Viscosities of Binary Mixtures of 2-Bromobutane and 2-Bromo-2-Methylpropane with Isomeric Butanols at 298.15 and 313.15 K

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This paper reports viscosity data of the binary mixtures (2-bromobutane or 2-bromo-2-methylpropane) plus an isomer of butanol at temperatures of 298.15 and 313.15 K. Kinematic viscosities have been correlated with the equations of McAllister and Heric, and absolute viscosities with the Grunberg–Nissan equation. Viscosity deviations have been correlated by means of a Redlich–Kister type equation, and they give negative values over the complete composition range at both temperatures.

KEY WORDS: 2-bromobutane; 2-bromo-2-methylpropane; isomeric butanols; viscosities; viscosity deviations.

1. INTRODUCTION

The measurement of liquid viscosities provides information that will allow us to have a better knowledge about the structure of liquids as well as data to be used in many industrial processes (flow, mass transfer or heat transfer calculations). The interest in this field led to the formulation of a large number of methods for correlating or predicting the viscosity-composition data of liquid mixtures [1]. These methods require the availability of an extensive and accurate database: systematic investigations of mixtures containing all the chemical functional groups are clearly necessary. Thus our research group has contributed to this goal with the report of many data of thermodynamic and transport properties concerning haloalkane and butanol mixtures [2–15]. More specifically, this work completes a series of

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papers dedicated to expand experimental information about the Br-OH interaction with the study of viscosities and viscosity deviations of 2-bromobutane or 2-bromo-2-methylpropane with an isomer of butanol at the temperatures 298.15 and 313.15 K.

To our knowledge, no literature data are available for these mixtures.

2. EXPERIMENTAL

The liquids had the following purities: 1-butanol (better than 99.8 mol per cent), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol%), 2-butanol (better than 99.0 mol%) and 2-bromo-2-methylpropane (better than 98 mol%), all provided by Aldrich, and 2-bromobutane (better than 99 mol%) supplied by Across. The purity of the chemicals was checked by both gas chromatography and measurements of their density using an Anton Paar DMA-58 vibrating tube densimeter automatically thermostated at 298.15 ± 0.01 K. These purities are considered sufficiently high for our purposes, and thus no further purification was attempted.

Kinematic viscosities, ν , were obtained by means of an Ubbelohde viscometer and a Schott–Geräte automatic measuring unit Model AVS-440. The accuracy of the time flow measurements was ± 0.01 s, and the estimated uncertainty in the kinematic viscosity was $\pm 1 \times 10^{-4}$ mm² · s⁻¹. The experimental densities and viscosities of the pure compounds at both temperatures compared with literature data [16] are given in Table I.

For the mixtures, the mole fractions, x, were determined by mass and their uncertainty is estimated to be less than $\pm 1 \times 10^{-4}$. Densities, ρ , required to calculate absolute viscosities ($\eta = \rho v$) were measured with the densimeter mentioned above. The density-composition curves for all

	$ ho\left(g\cdot\right)$	cm ⁻³)	$\eta (mPa \cdot s)$		
Compound	Exp.	Lit.	Exp.	Lit.	
2-Bromobutane 2-Bromo-2-methylpropane 1-Butanol 2-Butanol 2-Methyl-1-propanol 2-Methyl-2-propanol	1.25170 1.21094 0.80570 0.80246 0.79777 0.78059	1.25354 1.2132 0.80575 0.80241 0.7978 0.7812	0.5596 0.7441 2.5439 3.0338 3.3932 4.3900	0.563 0.750 2.5710 2.998 3.3330 4.438	

Table I. Densities, ρ , and Absolute Viscosities, η , of Pure Compounds at 298.15 KCompared with Literature Data [16]

