Refraction in Some Binary Liquid Nonelectrolyte Mixtures

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Refractive indices and refractivity intercepts are given for mixtures in 14 binary liquid nonelectrolyte systems at 25° C. The data, and those for previously reported densities in these systems, are fitted to deviation equations from additivity in volume fraction. In the present systems, among the three properties the refractivity intercept usually shows the least departure from such additivity, and requires the fewest number of constants to fit the departure. The behavior illustrates the convenience of the refractivity intercept for analysis.

Density and refractive index are properties frequently used in the physicochemical analysis of mixtures. Sumer and Thompson (*7*) have shown the usefulness of the refractivity intercept (*6*), $n_D - d/2$, as a substitute for these properties when their variation with mixture composition is inadequate for their use in analysis.

More extensive description of refractivity intercept behavior in mixtures involving nonspecific interacting components is needed for predicting the general usefulness of this property in analysis. In the present work, the refractive indices and refractivity intercepts of 14 such binary systems at 25° C. are reported. The components include aliphatic, alicyclic, and aromatic compounds, with a significant difference in molecular size between some of them. The results of a similar study of 11 ternary and three quaternary systems formed from the present binary systems are described elsewhere (*3*).

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The densities of the present mixtures have been reported as part of a concurrent study of viscometric behavior (*2*). Refractometric measurements were also made at that time, but presentation of the results was delayed until the behavior in the ternary and quaternary systems could also be described.

In a somewhat similar work, Heric and Coursey (*4*) have described refractivity intercept behavior in a series of binary systems containing *n*-hexadecane with 1-chloroalkane homologs. They found that the dependence of refractivity intercept on the volume fraction composition of a system (*5*) was essentially linear there. The purpose there was to investigate the behavior in related systems. In the present work, the purpose is different. The components are generally not homologous, but are combined with a variety of the other components to provide systems of different types.

EXPERIMENTAL

Equipment. The equipment and techniques have been described (*2*). A water bath thermostatically controlled

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 (*1*). [b] From 9 sources identified in (*1*).

Table II. Properties of Binary Mixtures at 25° C.

First-Named Component Volume Fraction	Refractive Index, n_D	Refractivity Intercept, $n_D - d/2$	First-Named Component Volume Fraction	Refractive Index, n_D	Refractivity Intercept, $n_D - d/2$
	n-Hexadecane–*n*-Hexane				
0.8797	1.42608	1.0471	0.6150	1.41093	1.0467
0.8704	1.42559	1.0472	0.5980	1.40994	1.0467
0.8651	1.42525	1.0471	0.5348	1.40604	1.0465
0.8468	1.42421	1.0471	0.4448	1.40068	1.0463
0.8017	1.42185	1.0472	0.3741	1.39617	1.0459
0.7928	1.42109	1.0470	0.2928	1.39116	1.0458
0.7905	1.42098	1.0469	0.2060	1.38568	1.0455
0.7864	1.42098	1.0471	0.1157	1.37996	1.0452
0.7118	1.41659	1.0469			
0.7112	1.41662	1.0470		*n*-Hexadecane–2-Bromobutane	
0.7045	1.41621	1.0469	0.8688	1.43199	1.0156
0.6181	1.41117	1.0467	0.7886	1.43176	0.9964

(*Continued on next page*)

Table II. (*Continued*)

0.7067	1.43171	0.9766
0.6270	1.43176	0.9577
0.5303	1.43188	0.9346
0.4613	1.43202	0.9181
0.3541	1.43238	0.8925
0.2423	1.43290	0.8657
0.1662	1.43324	0.8474
0.0953	1.43369	0.8303

n-Hexadecane–Carbon Tetrachloride

0.8853	1.43488	1.0035
0.7937	1.43660	0.9686
0.6915	1.43870	0.9298
0.6106	1.44049	0.8990
0.5154	1.44270	0.8626
0.4420	1.44451	0.8347
0.3591	1.44661	0.8035
0.2840	1.44859	0.7744
0.1877	1.45138	0.7375
0.0968	1.45411	0.7026

n-Hexadecane–Benzene

0.9148	1.43685	1.0480
0.8142	1.44209	1.0489
0.7338	1.44666	1.0500
0.5967	1.45471	1.0517
0.5519	1.45744	1.0521
0.3553	1.47053	1.0549
0.2868	1.47537	1.0560
0.1880	1.48275	1.0577
0.0970	1.48973	1.0593

4-Methylcyclohexanone–*n*-Hexadecane

0.9114	1.44161	0.9923
0.8077	1.44008	0.9986
0.7232	1.43893	1.0037
0.6313	1.43769	1.0091
0.5423	1.43672	1.0146
0.3634	1.43480	1.0252
0.2798	1.43403	1.0302
0.1718	1.43324	1.0368
0.1087	1.43287	1.0405

n-Tetradecane–*n*-Hexane

0.8847	1.42153	1.0469
0.7938	1.41691	1.0468
0.6988	1.41188	1.0466
0.6121	1.40727	1.0465
0.5307	1.40291	1.0464
0.4506	1.39849	1.0462
0.3577	1.39334	1.0459
0.2812	1.38897	1.0457
0.1943	1.38394	1.0454
0.1026	1.37869	1.0453

n-Tetradecane–2-Bromobutane

0.8798	1.42742	1.0182
0.8026	1.42760	0.9996
0.7153	1.42800	0.9788
0.6203	1.42852	0.9560
0.5310	1.42903	0.9345
0.3670	1.43037	0.8954
0.2925	1.43120	0.8777
0.1955	1.43204	0.8544
0.1266	1.43278	0.8379

