86 J. Chem. Eng. Data **2000,** *45,* 86−91

Viscosity Measurements for the Binary Mixtures of 1,2-Dichloroethane or 1,2-Dibromoethane with Isomeric Butanols

Lelia Mussari and Miguel Postigo[†]

Cátedra de Fisicoquímica, Depto. de Química, Facultad de Ingeniería U. N. del Comahue,
Buenos Aires 1400, Neuquén (8300), Argentina

Carlos Lafuente, Félix M. Royo, and José S. Urieta*

Departamento de Química Orgánica y Química Física, Facultad de Ciencias, Universidad de Zaragoza,
Ciudad Universitaria, Zaragoza 50009, Spain

Viscosities and viscosity deviations are reported for the binary mixtures of 1,2-dichloroethane or 1,2-dibromoethane with 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol at 298.15 and 313.15 K. Viscosity deviations are negative for all the mixtures and decrease in absolute value when the temperature increases.The kinematic viscosities were correlated by the equations of McAllister and Heric. The Wu model was used to predict the viscosities of the systems.

Introduction

The viscosity behavior of binary mixtures containing isomeric butanols seems to be strongly dependent on the structure of butanol and weakly affected by the nature of the second component; this behavior is confirmed by the results present here. We report in this paper viscosity measurements for the binary mixtures of 1,2-dichloroethane or 1,2-dibromoethane with isomeric butanols (1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol) at 298.15 and 313.15 K.

This work follows our systematic study on transport properties of liquid mixtures containing isomeric butanols: 1,3-dichloropropane (Lafuente et al., 1994), 1-chloro- and 1,4-dichlorobutane (Lafuente et al., 1996), 2-chloro-2-methylpropane (Cea et al., 1994), 2-chlorobutane (Cea et al., 1995), cyclohexane (Artigas et al., 1995), and butylamine (Domínguez et al., 1995). The only literature data available for these systems were the viscosities of 1,2-dichloroethane with 1-butanol at 35 °C (Rajkumar et al., 1984).

The group contribution method proposed by Wu has been used to predict the viscosities of these mixtures.

Experimental Section

Chemicals. The liquids used were 1-butanol (>99.8%), 2-methyl-1-propanol and 2-methyl-2-propanol (>99.5%), and 2-butanol and 1,2-dibromoethane (>99%) obtained from Aldrich and 1,2-dichloroethane (>99.8%) provided by Lab-Scan. Their purities were checked by a chromatographic method, confirming the absence of other significant organic components. All liquids were used without further purification, and the isomeric butanols were stored over type 0.3 nm activated molecular sieves from Merck.

Methods. Kinematic viscosities ν were determined using an Ubbelhode viscosimeter (inner diameter = 0.63 mm) and a Schott-Geräte automatic measuring unit model AVS-440. The temperature was kept constant within ±0.01 K by means of a Schott-Geräte thermostat. The viscosimeter was calibrated with doubly-distilled water. At least four time flow measurements were performed for each composition and temperature, and the results were averaged. Kinetic energy corrections were applied to the experimental data. The uncertainty of the time flow measurements was ±0.01 s, and the corresponding uncertainty in the kinematic viscosity was $\pm 1 \times 10^{-4}$ $mm^2 \cdot s^{-1}$. Densities ρ, required for converting kinematic viscosities to absolute viscosities, $\eta = \nu\rho$, were measured with an Anton-Paar DMA-58 vibrating tube densimeter automatically thermostated at ±0.01 K. The uncertainty of the density measurements was $\pm 1 \times 10^{-2}$ $kg \cdot m^{-3}$. The calibration was carried out with deionized doubly-distilled water and dry air.

Table 1. Densities ρ and Viscosities η of the Pure Compounds at 298.15 and Comparison with Literature Data

	ρ/kg·m^{-3}		η/mPa·s	
compound	exptl	lit.	exptl	lit.
1,2-dichloroethane	1245.63	1245.61[a]	0.7644	0.779[c]
1,2-dibromoethane	2168.50	2168.70[b]	1.6291	1.595[c]
1-butanol	805.85	805.75	2.5562	2.5710
2-butanol	802.40	802.41	3.0596	2.998
2-methyl-1-propanol	797.98	797.8	3.3603	3.330
2-methyl-2-propanol	781.00	781.2	4.4126	4.438

[a] TRC (1980). [b] TRC (1964). [c] Lide (1992).

The mixtures were prepared by using a Mettler H20T balance. The possible error in the mole fractions is estimated to be <±0.0001.

Table 1 shows the comparison of the experimental values of density and viscosity of the chemicals with the literature values at 298.15 K (Riddick et al., 1986).

Results and Discussion

The experimental values of viscosities (kinematic and absolute) and densities for the binary mixtures are given in Table 2.

