Density–Composition Data for Eight Binary Systems Containing Toluene or Ethylbenzene and C_8–C_{16} *n*-Alkanes at 293.15, 298.15, 308.15, and 313.15 K

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Density–composition data for eight binary mixtures, viz., toluene–*n*-octane, toluene–*n*-decane, toluene–*n*-dodecane, toluene–*n*-tetradecane, toluene–*n*-hexadecane, ethylbenzene–*n*-octane, ethylbenzene–*n*-tetradecane, and ethylbenzene–*n*-hexadecane have been determined at 293.15, 298.15, 308.15, and 313.15 K over the entire composition range. The results have been correlated by polynomial expressions. The experimental data were also used to calculate excess volumes of mixing.

Introduction

Although a large volume of experimental data on binary mixture densities has been published to date, relatively few investigations deal with binary mixtures on *n*-alkanes and aromatic hydrocarbons. The results of this study represent a part of an ongoing program in our laboratory that aims at determining transport and excess properties of liquid mixtures at different temperatures. The binary mixture data reported in this study are for *n*-alkane binary mixtures with toluene and ethylbenzene. With the exception of data on toluene–*n*-tetradecane and ethylbenzene–*n*-tetradecane at 298.15 K (*1*), similar data for the systems reported here have not been published before.

Experimental Section

Procedure. The pure-component densities were measured first at each stated temperature. Second, binary mixtures over the entire composition range were prepared according to the procedure described by Asfour (*2*), and their densities were measured.

Preparation of Solutions. Solution compositions were determined gravimetrically. Special care was taken during solution preparation to avoid evaporation losses (*3*). A Mettler Model HK160 electronic balance with a stated precision of 2×10^{-7} kg was used.

Density Measurements. An Anton Paar precision density meter (Model DMA 60 with Model DMA 602 measuring cell) with a stated precision of 1.5×10^{-6} kg/L was employed. The density meter was housed in a temperature-controlled environment where temperature fluctuations were kept within ±0.1 K. Temperature fluctuations in the density meter were kept within ±0.01 K with a Haake Model N4-B circulator with a calibrated platinum temperature sensor (IPTS-68). The density was determined by the three-parameter equation

$$\rho = AT^2/(1.0 - BT^2) - C \qquad (1)$$

where ρ is the density and T is the period of oscillation. The best values of the parameters A, B, and C were determined at each temperature level by using the following substances, the densities (kg/L) of which were obtained from the literature: At 293.15 K, for double-distilled and degassed water, ρ = 0.998 23 (4), for carbon tetrachloride, ρ = 1.594 (*5*), for benzene, ρ = 0.879 03 (*5*), and for toluene, ρ = 0.866 83 (5). At 298.15 K, for double-distilled and degassed water, ρ = 0.997 07 (4), for carbon tetrachloride, ρ = 1.584 45 (*5*), for benzene, ρ= 0.873 63 (*6*), and for toluene, ρ = 0.862 20 (*5*). At 308.15 K, for double-distilled and degassed water, ρ = 0.994 061 (*4*), for benzene, ρ = 0.862 96 (*6*), for N1.0, ρ = 0.7818, and for S3.0, ρ = 0.8286, where N1.0 and S3.0 are viscosity standards supplied by Cannon Instruments Co. (These viscosity standards were used because densities of pure substances at 308.15 K were not readily available). At 313.15 K, for double-distilled and degassed water, ρ = 0.992 2497 (*4*), for benzene, ρ = 0.857 63 (*6*), for carbon tetrachloride, ρ = 1.554 98 (*6*), and for toluene, ρ = 0.848 36 (*6*). Detailed calibration and operation procedures are documented elsewhere (*2*, *3*).

Materials. All reagents used were purchased from Aldrich Chemical Co. A chromatographic test of reagent purity, with a 5 m × 0.53 mm methyl silicone capillary column and a flame

Table I

compound	specification, mol%	GC analysis, mass %
n-octane	99+	99.7
n-decane	99+	99.8
n-dodecane	99+	99.9
n-tetradecane	99	99.8
n-hexadecane	99+	99.2
toluene	99+	99.9
ethylbenzene	99+	99.8

Table II. Comparison between Experimental and Literature Density Values of the Pure Components

	density, kg/L			
compound	exptl value	lit. value (*7*)	exptl value	lit. value (*7*)
	293.15 K		298.15 K	
n-octane	0.7022	0.702 67	0.6984	0.698 62
n-decane	0.7297	0.730 12	0.7260	0.726 35
n-dodecane	0.7485	0.748 75	0.7443	0.745 18
n-tetradecane	0.7631	0.762 55	0.7598	0.759 20
n-hexadecane	0.7737	0.773 53	0.7703	0.769 94
toluene	0.8671	0.866 9	0.8619	0.868 5 (*2*)
ethylbenzene	0.8672	0.867 0	0.8620	0.862 1 (*8*)
	308.15 K		313.15 K	
n-octane	0.6901	0.690 42 (*9*)	0.6863	0.686 3
n-decane	0.7178	0.718 92 (*10*)	0.7151	0.715 0
n-dodecane	0.7376	0.737 92 (*11*)	0.7343	0.734 4
n-tetradecane	0.7527	0.752 53 (*12*)	0.7488	0.749 1
n-hexadecane	0.7635	0.763 20 (*13*)	0.7609	0.759 5
toluene	0.8517	0.852 7 (*8*)	0.8482	0.848 5
ethylbenzene	0.8533	0.854 8 (*14*)	0.8495	0.849 5

