310 J. Chem. Eng. Data 1993, 38, 310–319

A Study on Mixing Properties of Binary Mixtures of Bromoform with Aliphatic Alcohols[†]

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Densities, refractive indices, speeds of sound, and viscosities of the binary mixtures of bromoform with 2-chloroethanol, 1-butanol, 1-pentanol, 3-methyl-1-butanol, 2-methyl-1-propanol, 1-hexanol, 1-heptanol, 1-nonanol, 2-methoxyethanol, and 2-octanol are presented in the temperature interval of 298.15–308.15 K. From these data the excess molar volume, excess isentropic compressibility, and excess molar refraction have been calculated. The sign and magnitude of these quantities have been used to discuss the type and nature of binary interactions. Furthermore, the computed results are fitted to the Redlich–Kister polynomial relation to estimate the regression coefficients and standard errors. Viscosity data have been analyzed by using the viscosity equations suggested by McAllister, Auslaender, and Heric; a polynomial relation is also used.

Introduction

The study of molecular interactions in binary mixtures of bromoform has been actively investigated in our laboratories (*1–5*). Accurate knowledge of thermodynamic mixing properties of such binary mixtures has great relevance in theoretical and applied areas of research. These data are needed for design processes in chemical, petrochemical, and pharmaceutical industries. Usually, for nonideal mixtures, direct experimental measurements are performed over the entire composition range. Many times predictive methods for the excess quantities would be more useful than the direct experimental measurements especially when quick estimates are needed. Most empirical approaches for calculating the excess properties attempt to explain solution nonidealities in terms of specific or nonspecific intermolecular interactions.

Bromoform (BF) is a versatile organic solvent which finds applications in analytical chemistry and other areas. An understanding about the mixing properties of binary mixtures of bromoform with alcohols is of considerable interest from the viewpoint of specific interactions between the mixing components. The presence of three bromine atoms in BF allows the molecule to act as a σ-acceptor and be involved in hydrogen bond formation. The alcohols are selected in increasing order of chain length or decreasing order of polarity. A thorough search of the literature suggests that none of these mixtures have been attempted earlier.

As a further contribution in this area, we now present the experimental data of density, ρ, viscosity, η, refractive index, n_D, and ultrasonic velocity, u, of the binary mixtures of bromoform with aliphatic alcohols. From these data the mixing properties have been calculated, and these results are discussed in terms of molecular interactions between the mixing components. The systems chosen in this study possess a wide range of molecular size ratio and are, therefore, particularly suitable for testing McAllister's three-body interaction equation (*6*). For comparison purposes, other viscosity equations such as those proposed by Heric (*7*) and Auslaender (*8*) in addition to a polynomial relation (*9*) have also been used.

Table I. Comparison of the Literature Data for Pure Liquids at 298.15 K

solvent	density/(g cm^{-3}) lit.[a]	density/(g cm^{-3}) obsd	refractive index lit.[a]	refractive index obsd
bromoform	2.8779	2.8741	1.5956	1.5931
1-butanol	0.8058	0.8067	1.3974	1.3973
2-methyl-1-propanol	0.7978	0.7979	1.3939	1.3933
1-pentanol	0.8108	0.8111	1.4080	1.4065
3-methyl-1-butanol	0.8018[b]	0.8030[b]	1.4060[c]	1.4048
1-hexanol	0.8153	0.8156	1.4157	1.4149
1-heptanol	0.8219[c]	0.8199	1.4249[c]	1.4228
2-octanol	0.8171	0.8171	1.4241	1.4233
1-nonanol	0.827[c]	0.8258	1.433	1.4309
2-chloroethanol	1.1912[b]	1.1916[b]	1.4419[c]	1.4388
2-methoxy-ethanol	0.9602	0.9591	1.4002	1.4002

[a] Reference 11. [b] At 303.15 K. [c] At 293.15 K.

Experimental Section

Materials. Bromoform (Thomas Baker, Bombay) was used directly. However, other solvents, namely, 1-butanol (Sisco, Bombay), 2-methyl-1-propanol (s.d. fine, Bombay), 1-pentanol (E. Merk, Darmstadt), 1-hexanol (Fluka, A.G., Switzerland), 3-methyl-1-butanol (Thomas Baker, Bombay), 1-heptanol (BDH, England), 2-octanol (BDH, England), 1-nonanol (Fluka, A.G., Switzerland) and 2-chloroethanol (E. Merk, Darmstadt), were purified by the recommended methods (*10, 11*). The purities of all the solvents were ascertained by the constancy of their boiling temperatures during final distillations and also by comparing their densities and refractive indices at 298.15 K which agreed reasonably with the corresponding literature values (Table I). The gas chromatographic tests of the purified solvents showed a purity of 99+ mol %.

Mixtures were prepared by mixing the appropriate volumes of liquids in specially designed ground-glass air-tight ampules and weighed in a single-pan Mettler balance (Switzerland) to an accuracy of ±0.05 mg. Preferential evaporation losses of solvents from the mixtures were kept to a minimum as evidenced by a repeated measurement of the physical properties over an interval of 2–3 days during which time no changes in the physical properties were observed. The possible error in the mole fractions is estimated to be around 0.0001.

Measurements. Densities of pure liquids and their binary mixtures in the composition range 0.1–0.9 at 0.1 mole fraction

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[†] Dedicated to Professor Petr Munk of the University of Texas, on the occasion of his 60th birthday.

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Table II. Experimental Densities, ρ, Viscosities, η, Refractive Indices, n_D, and Speeds of Sound, u, of Binary Mixtures