4-Methylcyclohexanone–*n*-Tetradecane

0.9018	1.44117	0.9931
0.8166	1.43946	0.9982
0.7232	1.43764	1.0037
0.6306	1.43592	1.0091
0.5466	1.43454	1.0142
0.4513	1.43298	1.0198
0.2836	1.43046	1.0300
0.1941	1.42926	1.0353
0.0917	1.42818	1.0417

2-Bromobutane–*n*-Hexane

0.8708	1.42590	0.8377
0.7813	1.42016	0.8588
0.7102	1.41575	0.8759
0.6250	1.41029	0.8959
0.5389	1.40422	0.9187
0.4389	1.39879	0.9403
0.2897	1.38946	0.9756
0.1905	1.38345	0.9992
0.0908	1.37758	1.0232

Carbon Tetrachloride–*n*-Hexane

0.8531	1.44428	0.7210
0.7887	1.43870	0.7454
0.7144	1.43233	0.7735
0.5350	1.41697	0.8417
0.4593	1.41058	0.8702
0.3691	1.40300	0.9046
0.2152	1.39013	0.9631
0.1110	1.38140	1.0026

Benzene–*n*-Hexane

0.8939	1.48346	1.0589
0.7989	1.47080	1.0570
0.7043	1.45838	1.0551
0.6327	1.44919	1.0538
0.5464	1.43825	1.0525
0.4615	1.42748	1.0510
0.3790	1.41726	1.0498
0.2873	1.40609	1.0483
0.1886	1.39419	1.0469
0.1294	1.38720	1.0462

4-Methylcyclohexanone–*n*-Hexane

0.8699	1.43446	0.9944
0.7921	1.42903	0.9987
0.7035	1.42323	1.0041
0.6194	1.41738	1.0090
0.5392	1.41176	1.0137
0.4422	1.40485	1.0193
0.3619	1.39906	1.0239
0.2705	1.39240	1.0293
0.1870	1.38635	1.0343
0.1000	1.37983	1.0391

Carbon Tetrachloride–Benzene

0.8966	1.46176	0.7068
0.7875	1.46648	0.7503
0.7114	1.46965	0.7801
0.6144	1.47366	0.8190
0.4634	1.47990	0.8788
0.3683	1.48377	0.9165
0.2736	1.48739	0.9538
0.1792	1.49102	0.9906
0.0999	1.49398	1.0220

n-Hexadecane–*n*-Tetradecane

0.9759	1.43253	1.0474
0.9460	1.43233	1.0473
0.9030	1.43204	1.0473
0.8166	1.43165	1.0474
0.7165	1.43114	1.0474
0.6268	1.43063	1.0473
0.5441	1.43020	1.0472
0.4938	1.42994	1.0473
0.3701	1.42926	1.0472
0.2852	1.42892	1.0472
0.2741	1.42883	1.0473
0.2005	1.42846	1.0471
0.1820	1.42835	1.0472
0.0959	1.42789	1.0471
0.0845	1.42777	1.0471

Table III. Constants of Equation 1

Component 1 is first-named of pair

	Density, Volume Fraction			10^4 Error, G. per Ml.		Refractive Index, Volume Fraction			10^5 Error, Refractive Index		Refractivity Intercept, Volume fraction		10^4 Error, Refractivity Intercept	
	A	*B*	*C*	Stand.[a]	Max.	*A*	*B*	*C*	Stand.[a]	Max.	*A*	*B*	Stand.[a]	Max.
n-Hexadecane–*n*-hexane	0.0091			1	2	0.00627			8	16	0.0018		1	2
n-Hexadecane–2-bromobutane	−0.0142	0.0029		1	2	−0.00541	−0.00036	−0.00401	3	4	0.0025	−0.0051	0	1
n-Hexadecane–carbon tetrachloride	−0.0282	0.0158		3	6	−0.00814	0.00134		3	6	0.0059	0.0065	1	3
n-Hexadecane–benzene	−0.0287	0.0101	−0.0060	1	2	−0.01851	0.00128		6	9	−0.0051		1	1
4-Methylcyclohexanone–*n*-hexadecane	−0.0158	0.0104	−0.0069	1	3	−0.01144	0.01529	−0.01286	3	6	−0.0012		1	2
n-Tetradecane–*n*-hexane	0.0108	−0.0108	0.0118	1	2	0.00849	−0.00871	0.00664	6	15	0.0029	−0.0026	1	2
n-Tetradecane–2-bromobutane	−0.0154	0.0133	−0.0105	1	2	−0.00482	−0.00228		4	9	0.0018	−0.0038	1	1
4-Methylcyclohexanone–*n*-tetradecane	−0.0149	0.0165	−0.0136	1	2	−0.00723	0.00201		4	6	−0.0010		1	1
2-Bromobutane–*n*-hexane	−0.0059	0.0044		1	3	−0.00303			7	9	−0.0012		1	2
Carbon tetrachloride–*n*-hexane	−0.0059			2	3	−0.00189	−0.00130		1	2	0.0028		1	2
Benzene–*n*-hexane	−0.0121			1	2	−0.01088	0.00072		4	6	−0.0045		1	1
4-Methylcyclohexanone–*n*-hexane	0.0052	0.0097	−0.0006	1	2	0.00578	−0.00160		7	16	0.0031	−0.0061	1	2
Carbon tetrachloride–benzene	−0.0026			3	5	0.00397			4	6	0.0053		2	3
n-Hexadecane–*n*-tetradecane	0.0012	−0.0021	−0.0031	1	2	0.00061	−0.00159		4	8	0		1	1

