.325			
				T = 313.15 K				
0.0694	0.770 41	0.141	0.3940	0.765 86	0.395	0.7605	0.764 46	0.253
0.1378	0.769 00	0.245	0.4804	0.765 22	0.399	0.8784	0.764 62	0.132
0.1953	0.768 07	0.304	0.5844	0.764 73	0.370	0.9388	0.764 72	0.068
0.2926	0.766 79	0.371	0.6935	0.764 49	0.306			
				T = 318.15 K				
0.0710	0.765 73	0.139	0.3882	0.761 01	0.392	0.7893	0.759 42	0.202
0.1338	0.764 43	0.231	0.4866	0.760 31	0.383	0.8745	0.759 44	0.117
0.2199	0.762 98	0.318	0.5852	0.759 77	0.354	0.9385	0.759 51	0.046
0.2908	0.762 02	0.365	0.6846	0.759 50	0.292			

Table 3. Absolute Viscosities η (mPa·s) and Viscosity Deviations $\Delta\eta$ (mPa·s) for Butanenitrile (1) + Butanol (2) Isomers at Different Temperatures

	T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
x_2	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
				Butanenitrile (1) + 1-Butanol (2)				
0.1001	0.660	−0.241	0.580	−0.176	0.515	−0.130	0.461	−0.098
0.1981	0.714	−0.454	0.623	−0.330	0.547	−0.245	0.487	−0.182
0.2994	0.792	−0.651	0.684	−0.472	0.596	−0.347	0.526	−0.258
0.3979	0.897	−0.816	0.764	−0.589	0.660	−0.431	0.575	−0.320
0.4953	1.034	−0.944	0.869	−0.680	0.741	−0.495	0.640	−0.365
0.5961	1.223	−1.030	1.012	−0.738	0.852	−0.535	0.726	−0.393
0.6981	1.487	−1.044	1.211	−0.744	1.003	−0.537	0.842	−0.392
0.7984	1.852	−0.952	1.482	−0.674	1.208	−0.481	1.002	−0.345
0.8991	2.402	−0.677	1.885	−0.473	1.506	−0.334	1.221	−0.240
				Butanenitrile (1) + 2-Methyl-1-propanol (2)				
0.0997	0.662	−0.380	0.582	−0.258	0.516	−0.178	0.462	−0.125
0.2000	0.721	−0.740	0.626	−0.500	0.551	−0.344	0.489	−0.240
0.2986	0.804	−1.067	0.690	−0.718	0.600	−0.491	0.528	−0.340
0.3982	0.920	−1.366	0.778	−0.914	0.667	−0.623	0.580	−0.430
0.4962	1.075	−1.618	0.895	−1.077	0.756	−0.729	0.648	−0.500
0.5918	1.288	−1.803	1.051	−1.194	0.874	−0.802	0.737	−0.547
0.7022	1.654	−1.898	1.315	−1.244	1.069	−0.826	0.881	−0.558
0.8004	2.159	−1.802	1.672	−1.168	1.323	−0.768	1.066	−0.512
0.8991	3.037	−1.334	2.273	−0.849	1.742	−0.546	1.363	−0.355
				Butanenitrile (1) + 2-Butanol (2)				
0.1016	0.650	−0.378	0.572	−0.240	0.508	−0.154	0.454	−0.102
0.1946	0.694	−0.699	0.605	−0.440	0.532	−0.281	0.472	−0.185
0.2965	0.758	−1.037	0.652	−0.649	0.567	−0.413	0.499	−0.270
0.3938	0.847	−1.331	0.717	−0.828	0.616	−0.523	0.536	−0.338
0.4949	0.979	−1.597	0.811	−0.988	0.685	−0.618	0.590	−0.394
0.5951	1.164	−1.807	0.945	−1.106	0.782	−0.685	0.658	−0.435
0.6966	1.445	−1.925	1.141	−1.165	0.921	−0.712	0.758	−0.446
0.7945	1.877	−1.879	1.435	−1.116	1.123	−0.670	0.898	−0.412
0.8999	2.723	−1.447	1.982	−0.834	1.478	−0.487	1.135	−0.290