x_1	$\rho/(g\ cm^{-3})$	$\eta/(mPa\ s)$	n_D	$u/(m\ s^{-1})$	x_1	$\rho/(g\ cm^{-3})$	$\eta/(mPa\ s)$	n_D	$u/(m\ s^{-1})$
Bromoform (1) + 1-Butanol (2)									
298.15 K									
0.000	0.8067	2.442	1.3973	1244	0.602	2.0280	1.887	1.5096	0952
0.099	1.0038	2.482	1.4146	1155	0.699	2.2318	1.847	1.5293	0936
0.205	1.2171	2.339	1.4331	1086	0.803	2.4507	1.817	1.5507	0928
0.300	1.4083	2.196	1.4506	1040	0.899	2.6546	1.827	1.5717	0923
0.401	1.6139	2.063	1.4702	1002	1.000	2.8741	1.912	1.5931	0926
0.501	1.8201	1.955	1.4892	0974					
303.15 K									
0.000	0.8028	2.129	1.3947		0.602	2.0179	1.718	1.5070	
0.099	0.9990	2.183	1.4122		0.699	2.2207	1.695	1.5269	
0.205	1.2108	2.070	1.4306		0.803	2.4394	1.684	1.5479	
0.300	1.4013	1.942	1.4482		0.899	2.6422	1.709	1.5685	
0.401	1.6058	1.841	1.4673		1.000	2.8610	1.790	1.5903	
0.501	1.8109	1.768	1.4868						
308.15 K									
0.000	0.7988	1.856	1.3922		0.602	2.0078	1.573	1.5041	
0.099	0.9940	1.915	1.4100		0.699	2.2095	1.559	1.5246	
0.205	1.2049	1.828	1.4280		0.803	2.4268	1.564	1.5458	
0.300	1.3941	1.738	1.4460		0.899	2.6294	1.588	1.5660	
0.401	1.5977	1.662	1.4648		1.000	2.8476	1.684	1.5872	
0.501	1.8017	1.607	1.4842						
Bromoform (1) + 2-Methyl-1-propanol (2)									
298.15 K									
0.000	0.7979	3.256	1.3933	1189	0.597	2.0089	1.905	1.5069	0947
0.099	0.9945	2.980	1.4107	1110	0.701	2.2256	1.849	1.5279	0930
0.197	1.1897	2.604	1.4287	1060	0.798	2.4323	1.815	1.5487	0923
0.300	1.3969	2.336	1.4479	1015	0.901	2.6542	1.823	1.5708	0921
0.395	1.5887	2.134	1.4664	0986	1.000	2.8741	1.912	1.5931	0920
0.498	1.8029	2.017	1.4873	0960					
303.15 K									
0.000	0.7941	2.743	1.3910		0.597	1.9990	1.732	1.5042	
0.099	0.9894	2.544	1.4083		0.701	2.2143	1.693	1.5254	
0.197	1.1836	2.272	1.4264		0.798	2.4204	1.679	1.5464	
0.300	1.3898	2.045	1.4457		0.901	2.6414	1.699	1.5681	
0.395	1.5805	1.901	1.4640		1.000	2.8610	1.790	1.5903	
0.498	1.7938	1.808	1.4843						
308.15 K									
0.000	0.7901	2.317	1.3887		0.597	1.9886	1.579	1.5017	
0.099	0.9844	2.193	1.4063		0.701	2.2032	1.559	1.5230	
0.197	1.1774	2.011	1.4244		0.798	2.4083	1.558	1.5436	
0.300	1.3826	1.803	1.4434		0.901	2.6287	1.591	1.5651	
0.395	1.5722	1.687	1.4612		1.000	2.8476	1.684	1.5872	
0.498	1.7844	1.633	1.4815						
Bromoform (1) + 1-Pentanol (2)									
298.15 K									
0.000	0.8111	3.302	1.4065	1279	0.600	1.9397	2.114	1.5054	0970
0.097	0.9764	3.255	1.4209	1192	0.701	2.1583	1.997	1.5256	0947
0.200	1.1589	3.006	1.4363	1125	0.800	2.3831	1.910	1.5465	0932
0.296	1.3332	2.729	1.4520	1077	0.900	2.6225	1.873	1.5690	0923
0.400	1.5329	2.477	1.4691	1031	1.000	2.8741	1.912	1.5931	0920
0.499	1.7288	2.275	1.4867	0998					
303.15 K									
0.000	0.8073	2.841	1.4048		0.600	1.9300	1.928	1.5033	
0.097	0.9717	2.831	1.4184		0.701	2.1478	1.822	1.5230	
0.200	1.1530	2.621	1.4337		0.800	1.3712	1.762	1.5438	
0.296	1.3266	2.399	1.4490		0.900	2.6100	1.742	1.5661	
0.400	1.5256	2.200	1.4664		1.000	2.8610	1.790	1.5903	
0.499	1.7202	2.039	1.4835						
308.15 K									
0.000	0.8037	2.449	1.4030		0.600	1.9205	1.741	1.5028	
0.097	0.9670	2.452	1.4162		0.701	2.1372	1.670	1.5195	
0.200	1.1475	2.296	1.4319		0.800	2.3597	1.631	1.5404	
0.296	1.3202	2.113	1.4469		0.900	2.5971	1.628	1.5632	
0.400	1.5179	1.954	1.4642		1.000	2.8476	1.684	1.5872	
0.499	1.7116	1.829	1.4811						
Bromoform (1) + 3-Methyl-1-butanol (2)									
298.15 K									
0.000	0.8069	3.581	1.4048	1236	0.599	1.9327	2.111	1.5047	0959
0.099	0.9750	3.419	1.4191	1161	0.702	2.1565	1.957	1.5272	0939
0.203	1.1595	3.063	1.4355	1097	0.803	2.3877	1.888	1.5475	0929

