Refraction in Some Ternary and Quaternary Liquid Nonelectrolyte Systems

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Refractive indices and refractivity intercepts at 25° C. are given for three quaternary liquid nonelectrolyte systems and the 11 ternary subsystems of the quaternaries. The data, and those for the previously reported densities in these systems, are fitted to deviation equations from additivity in volume fraction. In both present ternary and quaternary systems, the deviation equations for refractivity intercepts tend to be less complex in form than those for densities.

In a previous paper (*7*), densities (d), refractive indices (n_D), and refractivity intercepts ($n_D - d/2$) were considered for seven liquid nonelectrolytes and 14 binary systems of those compounds. For each of the properties, deviation from additivity in volume fraction (*8*) was fitted through an equation which may be expressed for present use as

$$p = \phi_i p_i + \phi_j p_j + \phi_i \phi_j [A_{ij} + B_{ij}\phi_i + C_{ij}\phi_i^2 + \dots] \quad (1)$$

where ϕ is the volume fraction of the indicated component, p is the property of the mixture, and subscripted p is that of the indicated component. A, B, and C are empirical constants.

The study is extended here to systems higher than binary. The ternaries are made up of a number of different combinations of the binaries, and, in turn, the quaternaries of several different combinations of the ternaries. Ternary and quaternary deviation terms are introduced through consideration of differences between experimental results and those predicted on the assumption that deviations from additivity previously established in the subsystems should apply to the combination of subsystems.

The purpose of the work is a further consideration of the approach of Sumer and Thompson (*9*) to the use of

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Table I. Properties of Purified Components at 25° C.

	Density, Grams Ml.$^{-1}$		Refractive Index, n_D		Refractivity Intercept, $n_D - d/2$
	Exptl.	Literature[a]	Exptl.	Literature[b]	Exptl.
Benzene	0.87355	0.87351–0.87370	1.49772	1.4979	1.06094
Carbon tetrachloride	1.58406	1.5842–1.5846	1.45714	1.45704–1.45759	0.66511
2-Bromobutane	1.25391	1.2510	1.43427	1.4342	0.80731
4-Methylcyclohexanone	0.91196	0.912 (24.4° C.)	1.44323	1.44322 (24.4° C.)	0.98725
n-Hexane	0.65518	0.65482–0.6550	1.37219	1.37226	1.04460
n-Tetradecane	0.76032	0.75917–0.7593	1.42731	1.4268	1.04715
n-Hexadecane	0.77079	0.7698–0.7712	1.43273	1.43250	1.04733

[a] From 12 sources identified in (*3*). [b] From 9 sources identified in (*3*).

Table II. Refractometric Properties of Ternary Mixtures at 25° C.

Volume Fraction				Volume Fraction			
First-named component	Second-named component	Refractive Index, n_D	Refractivity Intercept, $n_D - d/2$	First-named component	Second-named component	Refractive Index, n_D	Refractivity Intercept, $n_D - d/2$
n-Hexadecane–*n*-Hexane–2-Bromobutane				*n*-Hexadecane–Benzene–*n*-Hexane			
0.7000	0.1539	1.42340	1.0117	0.7586	0.1232	1.43244	1.0484
0.5976	0.1932	1.42101	0.9964	0.5283[a]	0.1950	1.42734	1.0486
0.5133	0.1969	1.42069	0.9770	0.5121	0.2862	1.43674	1.0498
0.5246	0.2609	1.41706	0.9952	0.3604	0.1513	1.41253	1.0479
0.4451	0.2839	1.41575	0.9816	0.3873	0.2961	1.43085	1.0498
0.3481	0.1482	1.42358	0.9259	0.3597[b]	0.4942	1.45256	1.0526
0.3566	0.3235	1.41329	0.9695	0.1755	0.1731	1.40357	1.0475
0.3507	0.4971	1.40336	1.0097	0.1795	0.3409	1.42369	1.0498
0.2710	0.1846	1.42156	0.9160	0.1807	0.5186	1.44544	1.0525
0.2752	0.3518	1.41161	0.9567	0.1863	0.6787	1.46585	1.0552
0.2673	0.5383	1.40071	0.9992	0.6112	0.2054	1.43310	1.0488
0.1843	0.1350	1.42496	0.8836	0.4436	0.2809	1.43216	1.0495
0.1779	0.3206	1.41352	0.9259	0.2704	0.2004	1.41279	1.0482
0.1968	0.4901	1.40333	0.9708	0.2789	0.3760	1.43380	1.0505
0.1772	0.6654	1.39292	1.0079	0.2659	0.5429	1.45335	1.0530