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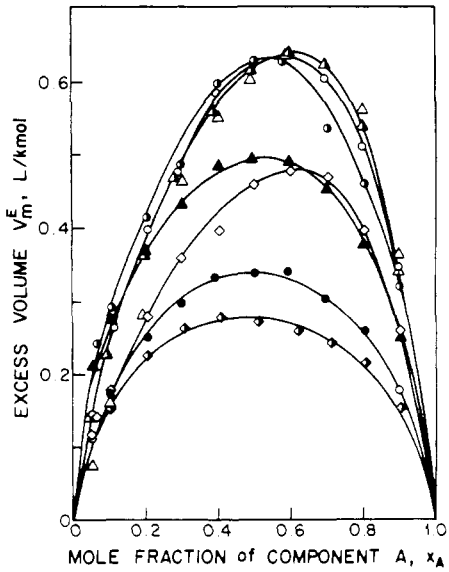

Figure 1. Variation of excess volume of mixing with composition at 293.15 K. Key: (●) toluene (A)–*n*-octane (B); (▲) toluene (A)–*n*-decane (B); (◇) toluene (A)–*n*-dodecane (B); (◑) toluene (A)–*n*-tetradecane (B); (▲) toluene (A)–*n*-hexadecane (B); (◆) ethylbenzene (A)–*n*-octane (B); (○) ethylbenzene (A)–*n*-tetradecane (B); (△) ethylbenzene (A)–*n*-hexadecane (B).

ionization detector (FID), produced the results in Table I.

Results and Discussion

Table II lists all the pure-component densities determined in this study. As it can be seen from this table, there is an excellent agreement between the experimental values reported here and those available from the TRC Tables (*7*). In cases where TRC Table values were unavailable, data substituted from other literature sources have also shown good agreement with the experimental data of this study.

The experimental densities of the systems studied are listed in Table III. Each value is the average of three measurements with a better than 8 × 10^{-5} kg/L reproducibility. Experimental densities were fitted by polynomial expressions of the form

$$\rho_m = \sum_{i=0}^{n} A_i x_A^i \qquad (2)$$

The adjustable parameters A_i were determined by least squares. The degree of the polynomial was varied so as to minimize the standard deviation of the fit. The values of the parameters A_i and the standard deviations for each system studied are given in Table IV. As it can be seen from the standard deviations listed in this table, the correlating expressions fit the experimental data very well.

The experimental binary mixture density–composition data were also used to calculate excess molar volumes of mixing from the equation

$$V_m^E = (M_A x_A + M_B x_B)/\rho_m - (M_A x_A/\rho_A + M_B x_B/\rho_B) \qquad (3)$$

The calculated excess volume values are shown in Table III. The maximum expected error has been estimated as 0.006 L/kmol. The calculated V_m^E values are shown plotted versus composition in Figures 1–4 for each of the temperatures considered here.

All the systems studied are of the nonassociating type. For all systems, the density increased monotonically with the mole fraction of the aromatic component at all temperatures studied. All systems exhibited positive V_m^E values at each temperature level and over the entire composition range with the exception of the systems toluene–*n*-octane, toluene–*n*-decane, and toluene–*n*-tetradecane, which exhibited small negative V_m^E values at 298.15, 308.15, and 308.15 K, respectively, over the toluene mole fraction range of 0.0–0.2 (Figures 2 and 3). Although the corresponding measurements were repeated three times for each system, it may still be possible that this behavior is due to some unaccounted source of experimental error.

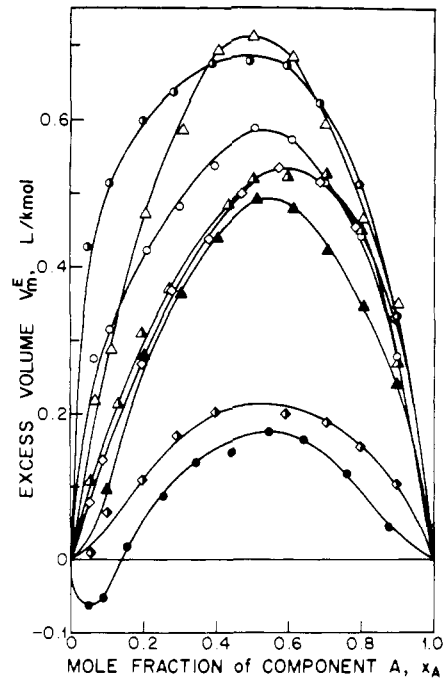

Figure 2. Variation of excess volume of mixing with composition at 298.15 K. Symbols defined in caption of Figure 1.