Table II. (Continued)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})	x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
Bromoform (1) + 3-Methyl-1-butanol (2)									
298.15 K									
0.299	1.3343	2.770	1.4503	1051	0.900	2.6216	1.873	1.5700	0921
0.422	1.5704	2.415	1.4719	1004	1.000	2.8741	1.912	1.5931	0920
0.498	1.7242	2.265	1.4861	0981					
303.15 K									
0.000	0.8030	3.033	1.4026		0.599	1.9232	1.909	1.5023	
0.099	0.9703	2.937	1.4172		0.702	2.1460	1.795	1.5247	
0.203	1.1536	2.643	1.4330		0.803	2.3762	1.739	1.5444	
0.299	1.3278	2.384	1.4484		0.900	2.6092	1.737	1.5674	
0.422	1.5627	2.145	1.4695		1.000	2.8610	1.790	1.5903	
0.498	1.7158	2.025	1.4831						
308.15 K									
0.000	0.7993	2.590	1.4008		0.599	1.9136	1.729	1.4996	
0.099	0.9655	2.527	1.4160		0.702	2.1356	1.647	1.5214	
0.203	1.1479	2.306	1.4305		0.803	2.3645	1.610	1.5416	
0.299	1.3212	2.111	1.4459		0.900	2.5968	1.605	1.5646	
0.422	1.5549	1.905	1.4670		1.000	2.8476	1.684	1.5872	
0.498	1.7071	1.815	1.4810						
Bromoform (1) + 1-Hexanol (2)									
298.15 K									
0.000	0.8156	4.342	1.4149	1306	0.601	1.8697	2.400	1.5032	0985
0.097	0.9600	4.186	1.4263	1228	0.701	2.0908	2.192	1.5221	0959
0.199	1.1207	3.770	1.4394	1159	0.798	2.3217	2.031	1.5428	0939
0.298	1.2870	3.340	1.4533	1104	0.900	2.5892	1.922	1.5670	0926
0.403	1.4737	2.965	1.4688	1055	1.000	2.8741	1.912	1.5931	0920
0.497	1.6542	2.667	1.4837	1018					
303.15 K									
0.000	0.8118	3.690	1.4130		0.601	1.8605	2.156	1.5003	
0.097	0.9555	3.573	1.4241		0.701	2.0807	1.988	1.5193	
0.199	1.1153	3.237	1.4370		0.798	2.3109	1.866	1.5402	
0.298	1.2809	2.907	1.4506		0.900	2.5768	1.784	1.5646	
0.403	1.4666	2.611	1.4664		1.000	2.8610	1.790	1.5903	
0.497	1.6462	2.370	1.4813						
308.15 K									
0.000	0.8079	3.139	1.4108		0.601	1.8513	1.943	1.4976	
0.097	0.9508	3.092	1.4224		0.701	2.0707	1.815	1.5168	
0.199	1.1099	2.811	1.4353		0.798	2.2996	1.719	1.5374	
0.298	1.2747	2.537	1.4480		0.900	2.5648	1.663	1.5613	
0.403	1.4596	2.301	1.4640		1.000	2.8476	1.684	1.5872	
0.497	1.6382	2.114	1.4788						
Bromoform (1) + 1-Heptanol (2)									
298.15 K									
0.000	0.8199	5.758	1.4228	1329	0.597	1.7987	2.755	1.5003	1000
0.102	0.9551	5.359	1.4327	1248	0.699	2.0274	2.440	1.5191	0970
0.204	1.0995	4.647	1.4436	1181	0.801	2.2807	2.170	1.5405	0945
0.301	1.2507	4.131	1.4555	1126	0.901	2.5607	1.982	1.5652	0929
0.405	1.4259	3.544	1.4693	1076	1.000	2.8741	1.912	1.5931	0920
0.503	1.6064	3.133	1.4843	1036					
303.15 K									
0.000	0.8161	4.814	1.4205		0.597	1.7901	2.457	1.4971	
0.102	0.9508	4.524	1.4303		0.699	2.0174	2.199	1.5165	
0.204	1.0945	3.988	1.4409		0.801	2.2698	1.992	1.5382	
0.301	1.2448	3.547	1.4532		0.901	2.5485	1.844	1.5626	
0.405	1.4192	3.093	1.4670		1.000	2.8610	1.790	1.5903	
0.503	1.5988	2.773	1.4815						
308.15 K									
0.000	0.8126	4.051	1.4182		0.597	1.7815	2.205	1.4947	
0.102	0.9465	3.863	1.4280		0.699	2.0078	1.990	1.5138	
0.204	1.0895	3.422	1.4395		0.801	2.2589	1.822	1.5349	
0.301	1.2390	3.084	1.4508		0.901	2.5365	1.713	1.5601	
0.405	1.4126	2.712	1.4645		1.000	2.8476	1.684	1.5872	
0.503	1.5911	2.461	1.4780						
Bromoform (1) + 2-Octanol (2)									
298.15 K									
0.000	0.8171	5.956	1.4233	1309	0.603	1.7459	2.623	1.4959	1003
0.104	0.9390	5.244	1.4321	1241	0.704	1.9744	2.337	1.5147	0972
0.199	1.0629	4.606	1.4414	1183	0.801	2.2256	2.123	1.5360	0948
0.300	1.2065	3.910	1.4526	1129	0.899	2.5184	1.969	1.5612	0929
0.403	1.3698	3.391	1.4663	1079	1.000	2.8741	1.912	1.5931	0920
0.502	1.5454	2.965	1.4799	1039					

Table II. (Continued)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})	x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
Bromoform (1) + 2-Octanol (2)									
303.15 K									
0.000	0.8130	4.803	1.4208		0.603	1.7370	2.335	1.4930	
0.104	0.9345	4.336	1.4304		0.704	1.9647	2.104	1.5122	
0.199	1.0578	3.855	1.4393		0.801	2.2132	1.943	1.5331	
0.300	1.2009	3.348	1.4505		0.899	2.5063	1.830	1.5586	
0.403	1.3632	2.937	1.4635		1.000	2.8610	1.790	1.5903	
0.502	1.5379	2.594	1.4769						
308.15 K									
0.000	0.8092	3.907	1.4190		0.603	1.7286	2.084	1.4904	
0.104	0.9300	3.625	1.4282		0.704	1.9551	1.913	1.5094	
0.199	1.0527	3.274	1.4368		0.801	2.2055	1.785	1.5300	
0.300	1.1949	2.894	1.4483		0.899	2.4944	1.698	1.5554	
0.403	1.3565	2.566	1.4606		1.000	2.8476	1.684	1.5872	
0.502	1.5303	2.288	1.4743						
Bromoform (1) 1-Nonanol (2)									
298.15 K									
0.000	0.8258	8.965	1.4309		0.604	1.7079	3.571	1.4965	
0.105	0.9389	7.847	1.4384		0.704	1.9327	2.984	1.5145	
0.299	1.1846	5.743	1.4569		0.802	2.1921	2.492	1.5357	
0.404	1.3416	5.079	1.4682		0.903	2.5070	2.120	1.5621	
0.504	1.5131	4.228	1.4813		1.000	2.8741	1.912	1.5931	
303.15 K									
0.000	0.8222	7.375	1.4288		0.604	1.7002	3.151	1.4943	
0.105	0.9346	6.517	1.4370		0.704	1.9236	2.669	1.5119	
0.299	1.1795	4.870	1.4547		0.802	2.1818	2.266	1.5331	
0.404	1.3355	4.380	1.4663		0.903	2.4954	1.963	1.5590	
0.504	1.5059	3.693	1.4788		1.000	2.8610	1.790	1.5903	
308.15 K									
0.000	0.8186	6.114	1.4272		0.604	1.6922	2.802	1.4915	
0.105	0.9303	5.421	1.4352		0.704	1.9146	2.399	1.5091	
0.299	1.1741	4.144	1.4523		0.802	2.1716	2.065	1.5298	
0.404	1.3295	3.777	1.4640		0.903	2.4835	1.818	1.5561	
0.504	1.4991	3.240	1.4764		1.000	2.8476	1.684	1.5872	
Bromoform (1) + 2-Chloroethanol (2)									
298.15 K									
0.000	1.1981	2.973	1.4388		0.595	2.2960	2.179	1.5382	
0.099	1.4081	2.878	1.4587		0.702	2.4577	2.067	1.5532	
0.198	1.6056	2.817	1.4752		0.801	2.6022	1.970	1.5671	
0.301	1.7993	2.587	1.4922		0.896	2.7340	1.915	1.5799	
0.396	1.9686	2.446	1.5079		1.000	2.8741	1.912	1.5931	
0.498	2.1402	2.300	1.5233						
303.15 K									
0.000	1.1916	2.611	1.4370		0.595	2.2847	1.982	1.5357	
0.099	1.4016	2.532	1.4562		0.702	2.4459	1.890	1.5507	
0.198	1.5977	2.487	1.4728		0.801	2.5898	1.825	1.5643	
0.301	1.7905	2.297	1.4897		0.896	2.7209	1.779	1.5769	
0.396	1.9593	2.191	1.5055		1.000	2.8610	1.790	1.5903	
0.498	2.1298	2.080	1.5209						
308.15 K									
0.000	1.1860	2.262	1.4352		0.595	2.2736	1.814	1.5327	
0.099	1.3949	2.237	1.4539		0.702	2.4340	1.746	1.5479	
0.198	1.5902	2.210	1.4701		0.801	2.5772	1.694	1.5611	
0.301	1.7819	2.055	1.4874		0.896	2.7081	1.666	1.5741	
0.396	1.9496	1.974	1.5025		1.000	2.8476	1.684	1.5872	
0.498	2.1193	1.884	1.5183						
Bromoform (1) + 2-Methoxyethanol (2)									
298.15 K									
0.000	0.9591	1.695	1.4002	1355	0.600	2.1498	2.183	1.5187	0980
0.097	1.1624	1.922	1.4202	1245	0.697	2.3288	2.094	1.5366	0957
0.198	1.3697	2.097	1.4415	1163	0.798	2.5136	2.003	1.5560	0937
0.297	1.5684	2.220	1.4597	1101	0.900	2.6966	1.932	1.5747	0925
0.401	1.7709	2.270	1.4802	1049	1.000	2.8741	1.912	1.5931	0920
0.499	1.9608	2.245	1.4989	1012					
303.15 K									
0.000	0.9544	1.525	1.3979		0.600	2.1392	1.972	1.5160	
0.097	1.1560	1.719	1.4176		0.697	2.3174	1.909	1.5339	
0.198	1.3629	1.872	1.4391		0.798	2.5014	1.842	1.5537	
0.297	1.5608	1.984	1.4571		0.900	2.6839	1.794	1.5719	
0.401	1.7621	2.030	1.4779		1.000	2.8610	1.790	1.5903	
0.499	1.9513	2.014	1.4964						