System	Т (К)	a (g·cm ⁻³)	b (g·cm ⁻³)	c (g·cm ⁻³)	d (g·cm ⁻³)
2-Bromobutane+					
1-Butanol	298.15	0.80609	0.53159	-0.11408	0.02807
2-Butanol		0.80330	0.50845	-0.08093	0.01804
2-Methyl-1-propanol		0.79783	0.53108	-0.09815	0.02043
2-Methyl-2-propanol		0.77995	0.51713	-0.05491	0.00774
1-Butanol	313.15	0.79433	0.51731	-0.10955	0.02706
2-Butanol		0.78864	0.51810	-0.13378	0.05770
2-Methyl-1-propanol		0.78654	0.51157	-0.08452	0.01528
2-Methyl-2-propanol		0.76400	0.51297	-0.06810	0.01992
2-Bromo-2-methyl	propane+				
1-Butanol	298.15	0.80593	0.49915	-0.11640	0.02205
2-Butanol		0.80241	0.49180	-0.11465	0.03154
2-Methyl-1-propanol		0.79831	0.50092	-0.11161	0.02354
2-Methyl-2-propanol		0.77972	0.48628	-0.06762	0.01213
1-Butanol	313.15	0.79409	0.48936	-0.12466	0.02872
2-Butanol		0.79086	0.47226	-0.10049	0.02403
2-Methyl-1-propanol		0.78639	0.47754	-0.08339	0.00605
2-Methyl-2-propanol		0.76527	0.47131	-0.06247	0.01229

Table II. Density Correlation Coefficients for Eq. (1) at Indicated Temperatures

systems studied at both temperatures were fitted to a polynomial type equation:

$$\rho = a + bx + cx^2 + dx^3 \tag{1}$$

The values of the adjustable coefficients a, b, c, d are collected in Table II.

The uncertainty of density measurements was $\pm 1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$, and for absolute viscosity, $\pm 1 \times 10^{-4} \text{ mPa} \cdot \text{s}$. Details for calibration and experimental procedures have been described elsewhere [17].

3. RESULTS AND DISCUSSION

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

$$\Delta \eta = \eta - \sum_{i=1}^{2} x_i \eta_i \tag{2}$$

where η and η_i are the absolute viscosities (mPa · s) of the mixture and pure component *i*, respectively, and x_i is the mole fraction of component *i*.

<i>x</i> ₁	$(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	η (mPa·s)	∆η (mPa·s)	x_1	$(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	η (mPa·s)	$\frac{\Delta\eta}{(\text{mPa}\cdot \text{s})}$			
2-Bromobutane (1) + 1-butanol (2) at 298.15 K										
0 1031	2,3673	2.0352	-0.3041	0 5983	0 7355	0.8012	-0 5555			
0.2031	1.7962	1.6338	-0.5071	0.7019	0.6213	0.7037	-0.4474			
0.3016	1.3848	1.3250	-0.6206	0.8026	0.5374	0.6308	-0.3205			
0.4044	1.0920	1.0967	-0.6447	0.9000	0.4812	0.5835	-0.1745			
0.5054	0.8843	0.9278	-0.6132							
		2-Bromobu	tane (1) + 2-	-butanol (2) at 298.15 K					
0.0514	2.9349	2.4336	-0.4730	0.5027	0.7768	0.8084	-0.9816			
0.1041	2.3220	1.9862	-0.7900	0.5839	0.6769	0.7285	-0.8606			
0.2027	1.5890	1.4352	-1.0971	0.7020	0.5733	0.6459	-0.6510			
0.2985	1.1970	1.1351	-1.1602	0.8019	0.5132	0.5996	-0.4501			
0.4321	0.8908	0.8991	-1.0656	0.9029	0.4685	0.5667	-0.2331			
	2-Bromobutane (1) + 2-methyl-1-propanol (2) at 298.15 K									
0.0474	3.5180	2.8946	-0.3643	0.6053	0.7338	0.7983	-0.8797			
0.1020	2.8562	2.4306	-0.6736	0.7043	0.6207	0.7016	-0.6959			
0.2030	2.0101	1.8127	-1.0053	0.8030	0.5387	0.6311	-0.4667			
0.3032	1.4803	1.4069	-1.1272	0.8948	0.4842	0.5854	-0.2723			
0.4043	1.1289	1.1265	-1.1211	0.9318	0.4670	0.5716	-0.1813			
0.5066	0.8921	0.9316	-1.0261							
	2-Bro	omobutane ((1) + 2-meth	yl-2-propa	anol (2) at 298	.15 K				
0.0500	3.9410	3.1753	-1.0232	0.5032	0.7966	0.8183	-1.6442			
0.1020	2.8392	2.3625	-1.6368	0.6203	0.6554	0.7087	-1.3053			
0.2043	1.7190	1.5186	-2.0888	0.7036	0.5836	0.6532	-1.0417			
0.3044	1.2350	1.1516	-2.0724	0.8056	0.5191	0.6048	-0.6994			
0.4041	0.9766	0.9576	-1.8845	0.9064	0.4728	0.5718	-0.3463			
		2-Bromobu	tane (1) + 1-	-butanol (2) at 313.15 K					
0.1031	1.6845	1.4259	-0.1973	0.5983	0.5969	0.6389	-0.3497			
0.2031	1.3116	1.1740	-0.3210	0.7019	0.5155	0.5736	-0.2823			
0.3016	1.0407	0.9794	-0.3896	0.8026	0.4536	0.5230	-0.2038			
0.4044	0.8451	0.8345	-0.4026	0.9000	0.4094	0.4876	-0.1144			
0.5054	0.6987	0.7206	-0.3871							
		2-Bromobu	tane (1) + 2-	-butanol (2) at 313.15 K					
0.0514	1.8351	1.4954	-0.2230	0.5027	0.6153	0.6292	-0.4971			
0.1041	1.5171	1.2762	-0.3730	0.5839	0.5482	0.5794	-0.4404			
0.2027	1.1315	1.0055	-0.5144	0.7020	0.4774	0.5282	-0.3366			
0.2985	0.8968	0.8366	-0.5576	0.8019	0.4322	0.4961	-0.2377			
0.4321	0.6903	0.6849	-0.5340	0.9029	0.3990	0.4774	-0.1266			