---

* Corresponding author. E-mail: urieta@posta.unizar.es.

[†] CONICET researcher.

10.1021/je990211n CCC: $19.00

Table 2. Experimental Viscosities and Viscosity Deviations for 1,2-Dichloroethane or 1,2-Dibromoethane with Isomeric Butanols

x_1	ν/mm^2·s^{-1}	ρ/kg·m^{-3}	η/mPa·s	$\Delta\eta$/mPa·s	x_1	ν/mm^2·s^{-1}	ρ/kg·m^{-3}	η/mPa·s	$\Delta\eta$/mPa·s
1,2-Dichloroethane (1) + 1-Butanol (2) at 298.15 K									
0.0000	3.1721	805.84	2.5562	0.0000	0.6047	0.8880	1052.03	0.9342	−0.5385
0.0967	2.5130	842.42	2.1170	−0.2659	0.7050	0.7747	1097.97	0.8506	−0.4424
0.1970	1.9770	881.18	1.7421	−0.4611	0.8027	0.6938	1144.57	0.7941	−0.3239
0.3011	1.5600	922.63	1.4393	−0.5774	0.9027	0.6400	1194.38	0.7644	−0.1744
0.4015	1.2610	963.92	1.2155	−0.6213	1.0000	0.6137	1245.56	0.7644	0.0000
0.5343	0.9916	1020.77	1.0122	−0.5867					
1,2-Dichloroethane (1) + 2-Butanol (2) at 298.15 K									
0.0000	3.8131	802.39	3.0596	0.0000	0.6034	0.7908	1045.27	0.8266	−0.8481
0.1002	2.4730	838.98	2.0748	−0.7548	0.7052	0.7072	1092.48	0.7726	−0.6684
0.2003	1.7504	876.83	1.5348	−1.0651	0.8039	0.6505	1140.81	0.7421	−0.4724
0.3217	1.2733	924.68	1.1774	−1.1438	0.8980	0.6184	1189.36	0.7355	−0.2630
0.4000	1.0912	956.84	1.0441	−1.0974	1.0000	0.6137	1245.56	0.7644	0.0000
0.5051	0.9073	1001.54	0.9087	−0.9916					
1,2-Dichloroethane (1) + 2-Methyl-1-propanol (2) at 298.15 K									
0.0000	4.2110	797.98	3.3603	0.0000	0.6087	0.8913	1049.25	0.9352	−0.8450
0.1033	2.9450	837.11	2.4653	−0.6268	0.7088	0.7600	1096.05	0.8330	−0.6873
0.2035	2.1560	876.39	1.8895	−0.9426	0.8037	0.6837	1142.46	0.7811	−0.4929
0.3040	1.6430	917.10	1.5068	−1.0644	0.8988	0.6300	1190.95	0.7503	−0.2768
0.4062	1.2940	959.89	1.2421	−1.0638	1.0000	0.6137	1245.56	0.7644	0.0000
0.5061	1.0500	1003.14	1.0533	−0.9932					
1,2-Dichloroethane (1) + 2-Methyl-2-propanol (2) at 298.15 K									
0.0000	5.6499	781.00	4.4126	0.0000	0.6020	0.8264	1032.07	0.8529	−1.3635
0.0999	3.1806	817.49	2.6001	−1.4481	0.7041	0.7323	1082.21	0.7925	−1.0514
0.2056	1.9961	858.42	1.7135	−1.9490	0.8009	0.6732	1132.35	0.7623	−0.7285
0.3032	1.4370	898.26	1.2908	−2.0157	0.9017	0.6319	1187.69	0.7505	−0.3725
0.4064	1.1431	942.44	1.0773	−1.8527	1.0000	0.6137	1245.56	0.7644	0.0000
0.5057	0.9496	986.94	0.9372	−1.6305					
1,2-Dichloroethane (1) + 1-Butanol (2) at 313.15 K									
0.0000	2.2090	794.57	1.7552	0.0000	0.6047	0.7050	1034.18	0.7291	−0.3462
0.0967	1.7740	829.99	1.4724	−0.1741	0.7050	0.6241	1079.15	0.6735	−0.2892
0.1970	1.4310	867.58	1.2415	−0.2922	0.8027	0.5659	1124.58	0.6364	−0.2164