Table II. (Continued)

x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})	x_1	ρ/(g cm^{-3})	η/(mPa s)	n_D	u/(m s^{-1})
				Bromoform (1) + 2-Methoxyethanol (2)					
				308.15 K					
0.000	0.9497	1.368	1.3956		0.600	2.1286	1.792	1.5134	
0.097	1.1502	1.549	1.4154		0.697	2.3060	1.748	1.5310	
0.198	1.3562	1.680	1.4367		0.798	2.4891	1.702	1.5504	
0.297	1.5528	1.774	1.4546		0.900	2.6709	1.676	1.5691	
0.401	1.7535	1.825	1.4753		1.000	2.8476	1.684	1.5872	
0.499	1.9416	1.817	1.4937						

increments were measured (Table II) by using a pycnometer having a bulb volume of about 10 cm^3 and a capillary with an internal diameter of 1 mm. For each measurement, sufficient time was allowed to attain thermal equilibrium in a INSREF (model 016 AP) precision thermostat, the bath temperature of which was monitored to ±0.01 K with a calibrated thermometer. The fluctuations in bath temperature did not exceed ±0.1 K, and evaporation losses remained insignificant during the time of actual measurement. The reported densities at 298.15, 303.15, and 308.15 K are considered significant to four figures. An average of triplicate measurements was taken into account, and these were reproducible within ±0.5%.

Viscosities were measured with Cannon Fenske viscometers (sizes 75 and 100 depending on the liquid flow times) ASTM D 445, supplied by the Industrial Research Glassware Ltd., New Jersey. An electronic stopwatch with a precision of ±0.01 s was used for flow time measurements. Triplicate measurements of flow times were reproducible within ±0.02%. The kinematic viscosity, ν, is given by $\nu \equiv \eta/\rho = At - B/t$, where η is the absolute viscosity, A and B are the viscometric constants, and t is the efflux time. The term B/t is the kinetic energy correction which may usually be neglected if the properly sized viscometer is used. In this case, the viscosity data can be readily obtained from the measurements of efflux times. The coefficients A for several viscometers were provided by the manufacturer at different temperatures, and these values were checked at room temperature by measurement of the viscosity of pure water. Absolute viscosities, η (mPa s), were then calculated by using the relation $\eta = \nu\rho$. The viscosities are accurate to ±0.001 mPa s, and the viscosities of pure liquids are of acceptable accuracy as evidenced by a good agreement of our data with the literature (*11*).

Refractive indices for the sodium D line were measured with a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) with an error of less than 0.0001 unit. However, these data were approximated to four places (see Table II). Water was circulated into the instrument through the thermostatically controlled bath. The refractometer was calibrated by using the glass test piece of known refractive index supplied with the instrument.

The speeds of sound were measured by using a variable-path single-crystal interferometer (Mittal Enterprises, New Delhi, model M-84). A crystal-controlled high-frequency generator was used to excite the transducer at a frequency of 1 MHz. The frequency was measured with an accuracy of 1 in 10^6 by using a digital frequency meter. The current variations across the transducer were observed on a microammeter. The interferometer cell was filled with the test liquid and was connected to the output terminal of the high-frequency generator through a shielded cable. Water was then circulated around the measuring cell from a thermostat maintained at the desired temperature. The other experimental details were given earlier (*1, 12*). The speed of sound data are accurate to ±2 m s^{-1}. The isentropic compressibilities were calculated as $\beta = 1/u^2\rho$.

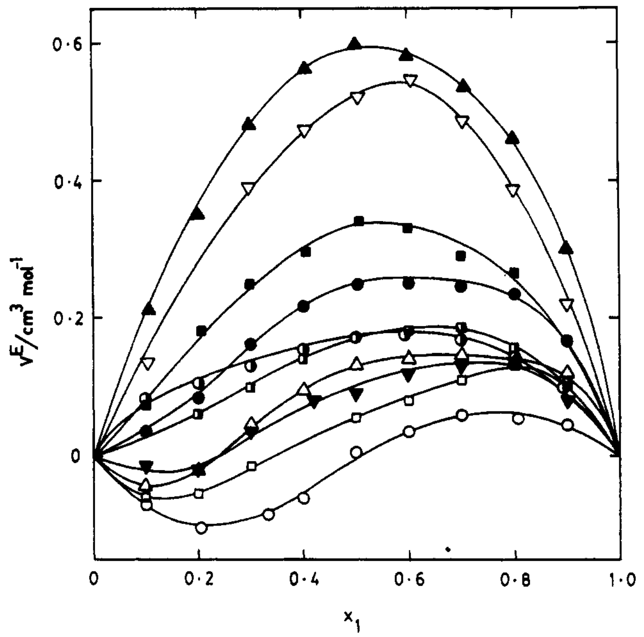

Figure 1. Dependence of excess molar volume on mole fraction at 298.15 K for mixtures of bromoform with (○) 1-butanol, (□) 2-methyl-1-propanol, (▼) 3-methyl-1-butanol, (△) 1-pentanol, (◧) 2-methoxyethanol, (◑) 2-chloroethanol, (●) 1-hexanol, (■) 1-heptanol, (▽) 1-nonanol, and (▲) 2-octanol.