Table III. Experimental Kinematic Viscosities, v, Absolute Viscosities, η , and ViscosityDeviations, $\Delta \eta$, for Binary Mixtures of 2-Bromobutane or 2-Bromo-2-Methylpropane (1) with
Isomeric Butanol (2) at 298.15 and 313.15 K

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>x</i> ₁	$(\mathrm{mm}^2\cdot\mathrm{s}^{-1})$	η (mPa·s)	$\frac{\Delta\eta}{(mPa\cdot s)}$	<i>x</i> ₁	$(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	$\eta \\ (mPa \cdot s)$	$\frac{\Delta\eta}{(mPa\cdot s)}$		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2-Bromobutane (1) + 2-methyl-1-propanol (2) at 313.15 K									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0474	2.2910	1.8571	-0.1975	0.6053	0.5910	0.6315	-0.4974		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1020	1.9050	1.5962	-0.3678	0.7043	0.5130	0.5696	-0.3950		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2030	1.4028	1.2443	-0.5521	0.8030	0.4532	0.5215	-0.2793		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.3032	1.0773	1.0065	-0.6237	0.8948	0.4115	0.4887	-0.1598		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.4043	0.8548	0.8382	-0.6242	0.9318	0.3989	0.4796	-0.1075		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.5066	0.6994	0.7176	-0.5750						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2-Bro	omobutane ((1) + 2-meth	yl-2-prop	anol (2) at 313	.15 K			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0500	2.0911	1.6509	-0.3257	0.5032	0.6290	0.6337	-0.6260		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1020	1.6670	1.3596	-0.5348	0.6203	0.5341	0.5665	-0.5080		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2043	1.1510	0.9969	-0.7356	0.7036	0.4842	0.5317	-0.4110		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.3044	0.8861	0.8102	-0.7640	0.8056	0.4361	0.4987	-0.2827		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.4041	0.7432	0.7146	-0.7019	0.9064	0.4022	0.4777	-0.1443		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2-Bromo-2-methylpropane $(1) + 1$ -butanol (2) at 298 15 K									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0518	2 7230	2 2642	0.1865	0.5054	1 0230	1.0550	0 5703		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0518	2.7230	2.2042	-0.1805	0.5054	0.8855	0.0468	-0.5733		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1000	1 8100	1 6379	-0.5313	0.0023	0.7768	0.9408	-0.3131		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2079	1.3100	1 3773	-0.5518	0.7004	0.7708	0.0391	-0.4242		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0.4067	1.2136	1.2029	-0.6090	0.9010	0.6309	0.7428	-0.1795		
0.1001 2.5560 2.1739 -0.6307 0.6050 0.8225 0.8760 -0.7725 0.2023 1.8147 1.6287 -0.9419 0.7049 0.7257 0.8006 -0.6192 0.3034 1.3820 1.3017 -1.0374 0.8014 0.6742 0.7680 -0.4308 0.4041 1.1224 1.1050 -1.0035 0.8997 0.6236 0.7327 -0.2411 0.5076 0.9321 0.9569 -0.9146 2-Bromo-2-methylpropane (1) + 2-methyl-1-propanol (2) at 298.15 K 0.1028 3.0426 2.5823 -0.5386 0.6029 0.9337 0.9943 -0.8018 0.2047 2.2550 2.0214 -0.8295 0.7033 0.8034 0.8866 -0.6435 0.3013 1.7449 1.6397 -0.9553 0.8031 0.7141 0.8146 -0.4511 0.4041 1.3729 1.3511 -0.9716 0.9050 0.6428 0.7570 -0.2388 0.5068 1.1082 1.1377 -0.9129 