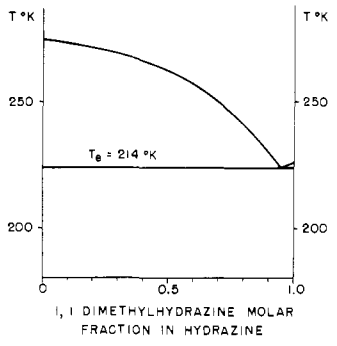

Figure 1. Solid-liquid phase diagram of the system hydrazine–1,1-dimethylhydrazine

straightforward. The components were purified by distillation in nitrogen atmosphere in the presence of sodium hydroxide in the case of hydrazine, and at reduced pressure in the presence of calcium hydride in the case of 1,1-dimethylhydrazine (*1*), collecting the middle fraction and discarding the first and last 25% of the distillate. Chromatographic runs did not show any appreciable peak owing to impurities in the case of hydrazine. A faint, unidentified peak was always present in the case of 1,1-dimethylhydrazine. The samples were prepared by weighing the pure components. The molar fractions are therefore certain to within ±0.005. The samples were sealed in borosilicate glass cells (*2*) in a nitrogen atmosphere and kept in the dark. Thermal analysis of these samples was repeated at intervals over a period of six months with very good reproducibility of results. Samples that were not kept in the dark showed visible signs of decomposition with development of a yellow color and exhibited, in general, depression of the liquidus and solidus points. Thermal analysis was performed following a procedure described elsewhere (*2*). The temperatures were measured with copper-constanant thermocouples and a recorder with a resolution of 0.2° K. Since the rates of cooling and warming were always kept well below one degree per minute, the thermal homogeneity of the sample was better than 0.2° K., which leads to a maximum uncertainty in the temperature of 0.2° K. Table I displays the solidus and liquidus temperatures for various compositions.

Table I. Solidus and Liquidus Temperatures of the System Hydrazine–1,1-Dimethylhydrazine

Molar Fraction of 1,1-Dimethylhydrazine	Solidus Temp., ° K.	Liquidus Temp., ° K.
0.00	...	275
0.01	214	275
0.05	214	274
0.20	214	271
0.35	214	269
0.50	214	262
0.55	214	260
0.59	214	257
0.72	214	250
0.83	214	225
0.90	214	220
0.95	214	215
0.99	...	216
1.00	...	216

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Refractive Indices of Some Ternary Systems Containing Naphthalene

Binary Solvent Mixtures Containing Hexane or Cyclohexane

E. L. HERIC and CECIL D. POSEY[1]
Department of Chemistry, University of Georgia, Athens, Ga.

IN PREVIOUS publications, refractive indices of some ternary systems containing naphthalene have been reported (*4*, *5*). Those studies were concerned with the six solvent pairs from among benzene, toluene, ethylbenzene, and carbon tetrachloride (*4*) and the six solvent pairs of hexadecane with each of benzene, toluene, ethylbenzene, carbon tetrachloride, hexane, and cyclohexane (*5*). Also included were the pertinent binary subsystems. The first set of ternary systems is characterized by a small energy of interaction between the components (*1*, *2*), and relatively small differences in component molar volumes. The second set involved systems containing components of greater dissimilarity.

The present work concludes the study of the set of naphthalene–mixed solvent systems, adding the remaining nine ternaries of the total of 21 possible for naphthalene with these solvent components. All of the present systems contain hexane or cyclohexane as one of the mixed solvent components. As in the previous two works, the question of the suitability of equations used in representing the experimental data is considered.

[1] Present address: Radiological Health Section, Georgia Department of Public Health, Atlanta, Ga.

Refractive indices have been determined at 25° C. for ternary systems of naphthalene with nine mixed solvents containing hexane or cyclohexane and for nine of the binary solvent 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 4 to 20 × 10^{-5} units among the systems.

EXPERIMENTAL DATA

Equipment, experimental procedure, and chemicals used have been described previously (*4*). All present refractive indices (n) refer to 25.00 ± 0.01° C. and the sodium D-line, 5893A. Binary solvent system data are given in Table I. Data for the naphthalene-solvent binaries have been reported previously (*4*, *5*).

Ternary system data are given in Table II. As previously (*4*, *5*), 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 for data fitting should obtain.