Results and Discussion

The results of excess molar volumes, V^E, presented at 298.15 K in Figure 1 have been calculated as

$$V^E = V_m - V_1x_1 - V_2x_2 \qquad (1)$$

where V_m stands for the molar volume of the mixture, V_1 and V_2 refer to the molar volumes of the two components forming the mixture, and x_1 and x_2 are the mole fractions of components, 1 and 2 respectively. It is observed that the values of V^E for the binary mixtures of bromoform with 2-octanol, 1-nonanol, 1-heptanol, 1-hexanol, 2-chloroethanol, or 2-methoxyethanol are positive over the entire mole fraction range. Alcohols are strongly self-associated through hydrogen bonding, but bromoform does not exhibit this property because it has no hydrogen atom having that ability. However, there is a possibility that a BF molecule interacts with another BF molecule through dipole–dipole interactions. At any rate, the mixing of BF with the above-mentioned alcohols results in breaking of the hydrogen bonds among alcohol molecules, and that of dipole–dipole interactions of the two BF molecules results in an increase in volume, giving positive V^E.

For mixtures of bromoform with 1-pentanol, 3-methyl-1-butanol, 2-methyl-1-propanol, or 1-butanol, negative V^E values are observed in the BF-poor region (i.e., x_1 up to 0.4) while positive V^E are observed at higher concentrations of bromoform in the mixture. Thus, sigmoidal shapes are observed for these mixtures. The only available data of V^E on mixtures of bromoform with methanol, ethanol, or 1-propanol measured

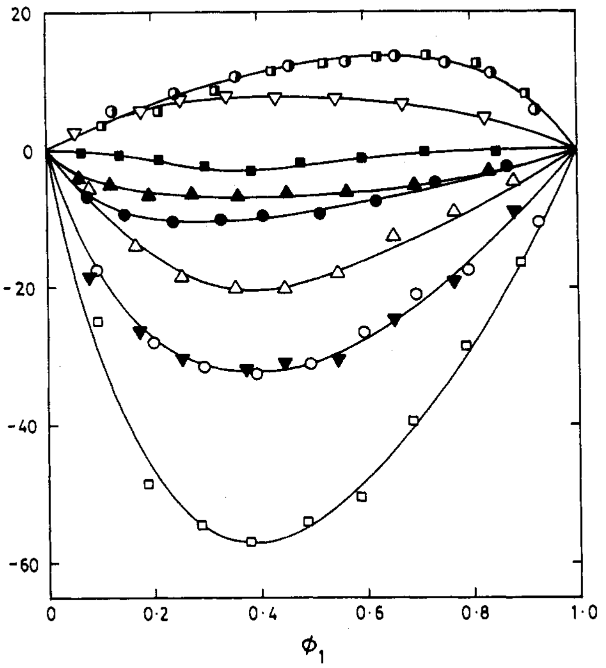

Figure 2. Dependence of excess isentropic compressibility on volume fraction at 298.15 K for the binary mixtures of bromoform with alcohols given in Figure 1.

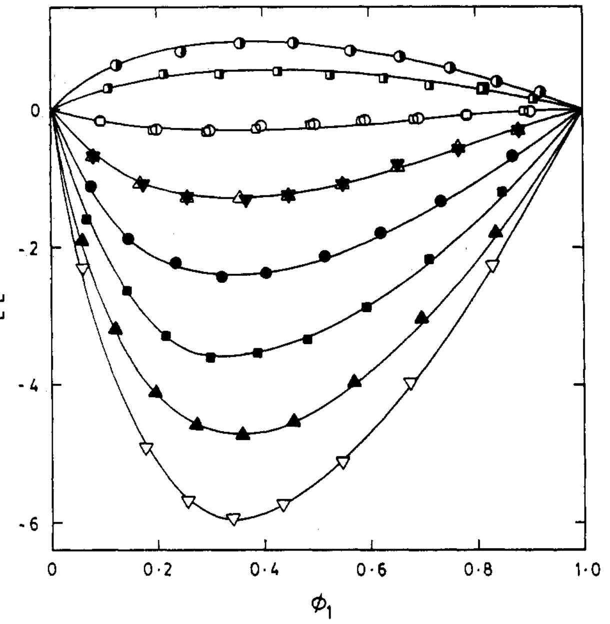

Figure 3. Dependence of Lorentz–Lorenz excess molar refraction on volume fraction at 298.15 K for the binary mixtures of bromoform with alcohols given in Figure 1.

at 303.15 K by Singh et al. (*13*) can be compared with our data. An incipient inversion was also observed for BF + ethanol or + 1-propanol mixtures (*13*). The observed V^E data for the present mixtures may be explained if it is assumed that (i) alcohols have a three-dimensional hydrogen-bonded network and the addition of a nearly globular molecule such as BF causes a rupture of some of these bonds, (ii) the alcohol chain fragments might interact with bromine atoms of BF due to specific interactions, and (iii) steric repulsion exists between the alkyl chain of the alcohol and the bromine atom of BF. The observed V^E would then be the cumulative sum of the contributions of these factors. Factors i and iii produce an expansion in volume, whereas factor ii results in a contraction. Thus, for the mixtures showing sigmoidal behavior, depending upon the values of x_1, these factors make appreciable contributions to the volume, so that V^E is either positive or negative. Furthermore, for the same BF molecule, since steric repulsion due to factor iii mentioned above would increase in the order 1-pentanol > 3-methyl-1-butanol > 2-methyl-1-propanol > 1-butanol, V^E for 1-pentanol should be more positive than that for 3-methyl-1-butanol, 2-methyl-1-propanol, or 1-butanol at higher values of x_1. The present V^E data support this conjecture.

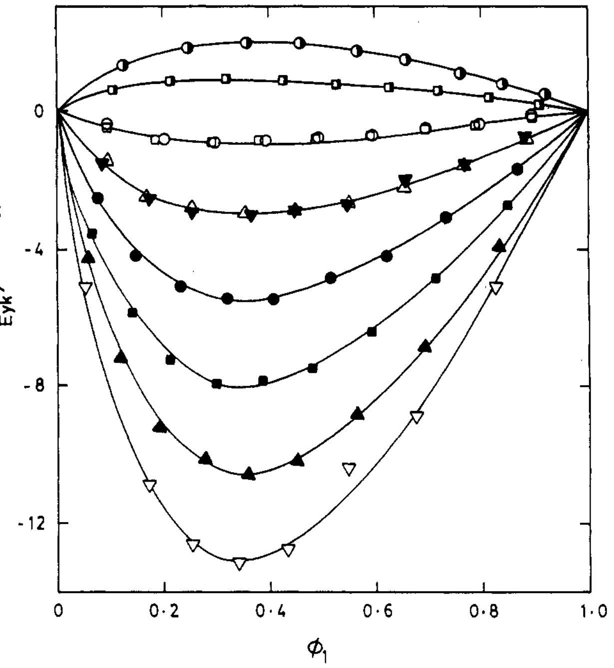

Figure 4. Dependence of Eykman excess molar refraction on volume fraction at 298.15 K for the binary mixtures of bromoform with alcohols given in Figure 1.