2-Bromo-2-methylpropane (1) + 2-methyl-2-propanol (2) at 298.15 K 0.1003 3.1987 2.6479 -1.3764 0.6049 0.8686 0.9136 -1.2710 0.2034 2.1210 1.8578 -1.7906 0.7050 0.7650 0.8363 -0.9833 0.3015 1.5840 1.4581 -1.8327 0.7981 0.6957 0.7868 -0.6934 0.4024 1.2510 1.2075 -1.7154 0.8958 0.6397 0.7483 -0.3757		2-Bro	omo-2-meth	vlpropane (1) + 2-but	anol (2) at 298	.15 K			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 1001	2 55 (0)	2 1720	0 (207	0 (050	0.8225	0.07(0	0 7725		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1001	2.5560	2.1739	-0.6307	0.6050	0.8225	0.8/60	-0.7/25		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2023	1.814/	1.028/	-0.9419	0.7049	0.7257	0.8000	-0.6192		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.3034	1.3820	1.301/	-1.03/4	0.8014	0.6742	0.7080	-0.4308		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.4041	1.1224	0.9569	-1.0035 -0.9146	0.8997	0.0230	0.7327	-0.2411		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.5070	0.7521	0.7507	-0.9140						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		2-Bromo-2	-methylproj	pane $(1) + 2$	-methyl-1-	-propanol (2) a	at 298.15 K			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1028	3.0426	2.5823	-0.5386	0.6029	0.9337	0.9943	-0.8018		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2047	2.2550	2.0214	-0.8295	0.7033	0.8034	0.8866	-0.6435		
0.4041 1.3729 1.3511 -0.9716 0.9050 0.6428 0.7570 -0.2388 0.5068 1.1082 1.1377 -0.9129 2-Bromo-2-methylpropane (1) + 2-methyl-2-propanol (2) at 298.15 K 0.1003 3.1987 2.6479 -1.3764 0.6049 0.8686 0.9136 -1.2710 0.2034 2.1210 1.8578 -1.7906 0.7050 0.7650 0.8363 -0.9833 0.3015 1.5840 1.4581 -1.8327 0.7981 0.6957 0.7868 -0.6934 0.4024 1.2510 1.2075 -1.7154 0.8958 0.6397 0.7483 -0.3757 0.5028 1.0170 1.0258 -1.5310	0.3013	1.7449	1.6397	-0.9553	0.8031	0.7141	0.8146	-0.4511		
0.5068 1.1082 1.1377 -0.9129 2-Bromo-2-methylpropane (1) + 2-methyl-2-propanol (2) at 298.15 K 0.1003 3.1987 2.6479 -1.3764 0.6049 0.8686 0.9136 -1.2710 0.2034 2.1210 1.8578 -1.7906 0.7050 0.7650 0.8363 -0.9833 0.3015 1.5840 1.4581 -1.8327 0.7981 0.6957 0.7868 -0.6934 0.4024 1.2510 1.2075 -1.7154 0.8958 0.6397 0.7483 -0.3757 0.5028 1.0170 1.0258 -1.5310 -1.5310 -1.5310	0.4041	1.3729	1.3511	-0.9716	0.9050	0.6428	0.7570	-0.2388		
2-Bromo-2-methylpropane (1) + 2-methyl-2-propanol (2) at 298.15 K 0.1003 3.1987 2.6479 -1.3764 0.6049 0.8686 0.9136 -1.2710 0.2034 2.1210 1.8578 -1.7906 0.7050 0.7650 0.8363 -0.9833 0.3015 1.5840 1.4581 -1.8327 0.7981 0.6957 0.7868 -0.6934 0.4024 1.2510 1.2075 -1.7154 0.8958 0.6397 0.7483 -0.3757 0.5028 1.0170 1.0258 -1.5310 -1.5310 -1.5310	0.5068	1.1082	1.1377	-0.9129						
		2-Bromo-2	-methylproj	pane (1) + 2-	-methyl-2-	-propanol (2) a	at 298.15 K			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1003	3.1987	2.6479	-1.3764	0.6049	0.8686	0.9136	-1.2710		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2034	2.1210	1.8578	-1.7906	0.7050	0.7650	0.8363	-0.9833		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.3015	1.5840	1.4581	-1.8327	0.7981	0.6957	0.7868	-0.6934		
0.5028 1.0170 1.0258 -1.5310	0.4024	1.2510	1.2075	-1.7154	0.8958	0.6397	0.7483	-0.3757		
	0.5028	1.0170	1.0258	-1.5310						

