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Ternary Liquid Mixture Viscosities and Densities

I-Chien Wei and Richard L. Rowley*

Department of Chemical Engineering, Rice University, Houston, Texas 77251

Liquid mixture viscosities and densities have been measured at 298.15 K and ambient pressure for 20 ternary systems. Twelve ternary compositions, encompassing the entire composition range, have been chosen for each system in an effort to test a newly proposed predictive equation based on local compositions. Viscosities calculated by using the local composition model agreed with the experimental data within an average absolute deviation of 6.4%. No adjustable parameters were used and only binary interactions in the form of NRTL constants were input. The results of these studies indicate that the local composition model predictions are generally as good for multicomponent systems as they are for the corresponding binaries.

Introduction

Many empirical or semiempirical equations can correlate binary mixture shear viscosity data using multiple adjustable parameters. In addition to the obvious disadvantage of requiring mixture viscosity data for parameter estimation, correlations may not be immediately extendable to multicomponent mixtures or they may require more parameters (such as three- and four-body interaction terms) for mixtures containing more than two components.

An equation based entirely on binary interaction parameters which are themselves obtained from equilibrium thermodynamic data has recently been reported (*1*) and tested for 24 binary systems (*2*). The model is similar to a local composition model first applied to liquid mixture thermal conductivity (*3*, *4*). To test its efficacy in multicomponent systems, shear viscosity measurements were made on 20 ternary systems. These systems were chosen to represent different types of interactions, including polar-polar, polar-nonpolar, and nonpolar-nonpolar. The experimental ternary mixture viscosity data reported in this work were felt to be a good basis for testing a model based only on binary interactions. To our knowledge, viscosity data for these ternary systems have not been previously reported.

Experimental Section

Pure components were used directly without further purification but they were purchased in their highest commercial purity. Pure-component densities and kinematic viscosities were measured and compared to average literature values to assure no significant effects due to impurities. Pure-component properties are listed and compared in Table I. Generally the measured pure-component property fell within the range of values obtained from the literature. Mixtures were gravimetrically prepared to the nearest 0.1 mg. Sample preparation flasks were stoppered to prevent evaporative composition changes; additions were made through a septum by displacement of an equal volume of vapor (for the added liquid) into a syringe.

Densities were measured to ±0.0001 g/cm^3 with a previously calibrated 4$^1/_2$ digit, Anton Paar, Model DMA45, calculating digital density meter. Air and distilled, deionized water were used as reference fluids to calibrate the densitometer. The density cell was water jacketed and maintained isothermal to ±0.002 K by circulating water from a Tamson 45-L visibility bath. The viscosity apparatus was submerged in this same bath. Temperature monitoring was done with a Hewlett-Packard digital quartz thermometer of ±0.0001 K resolution and ±0.04 K accuracy.

Kinematic viscosities were measured with an Ubbelohde capillary viscometer and a Schott AVS-300 automatic viscosity apparatus consisting of a support stand submerged in the viscosity bath and a control unit. The stand contains two optical sensors which initiate and stop a quartz digital timer as the meniscus passes through the respective light barriers. The controller has a time resolution of ±0.01 s. The capillary bore size was selected to provide an average residence time in the measuring portion of the capillary tube on the order of 500 s. Kinematic viscosities were computed from

$$\nu = k(t - \theta) \tag{1}$$

where k is a well-known constant for each capillary, dependent upon the bore size, and θ is the Hagenbach–Couette error correction supplied with each calibrated capillary. Experiments were generally performed in six replicates for each composition. Results of the first run for each new composition were disregarded and treated as a purge of the capillary tube. The remaining five runs were averaged to yield the reported value. All measurements were made at 298.15 ± 0.01 K. The capillary tube was thoroughly cleaned between mixtures and flushed several times with the new mixture before filling.

Results

Measured mixture viscosities and densities at 298.15 K and ambient pressure are shown in Table II. The average standard deviation, determined from replicate runs at each composition, was 0.2%. Table II results have an uncertainty of 0.4% at the 95% confidence level.