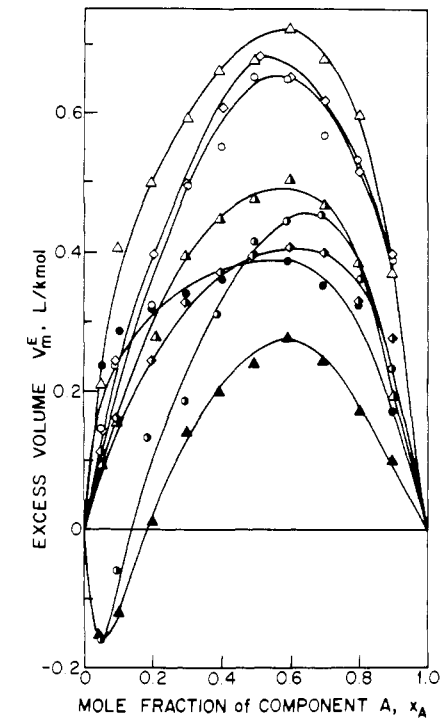

Figure 3. Variation of excess volume of mixing with composition at 308.15 K. Symbols defined in caption of Figure 1.

Excess volume of mixing generally increased with increasing chain length of the *n*-alkane component. This suggests that molecular size is probably a primary factor affecting the excess volume of mixing for the systems investigated. The pronounced molecular shape difference between the aromatic and *n*-alkane components, i.e., spherical versus rodlike, respectively, is probably another significant factor affecting V_m^E values.

Table III. Experimental Density–Composition Data and Calculated V_m^E Values for Binary Mixtures of Toluene and Ethylbenzene with *n*-Alkanes at 293.15, 298.15, 308.15, and 313.15 K

ω_A	x_A	ρ, kg/L	V_m^E, L/kmol	ω_A	x_A	ρ, kg/L	V_m^E, L/kmol
			Toluene–*n*-Octane				
		293.15 K				298.15 K	
0.0000	0.0000	0.7022	0.0000	0.0000	0.0000	0.6984	0.0000
0.0477	0.0584	0.7082	0.1139	0.0477	0.04995	0.7041	−0.0623
0.0840	0.1021	0.7128	0.1749	0.0747	0.0910	0.7087	−0.0503
0.1735	0.2065	0.72497	0.2529	0.1288	0.1548	0.7158	0.0164
0.2609	0.3044	0.7374	0.2972	0.2179	0.2566	0.7281	0.0875
0.3438	0.3937	0.7496	0.3323	0.3002	0.3472	0.7399	0.1336
0.4492	0.5027	0.7659	0.3370	0.3924	0.4447	0.7538	0.1469
0.5419	0.5946	0.7809	0.3401	0.4901	0.5437	0.76897	0.1746
0.6507	0.6979	0.7995	0.3016	0.58996	0.6408	0.7854	0.1632
0.7665	0.8028	0.8203	0.2587	0.7200	0.7612	0.8081	0.1168
0.8778	0.8990	0.8416	0.1774	0.8492	0.8747	0.8322	0.0444
1.0000	1.0000	0.8671	0.0000	1.0000	1.0000	0.8619	0.0000
		308.15 K				313.15 K	
0.0000	0.0000	0.6901	0.0000	0.0000	0.0000	0.6863	0.0000
0.0358	0.0440	0.6944	0.0915	0.0421	0.0517	0.6909	0.2357
0.0849	0.1032	0.7008	0.1322	0.0854	0.1038	0.6965	0.2855
0.1685	0.2008	0.7115	0.3035	0.1666	0.1986	0.7074	0.3197
0.2515	0.2940	0.7226	0.4274	0.2559	0.29896	0.7199	0.3396
0.3481	0.3983	0.7362	0.5275	0.3519	0.4023	0.7339	0.3597
0.4421	0.4956	0.7504	0.5245	0.4407	0.4942	0.7472	0.3960
0.5478	0.6003	0.7673	0.4786	0.5413	0.5939	0.7631	0.3874
0.6502	0.6974	0.7852	0.3218	0.6473	0.6947	0.7809	0.3514
0.7655	0.8019	0.8060	0.2004	0.7637	0.8003	0.8013	0.3247
0.8764	0.8979	0.8269	0.1149	0.8760	0.8976	0.8229	0.1704
1.0000	1.0000	0.8517	0.0000	1.0000	1.0000	0.8482	0.0000
			Toluene–*n*-Decane				