(*Continued on next page*)

Table II. (*Continued*)

n-Hexadecane–Carbon Tetrachloride–Benzene

0.7192	0.1515	1.44251	0.9910
0.5178	0.1886	1.45311	0.9791
0.5293	0.2956	1.44886	0.9371
0.3668	0.3204	1.45820	0.9295
0.3500	0.4878	1.45316	0.8639
0.1777	0.1366	1.47861	1.0044
0.1864	0.2980	1.47205	0.9412
0.1914	0.4924	1.46437	0.8647
0.1930	0.6747	1.45698	0.7925
0.6116	0.1716	1.44809	0.9844
0.4520	0.2743	1.45432	0.9464
0.2766	0.1928	1.46931	0.9809
0.2712	0.3705	1.46299	0.9112
0.2689	0.5334	1.45709	0.8472

n-Hexadecane–Carbon Tetrachloride–*n*-Hexane

0.6887	0.1441	1.42605	0.9920
0.5095	0.2022	1.42040	0.9696
0.5191	0.2738	1.42651	0.9425
0.3749	0.1316	1.40692	0.9960
0.3668	0.3274	1.42196	0.9216
0.1885	0.1267	1.39503	0.9974
0.1904	0.3232	1.41105	0.9225
0.1898	0.5081	1.42634	0.8526
0.1929	0.6677	1.43965	0.7921
0.6298	0.1976	1.42691	0.9716
0.4449	0.2682	1.42190	0.9443
0.2740	0.1814	1.40476	0.9766
0.2647	0.3752	1.41987	0.9032
0.2654	0.5413	1.43352	0.8404

n-Hexadecane–4-Methylcyclohexanone–*n*-Hexane

0.7330	0.1276	1.42548	1.0390
0.6228	0.1872	1.42312	1.0355
0.5272[c]	0.1845	1.41750	1.0355
0.5229	0.2745	1.42306	1.0300
0.4490	0.2634	1.41819	1.0306
0.3533	0.3113	1.41604	1.0275
0.3541	0.4978	1.42846	1.0169
0.2598	0.1867	1.40211	1.0348
0.2731	0.5396	1.42685	1.0142
0.1860	0.1325	1.39394	1.0378
0.1784	0.3278	1.40710	1.0263
0.1783	0.4790	1.41764	1.0176
0.1926	0.6778	1.43168	1.0060

n-Tetradecane–*n*-Hexane–2-Bromobutane

0.6943	0.1434	1.42022	1.0077
0.6280	0.1834	1.41819	1.0013
0.5072	0.2041	1.41750	0.9774
0.5283	0.2702	1.41370	0.9981
0.4325	0.2857	1.41312	0.9786
0.3658	0.1401	1.42199	0.9280
0.3530	0.3196	1.41140	0.9676
0.2806	0.1899	1.41976	0.9196
0.2823	0.3504	1.41002	0.9579
0.2792	0.5291	1.39966	0.9998
0.1959	0.1502	1.42277	0.8898
0.1785	0.3262	1.41212	0.9271
0.1811	0.4965	1.40181	0.9683
0.1891	0.6636	1.39195	1.0100

n-Tetradecane–4-Methylcylohexanone–*n*-Hexane

0.7059	0.1473	1.42127	1.0377
0.6274	0.1754	1.41895	1.0358
0.5424	0.1760	1.41475	1.0357
0.5358	0.2589	1.41985	1.0309
0.4473	0.2728	1.41618	1.0298
0.3825	0.1209	1.40285	1.0389
0.3644	0.3095	1.41458	1.0276
0.3770	0.4714	1.42599	1.0183
0.2771	0.1802	1.40106	1.0349
0.2869	0.3479	1.41312	1.0252
0.2832	0.5151	1.42421	1.0154
0.2110	0.1312	1.39407	1.0378
0.2093	0.2918	1.40523	1.0285
0.2136	0.4742	1.41802	1.0178

n-Hexadecane–*n*-Tetradecane–2-Bromobutane

0.1403	0.1551	1.43176	0.8784
0.1861	0.1796	1.43137	0.8952
0.2056	0.2693	1.43054	0.9213
0.2781	0.1831	1.43111	0.9182
0.2891	0.2739	1.43034	0.9424
0.1614	0.4872	1.42914	0.9629
0.3416	0.3172	1.43000	0.9653
0.4930	0.1551	1.43097	0.9630
0.1875	0.5437	1.42886	0.9827
0.3555	0.3657	1.42977	0.9801
0.5321	0.1879	1.43080	0.9801
0.1644	0.6640	1.42840	1.0060
0.3167	0.4835	1.42929	0.9992
0.5025	0.3299	1.43014	1.0069
0.6801	0.1407	1.43108	1.0042

n-Hexadecane–*n*-Tetradecane–*n*-Hexane

0.1857	0.1795	1.39479	1.0460
0.1793	0.2685	1.39930	1.0461
0.2612	0.1756	1.39924	1.0462
0.2664	0.2626	1.40425	1.0464
0.1337	0.4935	1.40882	1.0465
0.3190	0.3020	1.40947	1.0465
0.4884	0.1255	1.41012	1.0466
0.1841	0.5304	1.41375	1.0468
0.3663	0.3593	1.41531	1.0467
0.5435	0.1829	1.41630	1.0468
0.1480	0.6421	1.41738	1.0468
0.3306	0.4653	1.41866	1.0468
0.4873	0.3089	1.41856	1.0469
0.6570	0.1400	1.42048	1.0469

n-Hexadecane–*n*-Tetradecane–4-Methylcyclohexanone

0.6376	0.1849	1.43224	1.0364
0.5378	0.2783	1.43182	1.0361
0.4496	0.2800	1.43255	1.0308
0.3704	0.1441	1.43544	1.0180
0.3689	0.3190	1.43276	1.0284
0.3720	0.5038	1.43040	1.0396
0.2678	0.1878	1.43584	1.0145
0.2797	0.3745	1.43267	1.0262
0.2720	0.5387	1.43060	1.0356
0.1846	0.1543	1.43747	1.0075
0.2021	0.3130	1.43454	1.0179
0.1760	0.5136	1.43171	1.0284
0.1863	0.6763	1.42954	1.0387

Carbon Tetrachloride–*n*-Hexane–Benzene

0.6962	0.1572	1.44974	0.7837
0.5189	0.2014	1.45111	0.8532
0.5384	0.2819	1.43999	0.8442
0.3560	0.1671	1.46189	0.9181
0.3619	0.3181	1.44212	0.9130
0.3666	0.5057	1.41845	0.9078
0.1844	0.3142	1.44930	0.9829
0.1771	0.5018	1.42588	0.9824
0.2141	0.6503	1.40639	0.9656
0.6115	0.1939	1.44837	0.8170
0.4452	0.2552	1.44688	0.8809
0.2810	0.5396	1.41741	0.9409
0.2932	0.3050	1.44633	0.9399
0.2416	0.1858	1.46376	0.9625

Volume fractions previously reported (*5*) incorrectly, respectively, as 0.5287[a], 0.3579[b], and 0.5727[c].

Table III. Refractometric Properties of Quaternary Mixtures at 25° C.

Volume Fraction				
First-named component	Second-named component	Third-named component	Refractive Index, n_D	Refractivity Intercept, $n_D - d/2$
n-Hexadecane–*n*-Tetradecane–*n*-Hexane–2-Bromobutane				
0.8590	0.0506	0.0452	1.42977	1.0363
0.6854	0.1091	0.1041	1.42588	1.0226
0.4164	0.3944	0.0852	1.42536	1.0220
0.1245	0.5764	0.1451	1.42072	1.0097
0.3325	0.3261	0.1809	1.42005	1.0081
0.4437	0.1712	0.1934	1.42011	1.0006
0.1779	0.4291	0.1861	1.41906	0.9969
0.2547	0.2660	0.1842	1.41993	0.9758
0.3862	0.1012	0.4091	1.40825	1.0214
0.2472	0.2644	0.2893	1.41411	0.9986
0.2477	0.2574	0.2505	1.41630	0.9879
0.2903	0.1785	0.2004	1.41947	0.9671
0.1750	0.3092	0.3059	1.41276	0.9959
0.1852	0.2928	0.1896	1.41947	0.9668
0.0929	0.3811	0.4323	1.40526	1.0236
0.0922	0.3797	0.0914	1.42458	0.9420
0.2567	0.1759	0.2866	1.41449	0.9790
0.3289	0.0852	0.1056	1.42553	0.9316
0.1674	0.2690	0.2693	1.41492	0.9757
0.1677	0.1850	0.4502	1.40485	0.9987
0.1655	0.1878	0.1748	1.42092	0.9335
0.1225	0.1323	0.1428	1.42335	0.9022
0.1258	0.1169	0.6148	1.39545	1.0115
0.0833	0.0954	0.1045	1.42622	0.8749
0.0834	0.0843	0.7380	1.38818	1.0228
0.0482	0.0537	0.8475	1.38170	1.0330
n-Hexadecane–*n*-Tetradecane–4-Methylcyclohexanone–*n*-Hexane				
0.8450	0.0545	0.0566	1.43003	1.0437
0.6916	0.1057	0.0887	1.42596	1.0415
0.0572	0.8289	0.0603	1.42551	1.0433
0.3921	0.4145	0.0932	1.42519	1.0414
0.3887	0.3961	0.1021	1.42455	1.0407
0.5858	0.1466	0.1297	1.42467	1.0390
0.0906	0.7036	0.1002	1.42340	1.0407
0.3987	0.1102	0.3860	1.42889	1.0236
0.1486	0.5767	0.1438	1.42289	1.0380
0.4605	0.1757	0.1853	1.42266	1.0355
0.3042	0.3273	0.1822	1.42138	1.0356
0.3077	0.1990	0.3024	1.42295	1.0284
0.1793	0.4448	0.1755	1.41987	1.0359
0.2674	0.2754	0.2576	1.42153	1.0310
0.1379	0.1477	0.5901	1.43011	1.0113
0.1944	0.1775	0.4684	1.42651	1.0185
0.2729	0.2877	0.1789	1.41744	1.0355
0.2836	0.1982	0.2790	1.42002	1.0297
0.2439	0.2540	0.2416	1.41813	1.0318
0.1759	0.2614	0.2672	1.41633	1.0302
0.1821	0.2962	0.1761	1.41253	1.0358
0.1884	0.1802	0.3059	1.41546	1.0278
0.1684	0.1611	0.3304	1.41507	1.0264
0.0928	0.4041	0.0934	1.40763	1.0407
0.0904	0.1109	0.3982	1.41270	1.0222
0.1827	0.1697	0.1740	1.40577	1.0356
0.0927	0.0920	0.3972	1.41176	1.0222
0.1429	0.1335	0.1299	1.39834	1.0380
0.0889	0.0827	0.0992	1.39007	1.0396
n-Hexadecane–Carbon Tetrachloride–Benzene–*n*-Hexane				
0.7871	0.0645	0.0460	1.43060	1.0229
0.6720	0.0899	0.0928	1.43120	1.0138
0.4223	0.1961	0.1849	1.43592	0.9743
0.3766	0.4005	0.1002	1.44021	0.8959
0.3592	0.1019	0.4000	1.45005	1.0129
0.3800	0.1200	0.0931	1.41685	1.0016
0.2994	0.3044	0.1952	1.43915	0.9335
0.2925	0.1981	0.1806	1.42821	0.9732
0.2463	0.2257	0.2691	1.43837	0.9641
0.2489	0.1813	0.2953	1.43786	0.9812
0.2484	0.2832	0.1841	1.43307	0.9410
0.1391	0.1436	0.5818	1.46408	1.0000
0.1088	0.0925	0.6885	1.47135	1.0210
0.1716	0.1835	0.4562	1.45346	0.9829
0.1710	0.4581	0.1862	1.44381	0.8750
0.0472	0.0681	0.7873	1.47861	1.0318
0.1774	0.2800	0.2534	1.43719	0.9432
0.1648	0.1872	0.3290	1.43767	0.9794
0.1208	0.5998	0.1248	1.44539	0.8200
0.0828	0.3847	0.4119	1.46095	0.9064
0.1670	0.3344	0.1800	1.43213	0.9214
0.1631	0.2012	0.1729	1.41979	0.9714
0.0783	0.6957	0.0995	1.44818	0.7832
0.1255	0.1604	0.1556	1.41205	0.9865
0.1012	0.3965	0.1210	1.42643	0.8967
0.0922	0.1146	0.0962	1.39924	1.0032
0.0564	0.0744	0.0726	1.39087	1.0179

refractivity intercepts for physicochemical analysis of mixtures of nonelectrolytes. A previous paper (*7*) considered the question of the degree of complexity required in applying Equation 1 refractivity intercepts in binary systems. Here the question relative to fitting ternary and quaternary systems is considered. The complexity of the relationship has a clear bearing on the convenience of applying refractivity intercepts to analysis, particularly in multicomponent systems, where graphing techniques become impractical.

EXPERIMENTAL

Equipment. The equipment and techniques have been described (*4*). A water bath thermostatically controlled to ±0.01° C. was used. Bath temperature was set and monitored by a Beckman thermometer which had been set with a thermometer calibrated against an NBS certified standard. The cathetometer used in pycnometric density determinations indicated height to ±0.05 mm. All weighings were made with a Mettler 300-gram-capacity precision balance with certified balance weights.

Densities were determined with 3-ml. Lipkin pycnometers with precision capillary arms of 1-mm. i.d. The pycnometer was maintained in the bath until constant meniscus level was obtained. As room temperature was only slightly lower than 25° C., temperature equilibrium was established rapidly. Evaporation losses were negligible. The pycnometer was calibrated with distilled water, with heights of the liquid in the capillary arms measured relative to a single etch mark on each arm. Dissolved air was expelled from the water prior to calibration. Replication of measured densities of the pure components indicates an estimated precision of ±0.00005 gram per ml. in density.

Liquids were mixed in a 50-ml. modified glass syringe sealed by glass at the needle end. Again, evaporation rates were negligible. Transfer to the pycnometer was by overpressure through capillary tubing installed within the syringe plunger. The glass equipment was provided with ball and socket joints to minimize evaporation on transfer. Joints were treated with hexane to remove traces of nonvolatile components.

Refractive indices were measured with a Bausch and

Table IV. Ternary Constants of Equation 2[a]

	Density, Volume Fraction			10^4 Error, G./Ml.		Refractive Index, Volume Fraction			10^5 Error Refractive Index		Refractivity Intercept, Volume Fraction			10^4 Error Refractivity Intercept	
	A	*B*	*C*	Stand.[b]	Max.	*A*	*B*	*C*	Stand.[b]	Max.	*A*	*B*	*C*	Stand.[b]	Max.
n-Hexadecane–*n*-hexane–2-bromobutane	0.0317	−0.0323	−0.0399	1	2	0.01159	−0.02022	−0.01506	4	8	−0.0065			1	2
n-Hexadecane–benzene–*n*-hexane	0.0016	−0.0012	0.0404	2	3	0.00760			8	16	0			1	2
n-Hexdecane–carbon tetrachloride–benzene	0.0140	−0.0288	−0.0147	1	2	−0.00310	−0.00263	0.02172	12	22	0.0216	−0.1032	−0.0059	2	3
n-Hexadecane–carbon tetrachloride–*n*-hexane	0.0469	−0.0378	0.0125	1	2	0.00733			8	15	0.0051	−0.0808	−0.0452	2	3
n-Hexadecane–4-methylcyclohexanone–*n*-hexane	−0.0035	0.0302	0.0055	2	4	−0.00657	−0.00902	0.01827	5	9	−0.0090			1	3
n-Tetradecane–*n*-hexane–2-bromobutane	0.0218	−0.0338	−0.0072	1	2	−0.00562			8	15	−0.0101			1	2
n-Tetradecane–4-methylcyclohexanone–*n*-hexane	−0.0077	0.0074	0.0229	1	2	−0.01919	−0.00336	0.02848	8	16	−0.0131			1	2
n-Hexadecane–*n*-tetradecane–2-bromobutane	0.0101	−0.0069	−0.0328	1	3	−0.00545			6	12	−0.0048			1	2
n-Hexadecane–*n*-tetradecane–*n*-hexane	0			1	2	−0.00503			5	9	−0.0044			1	1
n-Hexadecane–*n*-tetradecane–4-methylcyclohexanone	0.0075	−0.0272	−0.0218	1	2	0.01634	−0.03408	−0.02900	4	7	0.0148	−0.0158	−0.0262	1	1
Carbon tetrachloride–*n*-hexane–benzene	−0.0011	−0.0715	0.0209	3	6	−0.01835	0.02626	0.02332	7	17	−0.0033	0.0262	−0.0194	2	4

[a] Component order as stated in Table II. [b] $\{\sum(\text{exptl.} - \text{calcd.})^2/\text{number of observations}\}^{1/2}$.

Table V. Quaternary Constants of Equation 2[a]

	Density, Volume Fraction				10^4 Error, G./Ml.		Refractive Index, Volume Fraction				10^5 Error, Refractive Index		Refractivity Intercept, Volume Fraction,	10^4 Error Refractivity Intercept	
	A	B	C	D	Stand.[b]	Max.	A	B	C	D	Stand.[b]	Max.	A	Stand.[b]	Max.
***n*-Hexadecane–*n*-tetradecene–*n*-hexane–2-bromobutane	−0.3493	1.2015	0.3019	−0.1806	2	5	−0.09120	0.42338	0.05039	−0.16831	8	24	−0.0209	1	1
***n*-Hexadecane–*n*-tetradecane–4-methylcyclohexanone–*n*-hexane	0.0272				1	3	−0.07508	0.04064	−0.04308	0.37829	6	12	−0.0262	1	2
***n*-Hexadecane–carbon tetrachloride–benzene–*n*-hexane	−0.2843	0.8112	−0.0868	0.0771	1	2	0.22462	−0.52925	−0.20659	−0.10641	15	28	0.0968	1	3

[a] Component order as stated in Table III. [b] Defined in Table IV.

Lomb Precision refractometer, thermostated at 25.00° ± 0.01° C., and using the sodium-D line, 5893 A. The refractometer was calibrated, and frequently rechecked, with air-free distilled water. For refractive indices the estimated precision is in agreement with the manufacturer's stated accuracy of the instrument, ±0.00003 unit.

Materials. Purification of the components has been described, and a comparison made between several experimental physical properties and literature values (*4*). The densities, refractive indices, and refractivity intercepts of the purified components are given in Table I.

RESULTS AND DISCUSSION

Refractive indices and refractivity intercepts are listed in Table II for the ternary systems and in Table III for the quaternary systems. Densities are not included in either table. They may be obtained from previously reported work (*5, 6*).

In multicomponent systems, an extension of Equation 1 has been used to fit the data. Thus for a quaternary system,

$$p = \phi_i p_i + \phi_j p_j + \phi_k p_k + \phi_l p_l + \sum_{\substack{i=1 \\ i<j}}^{n} \sum_{j=2}^{n} \phi_i \phi_j [A_{ij} + B_{iu}\phi_i + C_{ij}\phi_i^2 + \dots] + \sum_{\substack{i=1 \\ i<j<k}}^{n} \sum_{j=2}^{n} \sum_{k=3}^{n} \phi_i \phi_j \phi_k [A_{ijk} + B_{ijk}\phi_i + C_{uik}\phi_u + \dots] + \phi_i \phi_j \phi_k \phi_l [A_{ijkl} + B_{ijkl}\phi_i + C_{ijkl}\phi_j + D_{ijkl}\phi_k + \dots] \quad (2)$$

For a ternary system, Equation 2 is reduced, in that ϕ_l is zero, and the triple summation in $\phi_i\phi_j\phi_k$ becomes a single power series expansion in ϕ_i, ϕ_u.

Table IV lists the ternary constants for three properties fitted with Equation 2, and Table V lists the corresponding constants for the quaternary systems. Also included in these tables are the errors in fitting the experimental data thereby. Fitting was with a digital computer, using a weighted least-squares procedure (*3*). In establishing the ternary coefficients, a maximum of ten constants—i.e., through the third power of ϕ, including cross terms—was used in each system. The function was reduced by increments of one power of ϕ until the single constant A_{ijk} remained. The number of constants for a system reported in Table IV is that above which each increasing power of ϕ decreased the standard error by an amount less than the estimated precision of the property fitted. A similar approach was used in establishing the quaternary coefficients in Table V.

Three ternary constants are required to represent the densities for all systems but one. For six of the 11 systems, the ternary term represents both positive and negative values of the ternary deviation functions in the system. For *n*-hexadecane–*n*-tetradecane–*n*-hexane no ternary deviation term is needed. This is the only system consisting of three homologs, and the behavior may be a consequence of the principle of congruence (*1*). For densities in the quaternary systems, a maximum of four constants is required. All three systems show both positive and negative values for the quaternary deviation term. The typical error in representing the densities is ±0.0001 gram per ml. in both ternary and quaternary systems.

The excess molar volumes of mixing in the present ternary systems have been represented by (*5*)

$$\Delta V^E = \sum_{\substack{i=1 \\ i<j}}^{n} \sum_{j=2}^{n} x_i x_u (A_{ij} + B_{iu}x_i + C_{ij}x_i^2 + \dots) + x_i x_j x_k A_{ijk} \quad (3)$$

A comparison of the relative effectiveness of representing volumetric behavior in the ternary systems with excess volumes or densities is, therefore, possible. The ternary deviation terms in A_{ijk} of Equation 3 were significantly greater than zero in only half of the systems. In only two of these systems did this ternary deviation term assume both positive and negative values. For eight of the 11 systems, fitting through excess volumes produced smaller error than through densities. For the present ternary systems, treatment of the volumetric behavior through excess volumes is preferable to densities.

The two types of volumetric deviation functions are, of course, related. However, even for a binary system they are not simply related. Thus, let Equation 1 be restated for density in a binary system as $d = \phi_1 d_1 + \phi_2 d_2 + f(\phi)$, where $f(\phi)$ represents the deviation from additivity. Let Equation 3 be restated as $\Delta V^E = f(x)$. Then $f(\phi) = -(\phi_1 d_1 + \phi_2 d_2) f(x)/[x_1 V_1 + x_2 V_2 + f(x)]$. Although this expression reduces to $f(\phi) = 0$ when $f(x) = 0$, a simple relationship between $f(\phi)$ and $f(x)$ cannot be obtained. The problem grows more complicated as the number of components is increased.

For refractive indices in the ternary systems, a maximum of three constants is required. Five systems require only one constant. All of the systems requiring three constants, except *n*-tetradecane–4-methylcyclohexanone–*n*-hexane, exhibit both positive and negative values for the ternary deviation term. Unlike density, for refractive indices the system containing the three *n*-alkane homologs requires a ternary deviation term. For the quaternary systems, four constants are required for every system. There are positive and negative values for the quaternary deviation term in each system. Typical error in representing the refractive indices is ± 0.00007 unit in the ternary systems, and ± 0.0001 unit in the quaternary systems.

For refractivity intercepts in the ternary systems, a maximum of three constants is sufficient to fit the data. For the refractivity intercept, the average number of constants required is significantly fewer than for the density. For refractivity intercepts, six systems require one ternary constant and one system requires no ternary constant. Three of the systems requiring three ternary constants show both positive and negative values for the ternary deviation term. The fourth, *n*-hexadecane–carbon tetrachloride–*n*-hexane, exhibits only negative values for that term. The last-named system exhibits the largest values of that term among all of the ternary systems.

There is no apparent reason for the number of constants which a given system requires in representing the ternary deviation term for refractivity intercepts. Moreover, there is no consistent correlation between the sign of the ternary deviation term in density and that of refractive index and refractivity intercept. The typical error in fitting the refractivity intercepts in the systems is ± 0.0001 unit.

For refractivity intercepts in the quaternary systems, only one constant is required. For the three systems, all points in a system are of a fixed sign within experimental error. Typical error in fitting the refractivity intercepts in the quaternary systems is ± 0.0001 unit. As in the ternary systems, the refractivity intercepts tend to require fewer constants for representing the deviation term than do the densities.

The deviation functions used in the present work are empirical. No effort has been made to standardize the order of the components listed within each system. Equations for a transposition of components are available from a transformation table (2).

In summary, the ability to represent the refractivity intercepts in the systems higher than binary with fewer terms than required for the densities makes the former a convenient property to use for the analysis of present systems.

NOMENCLATURE

$A, B, C,$ D, E, F	=	constants for fitting of data
V	=	molar volume, ml. per mole
ΔV^E	=	$V - \Sigma x_i V_i$, molar excess volume of mixing, ml. per mole
d	=	density, g. per ml.
n_D	=	refractive index, Na-D line
$n_D - d/2$	=	refractivity intercept
p	=	physical property
x	=	mole fraction
ϕ	=	$x_i V_i / \Sigma x_i V_i$, volume fraction

SUBSCRIPTS. Letters or numbers indicate the component(s) associated with the given property or symbol.

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