[a] $\{\Sigma(\text{exptl.} - \text{calcd.})^2/\text{number of observations}\}^{1/2}$.

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. Replications of measured densities of the pure components indicate 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 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 (*2*). The densities, refractive indices, and refractivity intercepts of the purified components are given in Table I.

RESULTS AND DISCUSSION

The densities and refractive indices of the purified components are compared with literature values in Table I. For analysis in binary systems of these components, the difference in the densities of each component pair makes that property suitable for analysis with good precision. The difference is also sufficient, in combination with that of the refractive indices, to provide a variety of differences between the refractivity intercepts of the component pairs in the present systems. This is useful in delineating any systematic behavior of the refractivity intercepts.

Refractive indices and refractivity intercepts of mixtures in the binary systems are listed in Table II. Densities are not included, as they may be obtained for the same mixtures directly from the previous work. Except for the system *n*-hexadecane–2-bromobutane, in which there is a minimum in the property, the refractive indices vary monotonically without exception.

Departure of each of the three properties from additivity may be expressed through

$$p = \phi_1 p_1 + \phi_2 p_2 + \phi_1\phi_2[A + B\phi_1 + C\phi_1^2 + \dots] \quad (1)$$

where ϕ_i is the volume fraction of the ith component and p and p_i are, respectively, the property of the mixture and the ith component. For the density and refractive index, the first two terms on the right side represent ideal behavior, and the remaining term is the departure therefrom. For the refractivity intercept, linearity in ϕ is also obtained for ideal behavior of the density and refractive index, although the linearity may also be a consequence of compensating deviations from ideality by both density and refractive index.

Table III lists the constants for fitting the behavior of each of the three properties with Equation 1, and the errors in the fit. The constants were obtained by a least-squares analysis of the data using a digital computer. The data were weighted by a method described elsewhere (*1*). The number of constants given for each system is that number above which each additional constant decreased the standard error by an amount less than the estimated precision of the property fitted.

Except for the three systems 4-methylcyclohexanone–*n*-hexane, *n*-hexadecane–*n*-hexane, and *n*-tetradecane–*n*-hexane, all systems exhibit expansion on mixing. The system *n*-hexadecane–*n*-tetradecane has a change from expansion to contraction with decreasing average chain length.

Except for mixtures of carbon tetrachloride–benzene, refractive indices and densities show the same direction of deviation from ideality in the systems. Because of this agreement, the deviation of the refractivity intercept from linearity in ϕ tends to be smaller than that of the other two properties, and it becomes zero in the system *n*-hexadecane–*n*-tetradecane. The greatest deviation from linearity, at equimolal composition, is in the system *n*-hexadecane–carbon tetrachloride, 0.0022. That deviation is 0.6% of the difference between the refractivity intercepts of these two components.

No more than two constants are required to fit the refractivity intercept to ϕ in any of the systems, and the second constant is necessary in only five. The typical standard deviation in the fitting of the refractivity intercept is 0.0001. There is no evident systematic relationship between the algebraic signs of the fitting constants in a system for the refractivity intercept and the components of the system. In nine of the systems deviation of the refractivity intercept from additivity is of the same sign throughout the system. Four of the systems show a transition in the sign of the departure from additivity as the composition is varied: *n*-hexadecane–2-bromobutane, *n*-tetradecane–2-bromobutane, 4-methylcyclohexanone–*n*-tetradecane, and 4-methylcyclohexanone–*n*-hexane. The sign transition does not appear to be due to any noteworthy behavior in these systems.

The relatively small departure of the refractivity intercept from linearity in ϕ described here, and the small number of constants required to fit the departure illustrate the convenience of the property for analysis.

NOMENCLATURE

A, B, C	=	constants of Equation 1
d	=	density, grams per ml.
n_D	=	refractive index
$n_D - d/2$	=	refractivity intercept
x	=	mole fraction
V	=	molar volume
ϕ	=	volume fraction = $x_i V_i / \Sigma x_i V_i$

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