		293.15 K				298.15 K	
0.0000	0.0000	0.7297	0.0000	0.0000	0.0000	0.7260	0.0000
0.0383	0.05798	0.7333	0.2106	0.0342	0.0519	0.7299	0.0125
0.0733	0.1088	0.7372	0.2752	0.0675	0.1005	0.7335	0.0970
0.1452	0.2078	0.7453	0.3621	0.1408	0.20197	0.7414	0.2798
0.22099	0.3046	0.7542	0.4327	0.2202	0.3037	0.7505	0.3637
0.3056	0.4047	0.7645	0.4841	0.3068	0.4060	0.7609	0.4381
0.38997	0.4968	0.7752	0.4942	0.4039	0.5113	0.7729	0.4911
0.4919	0.5992	0.7887	0.4901	0.5038	0.6106	0.7860	0.4772
0.6013	0.6996	0.8038	0.4519	0.6075	0.7050	0.8004	0.4200
0.7208	0.7994	0.8213	0.3762	0.7241	0.8021	0.8173	0.3451
0.8579	0.9031	0.8427	0.2487	0.8476	0.8957	0.8363	0.2389
1.0000	1.0000	0.8671	0.0000	1.0000	1.0000	0.8619	0.0000
		308.15 K				313.15 K	
0.0000	0.0000	0.7178	0.0000	0.0000	0.0000	0.7151	0.0000
0.0326	0.0495	0.7211	0.1187	0.0284	0.0432	0.7189	−0.1765
0.0647	0.0966	0.7241	0.2834	0.0677	0.1008	0.7230	−0.07099
0.1366	0.1964	0.7316	0.4901	0.1409	0.2021	0.7312	0.0121
0.2155	0.2979	0.7404	0.6156	0.2167	0.2993	0.7396	0.1402
0.2954	0.3929	0.7499	0.6286	0.29596	0.3936	0.74899	0.1980
0.3894	0.4962	0.7614	0.6464	0.3880	0.4947	0.7603	0.2370
0.4890	0.5965	0.7742	0.6294	0.4856	0.5931	0.7726	0.2761
0.5996	0.6981	0.7894	0.5282	0.5971	0.6959	0.7876	0.2423
0.71995	0.7988	0.8065	0.4576	0.7226	0.8009	0.8055	0.1701
0.8506	0.8979	0.8269	0.2416	0.8483	0.8962	0.8242	0.0994
1.0000	1.0000	0.8516	0.0000	1.0000	1.0000	0.8482	0.0000
			Toluene–*n*-Dodecane				
		293.15 K				298.15 K	
0.0000	0.0000	0.7485	0.0000	0.0000	0.0000	0.7443	0.0000
0.03597	0.0645	0.7517	0.1433	0.0306	0.0551	0.7472	0.0795
0.0600	0.1056	0.7540	0.1795	0.0500	0.0887	0.7489	0.1373
0.1245	0.2082	0.7604	0.2785	0.1165	0.1959	0.7553	0.2660
0.1885	0.3004	0.7669	0.3590	0.1730	0.2789	0.7609	0.3673
0.2681	0.4037	0.7753	0.3952	0.2491	0.3802	0.7686	0.4386
0.3512	0.5002	0.7841	0.4568	0.3242	0.4701	0.7765	0.4975
0.4484	0.6005	0.79497	0.4755	0.4183	0.5707	0.7867	0.5344
0.5597	0.7015	0.8079	0.4674	0.5410	0.6854	0.8008	0.5131
0.6870	0.8023	0.8236	0.3954	0.6579	0.7805	0.8149	0.4524
0.8311	0.90099	0.8427	0.2563	0.8133	0.8895	0.8349	0.3269
1.0000	1.0000	0.8671	0.0000	1.0000	1.0000	0.8619	0.0000
		308.15 K				313.15 K	
0.0000	0.0000	0.7376	0.0000	0.0000	0.0000	0.7343	0.0000
0.0292	0.0527	0.7403	0.0637	0.0282	0.0508	0.7366	0.1439