Table III.	(Continued)
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x_1	$(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	η (mPa · s)	$\frac{\Delta\eta}{(\text{mPa}\cdot\text{s})}$	x_1	$(\mathrm{mm}^2 \cdot \mathrm{s}^{-1})$	η (mPa · s)	$\frac{\Delta\eta}{(\text{mPa}\cdot\text{s})}$			
2-Bromo-2-methylpropane (1) + 1-butanol (2) at 313.15 K										
0.0518	1.9229	1.5750	-0.1205	0.5054	0.8020	0.8127	-0.3589			
0.1060	1.6690	1.4096	-0.2233	0.6023	0.7005	0.7355	-0.3242			
0.2079	1.3360	1.1900	-0.3252	0.7004	0.6193	0.6723	-0.2741			
0.3109	1.0910	1.0201	-0.3761	0.7993	0.5591	0.6264	-0.2058			
0.4067	0.9313	0.9075	-0.3781	0.9010	0.5153	0.5951	-0.1196			
2-Bromo-2-methylpropane (1) + 2-butanol (2) at 313.15 K										
0.1001	1.6550	1.3856	-0.2815	0.6050	0.6368	0.6655	-0.4031			
0.2023	1.2554	1.1079	-0.4381	0.7049	0.5761	0.6235	-0.3267			
0.3034	1.0083	0.9333	-0.4928	0.8014	0.5391	0.6023	-0.2335			
0.4041	0.8350	0.8074	-0.4994	0.8997	0.5086	0.5859	-0.1334			
0.5076	0.7145	0.7201	-0.4640							
	2-Bromo-2	-methylproj	pane (1) + 2-	-methyl-1-	propanol (2) a	at 313.15 K				
0.1028	2.0588	1.7183	-0.2574	0.6029	0.7226	0.7553	-0.4538			
0.2047	1.5950	1.4047	-0.4148	0.7033	0.6352	0.6880	-0.3672			
0.3013	1.2651	1.1676	-0.5038	0.8031	0.5702	0.6382	-0.2640			
0.4041	1.0170	0.9825	-0.5314	0.9050	0.5234	0.6044	-0.1416			
0.5068	0.8420	0.8486	-0.5078							
	2-Bromo-2	-methylproj	pane (1) + 2-	-methyl-2-	propanol (2) a	at 313.15 K				
0.1003	1.8520	1.5036	-0.4061	0.6049	0.6654	0.6855	-0.4899			
0.2034	1.3570	1.1653	-0.5944	0.7050	0.5984	0.6408	-0.3889			
0.3015	1.0900	0.9832	-0.6337	0.7981	0.5523	0.6119	-0.2823			
0.4024	0.8980	0.8491	-0.6210	0.8958	0.5191	0.5950	-0.1570			
0.5028	0.7660	0.7568	-0.5672							

 Table III.
 (Continued)

Symbols without subscript refer to the mixture, subscript 1 is used for the brominated isomer and 2 for the isomeric butanol. The kinematic and absolute viscosities together with the viscosity deviations are reported in Table III and graphically shown in Figs. 1–4.

The kinematic viscosities were correlated using the following equations: *McAllister* [18]:

$$\ln v = x_1^3 \ln v_1 + 3x_1^2 x_2 \ln v_{12} + 3x_1 x_2^2 \ln v_{21} + x_2^3 \ln v_2 - \ln \left(x_1 + \frac{M_2}{M_1} x_2 \right) + 3x_1^2 x_2 \ln \left(\frac{2}{3} + \frac{M_2}{3M_1} \right) + 3x_1 x_2^2 \ln \left(\frac{1}{3} + \frac{2M_2}{3M_1} \right) + x_2^3 \ln \left(\frac{M_2}{M_1} \right)$$
(3)

0 -0.5 -1.0 ∆**η, mPa·s** -1.5 -2.0 0.2 0.4 0 0.6 0.8 X₁ 0 -0.1 -0.2 -0.3 ∆η**, mPa·s** -0.4 -0.5 -0.6 -0.7 -0.8 0 0.2 0.4 0.6 0.8 X 1

Fig. 1. Viscosity deviations of 2-bromobutane (1) + an isomer of butanol (2) at 298.15 K as a function of mole fraction x_1 : 1-butanol (\triangle); 2-butanol (\square); 2-methyl-1-propanol (\blacktriangle); 2-methyl-2-propanol (\blacksquare).