0.3011	1.1570	907.87	1.0504	−0.3663	0.9027	0.5274	1173.30	0.6188	−0.1215
0.4015	0.9573	948.19	0.9077	−0.3961	1.0000	0.5155	1224.05	0.6310	0.0000
0.5343	0.7762	1003.74	0.7791	−0.3754					
1,2-Dichloroethane (1) + 2-Butanol (2) at 313.15 K									
0.0000	2.2610	789.65	1.7854	0.0000	0.6034	0.6290	1027.66	0.6464	−0.4424
0.1002	1.6486	825.55	1.3610	−0.3087	0.7052	0.5743	1074.00	0.6168	−0.3545
0.2003	1.2473	862.58	1.0759	−0.4783	0.8039	0.5366	1121.13	0.6016	−0.2557
0.3217	0.9456	909.37	0.8599	−0.5541	0.8980	0.5148	1168.61	0.6016	−0.1471
0.4000	0.8201	940.86	0.7716	−0.5520	1.0000	0.5155	1224.05	0.6310	0.0000
0.5051	0.7056	984.84	0.6949	−0.5074					
1,2-Dichloroethane (1) + 2-Methyl-1-propanol (2) at 313.15 K									
0.0000	2.6630	785.77	2.0925	0.0000	0.6087	0.6997	1030.87	0.7213	−0.4815
0.1033	1.9633	823.92	1.6176	−0.3239	0.7088	0.6217	1076.89	0.6695	−0.3871
0.2035	1.5070	861.98	1.2990	−0.4960	0.8037	0.5622	1122.20	0.6309	−0.2869
0.3040	1.1940	901.59	1.0765	−0.5717	0.8988	0.5281	1170.04	0.6179	−0.1610
0.4062	0.9633	943.32	0.9087	−0.5901	1.0000	0.5155	1224.05	0.6310	0.0000
0.5061	0.8098	985.68	0.7982	−0.5546					
1,2-Dichloroethane (1) + 2-Methyl-2-propanol (2) at 313.15 K									
0.0000	2.7310	764.74	2.0885	0.0000	0.6020	0.6579	1011.86	0.6657	−0.5454
0.0999	1.8072	800.46	1.4466	−0.4963	0.7041	0.5942	1061.60	0.6308	−0.4315
0.2056	1.2852	840.80	1.0806	−0.7082	0.8009	0.5534	1111.31	0.6150	−0.3062
0.3032	1.0240	880.08	0.9012	−0.7454	0.9017	0.5287	1166.45	0.6167	−0.1576
0.4064	0.8528	923.55	0.7876	−0.7086	1.0000	0.5155	1224.05	0.6310	0.0000
0.5057	0.7347	967.47	0.7108	−0.6406					
1,2-Dibromoethane (1) + 1-Butanol (2) at 298.15 K									
0.0000	3.1721	805.84	2.5562	0.0000	0.6088	0.9299	1610.71	1.4978	−0.4940
0.1011	2.4532	935.35	2.2946	−0.1679	0.7057	0.8344	1745.09	1.4561	−0.4458
0.2045	1.8909	1069.49	2.0223	−0.3443	0.7989	0.7714	1876.72	1.4477	−0.3679
0.3026	1.5211	1198.28	1.8227	−0.4530	0.8972	0.7334	2018.00	1.4800	−0.2445
0.4200	1.2240	1354.41	1.6578	−0.5090	1.0000	0.7513	2168.37	1.6291	0.0000
0.4876	1.0951	1445.35	1.5828	−0.5213					
1,2-Dibromoethane (1) + 2-Butanol (2) at 298.15 K									
0.0000	3.8131	802.39	3.0596	0.0000	0.6015	0.8448	1593.99	1.3466	−0.8526
0.1035	2.3718	933.81	2.2148	−0.6967	0.7048	0.7749	1737.64	1.3465	−0.7049
0.2013	1.7050	1059.59	1.8066	−0.9650	0.7997	0.7335	1872.12	1.3732	−0.5424
0.3038	1.3187	1193.37	1.5737	−1.0513	0.9006	0.7193	2018.77	1.4521	−0.3192
0.3979	1.1023	1317.97	1.4528	−1.0376	1.0000	0.7513	2168.37	1.6291	0.0000
0.5007	0.9478	1456.21	1.3802	−0.9631					