While we do not have extensive literature data to compare the sigmoidal behavior of the present mixtures, there are other systems wherein such a behavior was prevalent. For instance, in a study by Choudary et al. (*14*) on excess volumes of 1,1,2,2-tetrachloroethane with normal alcohols (C_3–C_8) at 303.15 K, it was found that V^E varies with x_1 sigmoidally from negative to positive values. Their results have been explained in terms of two opposing contributions: (i) an expansion in volume due to depolymerization of alcohol aggregates and (ii) a contraction in volume due to interstitial accommodation of chloroalkane in the aggregate of alcohols and weak hydrogen bond interactions between unlike molecules. In accordance with these studies, our experimental results suggest that the above-mentioned two opposing contributions balance each other to varying degrees over the composition scale studied. Furthermore, the depolymerization effects become dominant with an increase in the chain length of alcohols.

The effect of temperature on V^E for the binary mixtures of this study shows a regular trend; i.e., it increases with a rise in temperature for all the mixtures except BF + 2-chloroethanol for which the effect is not so systematic. Such effects can also be seen in the work of Garcia et al. (*15*).

Excess isentropic compressibilities, β^E, have been calculated (*16, 17*) from the isentropic compressibility data of mixtures and those of the pure components by using

$$\beta^E = \beta^{mix} - \beta_1\phi_1 - \beta_2\phi_2 \qquad (2)$$

where ϕ_i is the volume fraction of the ith component of the mixture and is defined as

$$\phi_i = x_iV_i/\sum_{i=1}^{2} x_iV_i \qquad (3)$$

Table III. Estimated Parameters of Excess Quantities for Binary Mixtures

quantity	T/K	a_0	a_1	a_2	a_3	σ
Bromoform (1) + 1-Butanol (2)						
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	-0.019	-0.838	0.048	-0.509	0.012
	303.15	0.093	-0.807	-0.037	-0.759	0.014
	308.15	0.188	-0.892	-0.012	-0.580	0.008
$\beta^E/\mathrm{TPa^{-1}}$	298.15	-123.06	-68.54	20.97	-93.58	0.840
$R^E{}_{L-L}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-0.974	-0.879	-0.326	-0.462	0.019
	303.15	-0.923	-0.992	0.107	-0.651	0.016
	308.15	-0.851	-1.061	-0.035	-0.163	0.016
$E^E{}_{Eyk}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-3.245	-1.859	-0.789	-0.891	0.045
	303.15	-3.122	-2.144	0.297	-1.373	0.039
	308.15	-2.945	-2.313	-0.082	-0.161	0.038
$\Delta\eta/(\mathrm{mPa\ s})$	298.15	-0.884	0.578	0.894	1.535	0.006
	303.15	-0.789	0.450	0.880	1.466	0.007
	308.15	-0.664	0.441	0.643	1.288	0.006
Bromoform (1) + 2-Methyl-1-propanol (2)						
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	0.341	-0.051	-2.359	-0.828	0.044
	303.15	0.499	-0.030	-2.359	-0.597	0.048
	308.15	0.724	0.001	-2.436	-1.079	0.051
$\beta^E/\mathrm{TPa^{-1}}$	298.15	-223.74	-98.78	7.870	-56.25	2.919
$R^E{}_{L-L}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-0.970	-0.722	-0.911	-1.200	0.017
	303.15	-0.938	-0.710	-1.059	-0.990	0.013
	308.15	-0.887	-0.871	-0.547	-0.774	0.011
$R^E{}_{Eyk}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-3.233	-1.509	-2.001	-2.682	0.039
	303.15	-3.158	-1.484	-2.361	-2.164	0.030
	308.15	-3.028	-1.886	-1.106	-1.655	0.026
$\Delta\eta/(\mathrm{mPa\ s})$	298.15	-2.357	-0.627	0.191	1.668	0.019
	303.15	-1.896	-0.410	0.246	1.442	0.012
	308.15	-1.543	-0.265	0.450	1.514	0.012
Bromoform (1) + 1-Pentanol (2)						
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	0.483	-0.422	-1.102	-0.379	0.009
	303.15	0.635	-0.457	-0.929	0.110	0.009
	308.15	0.775	-0.416	-0.955	0.377	0.010
$\beta^E/\mathrm{TPa^{-1}}$	298.15	-76.13	-62.28	52.61	31.72	0.915
$R^E{}_{L-L}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-4.807	-2.710	-1.302	-3.044	0.022
	303.15	-4.860	-3.041	-0.951	-3.396	0.024
	308.15	-4.781	-2.929	-1.088	-3.722	0.064
$R^E{}_{Eyk}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-11.427	-5.816	-2.861	-6.616	0.048
	303.15	-11.554	-6.615	-1.985	-7.482	0.054
	308.15	-11.354	-6.340	-2.317	-8.293	0.155
$\Delta\eta/(\mathrm{mPa\ s})$	298.15	-1.358	0.734	1.235	1.721	0.007
	303.15	-1.119	0.576	1.045	1.739	0.010
	308.15	-0.966	0.548	0.931	1.424	0.007
Bromoform (1) + 3-Methyl-1-butanol (2)						
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	0.371	-0.577	-0.250	0.078	0.014
	303.15	0.452	-0.552	-0.445	0.030	0.009
	308.15	0.595	-0.550	-0.164	0.326	0.012
$\beta^E/\mathrm{TPa^{-1}}$	298.15	-124.17	-41.04	-70.48	-87.36	1.043
$R^E{}_{L-L}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-4.796	-3.328	-0.847	-3.148	0.032
	303.15	-4.785	-3.301	-0.755	-2.908	0.036
	308.15	-4.822	-3.347	-0.619	-2.359	0.043
$R^E{}_{Eyk}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-11.367	-7.322	-1.800	-6.762	0.077
	303.15	-11.339	-7.248	-1.587	-6.183	0.087
	308.15	-11.423	-7.336	-1.336	-4.860	0.100
$\Delta\eta/(\mathrm{mPa\ s})$	298.15	-1.966	0.449	1.060	1.547	0.017
	303.15	-1.593	0.205	0.854	1.864	0.019
	308.15	-1.311	0.261	0.678	1.672	0.008
Bromoform (1) + 1-Hexanol (2)						
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	0.958	-0.318	-1.045	0.362	0.011
	303.15	1.066	-0.332	-1.124	0.387	0.007
	308.15	1.123	-0.468	-0.749	0.464	0.007
$\beta^E/\mathrm{TPa^{-1}}$	298.15	-37.40	-22.98	-28.48	-44.69	0.338
$R^E{}_{L-L}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-9.025	-5.253	-1.753	-5.802	0.037
	303.15	-9.076	-5.234	-2.245	-5.739	0.038
	308.15	-9.050	-5.481	-1.222	-5.435	0.043
$R^E{}_{Eyk}/(\mathrm{cm^3\ mol^{-1}})$	298.15	-20.558	-11.434	-3.831	-12.678	0.082
	303.15	-20.676	-11.679	-5.041	-12.480	0.083
	308.15	-20.602	-11.976	-2.564	-11.792	0.095
$\Delta\eta/(\mathrm{mPa\ s})$	298.15	-1.906	0.666	1.414	2.275	0.013
	303.15	-1.529	0.633	1.067	1.753	0.013
	308.15	-1.251	0.510	1.062	1.911	0.016
Bromoform (1) + 1-Heptanol (2)						
$V^E/(\mathrm{cm^3\ mol^{-1}})$	298.15	1.384	-0.395	-0.348	-0.248	0.054
	303.15	2.326	-0.986	-2.892	3.192	0.049
	308.15	3.316	-1.560	-5.304	6.747	0.055
$\beta^E/\mathrm{TPa^{-1}}$	298.15	-6.701	-17.97	31.79	-0.735	0.559