Fig. 2. Viscosity deviations of 2-bromobutane (1) + an isomer of butanol (2) at 313.15 K as a function of mole fraction x_1 : 1-butanol (\triangle); 2-butanol (\square); 2-methyl-1-propanol (\blacktriangle); 2-methyl-2-propanol (\blacksquare).



Fig. 3. Viscosity deviations of 2-bromo-2-methylpropane (1)+an isomer of butanol (2) at 298.15 K as a function of mole fraction x_1 : 1-butanol (\triangle); 2-butanol (\square); 2-methyl-1-propanol (\blacktriangle); 2-methyl-2-propanol (\blacksquare).

Fig. 4. Viscosity deviations of 2-bromo-2-methylpropane (1)+an isomer of butanol (2) at 313.15 K as a function of mole fraction x_1 : 1-butanol (\triangle); 2-butanol (\square); 2-methyl-1-propanol (\blacktriangle); 2-methyl-2-propanol (\blacksquare).

where v and v_i are the kinematic viscosity (mm²·s⁻¹) of the mixture and pure component *i*, respectively, x_i and M_i are the mole fraction and the molar mass of component *i*, and v_{12} and v_{21} are adjustable parameters characteristic of the system.

Heric [19]:

$$\ln v = x_{1} \ln(v_{1}M_{1}) + x_{2} \ln(v_{2}M_{2}) - \ln(x_{1}M_{1} + x_{2}M_{2})$$
$$+ x_{1}x_{2}(\alpha_{12} + \alpha'_{12}(x_{1} - x_{2}))$$
(4)

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

The estimated parameters for Eqs. (3) and (4) together with the mean relative standard deviation (MRSD) between experimental and calculated kinematic viscosities are listed in Table IV. The MRSD is expressed as a percentage, and it is defined by the following expression:

$$\mathbf{MRSD} = 100 \times \left[\frac{1}{N} \sum_{i=1}^{i=N} \left(\frac{Y_i^{\mathrm{exp}} - Y_i^{\mathrm{calc}}}{Y_i^{\mathrm{exp}}}\right)^2\right]^{\frac{1}{2}}$$
(5)

where Y is the adjusted property and N is the number of experimental data. Both equations with two parameters give about the same MRSD values, and they correlate quite well the kinematic viscosity data, especially for mixtures containing primary butanols. On the other hand, systems with 2-methyl-2-propanol present the poorest correlations.

The *Grunberg–Nissan* equation [20] was used to correlate the absolute viscosity data:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \tag{6}$$

where d is an interaction parameter that is a function of the nature of the components and temperature. The values of d, obtained by fitting Eq. (6) to the viscosity data, along with the MRSD between experimental and calculated absolute viscosities, are also given in Table IV. The obtained deviations are smaller for the mixtures with primary alcohols (1- butanol or 2-methyl-1-propanol) independently of the brominated isomer, and the largest are those for systems containing 2-methyl-2-propanol. However, these results are indicative that this simple equation with only one adjustable parameter correlates satisfactorily the absolute viscosity data. The interaction parameter d is negative for all the mixtures at both temperatures, showing that the breaking of butanol self-association is the predominant effect [21].