Table III (Continued)

ω_A	x_A	ρ, kg/L	V_m^E, L/kmol	ω_A	x_A	ρ, kg/L	V_m^E, L/kmol
0.0564	0.0996	0.7429	0.0984	0.0522	0.0924	0.7387	0.2417
0.1224	0.2049	0.7494	0.1326	0.1213	0.2033	0.7450	0.3962
0.1819	0.2913	0.7550	0.2606	0.1884	0.3003	0.7514	0.4987
0.2667	0.4021	0.7634	0.3659	0.2702	0.4063	0.7594	0.6085
0.3497	0.4986	0.7720	0.4040	0.3606	0.5104	0.7685	0.6822
0.4422	0.5944	0.78199	0.4124	0.4467	0.5988	0.7779	0.6510
0.5544	0.69698	0.7947	0.3844	0.5597	0.7015	0.7906	0.6184
0.6811	0.7979	0.8101	0.2569	0.6838	0.7999	0.8054	0.5151
0.8266	0.8981	0.8285	0.1327	0.82799	0.89898	0.8234	0.3969
1.0000	1.0000	0.8517	0.0000	1.0000	1.0000	0.8482	0.0000
			Toluene–*n*-Tetradecane				
	293.15 K				298.15 K		
0.0000	0.0000	0.7631	0.0000	0.0000	0.0000	0.7598	0.0000
0.0318	0.0661	0.7653	0.2429	0.0223	0.0469	0.7606	0.4275
0.0537	0.1089	0.7671	0.2919	0.0528	0.1072	0.7630	0.5147
0.1082	0.2072	0.7717	0.4156	0.1022	0.1969	0.7672	0.59999
0.1678	0.3028	0.77699	0.4895	0.1565	0.2854	0.7719	0.6385
0.2360	0.3994	0.7830	0.5849	0.2259	0.3858	0.7781	0.6766
0.3201	0.5034	0.7909	0.6287	0.3100	0.4918	0.7859	0.6772
0.3927	0.5820	0.7979	0.6268	0.4049	0.5944	0.79496	0.6727
0.5232	0.7026	0.8113	0.5354	0.4984	0.6815	0.8043	0.6229
0.6569	0.8048	0.8256	0.4602	0.6400	0.7929	0.8191	0.5106
0.8100	0.9018	0.8430	0.3191	0.7978	0.8947	0.8369	0.3304
1.0000	1.0000	0.8671	0.0000	1.0000	1.0000	0.8619	0.0000
	308.15 K				313.15 K		
0.0000	0.0000	0.7527	0.0000	0.0000	0.0000	0.7488	0.0000
0.0245	0.0513	0.7545	0.1006	0.0240	0.0503	0.7514	−0.1592
0.0486	0.0991	0.7564	0.1907	0.0479	0.0977	0.7532	−0.0595
0.1027	0.1977	0.7608	0.2973	0.0957	0.1856	0.7569	0.1291
0.1638	0.29669	0.7660	0.3606	0.1627	0.2950	0.7627	0.1839
0.2266	0.3868	0.7715	0.4050	0.2284	0.3892	0.7683	0.3109
0.3150	0.4975	0.7794	0.4393	0.3132	0.4954	0.7756	0.4144
0.4079	0.5973	0.7880	0.4646	0.4008	0.5902	0.7837	0.4435
0.5180	0.6983	0.7986	0.4444	0.5092	0.6908	0.7938	0.5038
0.6448	0.7963	0.8118	0.3242	0.6566	0.8046	0.8091	0.3607
0.8052	0.89897	0.8291	0.1942	0.8029	0.8977	0.8250	0.2347
1.0000	1.0000	0.8517	0.0000	1.0000	1.0000	0.8482	0.0000
			Toluene–*n*-Hexadecane				
	293.15 K				298.15 K		
0.0000	0.0000	0.7737	0.0000	0.0000	0.0000	0.7703	0.0000
0.0186	0.0444	0.7749	0.1402	0.0284	0.06697	0.7724	0.1099
0.0414	0.0959	0.7765	0.2268	0.0578	0.13099	0.7745	0.2128
0.0941	0.2033	0.7805	0.3661	0.0886	0.1927	0.7767	0.3082
0.1373	0.2811	0.7838	0.4693	0.1313	0.2708	0.7801	0.3690
0.2057	0.38898	0.7892	0.5597	0.2373	0.4333	0.7885	0.4850
0.2866	0.4969	0.7959	0.6154	0.2914	0.5026	0.7929	0.5189
0.3794	0.6004	0.8038	0.6396	0.3763	0.5973	0.8001	0.5218
0.4843	0.6977	0.8132	0.6221	0.4890	0.7017	0.8099	0.5262
0.6163	0.7978	0.8256	0.5383	0.6170	0.7984	0.8218	0.4480
0.7863	0.9004	0.8430	0.3413	0.7818	0.89799	0.8383	0.2673
1.0000	1.0000	0.8671	0.0000	1.0000	1.0000	0.8619	0.0000
	308.15 K				313.15 K		
0.0000	0.0000	0.7635	0.0000	0.0000	0.0000	0.7609	0.0000
0.0151	0.0363	0.7646	0.0577	0.0224	0.0533	0.7624	0.0946
0.0427	0.0987	0.7664	0.2080	0.0415	0.0961	0.7637	0.1554
0.0984	0.2114	0.7702	0.3979	0.0986	0.2119	0.7679	0.2764
0.1532	0.3078	0.7738	0.6266	0.1455	0.2950	0.7712	0.3941
0.2128	0.3992	0.7781	0.7504	0.2103	0.3956	0.7762	0.4470
0.2918	0.5031	0.7843	0.7852	0.2879	0.4984	0.7823	0.4749
0.3754	0.5963	0.7912	0.7411	0.3786	0.5995	0.7896	0.5024
0.4904	0.7028	0.8014	0.60696	0.4865	0.6995	0.7987	0.4676
0.6149	0.7969	0.8131	0.4156	0.6116	0.7946	0.8099	0.3824
0.7813	0.8978	0.82995	0.1170	0.7856	0.9000	0.8266	0.1924
1.0000	1.0000	0.8517	0.0000	1.0000	1.0000	0.8482	0.0000
			Ethylbenzene–*n*-Octane				
	293.15 K				298.15 K		
0.0000	0.0000	0.7022	0.0000	0.0000	0.0000	0.6984	0.0000
0.0508	0.0544	0.7086	0.1156	0.0525	0.0562	0.7054	0.0084
0.0962	0.1028	0.7146	0.1542	0.0943	0.1008	0.7108	0.0658
0.1936	0.2053	0.7280	0.2261	0.18695	0.1983	0.7236	0.1087
0.2899	0.3052	0.7419	0.2618	0.2768	0.2917	0.7363	0.1700
0.3924	0.40997	0.7574	0.2770	0.3805	0.3979	0.7517	0.2018

Table III (Continued)