Table 2 (Continued)

x_1	ν/mm^2·s^{-1}	ρ/kg·m^{-3}	η/mPa·s	$\Delta\eta$/mPa·s	x_1	ν/mm^2·s^{-1}	ρ/kg·m^{-3}	η/mPa·s	$\Delta\eta$/mPa·s
1,2-Dibromoethane (1) + 2-Methyl-1-propanol (2) at 298.15 K									
0.0000	4.2110	797.98	3.3603	0.0000	0.5980	0.9543	1590.07	1.5174	−0.8076
0.1046	2.8460	931.90	2.6522	−0.5270	0.6783	0.8661	1702.00	1.4741	−0.7119
0.2018	2.0928	1057.87	2.2139	−0.7970	0.7952	0.7776	1867.93	1.4525	−0.5311
0.3054	1.5906	1193.95	1.8991	−0.9325	0.9005	0.7366	2020.64	1.4884	−0.3130
0.3845	1.3440	1299.26	1.7462	−0.9485	1.0000	0.7513	2168.37	1.6291	0.0000
0.5011	1.0876	1456.79	1.5844	−0.9084					
1,2-Dibromoethane (1) + 2-Methyl-2-propanol (2) at 298.15 K									
0.0000	5.6499	781.00	4.4126	0.0000	0.6110	0.8854	1588.43	1.4064	−1.3055
0.1079	3.0190	914.97	2.7623	−1.3500	0.7079	0.8032	1727.47	1.3875	−1.0547
0.2078	1.9175	1042.50	1.9990	−1.8352	0.8062	0.7504	1872.20	1.4049	−0.7636
0.3106	1.4464	1177.06	1.7025	−1.8455	0.9029	0.7278	2018.41	1.4690	−0.4304
0.4103	1.1726	1310.51	1.5367	−1.7338	1.0000	0.7513	2168.37	1.6291	0.0000
0.5130	0.9935	1451.13	1.4417	−1.5430					
1,2-Dibromoethane (1) + 1-Butanol (2) at 313.15 K									
0.0000	2.2090	794.57	1.7552	0.0000	0.6088	0.7260	1587.19	1.1523	−0.3302
0.1011	1.7280	922.45	1.5940	−0.1159	0.7004	0.6646	1712.46	1.1381	−0.3033
0.2045	1.3690	1054.42	1.4435	−0.2201	0.8022	0.6181	1853.91	1.1459	−0.2499
0.3026	1.1170	1181.02	1.3192	−0.3004	0.8972	0.5952	1988.58	1.1836	−0.1697
0.4191	0.9179	1333.37	1.2239	−0.3435	1.0000	0.6114	2138.04	1.3072	0.0000
0.4876	0.8360	1424.28	1.1907	−0.3461					
1,2-Dibromoethane (1) + 2-Butanol (2) at 313.15 K									
0.0000	2.2610	789.65	1.7854	0.0000	0.6015	0.6497	1568.88	1.0193	−0.4785
0.1035	1.5215	918.96	1.3982	−0.3377	0.7048	0.6085	1711.09	1.0412	−0.4072
0.2013	1.1581	1042.66	1.2075	−0.4816	0.7997	0.5869	1844.27	1.0824	−0.3206
0.3038	0.9355	1174.24	1.0985	−0.5416	0.9006	0.5840	1989.55	1.1619	−0.1928
0.3979	0.8062	1296.82	1.0455	−0.5496	1.0000	0.6114	2138.04	1.3072	0.0000
0.5007	0.7121	1433.09	1.0205	−0.5255					
1,2-Dibromoethane (1) + 2-Methyl-1-propanol (2) at 313.15 K									
0.0000	2.6630	785.77	2.0925	0.0000	0.5980	0.7231	1566.31	1.1326	−0.4903
0.1046	1.8646	917.78	1.7113	−0.2991	0.6783	0.6689	1677.08	1.1218	−0.4380
0.2018	1.4216	1041.92	1.4812	−0.4528	0.7952	0.6171	1841.03	1.1361	−0.3319
0.3054	1.1185	1176.04	1.3154	−0.5373	0.9005	0.5957	1992.28	1.1868	−0.1985
0.3845	0.9664	1279.70	1.2367	−0.5539	1.0000	0.6114	2138.04	1.3072	0.0000
0.5011	0.8113	1434.98	1.1642	−0.5348					
1,2-Dibromoethane (1) + 2-Methyl-2-propanol (2) at 313.15 K									
0.0000	2.7310	764.74	2.0885	0.0000	0.6110	0.6803	1562.25	1.0628	−0.5483
0.1079	1.6849	897.86	1.5128	−0.4914	0.7079	0.6317	1699.86	1.0738	−0.4616
0.2078	1.2488	1023.54	1.2782	−0.6479	0.8062	0.6046	1842.71	1.1141	−0.3445
0.3106	0.9998	1155.83	1.1556	−0.6902	0.9029	0.5978	1987.29	1.1880	−0.1951
0.4103	0.8560	1287.85	1.1024	−0.6653	1.0000	0.6114	2138.04	1.3072	0.0000
0.5130	0.7503	1426.36	1.0702	−0.6175					

The kinematic viscosities were correlated by using the following equations:

McAllister (1960)

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

where ν refers to the kinematic viscosity of the mixture, x_1 and x_2 are the mole fractions of components 1 and 2, ν_1 and ν_2 are the corresponding kinematic viscosities, M_1 and M_2 are molecular masses of the components, and ν_{12} and ν_{21} are adjustable parameters characteristic of the system.