	T = 298.15 K			Т	T = 313.15 K					
Equation	a	b	MRSD (%)	a	b	MRSD (%)				
2-Bromobutane (1) + 1-butanol (2)										
Grunberg–Nissan ^a	-0.9872		1.75	-0.9218		1.09				
McAllister ^b	0.5540	1.2302	0.42	0.4712	0.9150	0.43				
Heric ^c	-0.9677	-0.2275	0.42	-0.8965	-0.1306	0.43				
	2-Bro	omobutane (1	1) + 2-buta	nol (2)						
Grunberg–Nissan ^a	-1.9752		5.07	-1.5570		3.44				
McAllister ^b	0.5782	0.7416	1.65	0.4710	0.6212	1.31				
Heric ^c	-1.9329	0.6857	1.65	-1.5123	0.4614	1.31				
	2-Bromob	utane (1) + 2	-methyl-1-p	propanol (2)						
Grunberg–Nissan ^a	-1.5319		0.82	-1.3326		1.12				
McAllister ^b	0.5698	1.1210	0.45	0.4809	0.8375	0.64				
Heric ^{<i>c</i>}	-1.5119	0.1029	0.45	-1.3067	0.1357	0.64				
	2-Bromob	utane $(1) + 2$	-methyl-2-p	propanol (2)						
Grunberg–Nissan ^a	-2.7578		11.85	-1.8839		7.10				
McAllister ^b	0.6739	0.5618	3.48	0.5209	0.5364	2.40				
Heric ^{<i>c</i>}	-2.7153	1.5305	3.48	-1.8406	0.9188	2.40				
	2-Bromo-2	-methylprop	ane (1) + 1	-butanol (2)						
Grunberg-Nissan ^a	-1.0734		1.18	-0.9726		1.35				
McAllister ^b	0.7103	1.2467	1.15	0.5714	0.9561	1.31				
Heric ^{<i>c</i>}	-1.0521	-0.0340	1.15	-0.9496	-0.0432	1.31				
	2-Bromo-2	-methylprop	ane(1) + 2	-butanol (2)						
Grunberg–Nissan ^a	-1.7871		3.17	-1.4376		1.44				
McAllister ^b	0.6914	0.9604	1.10	0.5331	0.7755	0.69				
Heric ^e	-1.7540	0.4072	1.10	-1.4017	0.1784	0.69				
2-B	romo-2-meth	ylpropane (1	1) + 2-meth	yl-1-propanc	ol (2)					
Grunberg-Nissan ^a	-1.2987		0.60	-1.1067		1.33				
McAllister ^b	0.7223	1.4220	0.42	0.5599	1.0989	0.41				
Heric ^{<i>c</i>}	-1.2764	-0.0570	0.42	-1.0793	-0.1797	0.41				
2-В	romo-2-meth	ylpropane (1	1) + 2-meth	yl-2-propano	ol (2)					
Grunberg-Nissan ^a	-2.3269		7.79	-1.5882		3.31				
McAllister ^b	0.7955	0.8706	2.58	0.5802	0.7704	1.37				
Heric ^{<i>c</i>}	-2.2867	0.9633	2.58	-1.5441	0.4013	1.37				

 Table IV.
 Parameters and Mean Relative Standard Deviation (MRSD) for Viscosity Equations at Indicated Temperatures

a a = d.

 $^{b}a = v_{12}, b = v_{21}.$

 $a^{c} a = \alpha_{12}, b = \alpha'_{12}.$

The values of $\Delta \eta$ for the binary mixtures at both temperatures were fitted to a Redlich-Kister polynomial equation [22]:

$$\Delta \eta = x_1(1-x_1) \sum_{p=0}^{p} A_p(2x_1-1)^p$$
(7)

where x_1 denotes the mole fraction of bromoalkane, and A_p 's are adjustable parameters. In Table V are listed the parameters A_p and the standard deviations $\sigma(\Delta \eta)$ defined as

$$\sigma(\Delta \eta) = \left[\frac{\sum \left(\Delta \eta_{\exp} - \Delta \eta_{calc}\right)^2}{n-p}\right]^{\frac{1}{2}}$$
(8)

where n is the number of experimental data and p is the number of fitting parameters.

The values of the viscosity deviations for all systems at both temperatures are negative over the complete composition range. Considering the same bromoalkane, the mixtures with 2-methyl-2-propanol present the most negative $\Delta \eta$ values and those with 1-butanol the least negative ones.