	T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K		T = 318.15 K	
x_2	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
					Butanenitrile (1) + 2-Methyl-2-propanol (2)					
0.0953	0.575	−0.351	0.540	−0.255	0.510	−0.187	0.481	−0.142	0.456	−0.109
0.1938	0.613	−0.697	0.573	−0.502	0.537	−0.368	0.505	−0.276	0.476	−0.211
0.2941	0.669	−1.030	0.622	−0.737	0.579	−0.539	0.540	−0.402	0.506	−0.306
0.3922	0.749	−1.332	0.689	−0.948	0.636	−0.689	0.589	−0.511	0.546	−0.388
0.4949	0.867	−1.613	0.788	−1.141	0.719	−0.822	0.660	−0.605	0.607	−0.455
0.5910	1.030	−1.824	0.923	−1.278	0.834	−0.911	0.753	−0.667	0.685	−0.497
0.6950	1.297	−1.961	1.138	−1.358	1.006	−0.958	0.895	−0.692	0.802	−0.509
0.7957	1.727	−1.923	1.476	−1.306	1.272	−0.905	1.107	−0.642	0.974	−0.462
0.9002	2.573	−1.484	2.103	−0.975	1.746	−0.652	1.464	−0.452	1.245	−0.320

found in the literature. Excess volumes, dynamic viscosity, and viscosity deviations were calculated according to the following equations:

$$V^E = x_1M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2) \quad (2)$$

$$\eta = \nu\rho \quad (3)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

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

Tables 2 and 3 show the density and viscosity measurements at several temperatures together with excess vol-

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

	V^E/cm^3·mol^{-1}					$\Delta\eta$/mPa·s				
T/K	A_0	A_1	A_2	A_3	$\sigma(V^E)$	A_0	A_1	A_2	A_3	$\sigma(\Delta\eta)$
Butanenitrile (1) + 1-Butanol (2)										
288.15	0.237	0.252	0.036	0.207	0.002	−3.770	2.111	−1.862	1.344	0.010
298.15						−2.715	1.473	−1.255	0.862	0.006
308.15	0.500	0.243	0.063	0.174	0.002	−1.979	1.030	−0.856	0.557	0.004
318.15	0.630	0.228	0.057	0.139	0.002	−1.461	0.721	−0.572	0.367	0.004
Butanenitrile (1) + 2-Methyl-1-propanol (2)										
288.15	0.355	0.245	0.000	0.114	0.001	−6.441	4.395	−4.397	3.311	0.021
298.15	0.548	0.264	0.101		0.002	−4.295	2.821	−2.668	1.901	0.011
308.15	0.707	0.200	0.126	0.209	0.001	−2.909	1.820	−1.621	1.099	0.006
318.15	0.861	0.169	0.060	0.130	0.002	−2.000	1.204	−0.987	0.588	0.003
Butanenitrile (1) + 2-Butanol (2)										
288.15	1.180	0.095	0.218		0.002	−6.341	4.495	−5.267	4.481	0.034
298.15	1.396	0.078	0.339		0.004	−3.928	2.661	−2.843	2.262	0.017
308.15	1.547	0.015	0.486		0.006	−2.465	1.564	−1.539	1.160	0.008
318.15	1.701	0.068	0.336		0.002	−1.581	0.937	−0.851	0.573	0.004
Butanenitrile (1) + 2-Methyl-2-propanol (2)										
298.15						−6.400	4.696	−5.494	4.605	0.034
303.15	1.643	0.292	0.290	0.147	0.002	−4.538	3.195	−3.377	2.612	0.018
308.15	1.626	0.292	0.233	0.418	0.002	−3.280	2.194	−2.093	1.495	0.009
313.15	1.580	0.370	0.156	0.319	0.002	−2.420	1.533	−1.347	0.892	0.005
318.15	1.539	0.465	−0.013	0.327	0.003	−1.821	1.076	−0.862	0.540	0.004

Table 5. Mixed Kinematic Viscosity Parameters and Average Absolute Deviations (AAD) of Experimental and Calculated Kinematic Viscosities (10^{-6} m^2·s^{-1}) at Several Temperatures

	butanenitrile (1) +							
	1-butanol (2)		2-methyl-1-propanol (2)		2-butanol (2)		2-methyl-2-propanol (2)	
T/K	ν_{21}	ν_{12}	ν_{21}	ν_{12}	ν_{21}	ν_{12}	ν_{21}	ν_{12}
288.15	1.380	0.948	1.281	1.000	1.015	0.981		
298.15	1.160	0.828	1.087	0.864	0.888	0.840	0.897	0.894
303.15							0.874	0.815
308.15	0.994	0.730	0.940	0.756	0.790	0.729	0.847	0.750
313.15							0.809	0.700
318.15	0.864	0.652	0.823	0.672	0.710	0.642	0.772	0.649
AAD (%)	5.9		6.4		8.5		9.3	