REPRESENTATION OF DATA BY ANALYTICAL FUNCTIONS

In the binary systems, n has been expressed as

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

where n_1 and x_1 are the refractive index and mole fraction, 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. 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 only the binary coefficients A_{12}, A_{13}, and A_{23} leads to large errors in all present ternary systems. For the naphthalene-solvent systems, the constants are based upon the assignment of 1.62615 as n of the supercooled state of naphthalene (*4*).

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.

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

System	Mole Fraction First-Named Component	Exptl. Refr. Index
Cyclohexane-ethylbenzene	0.8187	1.43550
	0.5796	1.45232
	0.4097	1.46431
	0.2289	1.47690
	By Eq. 1: Std. and Av. Dev. 10^5 = 2	
Cyclohexane-toluene	0.7905	1.43573
	0.6193	1.44704
	0.4121	1.46176
	0.2558	1.47361
	By Eq. 1: Std. and Av. Dev. 10^5 = 1	
Cyclohexane-benzene	0.7624	1.43590
	0.5852	1.44715
	0.4042	1.46037
	0.2099	1.47688
	By Eq. 1: Std. and Av. Dev. 10^5 = 1	
Cyclohexane–carbon tetrachloride	0.7807	1.42970
	0.5900	1.43575
	0.4292	1.44113
	0.2638	1.44708
	By Eq. 1: Std. and Av. Dev. 10^5 = 2	
Hexane-ethylbenzene	0.8137	1.39373
	0.5773	1.42153
	0.4036	1.44245
	0.1844	1.46970
	By Eq. 1: Std. Dev. 10^5 = 3, Av. Dev. 10^5 = 2	
Hexane-toluene	0.7684	1.39587
	0.5880	1.41592
	0.4153	1.43669
	0.2351	1.46027
	By Eq. 1: Std. and Av. Dev. 10^5 = 2	
Hexane-benzene	0.7644	1.39249
	0.5864	1.41064
	0.4065	1.43211
	0.2007	1.46160
	By Eq. 1: Std. and Av. Dev. 10^5 = 2	
Hexane–carbon tetrachloride	0.8118	1.38459
	0.5617	1.40308
	0.4062	1.41600
	0.2185	1.43368
	By Eq. 1: Std. Dev. 10^5 = 4, Av. Dev. 10^5 = 3	
Cyclohexane-hexane	0.9102	1.41744
	0.5968	1.39981
	0.3989	1.39001
	0.2157	1.38164
	By Eq. 1: Std. and Av. Dev. 10^5 = 1	