A previously reported (*1*) local composition model in terms of volume fractions, ϕ_i, for liquid mixture shear viscosity can be written for an n-component system as

$$\eta = \exp(\xi)/V \tag{2}$$

$$\xi = \sum_i \phi_i \xi_i{}^0 + \sum_i \phi_i [\sum_j \phi_j G_{ji} (\xi_{ji} - \xi_i{}^0)/(\sum_l \phi_l G_{li})] - \sigma H^E/RT \tag{3}$$

$$\xi_{ji} = \xi_{ij} = \sum_i (\phi_i{}^* \phi_{ii}{}^* \xi_i{}^0)/\sum_j (\phi_j{}^* \phi_{jj}{}^*) \tag{4}$$

where the summations are over all n components and for the i, j ($i \neq j$) pair of interactions

$$G_{ji} = \exp(-\alpha A_{ji}/RT) \tag{5}$$

$$\phi_j{}^* = (1 + \Gamma_{ji})^{-1} \qquad \phi_{ii}{}^* = (1 + \phi_j{}^* G_{ji}/\phi_i{}^*)^{-1} \tag{6}$$

$$\Gamma_{ji} = (v_i/v_j)(G_{ij}/G_{ji})^{1/2} \exp[(\xi_i{}^0 - \xi_j{}^0)/2] \tag{7}$$

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* Address correspondence to this author at the Department of Chemical Engineering, Brigham Young University, Provo, UT 84602.

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Table I. Densities and Kinematic Viscosities of Pure Components at 298.15 K

compd	ρ, g/mL		ν, cSt	
	exptl	lit.	exptl[a]	lit.
acetone	0.7844	0.784 (*6, 9*)	0.3857	0.386 (*9, 21*)
carbon tetrachloride	1.5839	1.584 (*6, 8, 9*)	0.5675	0.567 (*8, 20, 21*)
chloroform	1.4718	1.477 (*6, 9, 11–13*)	0.3623	0.357 (*11, 19, 21*)
cyclohexane	0.7736	0.774 (*6, 9, 16, 17*)	1.1512	1.153 (*21*)
dimethyl sulfoxide	1.0951	1.096 (*6, 7, 19*)	1.8028	1.844 (*7, 21*)
ethanol	0.7852	0.785 (*9, 10*)	1.3770	1.409 (*9, 18*)
hexane	0.6562	0.655 (*8, 11, 14*)	0.4470	0.451 (*8, 9, 11, 14*)
2-propanol	0.7804	0.781 (*9, 15, 16*)	2.6086[b]	
methanol	0.7872	0.787 (*6, 9, 10*)	0.7020	0.694 (*9, 10, 18, 21*)
methyl acetate	0.9268	0.928 (*9*)	0.3881	0.392 (*9*)
propanol	0.8000	0.800 (*22–24*)	2.4272	2.438 (*22–24*)
triethylamine	0.7254	0.725 (*9, 19*)	0.4908	0.497 (*9, 18*)

[a] Standard deviation = 0.0001. [b] Standard deviation was 0.0020.

Table II. Ternary Mixture Kinematic Viscosities and Densities Measured at 298.15 K and Ambient Pressure