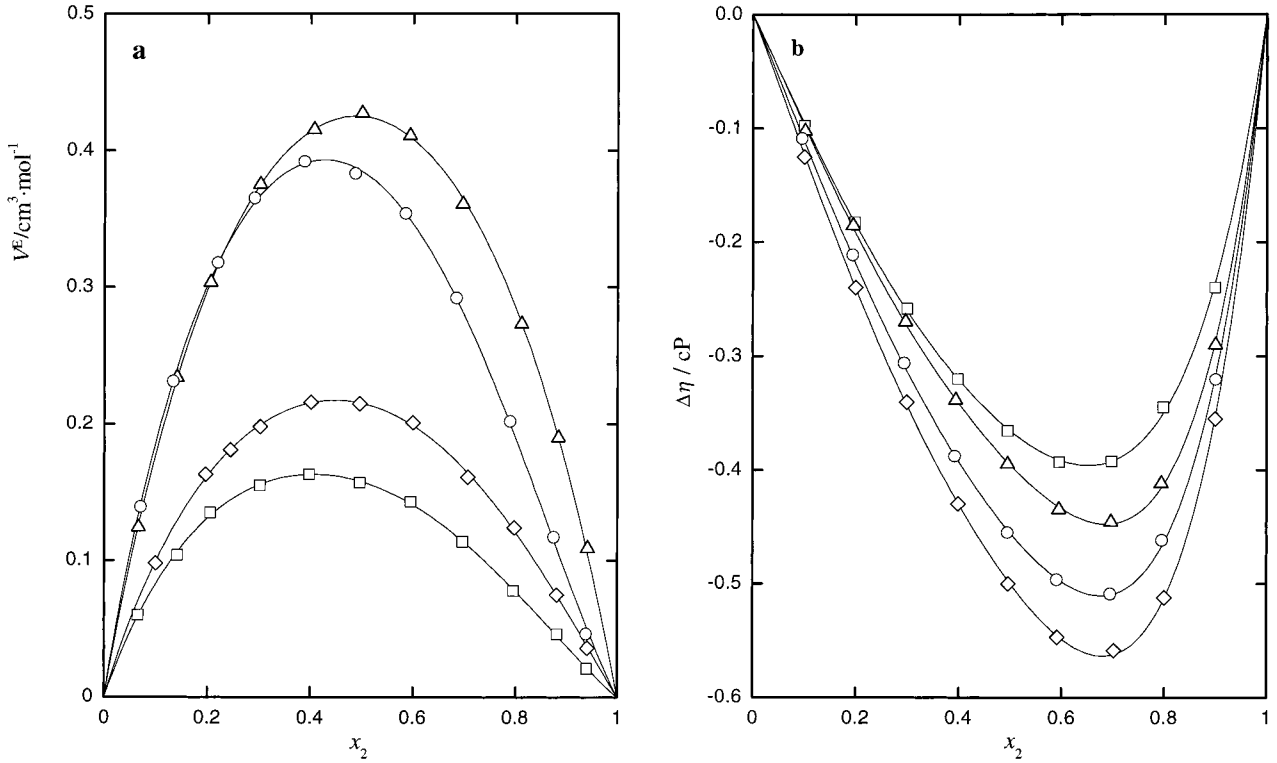

Figure 1. Excess volume (a) and viscosity deviation (b), at T = 318.15 K, for (□) {x_1 butanenitrile + x_2 1-butanol}, (◇) {x_1 butanenitrile + x_2 2-methyl-1-propanol}, (△) {x_1 butanenitrile + x_2 2-butanol}, and (○) {x_1 butanenitrile + x_2 2-methyl-2-propanol}. (—) from analytical equations.