ω_A	x_A	ρ, kg/L	V_m^E, L/kmol	ω_A	x_A	ρ, kg/L	V_m^E, L/kmol
0.49298	0.5113	0.7734	0.2705	0.5720	0.5898	0.7823	0.1988
0.6019	0.6193	0.7916	0.2579	0.6851	0.7007	0.8017	0.1858
0.6961	0.7113	0.80795	0.2416	0.7851	0.7972	0.8197	0.1539
0.7955	0.8071	0.8261	0.2139	0.8894	0.8964	0.8396	0.1030
0.8945	0.9012	0.8452	0.1515	1.0000	1.0000	0.8620	0.0000
1.0000	1.0000	0.8672	0.0000				
		308.15 K				313.15 K	
0.0000	0.0000	0.6901	0.0000	0.0000	0.0000	0.6863	0.0000
0.0480	0.0515	0.6963	0.0486	0.04497	0.0482	0.6918	0.1131
0.0908	0.0971	0.7018	0.1164	0.0913	0.0976	0.6979	0.1561
0.1757	0.1865	0.7131	0.2129	0.1858	0.1971	0.7106	0.2431
0.2819	0.2969	0.7281	0.2687	0.27996	0.2949	0.7238	0.3269
0.3809	0.3983	0.7428	0.3001	0.3800	0.3974	0.7386	0.3694
0.4718	0.4900	0.7568	0.3374	0.4719	0.4902	0.7527	0.3931
0.5742	0.5919	0.7734	0.3347	0.5788	0.5966	0.7700	0.4058
0.6861	0.7016	0.7926	0.2945	0.6798	0.6955	0.7871	0.3994
0.78596	0.7980	0.8108	0.2278	0.7846	0.7967	0.8062	0.3281
0.8918	0.8987	0.8311	0.1412	0.8895	0.8965	0.8260	0.2759
1.0000	1.0000	0.8533	0.0000	1.0000	1.0000	0.8495	0.0000
			Ethylbenzene–*n*-Tetradecane				
		293.15 K				298.15 K	
0.0000	0.0000	0.7631	0.0000	0.0000	0.0000	0.7598	0.0000
0.0286	0.0521	0.7653	0.1472	0.0347	0.0629	0.7622	0.2751
0.0651	0.1152	0.7683	0.2648	0.0595	0.1057	0.7643	0.2530
0.1246	0.2101	0.7734	0.3979	0.1251	0.2109	0.7699	0.4230
0.1817	0.2932	0.7784	0.4763	0.1889	0.3033	0.7755	0.4826
0.2664	0.4042	0.7860	0.5970	0.2586	0.3946	0.7818	0.5381
0.3452	0.4963	0.7935	0.6172	0.3492	0.5007	0.7902	0.5887
0.4428	0.5976	0.8031	0.6345	0.4459	0.6007	0.7997	0.5729
0.5526	0.6977	0.8143	0.6030	0.5555	0.7002	0.8109	0.5126
0.6798	0.7987	0.8281	0.5108	0.6783	0.7976	0.8239	0.4400
0.8279	0.8999	0.8452	0.3458	0.8242	0.8976	0.8404	0.2754
1.0000	1.0000	0.8672	0.0000	1.0000	1.0000	0.8620	0.0000
		308.15 K				313.15 K	
0.0000	0.0000	0.7527	0.0000	0.0000	0.0000	0.7488	0.0000
0.0290	0.0529	0.7547	0.1924	0.0279	0.0509	0.7509	0.14596
0.0567	0.1010	0.7565	0.4243	0.0516	0.0923	0.7527	0.2356
0.1178	0.1997	0.7613	0.6121	0.1174	0.1991	0.7584	0.3231
0.18298	0.2950	0.7668	0.7071	0.1889	0.3032	0.7643	0.4961
0.2573	0.39297	0.7734	0.7639	0.2633	0.4005	0.7709	0.5518
0.3463	0.4975	0.7816	0.7759	0.3451	0.4961	0.7782	0.6520
0.4264	0.5814	0.7892	0.7620	0.4369	0.5918	0.7869	0.6494
0.5527	0.6978	0.8020	0.6459	0.5558	0.7004	0.7989	0.5673
0.6827	0.8008	0.8158	0.5214	0.6782	0.7975	0.8115	0.5338
0.8240	0.8974	0.8316	0.3478	0.8276	0.8997	0.82798	0.3873
1.0000	1.0000	0.8533	0.0000	1.0000	1.0000	0.8495	0.0000
			Ethylbenzene–*n*-Hexadecane				
		293.15 K				298.15 K	
0.0000	0.0000	0.7737	0.0000	0.0000	0.0000	0.7703	0.0000
0.0260	0.0539	0.7757	0.0743	0.0337	0.0692	0.7725	0.2158
0.0510	0.1029	0.7775	0.1606	0.0570	0.1142	0.7742	0.2869
0.1039	0.1983	0.7816	0.2829	0.1083	0.2058	0.7779	0.4713
0.1687	0.3022	0.7865	0.46399	0.1729	0.3084	0.7829	0.5854
0.2402	0.4028	0.7923	0.5502	0.2421	0.4053	0.7883	0.6941
0.3129	0.4927	0.7984	0.6008	0.3215	0.5027	0.7949	0.7107
0.4082	0.5953	0.8066	0.6363	0.42296	0.6099	0.8037	0.6824
0.5199	0.6978	0.8167	0.6208	0.5201	0.69799	0.8127	0.5934
0.6511	0.7992	0.8291	0.5599	0.6564	0.8029	0.8257	0.4625
0.8087	0.9002	0.8454	0.3629	0.8098	0.9008	0.8408	0.3493
1.0000	1.0000	0.8672	0.0000	1.0000	1.0000	0.8620	0.0000
		308.15 K				313.15 K	
0.0000	0.0000	0.7635	0.0000	0.0000	0.0000	0.7609	0.0000
0.0243	0.0505	0.7643	0.4578	0.0242	0.0502	0.7623	0.2093
0.0449	0.0912	0.7657	0.5387	0.0488	0.0987	0.7637	0.4053
0.0998	0.1912	0.7698	0.3608	0.1039	0.1983	0.7678	0.4976
0.1671	0.2997	0.77497	0.7091	0.1695	0.3033	0.7727	0.5916
0.2401	0.4026	0.7808	0.7454	0.2333	0.3935	0.7776	0.6607
0.3188	0.4995	0.7872	0.7571	0.3176	0.4981	0.7845	0.6750
0.4097	0.5968	0.7949	0.7330	0.4115	0.5986	0.7921	0.7218
0.5217	0.6994	0.8047	0.7007	0.5218	0.6995	0.8016	0.6758
0.6509	0.7991	0.8165	0.6176	0.6558	0.8025	0.8137	0.5973
0.8061	0.8987	0.8316	0.4578	0.80599	0.8986	0.8286	0.3691
1.0000	1.0000	0.8533	0.0000	1.0000	1.0000	0.8495	0.0000