ϕ_1	ϕ_2	ρ, g/mL	ν, cSt	ϕ_1	ϕ_2	ρ, g/mL	ν, cSt
Ethanol (1)–Acetone (2)–Cyclohexane (3)							
0.1968	0.2165	0.7708	0.7249	0.5756	0.2383	0.7797	0.7726
0.2169	0.3887	0.7730	0.5861	0.2974	0.3028	0.7736	0.6538
0.2516	0.4986	0.7765	0.5305	0.2894	0.4015	0.7753	0.5836
0.3697	0.2333	0.7741	0.7258	0.1114	0.1128	0.7701	0.8617
0.3972	0.2973	0.7761	0.6757	0.1027	0.7947	0.7805	0.4251
0.3649	0.4047	0.7777	0.5954	0.7468	0.1521	0.7831	0.9538
Acetone (1)–Hexane (2)–Ethanol (3)							
0.2405	0.1755	0.7607	0.6978	0.5861	0.2343	0.7510	0.4323
0.1785	0.3907	0.7317	0.6219	0.3102	0.2959	0.7440	0.5589
0.2025	0.6024	0.7027	0.4833	0.3397	0.4007	0.7292	0.4890
0.3992	0.2353	0.7533	0.5397	0.1323	0.1230	0.7684	0.9079
0.4083	0.2968	0.7433	0.4931	0.1043	0.8235	0.6768	0.4454
0.4046	0.4125	0.7268	0.4487	0.8109	0.0798	0.7717	0.4053
Acetone (1)–Ethanol (2)–Methanol (3)							
0.2208	0.2328	0.7895	0.6538	0.6116	0.1733	0.7886	0.4703
0.2109	0.3968	0.7884	0.7175	0.2811	0.2994	0.7891	0.6364
0.2289	0.5784	0.7873	0.7731	0.2871	0.4077	0.7883	0.6677
0.3190	0.3280	0.7889	0.6219	0.0913	0.1750	0.7899	0.5626
0.3792	0.3077	0.7889	0.5880	0.1075	0.7602	0.7868	0.9901
0.3977	0.3833	0.7880	0.6000	0.7582	0.1275	0.7892	0.4235
Acetone (1)–Hexane (2)–Cyclohexane (3)							
0.1943	0.1561	0.7503	0.6558	0.5598	0.2327	0.7443	0.4348
0.1954	0.3751	0.7249	0.5483	0.3204	0.2628	0.7379	0.5250
0.1847	0.5818	0.7011	0.4797	0.3665	0.4055	0.7220	0.4575
0.3768	0.2356	0.7412	0.5062	0.0942	0.0860	0.7583	0.8235
0.3685	0.2938	0.7346	0.4903	0.1162	0.7885	0.6787	0.4466
0.3989	0.4117	0.7220	0.4442	0.7974	0.0747	0.7689	0.4060
Hexane (1)–Cyclohexane (2)–Ethanol (3)							
0.1870	0.2202	0.7542	1.0335	0.5683	0.1972	0.7067	0.6510
0.2204	0.3720	0.7480	0.9369	0.3015	0.3021	0.7390	0.8782
0.2030	0.5853	0.7480	0.8648	0.3045	0.3672	0.7375	0.8420
0.4009	0.2038	0.7280	0.8180	0.0815	0.1197	0.7706	1.2179
0.3798	0.3124	0.7291	0.7861	0.1214	0.7928	0.7585	0.9408
0.3966	0.4003	0.7257	0.7252	0.7421	0.0906	0.6869	0.5624
Methanol (1)–Ethanol (2)–2-Propanol (3)							
0.2040	0.2244	0.7831	1.5912	0.5910	0.1980	0.7860	0.9780
0.2048	0.4159	0.7840	1.4244	0.3047	0.3205	0.7843	1.3035
0.1813	0.6086	0.7847	1.3252	0.2855	0.4090	0.7846	1.2774
0.3939	0.1992	0.7844	1.2369	0.0964	0.0664	0.7814	2.0395
0.3946	0.3152	0.7850	1.1657	0.1451	0.7359	0.7847	1.3115
0.3979	0.4110	0.7854	1.1171	0.7564	0.1355	0.7857	0.8331
Acetone (1)–Ethanol (2)–2-Propanol (3)							
0.2056	0.2027	0.7813	1.1197	0.6005	0.2174	0.7831	0.5369
0.2129	0.4030	0.7830	1.0205	0.2998	0.2853	0.7823	0.8706
0.2256	0.5601	0.7841	0.9368	0.2998	0.3911	0.7832	0.8420
0.3976	0.2045	0.7818	0.7296	0.0706	0.1065	0.7807	1.7338
0.3795	0.3267	0.7829	0.7355	0.1086	0.7869	0.7848	1.1360
0.3835	0.3964	0.7838	0.7145	0.8073	0.0982	0.7836	0.4351

Table II (Continued)

ϕ_1	ϕ_2	ρ, g/mL	ν, cSt	ϕ_1	ϕ_2	ρ, g/mL	ν, cSt
Methyl Acetate (1)–Chloroform (2)–Methanol (3)							
0.1896	0.2068	0.9576	0.5539	0.5835	0.1948	1.0017	0.4229
0.1826	0.4014	1.0876	0.5133	0.2972	0.3127	1.0427	0.4909
0.1966	0.5980	1.2239	0.4458	0.3110	0.3792	1.0880	0.4715
0.3890	0.2304	0.9994	0.4773	0.1245	0.1324	0.8965	0.6067
0.3765	0.2823	1.0325	0.4698	0.1102	0.7537	1.3179	0.4133
0.3991	0.3889	1.1113	0.4390	0.7537	0.1191	0.9738	0.3968
Chloroform (1)–Ethanol (2)–Methanol (3)							
0.2186	0.2143	0.9393	0.7433	0.5887	0.2205	1.1894	0.5685
0.1891	0.4110	0.9176	0.8479	0.2804	0.3270	0.9804	0.7731
0.1921	0.6082	0.9189	0.9682	0.2543	0.4201	0.9730	0.8154
0.4021	0.2161	1.0640	0.6795	0.7620	0.1157	1.3124	0.4462
0.4722	0.3126	1.1123	0.6659	0.1177	0.7698	0.8698	1.1151
0.4062	0.3884	1.0719	0.7281	0.0749	0.1200	0.8391	0.7244
Ethanol (1)–Cyclohexane (2)–2-Propanol (3)							
0.2422	0.2283	0.7772	1.6792	0.5917	0.1940	0.7789	1.4322
0.2197	0.3914	0.7747	1.4563	0.3163	0.3207	0.7759	1.4798
0.2237	0.5735	0.7728	1.2449	0.3085	0.3749	0.7751	1.4159
0.3913	0.2239	0.7777	1.5542	0.1231	0.1214	0.7789	2.0081
0.3618	0.3362	0.7759	1.4277	0.1541	0.7344	0.7719	1.1288
0.3988	0.3867	0.7752	1.3390	0.7632	0.1130	0.7812	1.4037
Methyl Acetate (1)–Cyclohexane (2)–Ethanol (3)							
0.2024	0.2042	0.8061	0.8064	0.5992	0.2079	0.8585	0.4775
0.2046	0.3929	0.8009	0.7503	0.2849	0.2951	0.8136	0.6774
0.1992	0.5897	0.7965	0.7185	0.3134	0.3868	0.8148	0.6292
0.3894	0.2044	0.8302	0.6034	0.1267	0.1324	0.7985	0.9605
0.4128	0.3080	0.8302	0.5614	0.1171	0.7549	0.7847	0.8224
0.4055	0.3878	0.8266	0.5564	0.7621	0.1131	0.8849	0.4249
Triethylamine (1)–Methanol (2)–Chloroform (3)							
0.1770	0.4159	1.0696	0.6688	0.3233	0.3072	1.0415	0.7203
0.1728	0.6006	0.9435	0.7254	0.2884	0.3920	1.0077	0.7353
0.3977	0.2162	1.0506	0.7114	0.2008	0.2097	1.1908	0.5834
0.4119	0.3116	0.9745	0.7619	0.1146	0.1389	1.3007	0.4858
0.3897	0.3940	0.9298	0.7790	0.1323	0.7527	0.8707	0.7237
0.5754	0.2265	0.9109	0.7398	0.6784	0.1634	0.8757	0.6933
Triethylamine (1)–Ethanol (2)–Propanol (3)							
0.2048	0.2005	0.7906	1.7340	0.5907	0.2130	0.7666	0.9225
0.1933	0.4113	0.7877	1.5641	0.3045	0.2992	0.7845	1.4299
0.1990	0.5859	0.7848	1.4151	0.3318	0.3870	0.7819	1.3143
0.4005	0.2090	0.7804	1.2914	0.1498	0.1179	0.7937	1.9244
0.3834	0.3036	0.7801	1.2650	0.1199	0.7579	0.7852	1.4193
0.3899	0.3901	0.7786	1.2016	0.7678	0.1436	0.7518	0.7027
Triethylamine (1)–Methanol (2)–Ethanol (3)							
0.1813	0.0913	0.7859	1.2385	0.3708	0.3186	0.7793	0.9300
0.2556	0.1987	0.7819	1.0880	0.3794	0.4157	0.7797	0.9166
0.1891	0.3764	0.7837	0.9884	0.7947	0.1031	0.7514	0.6408
0.1494	0.7679	0.7852	0.7845	0.6177	0.1809	0.7659	0.7890
0.2120	0.5795	0.7840	0.8610	0.3176	0.2757	0.7803	0.9926
0.3740	0.2170	0.7789	0.9817	0.2830	0.3657	0.7818	0.9551
Acetone (1)–Carbon Tetrachloride (2)–Cyclohexane (3)							
0.2059	0.1930	0.9333	0.6494	0.5782	0.2279	0.9619	0.4349
0.2052	0.3904	1.0869	0.5740	0.2976	0.3272	1.0368	0.5300
0.1972	0.5982	1.2574	0.5244	0.2863	0.4246	1.1151	0.5125
0.3784	0.1979	0.9314	0.5272	0.1005	0.0931	0.8516	0.8081
0.3776	0.3118	1.0244	0.4951	0.1055	0.7890	1.4067	0.5449
0.3882	0.3914	1.0929	0.4714	0.7019	0.1855	0.9296	0.4080
Carbon Tetrachloride (1)–Cyclohexane (2)–2-Propanol (3)							
0.1946	0.2291	0.9340	1.2776	0.5429	0.2296	1.2087	0.7264
0.1837	0.3990	0.9200	1.0980	0.2947	0.3358	1.0091	0.9496
0.2048	0.6100	0.9350	0.9053	0.3127	0.3796	1.0233	0.8907
0.3927	0.1994	1.0864	0.9258	0.0921	0.1037	0.8577	1.8183
0.3853	0.2868	1.0799	0.8636	0.0916	0.8179	0.8469	1.0031
0.3994	0.3797	1.0966	0.7888	0.8097	0.1338	1.4218	0.6193
Dimethyl Sulfoxide (1)–Chloroform (2)–Methanol (3)							
0.1331	0.1318	0.9288	0.7378	0.3907	0.2732	1.1005	0.8586
0.1851	0.2056	0.9904	0.7407	0.4327	0.3889	1.1915	0.9245
0.2145	0.3942	1.1316	0.7520	0.7462	0.1298	1.1119	1.3016
0.1229	0.7426	1.3383	0.5649	0.5974	0.1921	1.1106	1.0916
0.1804	0.6321	1.2830	0.6469	0.2846	0.3262	1.1056	0.7783
0.4133	0.1924	1.0656	0.8835	0.2813	0.3935	1.1499	0.7791

Table II (Continued)

ϕ_1	ϕ_2	ρ, g/mL	ν, cSt	ϕ_1	ϕ_2	ρ, g/mL	ν, cSt
			Dimethyl Sulfoxide (1)–Acetone (2)–Chloroform (3)				
0.1300	0.1497	1.3248	0.5593	0.4006	0.3124	1.1101	0.7715
0.2220	0.2259	1.2407	0.6539	0.3530	0.4305	1.0527	0.6896
0.2144	0.3868	1.1326	0.5977	0.7262	0.1551	1.0966	1.1958
0.0754	0.7836	0.9134	0.4327	0.6271	0.1905	1.1095	1.1609
0.2080	0.2693	0.9656	0.5340	0.3434	0.3774	1.1538	0.7543
0.3986	0.1819	1.1942	0.8369	0.2979	0.3827	1.1052	0.6999
			Dimethyl Sulfoxide (1)–Carbon Tetrachloride (2)–Methanol (3)				
0.0825	0.1227	0.9171	0.7125	0.3804	0.3202	1.1748	0.8821
0.2088	0.1919	1.0111	0.7470	0.3680	0.3700	1.2157	0.8937
0.1968	0.3852	1.1608	0.7440	0.7899	0.9072	1.1154	1.3815
0.1033	0.7911	1.4478	0.6780	0.5932	0.2009	1.1434	1.1084
0.1833	0.5983	1.3394	0.7441	0.3072	0.2855	1.1250	0.8170
0.3921	0.2119	1.0950	0.8709	0.2771	0.3983	1.2033	0.8387
			Dimethyl Sulfoxide (1)–Carbon Tetrachloride (2)–Chloroform (3)				
0.1193	0.1322	1.4412	0.5487	0.4056	0.2505	1.3517	1.0156
0.1846	0.2085	1.4256	0.6572	0.4065	0.3794	1.3641	1.0773
0.2112	0.4072	1.4345	0.7538	0.7508	0.1093	1.2050	1.4516
0.1036	0.7733	1.5205	0.6477	0.5733	0.1893	1.2779	1.2289
0.2117	0.5736	1.4644	0.7822	0.3128	0.2845	1.3819	0.8818
0.3896	0.2310	1.3547	1.0033	0.2868	0.3459	1.4055	0.8790