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

System	Mole Fraction First-Named Component	Mole Fraction Second-Named Component	Exptl. Refr. Index
Cyclohexane-benzene-naphthalene	0.0456	0.7297	1.52951
	0.0430	0.6876	1.53632
	0.1603	0.6282	1.51635
	0.1574	0.6168	1.51879
	0.1513	0.5928	1.52379
	0.1999	0.7525	1.48634
	0.1913	0.7201	1.49423
	0.1729	0.6511	1.51014
	0.3271	0.4918	1.49684
	0.3145	0.4728	1.50276
	0.3866	0.5698	1.46955
	0.3530	0.5203	1.48639
	0.5557	0.3969	1.45758
	0.4993	0.3565	1.47778
	0.5057	0.3419	1.47821
	0.4868	0.3292	1.48466
	0.7259	0.2263	1.44633
	0.6585	0.2053	1.46528
	0.8355	0.0547	1.44985
	0.8066	0.0529	1.45652
	Std. Dev. 10^5: 14 (Eq. 3a), 20 (Eq. 3b) Av. Dev. 10^5: 11 (Eq. 3a), 14 (Eq. 3b)		
Cyclohexane-toluene-naphthalene	0.1673	0.6404	1.50925
	0.1604	0.6139	1.51454
	0.1567	0.5998	1.51735
	0.1545	0.5913	1.51906
	0.2428	0.7062	1.48260
	0.2203	0.6408	1.49755
	0.2101	0.6110	1.50429
	0.3332	0.4899	1.49442
	0.3179	0.4674	1.50108
	0.3102	0.4562	1.50443
	0.3887	0.5544	1.47247
	0.3695	0.5270	1.48108
	0.5889	0.3621	1.45696
	0.5559	0.3418	1.46749
	0.5256	0.3232	1.47704
	0.7253	0.1922	1.45297
	0.6964	0.1846	1.46057
	0.6931	0.1811	1.46154
	0.6704	0.1751	1.46744
	0.6584	0.1720	1.47051
	Std. Dev. 10^5: 10 (Eq. 3a), 21 (Eq. 3b) Av. Dev. 10^5: 8 (Eq. 3a), 15 (Eq. 3b)		
Cyclohexane-ethylbenzene-naphthalene	0.1656	0.6346	1.50885
	0.1580	0.6054	1.51428
	0.1540	0.5904	1.51708
	0.2164	0.7289	1.48562
	0.2025	0.6820	1.49496
	0.1897	0.6390	1.50353
	0.3302	0.4966	1.49407
	0.3166	0.4760	1.49972
	0.3093	0.4651	1.50278
	0.3857	0.5558	1.47429
	0.3615	0.5209	1.48427
	0.3459	0.4984	1.49058
	0.5426	0.3936	1.46410
	0.4996	0.3522	1.47901
	0.4823	0.3400	1.48432
	0.4694	0.3309	1.48831
	0.7730	0.1711	1.44688
	0.7335	0.1624	1.45680
	0.7473	0.1396	1.45700
	0.7192	0.1344	1.46380
	Std. Dev. 10^5: 8 (Eq. 3a), 19 (Eq. 3b) Av. Dev. 10^5: 6 (Eq. 3a), 15 (Eq. 3b)		
Cyclohexane–carbon tetrachloride–naphthalene	0.1970	0.6345	1.48420
	0.1883	0.6063	1.49193
	0.1824	0.5876	1.49687
	0.2438	0.6803	1.46400
	0.2238	0.6245	1.48026
	0.3534	0.5051	1.47252
	0.3470	0.4960	1.47576
	0.3322	0.4748	1.48323
	0.3988	0.5305	1.45696
	0.3695	0.4915	1.47179
	0.5557	0.3861	1.44864
	0.5198	0.3612	1.46190
	0.5283	0.3480	1.46213
	0.5165	0.3402	1.46638
	0.4919	0.3240	1.47510
	0.7345	0.2064	1.44270
	0.6994	0.1965	1.45254
	0.7148	0.1719	1.45348
	0.6872	0.1653	1.46082
	0.6765	0.1627	1.46362
	Std. Dev. 10^5: 14 (Eq. 3a), 27 (Eq. 3b) Av. Dev. 10^5: 10 (Eq. 3a), 20 (Eq. 3b)		
Hexane-benzene-naphthalene	0.0220	0.7520	1.53079
	0.0260	0.7054	1.53830
	0.0385	0.7421	1.52684
	0.0378	0.7286	1.52902
	0.0359	0.6920	1.53540
	0.1425	0.6571	1.50556
	0.1330	0.6133	1.51566
	0.1914	0.7625	1.47143
	0.1715	0.6832	1.49167
	0.1650	0.6572	1.49808
	0.3212	0.4721	1.47903
	0.3133	0.4605	1.48329
	0.3893	0.5684	1.44201
	0.3724	0.5437	1.45149
	0.3408	0.4975	1.46917
	0.5615	0.3960	1.42092
	0.5107	0.3602	1.44179
	0.4943	0.3447	1.44895
	0.7354	0.2267	1.40181
	0.6720	0.2071	1.42231
	Std. Dev. 10^5: 27 (Eq. 3a), 44 (Eq. 3b) Av. Dev. 10^5: 20 (Eq. 3a), 35 (Eq. 3b)		
Hexane-toluene-naphthalene	0.1645	0.6228	1.50143
	0.1609	0.6093	1.50439
	0.1560	0.5906	1.50845
	0.2231	0.7258	1.46979
	0.2137	0.6953	1.47709
	0.2028	0.6597	1.48554
	0.1917	0.6236	1.49396
	0.3385	0.4942	1.47134
	0.3312	0.4835	1.47494
	0.3182	0.4646	1.48140
	0.3934	0.5538	1.44743
	0.3742	0.5268	1.45704
	0.5334	0.2737	1.43646
	0.5105	0.3577	1.44489
	0.5041	0.3470	1.44798
	0.4936	0.3397	1.45193
	0.4832	0.3325	1.45591