Table IV. Least-Squares Constants for Equation 2

system	A_0	A_1	A_2	A_3	A_4	std dev, kg/L
			293.15 K			
toluene–*n*-octane	0.7022	0.0974	0.0657	−0.0320	0.0338	6.45×10^{-5}
toluene–*n*-decane	0.7296	0.0609	0.0785	−0.0628	0.0608	1.08×10^{-4}
toluene–*n*-dodecane	0.7485	0.0442	0.0733	−0.0783	0.0793	1.09×10^{-4}
toluene–*n*-tetradecane	0.7632	0.0272	0.0847	−0.1078	0.0997	2.42×10^{-4}
toluene–*n*-hexadecane	0.7739	0.0178	0.0947	−0.1447	0.1253	2.49×10^{-4}
ethylbenzene–*n*-octane	0.7022	0.1145	0.0592	−0.0335	0.0247	5.70×10^{-5}
ethylbenzene–*n*-tetradecane	0.7632	0.0366	0.0681	−0.0729	0.0721	1.51×10^{-4}
ethylbenzene–*n*-hexadecane	0.7739	0.0282	0.0663	−0.0878	0.0865	2.23×10^{-4}
			298.15 K			
toluene–*n*-octane	0.6986	0.1073	0.0227	0.0333		1.00×10^{-4}
toluene–*n*-decane	0.7259	0.0761	−0.0006	0.0602		3.08×10^{-4}
toluene–*n*-dodecane	0.7438	0.0636	−0.0278	0.0817		5.67×10^{-4}
toluene–*n*-tetradecane	0.7588	0.0486	−0.0318	0.0854		8.64×10^{-4}
toluene–*n*-hexadecane	0.7696	0.0478	−0.0555	0.0991		8.71×10^{-4}
ethylbenzene–*n*-octane	0.6984	0.1213	0.0256	0.0167		7.91×10^{-5}
ethylbenzene–*n*-tetradecane	0.7592	0.0526	−0.0156	0.0652		5.10×10^{-4}
ethylbenzene–*n*-hexadecane	0.7698	0.0442	−0.0285	0.0758		6.02×10^{-4}
			308.15 K			
toluene–*n*-octane	0.6900	0.1015	0.0136	0.0642	−0.0177	1.299×10^{-4}
toluene–*n*-decane	0.71797	0.0568	0.0720	−0.0448	0.0497	1.31×10^{-4}
toluene–*n*-dodecane	0.7376	0.0512	0.0283	−0.0042	0.0389	7.83×10^{-5}
toluene–*n*-tetradecane	0.7528	0.0301	0.0659	−0.0774	0.0803	9.35×10^{-5}
toluene–*n*-hexadecane	0.7636	0.0258	0.0258	−0.01899	0.0556	1.05×10^{-4}
ethylbenzene–*n*-octane	0.6901	0.1166	0.0379	−0.0004	0.0092	4.97×10^{-5}
ethylbenzene–*n*-tetradecane	0.7528	0.0293	0.0793	−0.0784	0.0702	1.41×10^{-4}
ethylbenzene–*n*-hexadecane	0.7635	0.0143	0.1175	−0.15996	0.1178	2.43×10^{-4}
			313.15 K			
toluene–*n*-octane	0.6861	0.0927	0.0790	−0.0549	0.0453	1.696×10^{-4}
toluene–*n*-decane	0.7152	0.0775	−0.0015	0.0569		1.90×10^{-4}
toluene–*n*-dodecane	0.7337	0.0602	−0.0265	0.0801		6.38×10^{-4}
toluene–*n*-tetradecane	0.7491	0.0366	0.0419	−0.0515	0.0719	2.41×10^{-4}
toluene–*n*-hexadecane	0.7610	0.0212	0.0666	−0.0939	0.0932	1.49×10^{-4}
ethylbenzene–*n*-octane	0.6863	0.11296	0.0561	−0.0346	0.0286	1.33×10^{-4}
ethylbenzene–*n*-tetradecane	0.7483	0.0542	−0.0241	0.0704		5.56×10^{-4}
ethylbenzene–*n*-hexadecane	0.76097	0.0201	0.0892	−0.1187	0.09795	1.25×10^{-4}