Table III. Average Absolute Deviation (AAD) of Experimental and Calculated Viscosities at 298.15 K

system	AAD, %	
	η	ξ
ethanol–acetone–cyclohexane	2.282	0.623
acetone–ethanol–methanol	4.776	1.414
acetone–hexane–ethanol	1.401	0.417
acetone–hexane–cyclohexane	4.553	1.308
hexane–cyclohexane–ethanol	3.050	0.789
methanol–ethanol–2-propanol	1.935	0.475
acetone–ethanol–2-propanol	3.103	0.797
acetone–carbon tetrachloride–cyclohexane	4.274	1.138
carbon tetrachloride–cyclohexane–2-propanol	12.31	2.561
methyl acetate–chloroform–methanol	8.785	2.460
chloroform–ethanol–methanol	1.737	0.469
ethanol–cyclohexane–2-propanol	9.241	1.976
methyl acetate–cyclohexane–ethanol	7.457	1.885
triethylamine–ethanol–propanol	9.847	2.347
triethylamine–methanol–chloroform	3.057	0.786
dimethyl sulfoxide–carbon tetrachloride–methanol	9.086	2.467
dimethyl sulfoxide–chloroform–methanol	4.652	1.214
triethylamine–methanol–ethanol	5.346	1.409
dimethyl sulfoxide–carbon tetrachloride–chloroform	16.33	3.885
dimethyl sulfoxide–acetone–chloroform	15.68	4.186
AAD for 20 systems, 240 points, %	6.445	1.630

and ξ_i^0 represents the pure-component i value given by

$$\xi_i^0 = \ln(\eta_i V_i) \tag{8}$$

In the above model, α, A_{ij}, and A_{ji} represent the NRTL parameters for each binary system. These parameters may be obtained directly from the literature or by fitting the NRTL equation to vapor–liquid or liquid–liquid equilibrium data. Molar volumes, V, for both the pure components and the mixtures were obtained from our density measurements. The factor σ was taken to be 0.25 for this work. Binary excess enthalpy data, H^E, were obtained from Christensen's compilation (*5*); raw data were curve fitted as a function of mole fraction by using the model

$$H^E = \sum_i x_i \frac{\sum_j H_{ji} G_{ji}' x_j}{\sum_k G_{ki}' x_k} \tag{9}$$

$$G_{ji}' = \exp[-(H_{ji} - TS_{ji})/RT] \tag{10}$$

where H_{ji} and S_{ji} are adjustable parameters. Ternary excess enthalpies were thus obtained by using only binary adjustable parameters in accordance with eq 9. Results of the comparison between calculated and experimental mixture shear viscosities are shown in Table III. In terms of the dynamic viscosity, η, the average absolute deviation for the 20 systems is 6.4%. For the property ξ, utilized in this model, the average absolute deviation is 1.6%. This compares favorably with the agreement reported (*2*) for ξ for binary systems of similar type constituency. The local composition model evidently produces reliable predictions for multicomponent viscosity although it is based only on binary interactions. The poor results obtained on the dimethyl sulfoxide–carbon tetrachloride–chloroform and dimethyl sulfoxide–acetone–chloroform ternary systems are reflected in equally poor predictions of the corresponding binaries containing dimethyl sulfoxide as one of the components. The lack of agreement in these systems, therefore, appears to be a result of the inadequacies of the interaction parameters for complete binary property prediction and probably not an inability of the multicomponent model to predict properties based solely on binary interactions.