Heric (1966)

$$\ln \nu = x_1 \ln(\nu_1 M_1) + x_2 \ln(\nu_2 M_2) - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2[\alpha_{12} + \alpha'_{12}(x_1 - x_2)] \quad (2) \tag{2}$$

in which α_{12} and α'_{12} are also adjustable parameters.

The estimated parameters of the viscosity equations and the corresponding mean relative standard deviation (MRSD) are shown in Table 3. The MSRD, expressed in percent, is defined as

$$\mathrm{MSRD} = 100 \times \left[\frac{1}{N} \sum_{i=1}^{i=\mathrm{N}} \left(\frac{\mathrm{viscosity}_i^{\mathrm{exp}} - \mathrm{viscosity}_i^{\mathrm{cal}}}{\mathrm{viscosity}_i^{\mathrm{exp}}}\right)^2\right]^{1/2} \tag{3}$$

where N is the number of experimental data.

The equations of McAllister and Heric correlated very well the viscosity data, especially those corresponding to mixtures containing 1-butanol and 2-methyl-1-propanol, and they give about the same results.

Viscosity deviations were calculated from our measurements according to the following equation:

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

where η is the absolute viscosity of the mixture and η_1 and η_2 are the absolute viscosities of components 1 and 2.

This function is gathered in Table 2 and graphically represented in Figures 1−4.

The values of viscosity deviations at each temperature

Table 3. Correlation and Prediction of Viscosities for 1,2-Dichloroethane or 1,2-Dibromoethane with Isomeric Butanols

	T = 298.15 K			T = 313.15 K		
model	a	b	MRSD/%	a	b	MRSD/%
		1,2-Dichloroethane + 1-Butanol				
McAllister[a]	0.6722	1.3845	0.33	0.5461	1.0298	0.42
Heric[b]	−1.0792	−0.2633	0.33	−1.0306	−0.2250	0.42
Wu-UNIFAC			9.90			8.19
Wu-ASOG			1.20			1.18
		1,2-Dichloroethane + 2-Butanol				
McAllister	0.6669	0.8558	1.59	0.5210	0.7269	0.68
Heric	−2.0887	0.5383	1.59	−1.6583	0.2388	0.68
Wu-UNIFAC			14.95			8.01
Wu-ASOG			22.65			12.55
		1,2-Dichloroethane + 2-Methyl-1-propanol				
McAllister	0.6704	1.2809	0.90	0.5515	0.9617	0.56
Heric	−1.6248	−0.0090	0.90	−1.3987	−0.0139	0.56
Wu-UNIFAC			3.24			3.00
Wu-ASOG			11.03			6.43
		1,2-Dichloroethane + 2-Methyl-2-propanol				
McAllister	0.7618	0.7309	2.08	0.5987	0.6451	1.60
Heric	−2.7155	1.1712	2.08	−1.9122	0.7209	1.60
Wu-UNIFAC			36.86			14.71
Wu-ASOG			40.18			19.21
		1,2-Dibromoethane + 1-Butanol				
McAllister	0.6989	1.4095	0.86	0.5670	1.0256	0.81
Heric	−1.0436	−0.3597	0.86	−0.9825	−0.2745	0.81
Wu-UNIFAC			7.93			7.12
Wu-ASOG			20.33			23.60
		1,2-Dibromoethane + 2-Butanol				
McAllister	0.7281	0.8617	2.23	0.5706	0.6635	1.74
Heric	−1.9964	0.5317	2.23	−1.6612	0.3997	1.74
Wu-UNIFAC			13.90			8.90
Wu-ASOG			7.64			13.31
		1,2-Dibromoethane + 2-Methyl-1-propanol				
McAllister	0.7456	1.2335	1.22	0.5890	0.8817	1.06
Heric	−1.5717	0.0788	1.22	−1.4326	0.1028	1.06
Wu-UNIFAC			3.22			2.81
Wu-ASOG			12.19			16.80
		1,2-Dibromoethane + 2-Methyl-2-propanol				
McAllister	0.8192	0.7750	3.40	0.6316	0.6556	2.57
Heric	−2.5684	1.0643	3.40	−1.8100	0.6647	2.57
Wu-UNIFAC			27.78			12.16
Wu-ASOG			13.60			11.64

[a] $a = \nu_{12}$, $b = \nu_{21}$. [b] $a = \alpha_{12}$, $b = \alpha'_{12}$.