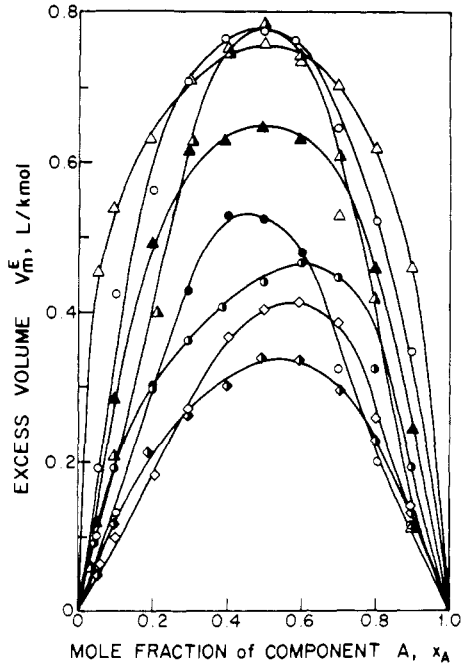

Figure 4. Variation of excess volume of mixing with composition at 313.15 K. Symbols defined in caption of Figure 1.

As the temperature increases, the free volume of a liquid is expected to increase. Thus, a decrease in V_m^E values should be expected with an increase in temperature. However, only some of the systems studied behaved in this manner. Other systems displayed an increase in V_m^E values with increasing temperature (Figures 1–4). This apparent inconsistency is in agreement with the results reported by Dieter and Heinz (*15*) and by Garcia et al. (*16*) who similarly reported V_m^E values increasing with increasing temperature.

As mentioned earlier, V_m^E data for the systems ethylbenzene–*n*-tetradecane and toluene–*n*-tetradecane at 298.15 K have been previously published by Grolier and Faradjadeh (*1*). When these data are compared to the ones obtained in this study (Table III), it can be seen that the V_m^E values calculated here are somewhat higher than the ones reported by Grolier and Faradjadeh. In addition, the maximum of the V_m^E composition curve reported by Grolier and Faradjadeh is shifted to the right relative to the V_m^E–composition curve reported in this study (Figure 2).

Specifically, the maximum of this curve for the ethylbenzene–*n*-tetradecane system was 0.5887 L/kmol at an ethylbenzene mole fraction of 0.5007 in this study versus the 0.5163 L/kmol at 0.6070 mole fraction reported by Grolier and Faradjadeh. The remaining V_m^E values reported here are similarly slightly higher than those reported by Grolier and Faradjadeh throughout the entire composition range. For the toluene–*n*-tetradecane system, the same behavior is also evident but with the difference between the values calculated here and those reported by Grolier and Faradjadeh being somewhat greater. Thus, the maximum calculated in this study was 0.6772 L/kmol at 0.4918 vs 0.5232 L/kmol at 0.6305 reported by Grolier and Faradjadeh.

To better explain these apparent differences, it should be noted that two factors may have affected the accuracy of the data reported by Grolier and Faradjadeh. The first is reagent purity. Although the reagents used in both studies had the same stated purity, they were obtained from different suppliers. In addition, the reagents used here were proven by chromatographic analysis to exceed their stated purity. No such purity

verification is reported by Grolier and Faradjadeh. The second factor stems from the fact that Grolier and Faradjadeh used double-distilled degassed water and dry nitrogen at atmospheric pressure as density meter calibration standards. However, the densities of these standards represent too wide a range in comparison with the range of the density measurements taken. This may have contributed to some errors in subsequent density measurements. The density calibration standards employed in this study provided a narrow density calibration range more appropriate for the density measurements taken.

Conclusions

Densities of eight binary mixtures were determined at 293.15, 298.15, 308.15, and 313.15 K with a maximum error of 1.5×10^{-6} kg/L. The experimental values were correlated by using polynomial expressions that fitted the data well. The experimental density–composition data were also used to calculate excess molar volumes of mixing with a maximum error of 0.006 L/kmol.

For all systems, the density increased monotonically with the mole fraction of the aromatic component at all temperatures studied. All systems exhibited positive V_m^E values over the entire composition range, with the exception of the systems toluene–*n*-octane at 298.15 K and toluene–*n*-decane and toluene–*n*-tetradecane at 308.15 K, which exhibited small negative V_m^E values in the toluene mole fraction range of 0.0–0.2.

The excess volumes of mixing of the systems investigated here were found to generally increase with the chain length of the *n*-alkane component. The effect of increasing temperature has been mixed, leading to increased V_m^E values in some systems and decreased in others.

A comparison with available V_m^E literature values indicated reasonable agreement.

Nomenclature

A = calibration constant or adjustable parameter
B = calibration constant
C = calibration constant
M = molecular weight
V = molar volume
x = mole fraction
ρ = density

Subscripts

A = first-named component in a binary mixture
m = mixture

Superscripts

E = excess

Registry No. Toluene, 108-88-3; ethylbenzene, 100-41-4; octane, 111-65-9; decane, 124-18-5; dodecane, 112-40-3; tetradecane, 629-59-4; hexadecane, 544-76-3.

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Received for review October 3, 1989. Accepted December 18, 1989. We acknowledge with thanks financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC).