Refractive Indices of Some Ternary Systems Containing Naphthalene

Binary Solvent Mixtures Containing Hexadecane

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Refractive indices have been determined at 25° C. for the ternary systems of naphthalene and hexadecane with each of benzene, toluene, ethylbenzene, carbon tetrachloride, hexane and cyclohexane; and for several of the binary subsystems. Equations are given relating refractive index to solution composition in mole fraction. The average deviations in the ternary systems from predicted refractive indices by these equations range from 5 to 10 × 10^{-5} units among the systems. The deviations are nonrandomly distributed in each system.

IN A PREVIOUS PUBLICATION refractive indices of some ternary systems containing naphthalene were reported (*4*). That study was concerned with solvent pairs from among benzene, toluene, ethylbenzene, and carbon tetrachloride. Those systems are characterized by a small energy of interaction between the components (*1*, *2*), and relatively small differences in their molar volumes. The present work is concerned with an extension of the study to ternary systems containing components of greater dissimilarity, with consideration of this effect on the suitability of equations used in representing the experimental data.

EXPERIMENTAL DATA

Equipment, experimental procedure, and chemicals used have been described previously (*1*). All present refractive indices (n) refer to 25.00 ± 0.01° C. and the sodium D-line, 5893 A.

Table I. Refractive Indices of Binary Systems at 25° C.

System	Mole Fraction of First-named Component	Exptl. Refr. Index
Benzene-hexadecane	0.8569	1.47057
	0.6185	1.45005
	0.4587	1.44324
	0.2339	1.43673
	By Eq. 1: Std. Dev. 10^5 = 16, Av. Dev. 10^5 = 13	
Toluene-hexadecane	0.8293	1.46960
	0.6026	1.45227
	0.4301	1.44426
	0.2096	1.43725
	By Eq. 1: Std. Dev. 10^5 = 12, Av. Dev. 10^5 = 10	
Ethylbenzene-hexadecane	0.8448	1.47286
	0.6314	1.45588
	0.4467	1.44633
	0.2410	1.43885
	By Eq. 1: Std. Dev. 10^5 = 9, Av. Dev. 10^5 = 7	
Carbon tetrachloride–hexadecane	0.8353	1.44620
	0.5988	1.43906
	0.4323	1.43631
	0.2555	1.43437
	By Eq. 1: Std. Dev. 10^5 = 8, Av. Dev. 10^5 = 7	
Hexane-hexadecane	0.8462	1.39104
	0.6030	1.40953
	0.4281	1.41854
	0.1897	1.42744
	By Eq. 1: Std. Dev. 10^5 = 7, Av. Dev. 10^5 = 6	
Cyclohexane-hexadecane	0.8216	1.42496
	0.5696	1.42766
	0.4237	1.42941
	0.1954	1.43131
	By Eq. 1: Std. Dev. 10^5 = 8, Av. Dev. 10^5 = 6	
Naphthalene-hexadecane	0.1618	1.44644
	0.1473	1.44508
	0.1272	1.44326
	0.1267	1.44323
	0.1050	1.44136
	0.0824	1.43943
	0.0676	1.43809
	By Eq. 1: Std. Dev. 10^5 = 3, Av. Dev. 10^5 = 2	
Naphthalene-hexane	0.1116	1.40026
	0.1035	1.39810
	0.0926	1.39552
	0.0922	1.39537
	0.0901	1.39485
	0.0804	1.39229
	0.0779	1.39180
	0.0688	1.38940
	0.0682	1.38928
	0.0676	1.38928
	0.0651	1.38848
	0.0402	1.38237
	By Eq. 1: Std. Dev. 10^5 = 7, Av. Dev. 10^5 = 5	
Naphthalene-cyclohexane	0.1233	1.44983
	0.1134	1.44782
	0.0968	1.44417
	0.0808	1.44070
	0.0727	1.43887
	0.0400	1.43176
	By Eq. 1: Std. Dev. 10^5 = 4, Av. Dev. 10^5 = 3	

Binary system data are given in Table I. In the naphthalene-solvent binaries, the data extend to within 0.01, 0.03, and 0.04 mole fraction of saturation for hexane, cyclohexane, and hexadecane, respectively.

Ternary system data are given in Table II. As previously (*4*), the data reported in each system have been reduced to 20 points from the total number recorded. The reported data represent the extent of the concentration range covered, and include several points within a few hundredths mole fraction of naphthalene saturation. All data are quite removed in concentration from the binaries, so that rigorous tests of the ternary equations used should obtain.

REPRESENTATION OF DATA BY ANALYTICAL FUNCTIONS

In the binary systems, n has been expressed as

$$n = n_1x_1 + n_2x_2 + x_1x_2A_{12} \qquad (1)$$

where n_i and x_i are the refractive index and mole fraction,

Table II. Refractive Indices of Ternary Systems at 25° C.

System	Mole Fraction of First-named Component	Mole Fraction of Second-named Component	Exptl. Refr. Index
Benzene-hexadecane-naphthalene	0.1544	0.7313	1.44620
	0.1500	0.7103	1.44864
	0.1404	0.6649	1.45443
	0.2141	0.7010	1.44483
	0.1977	0.6476	1.45202
	0.3638	0.4986	1.45735
	0.3436	0.4709	1.46309
	0.3311	0.4538	1.46680
	0.4243	0.5007	1.45155
	0.3902	0.4605	1.46051
	0.5018	0.3313	1.47132
	0.4634	0.3060	1.48020
	0.5784	0.3567	1.45866
	0.5386	0.3322	1.46728
	0.5022	0.3097	1.47553
	0.8043	0.1343	1.48052
	0.7574	0.1265	1.48939
	0.6971	0.1132	1.50147
	0.6837	0.1110	1.50388
	0.6470	0.1050	1.51066
	Std. Dev. 10^5: 23(Eq. 3a), 50(Eq. 3b)		
	Av. Dev. 10^5: 19(Eq. 3a), 42(Eq. 3b)		
Toluene-hexadecane-naphthalene	0.1956	0.7374	1.44334
	0.1812	0.6834	1.44996
	0.3426	0.5206	1.45768
	0.3343	0.5080	1.45996
	0.3230	0.4909	1.46328
	0.3126	0.4750	1.46643
	0.3953	0.5238	1.45275
	0.3648	0.4835	1.46059
	0.4853	0.3386	1.47309
	0.4690	0.3272	1.47672
	0.4573	0.3190	1.47934
	0.5574	0.3675	1.46117
	0.5154	0.3398	1.46981
	0.4841	0.3192	1.47646
	0.7575	0.1560	1.48168
	0.7232	0.1489	1.48749
	0.6766	0.1393	1.49545
	0.6711	0.1280	1.49913
	0.6401	0.1221	1.50439
	0.6210	0.1184	1.50767
	Std. Dev. 10^5: 13(Eq. 3a), 34(Eq. 3b)		
	Av. Dev. 10^5: 9(Eq. 3a), 28(Eq. 3b)		
Ethylbenzene-hexadecane-naphthalene	0.1709	0.7407	1.44517
	0.1554	0.6738	1.45326
	0.1511	0.6551	1.45563
	0.2178	0.6859	1.44770
	0.1998	0.6290	1.45515
	0.3685	0.4987	1.45919
	0.3534	0.4782	1.46317
	0.4093	0.5070	1.45488
	0.3843	0.4760	1.46084
	0.5266	0.3242	1.47236
	0.5101	0.3141	1.47565
	0.4843	0.2982	1.48090
	0.5823	0.3399	1.46470
	0.5462	0.3189	1.47130
	0.7833	0.1439	1.48210
	0.7422	0.1364	1.48829
	0.6975	0.1282	1.49521
	0.6872	0.1200	1.49866
	0.6688	0.1167	1.50156
	0.6550	0.1143	1.50371
	Std. Dev. 10^5: 10(Eq. 3a), 20(Eq. 3b)		
	Av. Dev. 10^5: 8(Eq. 3a), 15(Eq. 3b)		
Carbon tetrachloride-hexadecane-naphthalene	0.1390	0.7778	1.44125
	0.1339	0.7492	1.44447
	0.1294	0.7240	1.44743
	0.1249	0.6987	1.45056
	0.2420	0.7050	1.43937
	0.2262	0.6589	1.44572
	0.3711	0.5435	1.44560
	0.3588	0.5255	1.44912
	0.3324	0.4869	1.45703
	0.4041	0.5306	1.44362
	0.3798	0.4987	1.45013
	0.4983	0.3579	1.45800
	0.4653	0.3342	1.46604
	0.5510	0.3692	1.44961
	0.5052	0.3385	1.46005
	0.7651	0.1508	1.46096
	0.7103	0.1400	1.47229
	0.7387	0.1385	1.46841
	0.7173	0.1345	1.47296
	0.6759	0.1267	1.48171
	Std. Dev. 10^5: 18(Eq. 3a), 28(Eq. 3b)		
	Av. Dev. 10^5: 13(Eq. 3a), 23(Eq. 3b)		
Hexane-hexadecane-naphthalene	0.1468	0.7865	1.43459
	0.1425	0.7638	1.43712
	0.1370	0.7340	1.44057
	0.1321	0.7079	1.44381
	0.1778	0.7594	1.43324
	0.1668	0.7127	1.43887
	0.3630	0.5529	1.42942
	0.3528	0.5373	1.43249
	0.3423	0.5214	1.43569
	0.3333	0.5076	1.43856
	0.5485	0.3840	1.41966
	0.5363	0.3755	1.42263
	0.5224	0.3658	1.42604
	0.5103	0.3573	1.42900
	0.8191	0.1489	1.39708
	0.7991	0.1453	1.40157
	0.8082	0.1414	1.40025
	0.7944	0.1390	1.40338
	0.7712	0.1349	1.40872
	0.7565	0.1323	1.41216
	Std. Dev. 10^5: 6(Eq. 3a), 10(Eq. 3b)		
	Av. Dev. 10^5: 5(Eq. 3a), 7(Eq. 3b)		
Cyclohexane-hexadecane-naphthalene	0.1564	0.7699	1.43833
	0.1459	0.7183	1.44439
	0.1415	0.6967	1.44704
	0.1839	0.7573	1.43669
	0.1746	0.7187	1.44133
	0.3688	0.5382	1.43995
	0.3478	0.5076	1.44605
	0.3397	0.4957	1.44847
	0.3772	0.5248	1.44038
	0.3573	0.4972	1.44608
	0.3493	0.4860	1.44847
	0.3976	0.5408	1.43618
	0.3770	0.5129	1.44184
	0.5364	0.4053	1.43539
	0.5070	0.3831	1.44217
	0.5091	0.3785	1.44261
	0.4923	0.3660	1.44659
	0.4802	0.3570	1.44960
	0.7580	0.1564	1.43962
	0.7067	0.1458	1.45059
	Std. Dev. 10^5: 7(Eq. 3a), 11(Eq. 3b)		
	Av. Dev. 10^5: 6(Eq. 3a), 9(Eq. 3b)		

Table III. Binary System Constants

System	Constants of Equation 2 (x_1 is First-named Component)		
	B_{12}	C_{12}	D_{12}
Benzene-hexadecane	−0.08148	−0.05832	−0.04312
Toluene-hexadecane	−0.06494	−0.03750	−0.02188
Ethylbenzene-hexadecane	−0.05653	−0.02791	−0.01532
Carbon tetrachloride–hexadecane	−0.03071	−0.02032	−0.01543
Hexane-hexadecane	0.05004	0.02228	0.01082
Cyclohexane-hexadecane	0.00223	−0.00261	−0.00140
Naphthalene-hexadecane	−0.17149	−0.07508	−0.01900
Naphthalene-hexane	−0.08344	−0.20772	−0.13997
Naphthalene-cyclohexane	−0.14441	−0.40906	−0.26248

respectively, of pure component i. A_{12} is a concentration dependent function defined by

$$A_{12} = B_{12} + C_{12}\,(x_1 - x_2) + D_{12}\,(x_1 - x_2)^2 \quad (2)$$

where B_{12}, C_{12}, D_{12} are empirical constants evaluated from experimental n data. The constants of Equation 2 are listed in Table III. For the naphthalene-solvent systems the constants are based upon the assignment of 1.62615 as n of the supercooled state (*4*). Columns 4 and 5 of Table I list the standard and average deviations of experimental n from those predicted with Equation 1.

In representing ternary behavior the equation has been used:

$$n = n_1x_1 + n_2x_2 + n_3x_3 + x_1x_2A_{12} + x_1x_3A_{13} + x_2x_3A_{23} + A_{123} \quad (3)$$

A_{123} is a three-component difference term which will be zero if the binary coefficients only are needed to calculate refractive index for the ternary mixtures. The data show that calculation of the refractive index using the binary coefficients A_{12}, A_{13}, and A_{23} leads to errors so that the term A_{123} can amount to as much as from 200×10^{-4} in the hexane-hexadecane-naphthalene system to 600×10^{-4} in the benzene-hexadecane-naphthalene system. Differences are constantly of the same sign in some systems (positive or negative), while within other systems differences range over both positive and negative values.

The difference term A_{123} can be represented by Equation 4:

$$A_{123} = B_{123} + C_{123}x_1 + D_{123}x_2 + E_{123}x_1^2 + F_{123}x_2^2 + G_{123}x_1x_2 \quad (4)$$

Combining Equations 3 and 4 gives Equation 3a. An attempt to simplify Equation 3a by assigning the value zero to E_{123}, F_{123}, G_{123} gives an Equation 3b which is less adequate. In using Equation 3a or 3b it is, of course, understood that the binary coefficients are first calculated using Equation 2 (see Table III). The ternary coefficients are taken from Table IV.

Columns 5 to 8 of Table II list the standard and average deviations of the experimental n from those predicted with Equations 3a and 3b. As in previous work (*4*), computations in the present work were programmed for a digital computer.

DISCUSSION

In the present binary solvent-solvent systems, the deviations from Equation 1 are significantly greater than those encountered previously (*4*). This contrast apparently does not depend as much upon the difference of n values of the two pure components as upon both the difference in molal volumes and the energy of interaction between them (*1*, *2*, *3*). The relationship is not clearly consistent, however.

In the present binary naphthalene-solvent systems, deviations from Equation 1 are comparable with those found in earlier work (*4*). It may be, however, that the reduced range of observable concentrations in the present work—due to decreased naphthalene solubility (*1*)—has masked what might actually be a relatively poorer fit of the data in the hexadecane-naphthalene system.

In the present ternary systems, experimental n shows a systematic deviation from values calculated when A_{123} is assumed to be zero. Only in the two systems containing cyclohexane or hexane are both positive and negative deviations found within a system. The sign of the deviations in the other systems is not predictable, nor is their magnitude related to the difference of n of the pure solvents.

The use of Equations 3a or 3b yields deviations from experimental results comparable with those found before (*4*), despite the larger deviations from Equation 1 for the present binary solvent-solvent subsystems. Both the average and extreme deviations in all present systems are greater by Equation 3b than by 3a, and the deviations are nonrandomly distributed in a system. With the former and later equations, the greatest differences in any single system are 90 and 40×10^{-5} units respectively.

It appears that the degree of usefulness of Equation 3a in ternary systems is not markedly affected by increasing dissimilarity between the solvent pair. In the present work, the deviations accompanying the application of Equation 1 to the constituent binaries are comparable to those encountered in the ternaries. The apparently small effect in the ternary systems resulting from deviations in the binary systems reflects the decreasing significance of the latter in concentration regions quite far removed from the constituent binary subsystems. While the desirability of higher terms in $(x_1 - x_2)$ in Equation 1 for representing present solvent-solvent pairs is indicated, there is no assurance that this would lead to decreased deviations in the ternary systems. It appears probable that this indicated need for a larger number of terms in the solvent-solvent binaries results from the difference in the molal volumes. Scatchard and Ticknor (*5*) have shown that n is rather simply related to the volume fractions in ternary systems. Thus, it is not

Table IV. Ternary System Constants

System	Equation 3a						Equation 3b		
	B_{123}	C_{123}	D_{123}	E_{123}	F_{123}	G_{123}	B_{123}	C_{123}	D_{123}
Benzene-hexadecane-naphthalene	−0.0750	−0.7073	0.1321	0.3436	−0.1892	0.6768	−0.2523	−0.1333	0.2764
Toluene-hexadecane-naphthalene	0.2378	−1.2768	−0.4105	0.7769	0.0606	1.1780	−0.1549	−0.1110	0.1771
Ethylbenzene-hexadecane-naphthalene	0.1329	−0.7802	−0.3811	0.4570	0.1837	0.8585	−0.1728	0.0007	0.1728
Carbon tetrachloride–hexadecane–naphthalene	1.8926	−5.2931	−3.2176	3.1323	1.3121	4.4684	0.2135	−0.6359	−0.1417
Hexane-hexadecane-naphthalene	2.2721	−4.9894	−4.3572	2.6744	2.1517	4.8492	0.3226	−0.4004	−0.2489
Cyclohexane-hexadecane-naphthalene	2.9111	−5.8742	−5.3153	2.7339	2.5233	5.3857	0.8367	−1.0826	−0.7128

In applying these constants in Equation 3a or 3b to a system, subscripts 1, 2, 3, refer to the components in the order listed in column 1 of this table.

unexpected that the mole fraction becomes increasingly less suitable as the concentration variable as the difference in molal volumes increases.

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NOMENCLATURE

A_{ij} = function defined in Equation 2
A_{ijk} = function defined in Equation 4
B_{ij}, C_{ij}, D_{ij} = constants in Equation 2
$B_{ijk}, C_{ijk}, D_{ijk}, E_{ijk}, F_{ijk}, G_{ijk}$ = constants in Equation 4
n = refractive index
n_i = refractive index of pure component i
x_i = mole fraction of component i

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Enthalpies, Entropies, and Free Energy Functions of TlF, TlBr, and TlI Above Room Temperature

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The enthalpy increments above 298° K. for solid and liquid thallous fluoride, bromide, and iodide were measured with a drop calorimeter. These data together with literature values for the absolute entropies were used to calculate the enthalpy, entropy, and free energy for these compounds. The thermodynamic functions for the gaseous phases of these compounds were calculated from molecular constant data.

As A PART of our studies of the thermodynamics of evaporation of thallous fluoride (*5*), bromide (*3*), and iodide (*4*), it was necessary to determine the enthalpies of these salts in their condensed phases from room temperature to their boiling points. These results can be combined with the absolute entropies of the crystals at room temperature to yield the free energy function for the condensed phases. In addition, there is sufficient molecular constant data available to calculate the thermodynamic functions (entropy, enthalpy, and free energy function) for the gas phases. Results of this type for thallous chloride have already been reported (*6*).

EXPERIMENTAL

Enthalpy Measurements. The calorimeter was essentially the same as that used for thallous chloride (*6*) except that the calorimeter bucket of the original Parr equipment was replaced by a metal block containing two cavities. The samples dropped into one cavity, while the other cavity contained a small amount of silicone oil in which the calorimetric thermometer was oscillated and registered the temperature rise of the unit.

Preparation of Samples. The halides were prepared by the methods described in the respective papers (*3–5*) on vapor pressures. The purities are also reported there. Samples of approximately 20 grams of each of the halides were sealed into platinum-10% rhodium containers (5/16 inch O.D. × 3 inches long). Proper taring resulted in information on the weights of the containers and contents. Their closures were tested for leaks by heating the containers to the boiling points of their contents and finding no weight loss.

The melting and any transition points were determined by cooling curves. A platinum-10% rhodium thermocouple, checked against one calibrated by the NBS was tightly wired to the outside middle of the capsule. Cooling and heating curves made on these gave sharp breaks for freezing and melting and somewhat less sharp ones at transition points. The values obtained are given in Table I.

ENTHALPIES FOR CONDENSED PHASES

The measured enthalpy increments above 298° K. are shown as data points in Figure 1. To the authors' knowledge, there have been no other measurements on the fluoride and iodide. For the bromide, Goodwin and Kalmus (*7*) have given values to temperature somewhat above the melting point. Their results are shown for comparison. They agree, in general, with the authors' data, but the derived heat capacities, especially of the liquid, differ appreciably.

The enthalpies were fitted to analytical expressions that were first and second order in temperature. These expressions fit the experimental points to somewhat better than