Table 4. Coefficients A_0 and Standard Deviations for Eq 5

system	T/K	A_0	A_1	A_2	A_3	σ
1,2-dichloroethane + 1-butanol	298.15	−2.4153	0.8118	−0.1625	−0.2464	0.0011
	313.15	−1.5391	0.4667	−0.2031	−0.1577	0.0020
2-butanol	298.15	−3.9648	2.5333	−2.4771	1.4259	0.0066
	313.15	−2.0451	1.1216	−0.7302	0.0295	0.0008
2-methyl-1-propanol	298.15	−3.9682	2.1066	−1.4620	0.3897	0.0052
	313.15	−2.2194	1.0280	−0.6265	0.0769	0.0035
2-methyl-2-propanol	298.15	−6.5193	5.0256	−5.3333	3.6804	0.0190
	313.15	−2.5614	1.6678	−1.6606	1.0360	0.0033
1,2-dibromoethane + 1-butanol	298.15	−2.0811	0.1757	−0.3143	−1.0186	0.0046
	313.15	−1.3882	0.0830	−0.2430	−0.7084	0.0025
2-butanol	298.15	−3.8250	1.8469	−2.5452	1.0054	0.0097
	313.15	−2.0896	0.7121	−1.1977	0.3570	0.0044
2-methyl-1-propanol	298.15	−3.6051	1.4923	−1.4563	−0.2179	0.0051
	313.15	−2.1382	0.6855	−0.8559	−0.1004	0.0024
2-methyl-2-propanol	298.15	−6.2138	4.2930	−5.2269	2.6358	0.0180
	313.15	−2.4795	1.1156	−1.8262	1.1414	0.0061

were correlated with a Redlich−Kister polynomial equation:

$$\Delta\eta = x_1(1 - x_1)\sum_{i=0}^{i=N} A_i(2x_1 - 1)^i \qquad (5)$$

where A_i are adjustable parameters and x_1 is the mole fraction of 1,2-dihaloethane. Table 4 lists the values of the parameters together with the standard deviations.

Viscosity deviations are negative over the whole composition range for all the mixtures. For a given 1,2-dihaloethane, viscosity deviations as absolute values at 298.15 K follow the sequence 1-butanol < 2-methyl-1-propanol < 2-butanol < 2-methyl-2-propanol. At 313.15 K this se-

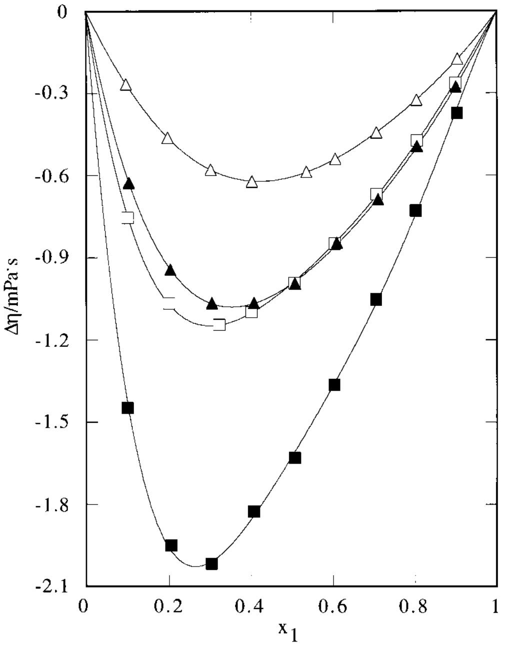

Figure 1. Viscosity deviations of 1,2-dichloroethane (1) + isomeric butanol (2) at $T = 298.15$ K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■); Redlich−Kister equation (—).

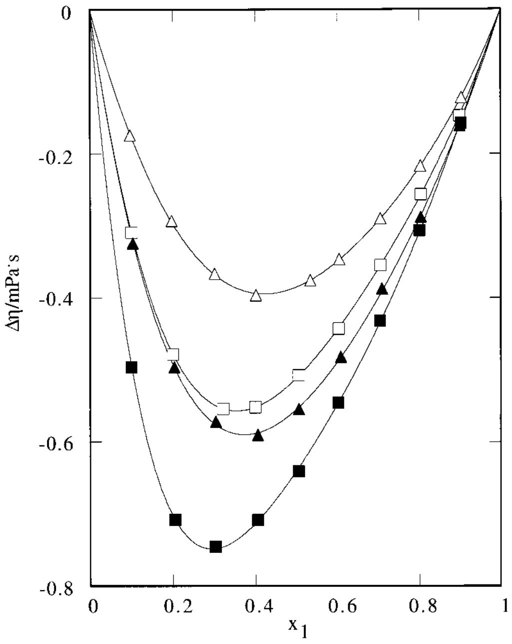

Figure 2. Viscosity deviations of 1,2-dichloroethane (1) + isomeric butanol (2) at $T = 313.15$ K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■); Redlich−Kister equation (—).

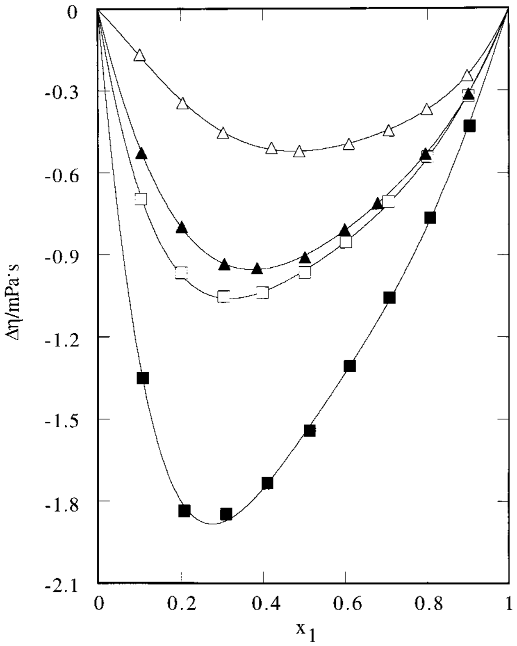

Figure 3. Viscosity deviations of 1,2-dibromoethane (1) + isomeric butanol (2) at $T = 298.15$ K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■); Redlich−Kister equation (—).

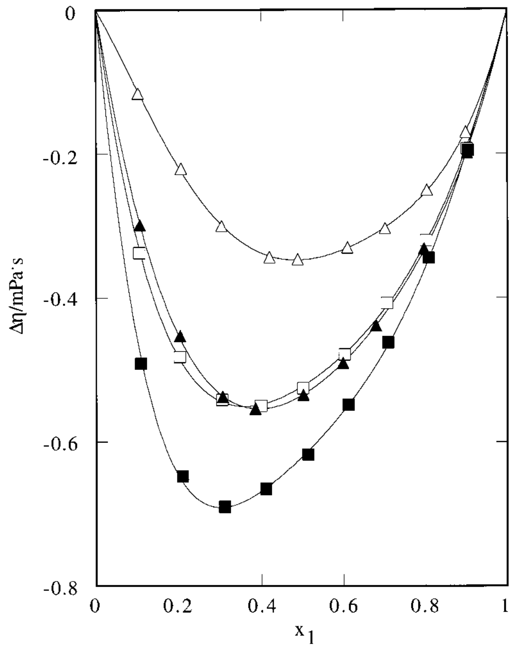

Figure 4. Viscosity deviations of 1,2-dibromoethane (1) + isomeric butanol (2) at $T = 313.15$ K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■); Redlich−Kister equation (—).

quence changes a little because in the case of 1,2-dichloroethane the $\Delta\eta$ values for the mixture with 2-methyl-1-propanol are more negative than those for the mixture with 2-butanol while in the case of 1,2-dibromoethane the $\Delta\eta$ values for the mixtures containing 2-methyl-1-propanol or 2-butanol are very similar. Minimum $\Delta\eta$ values for branched butanols are clearly shifted toward lower concentrations of 1,2-dihaloethane. Viscosity deviations decrease in absolute value when the temperature increases in such a way that mixtures with 1-butanol show the lowest decrease and mixtures with 2-methyl-2-propanol show the largest one. Considering each isomeric butanol separately, the viscosity deviations slightly decrease in absolute value from 1,2-dichloroethane to 1,2-dibromoethane.

The predominant effect that governs the viscosity behavior is the breaking of the liquid-associated structure of isomeric butanols by the mixing process that leads to negative viscosity deviations (Fort and Moore, 1966). This disassociation and breaking of the liquid structure of butanols increases with branching, and therefore viscosity deviations as absolute values for the mixtures containing 2-methyl-2-propanol are greater than those for the mixtures containing the other butanols. The existence of the X−OH interaction, X = Cl or Br, which leads to a positive viscosity deviation, has a minor importance, as is shown by the similar viscosity behavior for systems containing isomeric butanols and α,ω-dichloroalkanes or haloalkanes (Cea et al., 1994; Cea et al., 1995; Lafuente et al., 1994; Lafuente et al., 1996) or even hexane (Franjo et al., 1995).

Viscosity Predictions. The Wu model was used to predict the viscosities of the systems. This model is based on the following modified Eyring viscosity equation for liquid mixtures (Eyring et al., 1941):

$$\eta = \frac{hN}{V}\exp\left[\frac{(x_i G_i^*) - \dfrac{G^{\mathrm{E}}}{\mathrm{A}}}{RT}\right] \qquad (6)$$

where h is Planck's constant, N is Avogadro's number, V is the molar volume of the liquid mixture, x_i and G_i^* are the mole fraction and the Gibbs energy of activation for viscous flow of component i, respectively, G^{E} is the Gibbs excess energy of the liquid mixture at the corresponding mole fraction, A is an empirical factor, T is the absolute temperature, and R is the gas constant. G_i^* can be obtained from the corresponding viscosity and molar volume of the pure compound by using eq 6 with $x_i = 1$ and $G^{\mathrm{E}} = 0$. G^{E} can be estimated by using several group contribution methods; here we have employed the UNIFAC method (Gmehling et al., 1993) and the ASOG method (Tochigi et al., 1990), and the empirical factor $A = 1$ is used.

For all the systems the viscosities obtained experimentally were compared with the predictions, and the mean relative standard deviations are given in Table 4. These values indicate that both the Wu-UNIFAC method and the Wu-ASOG method provide a rather good prediction of viscosity data except for mixtures containing 2-methyl-2-propanol. The overall average MSRD is 11.4% for Wu-UNIFAC and 14.6% for Wu-ASOG; the major average deviation appears in the mixture of 1,2-dichloroethane with 2-methyl-2-propanol at 298.15 K.

Literature Cited

Artigas, H.; Sanz, M. L.; Mainar, A. M.; Royo, F. M.; Urieta, J. S. Excess Volumes and Excess Viscosities of Binary Mixtures of Cyclohexane + an Isomer of Butanol at Several Temperatures. *Phys. Chem. Liquids* **1995**, *30*, 17−28.

Cea, P.; Lafuente, C.; Artigas, H.; Royo, F. M.; Urieta, J. S. Excess Volumes and Excess Viscosities of Binary Mixtures of 2-Chloro-2-methylpropane with Isomeric Butanols at 298.15 K. *Can. J. Chem.* **1994**, *72*, 1921−1925.

Cea, P.; Lafuente, C.; Morand, J. P.; Royo, F. M.; Urieta, J. S. Excess Volumes and Excess Viscosities of Binary Mixtures of 2-Chlorobuthane with Isomeric Butanols at 298.15 K. *Phys. Chem. Liq.* **1995**, *29*, 69−77.

Domínguez, M.; Rodríguez, S.; López, M. C.; Royo, F. M.; Urieta, J. S. Densities and Viscosities of the Ternary Mixtures 1-Butanol + 1-Chlorobutane + 1-Butylamine and 2-Methyl-1-propanol + 1-Chlorobutane + 1-Butylamine at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 37−42.

Fort, R. J.; Moore, W. R. Viscosities of Binary Liquid Mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−1119.

Franjo, C.; Jiménez, E.; Iglesias, T. P.; Legido, J. L.; Andrade, M. I. Viscosities and Densities of Hexane + Butan-1-ol, + Hexan-1-ol, and + Octan-1-ol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 68−70.

Gmehling, J.; Li, J.; Schiller, M. Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

Heric, E. L. Viscosity of Ternary Mixtures. *J. Chem. Eng. Data* **1966**, *11*, 66−68.

Lafuente, C.; Artigas, H.; López, M. C.; Royo, F. M.; Urieta, J. S. Viscosimetric Study of Binary Mixtures of 1,3-Dichloropropane with Isomeric Butanols. *J. Mol. Liq.* **1994**, *62*, 199−208.

Lafuente, C.; Artigas, H.; Pardo, J.; Royo, F. M.; Urieta, J. S. Viscosities of 1-Chlorobutane and 1,4-Dichlorobutane with Isomeric Butanols at 25 and 40 °C. *J. Solution Chem.* **1996**, *25*, 303−313.

Lide, D. R. *CRC Handbook of Physics and Chemistry*, 73rd ed.; CRC Press: Boca Raton, FL, 1992; p 6-167.

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

Powell, R. E.; Roseveare, W. E.; Eyring, H. Diffusion, Thermal Conductivy and Viscosity of Liquids. *Ind. Eng. Chem.* **1941**, *33*, 430−435.

Rajkumar, X. R.; Arulraj, S. J.; Raman, K. V. Adiabatic Compressibilties and Viscosities of Binary Systems of Alcohol with Alkane or 1,2-Dichloroethane. *Ind. J. Pure Appl. Phys.* **1984**, *22*, 241−243.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Techniques of Chemistry, Vol. II; Wiley-Interscience: New York, 1986; pp 198, 200, 202, and 204.

Tochigi, K. D.; Tiegs, D.; Gmehling, J.; Kojima, K. Determination of New ASOG Parameters. *J. Chem. Eng. Jpn.* **1990**, *23*, 453−463.

TRC−Thermodynamic Tables Non-Hydrocarbons; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1964; p a-7580; 1980; p d-7242.

Wu, D. T. Prediction of Viscosities of Liquid Mixtures by a Group Contribution Method *Fluid Phase Equilib.* **1986**, *30*, 149−156.

Received for review July 26, 1999. Accepted October 7, 1999. The authors are grateful to U. N. Comahue and to Universidad de Zaragoza (Proyecto UZ:96-232-47) and Diputación General de Aragón (Proyecto PCB-0894).

JE990211N