Because the local composition model for shear viscosity is not presently amenable to aqueous systems, we have limited our studies to nonaqueous mixtures. Furthermore, all viscosity data were measured at 298.15 K; additional viscosity measurements over a wide range of temperatures should be performed to test the temperature dependence of this model.

Glossary

A_{ji}	NRTL parameters
AAD	average absolute deviation
G_{ji}	NRTL nonrandomness factors
G_{ji}'	nonrandomness factors of excess enthalpy model
H^E	excess enthalpy
H_{ji}	binary enthalpy parameter
k	capillary viscometer constant
R	gas constant
S_{ji}	binary entropy parameter
T	absolute temperature
t	time

V	molar volume
x	mole fraction

Greek Letters

α	nonrandomness parameter
Γ_{ji}	ratio defined by eq 7
η	shear viscosity
ν	kinematic viscosity
ρ	density
ξ	$\ln(\eta V)$
σ	free energy of activation parameter
θ	Hagenbach–Couette error correction factor
ϕ	volume fraction
$\phi_i{}^*$	volume fraction at specific composition defined by eq 6
ϕ_{ji}	local volume fraction of j around component i

Registry No. Acetone, 67-64-1; carbon tetrachloride, 56-23-5; chloroform, 67-66-3; cyclohexane, 110-82-7; dimethyl sulfoxide, 67-68-5; ethanol, 64-17-5; hexane, 110-54-3; 2-propanol, 67-63-0; methanol, 67-56-1; methyl acetate, 79-20-9; propanol, 71-23-8; triethylamine, 121-44-8.

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Excess Volumes of Benzene + 1-Hexanol and + 3-Methyl-3-pentanol at Three Different Temperatures

Juan Ortega* and M. Carmen Angulo

Cátedra de Termodinâmica y Fisicoquimica de la Escuela Superior de Ingenieros Industriales, Polytechnic University of Las Palmas, Las Palmas, Canary Islands, Spain

Excess volumes for benzene with 1-hexanol and 3-methyl-3-pentanol have been measured over the entire composition range at 298.15, 303.15, and 308.15 K. V^E values were obtained with an oscillator type densimeter and the analytical expressions which represent the composition dependences of the excess volume are reported.

Experimental excess properties are needed to relate and compute the properties of liquid mixtures and then to be compared with those derived from theoretical formalism of classical thermodynamics. Studies of the thermodynamic properties of pure alcohols and of their mixtures with other molecular species are very important because they may provide information about the variation of these properties with the number and positions of the hydroxyl group in the alcohol. The purpose of this investigation is to measure the excess volumes for two binary systems formed by benzene with 1-hexanol and 3-methyl-3-pentanol (3-M-3-P) from density values as a function of temperature between 298.15 and 308.15 K. Likewise, from excess volumes at those temperatures, the temperature coefficients of V^E were calculated.

Experimental Section

The benzene used was supplied by Carloerba with a stated purity of ≥99.5 mol %; however, 1-hexanol and 3-M-3-P were "puriss" grade from Fluka (AG) and their purity was ≥99.0 mol %. Both the benzene and the alcohols were used as received without further purification.

The physical properties of the pure liquids are compared with literature values in Table I. In general, agreement with them is satisfactory; however, there appear to exist no reliable recent measurements for 3-M-3-P.

All mixtures were prepared by weight on a Mettler H10 analytical balance. The probable error in the mole fraction is estimated to be less than 10^{-4}. The densities ρ were measured with a digital density meter DMA-55 (Anton Paar, KG, Graz, Austria) with a reproducibility of $\pm 0.000\,01$ g cm^{-3}. The apparatus was calibrated at each temperature with redistilled and degassed water and dry air at atmospheric pressure. The samples in the densimeter were thermostated by a Heto Birkeroad ultrathermostat, the temperature being controlled within ±0.01 K by a digital thermometer DT-100 (Anton Paar) with a thermistor calibrated previously.

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