Table III. (Continued)

quantity	T/K	a_0	a_1	a_2	a_3	σ
Bromoform (1) + 1-Heptanol (2)						
$R^{E}_{\mathrm{L-L}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	−13.437	−7.607	−2.480	−9.145	0.067
	303.15	−13.424	−7.656	−2.605	−9.055	0.052
	308.15	−13.419	−7.720	−2.267	−8.228	0.058
$R^{E}_{\mathrm{Eyk}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	−30.167	−16.592	−5.496	−20.088	0.149
	303.15	−30.131	−16.710	−5.797	−19.838	−0.113
	308.15	−30.117	−16.855	−5.037	−17.797	0.129
$\Delta\eta/(\mathrm{mPa\,s})$	298.15	−2.843	0.371	1.251	2.481	0.036
	303.15	−2.188	0.437	1.123	2.055	0.025
	308.15	−1.700	0.467	0.949	1.941	0.027
Bromoform (1) + 2-Octanol (2)						
$V^{E}/(\mathrm{cm^3\,mol^{-1}})$	298.15	2.391	−0.295	−0.809	1.194	0.017
	303.15	2.476	−0.705	−0.778	1.265	0.040
	308.15	2.578	−0.425	−0.492	−0.841	0.010
$\beta^{E}/\mathrm{TPa^{-1}}$	298.15	−25.58	2.750	−42.98	−26.50	0.721
$R^{E}_{\mathrm{L-L}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	−17.736	−10.082	−2.524	−12.370	0.059
	303.15	−17.740	−10.458	−1.491	−11.713	0.062
	308.15	−17.852	−10.309	−1.859	−11.898	0.076
$R^{E}_{\mathrm{Eyk}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	−39.526	−21.940	−5.670	−27.212	0.128
	303.15	−39.533	−22.814	−3.225	−25.574	0.136
	308.15	−39.783	−22.486	−4.020	−26.076	0.170
$\Delta\eta/(\mathrm{mPa\,s})$	298.15	−3.856	−0.452	0.610	1.578	0.017
	303.15	−2.771	0.014	0.740	1.265	0.008
	308.15	−1.981	0.344	0.868	1.210	0.005
Bromoform (1) + 1-Nonanol (2)						
$V^{E}/(\mathrm{cm^3\,mol^{-1}})$	298.15	2.070	−0.632	−0.012	−0.268	0.018
	303.15	2.145	−0.822	0.237	−0.135	0.009
	308.15	2.216	−0.900	0.707	0.522	0.007
$\beta^{E}/\mathrm{TPa^{-1}}$	298.15	29.56	10.47	−8.428	32.70	0.601
$R^{E}_{\mathrm{L-L}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	−22.067	−12.870	−2.307	−15.426	0.083
	303.15	−22.050	−13.017	−1.333	−14.971	0.094
	308.15	−22.195	−12.962	−1.777	−14.792	0.009
$R^{E}_{\mathrm{Eyk}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	−48.984	−29.185	−5.176	−33.799	0.179
	303.15	−48.932	−28.537	−2.778	−32.752	0.206
	308.15	−49.269	−28.372	−3.908	−32.313	0.219
$\Delta\eta/(\mathrm{mPa\,s})$	298.15	−4.704	−0.273	−0.588	1.613	0.080
	303.15	−3.464	−0.037	−0.661	1.155	0.075
	308.15	−2.573	−0.021	−0.978	0.804	0.061
Bromoform (1) + 2-Chloroethanol (2)						
$V^{E}/(\mathrm{cm^3\,mol^{-1}})$	298.15	0.685	−0.252	0.207	0.708	0.004
	303.15	0.669	−0.316	−0.265	0.305	0.007
	308.15	0.742	−0.343	−0.233	−0.322	0.003
$\beta^{E}/\mathrm{TPa^{-1}}$	298.15	51.04	−27.75	19.76	50.98	0.845
$R^{E}_{\mathrm{L-L}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	3.770	1.276	0.960	2.249	0.010
	303.15	3.735	1.158	0.862	1.746	0.010
	308.15	3.706	1.134	0.744	1.730	0.009
$R^{E}_{\mathrm{Eyk}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	7.413	2.826	2.204	5.140	0.023
	303.15	7.339	2.534	2.029	3.922	0.022
	308.15	7.268	2.484	1.725	3.894	0.022
$\Delta\eta/(\mathrm{mPa\,s})$	298.15	−0.574	0.630	0.379	0.568	0.026
	303.15	−0.498	0.511	0.248	0.473	0.023
	308.15	−0.361	0.469	0.370	0.656	0.018
Bromoform (1) + 2-Methoxyethanol (2)						
$V^{E}/(\mathrm{cm^3\,mol^{-1}})$	298.15	0.671	−0.502	0.148	0.067	0.003
	303.15	0.724	−0.698	0.716	0.664	0.010
	308.15	0.790	−0.734	0.747	0.814	0.012
$\beta^{E}/\mathrm{TPa^{-1}}$	298.15	49.94	−33.76	−9.359	40.50	0.368
$R^{E}_{\mathrm{L-L}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	2.110	0.664	0.546	1.279	0.025
	303.15	2.115	0.648	0.382	1.407	0.030
	308.15	2.141	0.640	0.467	1.510	0.025
$R^{E}_{\mathrm{Eyk}}/(\mathrm{cm^3\,mol^{-1}})$	298.15	3.527	1.496	1.239	2.883	0.059
	303.15	3.542	1.469	0.804	3.180	0.072
	308.15	3.608	1.454	0.997	3.416	0.061
$\Delta\eta/(\mathrm{mPa\,s})$	298.15	1.776	1.330	−0.610	−0.284	0.004
	303.15	1.444	1.134	−0.491	−0.267	0.004
	308.15	1.177	0.951	−0.336	−0.115	0.004

The variation of the excess isentropic compressibility with the volume fraction of BF at 298.15 K is shown in Figure 2. It is observed that, for mixtures of BF with 2-methoxyethanol or 2-chloroethanol, the values of β^{E} change almost identically over the whole range of mixture compositions. Therefore, their dependencies are shown by a single curve. In the case of BF + 1-nonanol mixture, β^{E} is positive. However, for mixtures of BF with 1-heptanol, 2-octanol, or 1-hexanol, β^{E} values are small and negative without sharp minima. On the other hand, for mixtures of BF with 1-pentanol, 3-methyl-1-butanol, or 2-methyl-1-propanol, β^{E} values are negative; the largest negative β^{E} is shown by the BF + 2-methyl-1-propanol mixture, suggesting a nonideal behavior due to structural differences between the mixing components. These results also support the explanations advanced before for excess molar volumes.