(*Continued on page 43*)

TABLE II (Continued)

System	Mole Fraction First-Named Component	Mole Fraction Second-Named Component	Exptl. Refr. Index
Hexane-toluene-naphthalene, cont'd.	0.6906	0.1898	1.42209
	0.6747	0.1854	1.42693
	0.6588	0.1811	1.43179
	Std. Dev. 10^5: 11 (Eq. 3a), 14 (Eq. 3b) Av. Dev. 10^5: 9 (Eq. 3a), 10 (Eq. 3b)		
Hexane-ethylbenzene-naphthalene	0.1257	0.6826	1.50275
	0.1198	0.6509	1.50848
	0.1730	0.7649	1.47945
	0.1622	0.7171	1.48869
	0.1524	0.6737	1.49711
	0.3310	0.5075	1.47303
	0.3224	0.4945	1.47698
	0.3105	0.4761	1.48273
	0.3817	0.5641	1.45249
	0.3448	0.5096	1.46939
	0.5492	0.4022	1.43146
	0.5225	0.3826	1.44097
	0.4959	0.3569	1.45097
	0.4869	0.3505	1.45423
	0.4763	0.3429	1.45796
	0.7568	0.1509	1.41273
	0.7456	0.1487	1.41588
	0.7353	0.1466	1.41876
	0.7230	0.1441	1.42232
	Std. Dev. 10^5: 7 (Eq. 3a), 9 (Eq. 3b) Av. Dev. 10^5: 4 (Eq. 3a), 6 (Eq. 3b)		
Hexane–carbon tetrachloride–naphthalene	0.0809	0.7415	1.48568
	0.0768	0.7030	1.49465
	0.0750	0.6869	1.49854
	0.1384	0.6907	1.47755
	0.1351	0.6743	1.48183
	0.1672	0.6676	1.47348
	0.1590	0.6350	1.48229
	0.1552	0.6200	1.48653
	0.2022	0.7233	1.45117
Hexane–carbon tetrachloride–naphthalene, cont'd.	0.3391	0.5026	1.45390
	0.3242	0.4805	1.46312
	0.5253	0.4098	1.41888
	0.4962	0.3871	1.43152
	0.7157	0.1821	1.41100
	0.6970	0.1774	1.41676
	0.6863	0.1746	1.42019
	0.9108	0.0205	1.39092
	0.8951	0.0202	1.39495
	0.8731	0.0197	1.40057
	0.8623	0.0194	1.40349
	Std. Dev. 10^5: 24 (Eq. 3a), 39 (Eq. 3b) Av. Dev. 10^5: 18 (Eq. 3a), 31 (Eq. 3b)		
Cyclohexane-hexane-naphthalene	0.1881	0.7459	1.39699
	0.1843	0.7309	1.40151
	0.1806	0.7162	1.40604
	0.1772	0.7029	1.41009
	0.2067	0.7516	1.39177
	0.1975	0.7184	1.40205
	0.3709	0.5593	1.40657
	0.3656	0.5513	1.40976
	0.3590	0.5414	1.41375
	0.3511	0.5294	1.41866
	0.5506	0.3665	1.41921
	0.5418	0.3606	1.42264
	0.5329	0.3547	1.42611
	0.5245	0.3491	1.42949
	0.7706	0.1416	1.43307
	0.7604	0.1398	1.43578
	0.7452	0.1370	1.43977
	0.7385	0.1357	1.44170
	0.8661	0.0854	1.42824
	0.8240	0.0812	1.43846
	Std. Dev. 10^5: 12 (Eq. 3a), 13 (Eq. 3b) Av. Dev. 10^5: 9 (Eq. 3a), 10 (Eq. 3b)		

Table III. Binary System Constants

System	Constants of Equation 2 (x_1 is First-Named Component) B_{12}	C_{12}	D_{12}
Cyclohexane-ethylbenzene	−0.00109	−0.00086	−0.00325
Cyclohexane-toluene	−0.01337	−0.00133	−0.00061
Cyclohexane-benzene	−0.02948	0.00338	0.00058
Cyclohexane–carbon tetrachloride	−0.00632	0.00064	−0.00005
Hexane-ethylbenzene	−0.00841	0.00006	−0.00016
Hexane-toluene	−0.02833	0.00226	−0.00057
Hexane-benzene	−0.05854	0.01336	−0.00610
Hexane–carbon tetrachloride	−0.02766	0.00402	−0.00119
Cyclohexane-hexane	−0.01195	−0.00265	−0.00175

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 was done previously (*4*, *5*), computations in the present work were programmed for a digital computer.