System	Т (К)	$\begin{array}{c} A_0 \\ (\text{mPa} \cdot \text{s}) \end{array}$	$\begin{array}{c} A_1 \\ (\mathbf{mPa} \cdot \mathbf{s}) \end{array}$	$\begin{array}{c} A_2 \\ (\text{mPa} \cdot \text{s}) \end{array}$	$\begin{array}{c} A_3 \\ (\text{mPa} \cdot \text{s}) \end{array}$	$\begin{array}{c} A_4 \\ (\mathrm{mPa} \cdot \mathrm{s}) \end{array}$	$\sigma \left(\varDelta \eta \right) \\ (\text{mPa} \cdot \text{s})$
2-Bromobutane +							
1-Butanol 2-Butanol 2-Methyl-1-propanol 2-Methyl-2-propanol 1-Butanol 2 Butanol	298.15 313.15	-2.4864 -3.9238 -4.1248 -6.6086 -1.5579 1.0801	1.0275 2.7533 2.4144 5.2086 0.6237	-0.2542 -2.5811 -1.5393 -4.6473 -0.2319 1.0874	-0.2727 1.5315 0.6039 5.4177 0.1157 0.7668	-3.6475	0.0048 0.0053 0.0031 0.0056 0.0024 0.0053
2-Methyl-1-propanol 2-Methyl-2-propanol 2-Bromo-2-methy	lpropan	-2.3107 -2.4947 e+	1.1870 1.2833 1.8467	-0.8326 -1.9987	0.2656 1.2557		0.0033 0.0022 0.0055
1-Butanol 2-Butanol 2-Methyl-1-propanol 2-Methyl-2-propanol 1-Butanol 2-Butanol 2-Methyl-1-propanol 2-Methyl-2-propanol	298.15 313.15	$\begin{array}{r} -2.3169 \\ -3.6676 \\ -3.3666 \\ -6.1386 \\ -1.4419 \\ -1.8618 \\ -2.0428 \\ -2.2676 \end{array}$	1.0573 2.3619 1.7704 4.2759 0.5658 0.9626 0.7995 1.3236	$\begin{array}{c} - 0.8228 \\ - 1.7765 \\ - 0.9617 \\ - 3.1077 \\ - 0.5993 \\ - 0.6602 \\ - 0.2389 \\ - 1.2530 \end{array}$	$\begin{array}{c} - \ 0.0116 \\ 0.6003 \\ 0.2733 \\ 4.2030 \\ - \ 0.1020 \\ 0.1419 \\ - \ 0.1385 \\ 0.7326 \end{array}$	- 3.6952	0.0042 0.0064 0.0039 0.0073 0.0029 0.0033 0.0025 0.0042

Table V. Coefficients of Eq. (7) and Standard Deviations at Indicated Temperatures

Systems containing 2-butanol and 2-methyl-1-propanol show similar values, and they are intermediate between those mentioned above. The shape of the curves shows that the mole fractions corresponding to the minimum values appear in regions richer in the brominated derivative when the system involves the primary alcohols (2-methyl-1-propanol or 1-butanol), and they shift towards minor mole fractions with 2-methyl-2-propanol. An increase in the temperature of the measurements leads to less negative viscosity deviations, with the more pronounced effect for 2-methyl-2-propanol mixtures. All these observations are in agreement with those obtained in other studies of thermodynamic and transport properties containing an isomeric butanol [2-15], and point out again that the breaking of the self-associated structure of butanols is the main effect to be considered in these systems. The differences observed with each isomeric butanol can be explained in terms of both the position of the OH group and the branching of the alkyl chain that carries this functional group [23–25].

From the viewpoint of a given butanol, the different viscosity deviation values obtained with 2-bromobutane or 2-bromo-2-methylpropane can be interpreted as the result of both the different ability for breaking the hydrogen bond by the alkyl brominated chain, and the different extent of the Br-OH interaction. These values can be compared with those for systems with the primary isomers: 1-bromobutane [12] and 1-bromo-2-methylpropane [15]. The most noticeable observation is that the same butanol mixed with any isomeric bromobutane presents both similar viscosity deviation values and a similar position of the minimum. The small differences seem to depend on the branching of the alkyl chain of the brominated derivative instead of the position of the bromine atom. Consequently, systems involving linear brominated isomers (1-bromobutane or 2-bromobutane) yield similar values. Also, the $\Delta \eta$ values obtained for mixtures containing these linear isomers are the most negative, meanwhile those with 2-bromo-2-methylpropane present the most positive. It can be deduced that the presence of linear bromoalkanes leads to a greater breaking of the structure of the butanols; nevertheless, the difference in absolute value is only about 5 to 10% of the minimum measured $\Delta \eta$, independent of temperature.

A similar behavior was observed when the halogenated derivatives contain a chlorine atom instead of the bromine one [9–11, 14]. The only difference is that the corresponding viscosity deviations are slightly more negative in systems with chloroalkanes, indicating that the structure of the butanols is more affected by the presence of the chloroderivatives. This effect was previously observed in systems for which different properties of mixtures containing α , ω -dihaloalkanes and isomeric butanols were considered [8, 11, 13, 15].

Obviously, there are other effects that contribute to the observed behavior [9], but their relative strength compared with the breaking of the self-associated structure of the alcohols gives little influence on the values of the different properties.

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