Table IV. Standard Error, σ, Values for the Viscosity Equations

	standard error, $\sigma \times 10^2$			
T/K	McAllister	Auslaender	Heric	polynomial
	BF (1) + 1-Butanol (2)			
298.15	2.71	4.30	1.47	1.86
303.15	3.14	4.41	1.66	1.93
308.15	2.34	4.24	1.39	4.24
	BF (1) + 2-Methyl-1-propanol (2)			
298.15	2.75	3.33	2.20	1.45
303.15	2.24	2.70	1.64	0.95
308.15	2.36	2.89	1.50	1.16
	BF (1) + 1-Pentanol (2)			
298.15	2.93	3.43	1.38	2.51
303.15	3.03	3.75	0.67	2.67
308.15	2.63	3.39	1.29	2.17
	BF (1) + 3-Methyl-1-butanol (2)			
298.15	2.80	3.30	1.60	2.28
303.15	3.23	3.73	2.14	2.79
308.15	2.55	3.11	1.63	2.09
	BF (1) + 1-Hexanol (2)			
298.15	3.48	3.74	2.05	3.78
303.15	2.85	3.36	1.81	3.03
308.15	3.39	3.67	2.17	3.51
	BF (1) + 1-Heptanol (2)			
298.15	4.28	5.00	3.73	5.09
303.15	3.41	3.85	2.67	4.03
308.15	3.49	4.09	2.89	4.08
	BF (1) + 2-Octanol (2)			
298.15	2.11	2.77	1.72	2.25
303.15	1.75	1.96	0.99	1.91
308.15	1.80	1.85	0.79	1.99
	BF (1) + 1-Nonanol (2)			
298.15	6.08	7.67	6.63	6.24
303.15	5.63	6.94	6.11	5.71
308.15	4.88	5.80	5.11	4.56
	BF (1) + 2-Chloroethanol (2)			
298.15	1.42	2.68	1.47	1.48
303.15	1.23	2.38	1.30	1.31
308.15	1.18	2.24	1.09	1.09
	BF (1) + 2-Methoxyethanol (2)			
298.15	0.80	2.11	0.25	0.43
303.15	0.65	1.94	0.24	0.42
308.15	0.40	9.60	0.31	0.29

The excess molar refraction, R^E, which represents the electronic perturbation due to orbital mixing of the molecules is a quantity of interest which has been studied extensively in the literature (*18–23*). This quantity can be calculated by using any of the refractive index mixing rules. Thus,

$$R^E = R_m - R_1\phi_1 - R_2\phi_2 \qquad (4)$$

where R_m is the molar refraction of the binary mixture calculated from refractive index mixing rules. The quantities R_1 and R_2 refer to molar refractions of pure components. Of the many refractive index mixing rules, the Lorentz–Lorenz (L–L) and Eykman (Eyk) relations have been widely used (*24*) to calculate $R^E{}_{L-L}$ and $R^E{}_{Eyk}$ from the refractive indices and densities of mixtures. Their dependencies on ϕ_1 are shown in Figures 3 and 4, respectively. It is found that the trends in the variation of the excess molar refraction for both L–L and Eyk mixing rules are the same, but in general, the magnitudes of $R^E{}_{L-L}$ are smaller than those of $R^E{}_{Eyk}$. From both the mixing rules, we find that R^E data are positive for mixtures of BF with 2-chloroethanol or 2-methoxyethanol while, for the remaining mixtures, $R^E{}_{L-L}$ and $R^E{}_{Eyk}$ are negative. However, for mixtures of BF with 1-butanol or 2-methyl-1-propanol, the R^E data are almost identical; similarly, it is true of BF + 3-methyl-1-butanol or + 1-pentanol mixtures. Hence, the R^E dependencies for these mixtures are shown by a single curve representing the common behavior for both the mixtures. A temperature dependence of these properties is not extremely systematic within the range of experimental temperatures used in this research.

Each set of the derived quantities Y^E ($= V^E$, β^E, and R^E) discussed above has been fitted to the Redlich–Kister (*25*) polynomial relation of the type

$$Y^E = c_1c_2\sum_{i=0}^{3} a_i(c_2 - c_1)^i \qquad (5)$$

to estimate the regression coefficients, a_i, and standard errors, σ. Here, c_i represent the values of mole or volume fractions. The β^E and R^E results are fitted by using the volume fraction differences while those of V^E are fitted by using mole fraction differences. These values are summarized in Table III. A third-order fit in almost all cases reproduced insignificant differences between the calculated and observed excess quantities. The back-calculated values of V^E, β^E, and R^E are used as guidelines to draw the smooth curves given in Figures 1–4. Different symbols in all these figures represent the observed points.

The kinematic viscosities of the binary mixtures have been used to test the validity of the empirical viscosity relations suggested by McAllister (*6*), Heric (*7*), and Auslaender (*8*). Quite frequently, a polynomial relation as given by eq 6 with

$$\nu = x_1\nu_1 + x_2\nu_2 + x_1x_2[a + b(x_2 - x_1) + c(x_2 - x_1)^2] \qquad (6)$$

three adjustable parameters was also used (*9*). The parameters a, b, and c of these equations and those of the others have been determined by the method of least squares by using the binary viscosity data. The standard errors, σ, between the experimental data and the calculated values are given in Table IV. Such correlations were also attempted earlier in the literature (*9, 26–29*).

Analysis of the viscosity data suggests that it is difficult to judge the relative validity of one equation over the other. However, for a better comparison, the kinematic viscosities were calculated by converting the logarithmic terms of the McAllister and Heric equations. When these values are compared on a relative basis, it is found that for the majority of mixtures, the Heric equation gives the least deviation and thus predicts the binary viscosities much better (i.e., closer to the experimental viscosities) than the other relations. However, the Auslaender relation gives the largest standard errors among the equations tested in this work. For a few mixtures, the McAllister relation also gives the best prediction. In keeping with McAllister's analysis, there is a general downward trend in errors with a decrease in the molecular size ratio. Also, the values of the parameters decrease with a rise in temperature, consistent with the viscosity–temperature behavior of liquids, a fact that was also observed in the literature (*27*).

Acknowledgment

We thank Mr. R. S. Khinnavar for his help on this project.

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Received for review August 5, 1992. Revised November 23, 1992. Accepted December 18, 1992. We thank the University Grants Commission, New Delhi, for major research support, Grant No. F.12-55/88(SR-III).