DISCUSSION

In the present binary solvent-solvent systems, the deviations from Equation 1 resemble more closely those of the first set of systems (*4*) than the second set (*5*). The error thus appears to be more dependent upon the difference in molal volumes than upon the molecular interaction between the solvent component pair (*1–3*) or the difference in n of the pure components.

In the ternary systems, n values calculated with Equation 3 are systematically below the experimental values in all present systems if $A_{123} = 0$ is assumed. Both the average and extreme deviations in all present systems are greater by Equation 3b than by 3a. The use of Equations 3a or 3b yields deviations from experimental results comparable to those found previously (*4*, *5*), with no apparent correlation between the error thereby and any of molecular interaction, difference in molal volumes of the pure components or difference in refractive indices of the pure components.

While the usefulness of Equation 3a in the 21 ternary systems considered in these works is limited, it is not markedly affected by increasing dissimilarity between the solvent pair.

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}
Cyclohexane-benzene-naphthalene	2.5907	−4.5198	−4.7043	1.8113	2.3196	4.2806	0.9763	−1.0664	−0.7895
Cyclohexane-toluene-naphthalene	2.9673	−5.5511	−5.4788	2.5181	2.6979	5.2945	1.0205	−1.1092	−0.8600
Cyclohexane-ethylbenzene-naphthalene	2.7167	−4.8873	−4.9902	2.0938	2.5301	4.4972	1.0100	−1.1220	−0.8365
Cyclohexane–carbon tetrachloride–naphthalene	5.4585	−10.1942	−11.3500	4.7299	6.1260	10.7561	1.3594	−1.3802	−1.3127
Hexane-benzene-naphthalene	3.1835	−6.7509	−6.2560	3.6274	3.2043	6.5781	0.8402	−0.9703	−0.7633
Hexane-toluene-naphthalene	1.5487	−2.8260	−2.9444	1.2195	1.5036	2.7235	0.5160	−0.5800	−0.4395
Hexane-ethylbenzene-naphthalene	1.2323	−2.2293	−2.1376	0.9425	0.9983	1.9447	0.5049	−0.5726	−0.4261
Hexane–carbon tetrachloride–naphthalene	6.7871	−13.1284	−15.4595	6.4527	8.9758	14.8240	1.0988	−1.0474	−1.2149
Cyclohexane-hexane-naphthalene	10.9516	−23.0937	−22.3052	12.2495	11.4918	23.7388	1.0097	−1.0103	−0.9092

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.

ACKNOWLEDGMENT

The University of Georgia Institute of Statistics provided vital assistance in computation.

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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Viscosity of a Mixture of Methane and *n*-Butane

L. T. CARMICHAEL, VIRGINIA BERRY, and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

Measurements of the viscosity of a mixture of methane and *n*-butane containing 0.394 mole fraction methane have been carried out with a couette-type instrument at pressures up to 5000 p.s.i. in the temperature interval between 40° and 400° F. Good agreement with an earlier investigation involving an effusion-type instrument was realized. The present results and comparisons with the earlier data are depicted in both graphical and tabular form.

THE VISCOSITY of the paraffin hydrocarbons at atmospheric and elevated pressure has been the subject of many investigations over the past two decades. In the case of methane, the viscosity has been investigated experimentally in some detail (*1-4, 6, 7, 10, 13, 14*). Likewise, the viscosity of *n*-butane has been investigated rather completely (*5, 9, 11, 15-18*). Satisfactory agreement for both methane and *n*-butane was obtained between effusion and couette-flow equipment. The agreement as to the viscosity of a particular state as measured with widely different types of equipment lends credence to the accuracy of the absolute values for these compounds.

Recently, the viscosity of four mixtures of methane and *n*-butane was established by Dolan, Ellington, and Lee (*8*) at pressures as high as 5000 p.s.i.a. in the temperature interval between 70° and 340° F. The measurements upon