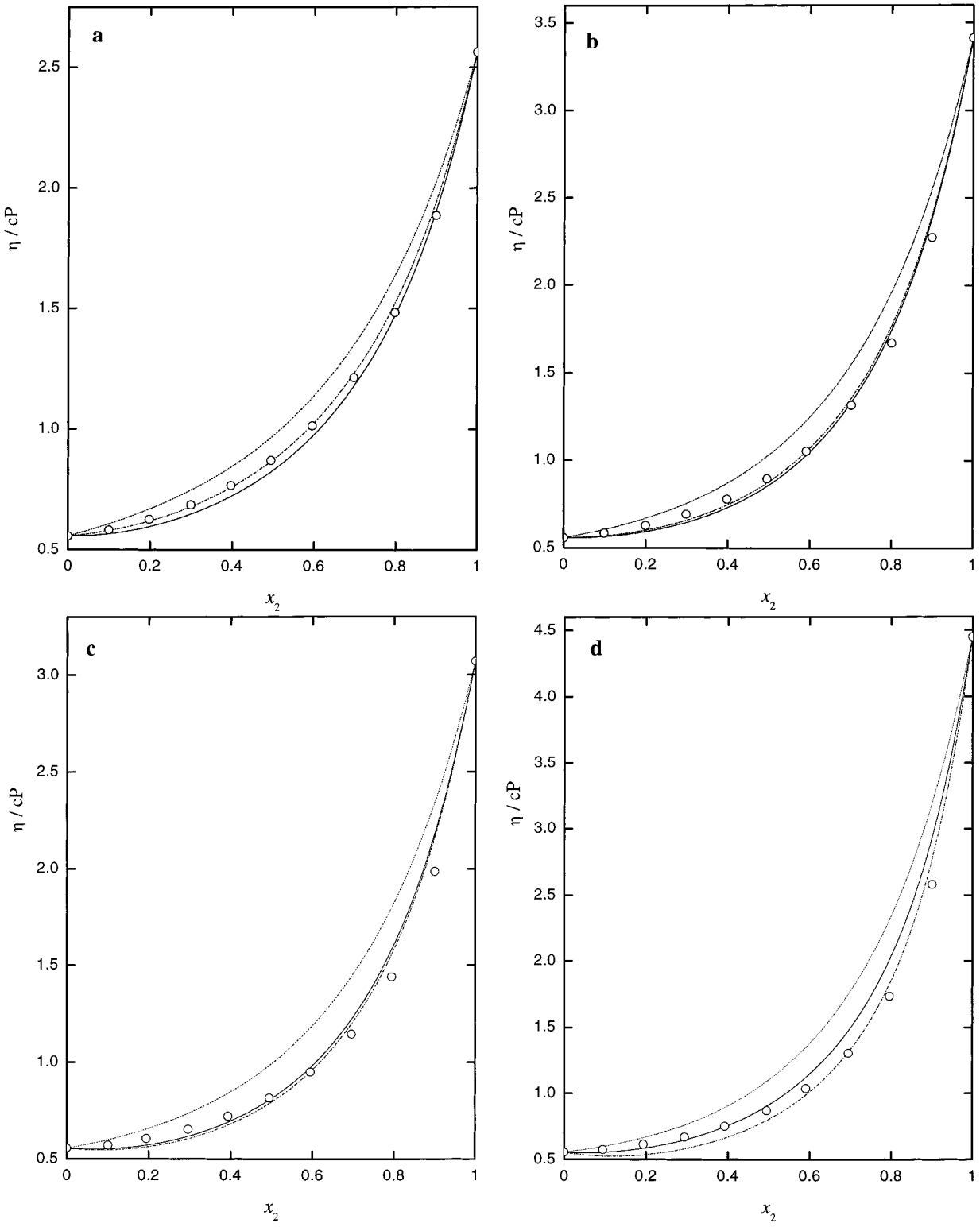

Figure 2. Dynamic viscosity, at $T = 298.15$ K, for (a) {x_1 butanenitrile + x_2 1-butanol}, (b) {x_1 butanenitrile + x_2 2-methyl-1-propanol}, (c) {x_1 butanenitrile + x_2 2-butanol}, and (d) {x_1 butanenitrile + x_2 2-methyl-2-propanol}. (○) Experimental, from the NRTL model: (···) with $\sigma = 0.00$, (—) with $\sigma = 0.25$ (predictive), (— · —) with σ (fitted).

umes and viscosity deviations, which were fitted to a polynomial

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

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

$$\sigma(Q) = \left[\frac{\sum (Q_{exp} - Q_{cal})^2}{N - m}\right] \qquad (6)$$

where N is the number of experimental points and m is the number of parameters in the corresponding analytical

Table 6. Average Absolute Deviations (AAD) for Experimental and Calculated Dynamic Viscosities According to the Wei and Rowley Model, at $T = 298.15$ K, for $\sigma = 0.00$, $\sigma = 0.25$, and σ (Fitted)

	AAD (%)					
system	σ	η	σ	η	σ	η
butanenitrile (1) + 1-butanol (2)	0.00	9.3	0.25	3.2	0.17	1.5
butanenitrile (1) + 2-methyl-1-propanol (2)	0.00	14.4	0.25	4.5	0.22	4.3
butanenitrile (1) + 2-butanol (2)	0.00	18.5	0.25	6.1	0.28	5.8
butanenitrile (1) + 2-methyl-2-propanol (2)	0.00	27.1	0.25	10.6	0.42	7.7

equation. In Figure 1 the experimental results and the results of the fit are plotted at $T = 318.15$ K.

Discussion

For all systems, both V^E and $\Delta\eta$ increase with increasing temperature except for mixtures containing 2-methyl-2-propanol, where a minor and opposite variation is observed. At $T = 318.15$ K, Figure 1 shows the experimental behavior for the four mixtures (butanenitrile + butanol isomers). The excess volume increases with the branching around the OH group, whereas for $\Delta\eta$ the more negative values are observed in mixtures containing 2-methyl-1-propanol.

Many semitheoretical and empirical equations have been used to fit 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.[13] We have selected McAllister's two-parameter equation,[14] based on Eyring's equation, which takes into account interactions of both like and unlike molecules by a two-dimensional, three-body model. The McAllister equation is given by

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

ν_i is the kinematic viscosity of the pure compounds ($i = 1$ for butanenitrile, and $i = 2$ for alcohol), x_i are the mole fractions, M_i are the molar masses, ν_{12} and ν_{21} are fit parameters which denote viscosity contributions for 112 and 221 interactions, respectively, and which have been calculated for each temperature by a least-squares method. For each system at several temperatures, the mixed viscosity parameters are collected in Table 5 together with the average absolute deviations (AAD). For butanenitrile + 1-butanol, + 2-methyl-1-propanol, + 2-butanol, or + 2-methyl-2-propanol, the AADs were 5.9%, 6.4%, 8.5%, and 9.3%, respectively.

Wei and Rowley[15,16] proposed a local composition model for multicomponent nonelectrolyte liquid mixture viscosity, which requires only binary equilibrium thermodynamic information (H^E and 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

$$\eta = \exp(\xi)/V \quad (8)$$

$$\xi = \sum_i \phi_i \xi_i^0 + \sum_i \phi_i \left[\sum_j \phi_j G_{ji} (\xi_{ji} - \xi_j^0)/\left(\sum_l \phi_l G_{li}\right)\right] - \sigma H^E/RT \quad (9)$$

$$\xi_{ji} = \xi_{ij} = \sum_i (\phi_i^* \phi_{ii}^* \xi_i^0)/\sum_j (\phi_j^* \phi_{jj}^*) \quad (10)$$

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

$$G_{ji} = \exp(-\alpha A_{ji}/RT) \quad (11)$$

$$\phi_j^* = (1 + \Gamma_{ji})^{-1} \qquad \phi_{ii}^* = (1 + \phi_j^* G_{ji}/\phi_i^*)^{-1} \quad (12)$$

$$\Gamma_{ji} = (V_i/V_j)(G_{ij}/G_{ji})^{1/2} \exp[(\xi_i^0 - \xi_j^0)/2] \quad (13)$$

The asterisk stands for the volume fraction at a specific composition defined by eq 12, and ξ_i^0 denotes the pure component i value

$$\xi_i^0 = \ln(\eta_i V_i) \quad (14)$$

The same notation as that 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.[5−7] ϕ represents the volume fraction and V the molar volume. If the factor σ in eq 9 is taken as 0.25, as in the original paper, the validity of the model as a nonparametric predictive method is then tested. In Table 6, AADs 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 2. For these systems, η is well described by the predictive model ($\sigma = 0.25$). For butanenitrile + 1-butanol, + 2-methyl-1-propanol, + 2-butanol, or + 2-methyl-2-propanol, the AAD s were 3.2%, 4.5%, 6.1%, and 10.6%, respectively. The agreement with the experimental results is comparable to that obtained with σ fitted (monoparametric) or with the McAllister biparametric equation. In all cases, for mixtures containing 2-methyl-2-propanol, the AAD is somewhat worse. A previous study of mixtures of butanol isomers with butanone yielded a similar agreement between experimental and calculated results. By taking into account the strong interactions in these mixtures, we can conclude that the NRTL model (predictive) gives an adequate representation of these systems.

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