Densities and Refraction in Some Binary Systems of Hexadecane and Normal Chloroalkanes at 25° C.

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Densities, refractive indices, and refractivity intercepts are reported for nine binary systems of *n*-hexadecane with 1-chloroalkanes at 25° C. Both densities and refractive indices significantly depart from ideal behavior for most of the systems, but refractivity intercepts closely approach a linear dependence on volume fraction for all of the systems.

IN the analysis of *n*-component mixtures by measurement of physical properties, $n - 1$ properties are required. Thus, in a ternary system one must measure two properties. Even for systems restricted to the inclusion of components of no more than two homologous series, the analysis may be complicated because of similar values of a property for different components. The problem is considered here, in terms of density and refractometric behavior in binary mixtures of an *n*-alkane and 1-chloroalkanes. Results of measurement of these properties and the refractivity intercepts derived therefrom (*5*), n_D-d/2, are described. The alkane is *n*-hexadecane and the 1-chloroalkanes include members between 4 and 18 carbons. The fitting of the data by analytical functions of composition is also considered. Mixtures are the same as those for which viscometric measurements have been reported earlier, except for lost samples. Presentation of present results was delayed until refractometric behavior in mixtures of 1-chloroalkane homologs could be studied (*4*).

EXPERIMENTAL

Equipment. The equipment and techniques have been involved in a related work (*4*). A water bath thermostatically controlled to ±0.01° C. was used. Bath temperature was monitored with 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 a 4.5-ml. Lipkin pycnometer with precision-bore 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. The standard error in calibrated pycnometer volume *vs.* capillary height was ±0.00007 ml. Replication of measured densities of the pure components indicates a standard error of ±0.00003 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 & Lomb Precision refractometer, thermostated at 25.00° ± 0.01° C. and using the sodium-*D* line, 5893A. The refractometer was calibrated, and frequently rechecked, with air-free distilled water.

Materials. Purification of the components has been described, and a comparison made between several experimental physical properties and literature values (*1*). The densities, refractive indices, and refractivity intercepts of the purified components are given in Table I.

RESULTS AND DISCUSSION

From Table I it is evident that density determination is a suitable means of analyzing *n*-alkane–1-chloroalkane mixtures. Thus, an uncertainty of ±0.00003 gram per ml. corresponds to about 0.03% of the density difference between *n*-hexadecane and the 1-chloroalkanes, and this decreases to about 0.01% when the *n*-alkane is *n*-hexane. For refractive index, however, the suitability is variable. When the *n*-alkane is *n*-hexadecane, an uncertainty of ±0.00003 in refractive index corresponds to, respectively, 0.1, 1, 0.2, and 0.1% of the difference of that property between the *n*-alkane and the halides of 4, 10, 18, and 40 (*2*) carbons. Clearly, there is a range of chain lengths in which the refractive index is unsuitable for precise analysis, although this difficulty is rapidly removed at lower *n*-alkane chain lengths.

Refractivity intercepts of the *n*-alkanes vary little with chain length, so that the behavior of that property shown in Table I applies not only toward *n*-hexadecane, but toward

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

	Density, G. per Ml.	Refractive Index	Refractivity Intercept, n_D-d/2
n-Hexadecane	0.77090	1.43286	1.04741
1-Chlorobutane	0.88095	1.39996	0.95948
1-Chloropentane	0.87700	1.41000	0.97150
1-Chlorohexane	0.87338	1.41762	0.98093
1-Chlorooctane	0.86922	1.42850	0.99389
1-Chlorodecane	0.86586	1.43603	1.00310
1-Chlorododecane	0.86363	1.44151	1.00969
1-Chlorotetradecane	0.86190	1.44479	1.01384
1-Chlorohexadecane	0.86065	1.44815	1.01782
1-Chlorooctadecane[a]	0.85968	1.45062	1.02078

[a] Supercooled liquid.

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

n-Hexadecane			Refractive	Refractivity
Mole fraction	Volume fraction	Density, G. per Ml.	Index, n_D	Intercept, n_D-d/2
		n-Hexadecane–1-Chlorobutane		
0.1495	0.3294	0.84309	1.40988	0.98834
0.2967	0.5412	0.81937	1.41662	1.00693
0.4418	0.6887	0.80328	1.42150	1.01986
0.5454	0.7703	0.79462	1.42445	1.02714
0.6777	0.8546	0.78565	1.42737	1.03454
0.8309	0.9322	0.77771	1.43018	1.04132
		n-Hexadecane–1-Chloropentane		
0.1532	0.3042	0.84325	1.41621	0.99459
0.2897	0.4964	0.82263	1.42046	1.00914
0.4420	0.6569	0.80570	1.42416	1.02131
0.5367	0.7368	0.79728	1.42623	1.02759
0.6903	0.8434	0.78633	1.42841	1.03524
0.8323	0.9231	0.77850	1.43084	1.04159
		n-Hexadecane–1-Chlorohexane		
0.1413	0.2593	0.84569	1.42079	0.99795
0.1478	0.2695	0.84457	1.42109	0.99881
0.1944	0.3392	0.83739	1.42220	1.00350
0.2058	0.3554	0.83570	1.42266	1.00481
0.3072	0.4854	0.82210	1.42424	1.01319
0.4454	0.6308	0.80738	1.42670	1.02301
0.5320	0.7074	0.79949	1.42806	1.02831
0.5438	0.7171	0.79848	1.42829	1.02905
0.6893	0.8251	0.78773	1.42967	1.03589
0.8311	0.9128	0.77914	1.43122	1.04165
		n-Hexadecane–1-Chlorooctane		
0.1502	0.2329	0.84568	1.42932	1.00648
0.2936	0.4165	0.82728	1.42989	1.01625
0.3835	0.5165	0.81739	1.43003	1.02133
0.4348	0.5692	0.81221	1.43029	1.02418
0.5265	0.6563	0.80371	1.43106	1.02920
0.6890	0.7918	0.79055	1.43166	1.03638
0.8454	0.9038	0.77987	1.43217	1.04223
		n-Hexadecane–1-Chlorodecane		
0.1457	0.1971	0.84659	1.43540	1.01210
0.2910	0.3713	0.82990	1.43485	1.01990
0.4463	0.5370	0.81408	1.43432	1.02728
0.4487	0.5394	0.81382	1.43432	1.02741
0.5414	0.6295	0.80541	1.43403	1.03132
0.5466	0.6343	0.80484	1.43401	1.03159
0.5758	0.6614	0.80231	1.43393	1.03277
0.6979	0.7688	0.79220	1.43359	1.03749
0.8427	0.8852	0.78129	1.43322	1.04257
0.8464	0.8880	0.78110	1.43321	1.04266

n-Hexadecane			Refractive	Refractivity
Mole fraction	Volume fraction	Density, G. per Ml.	Index, n_D	Intercept, n_D-d/2
		n-Hexadecane–1-Chlorododecane		
0.1515	0.1812	0.84669	1.43984	1.01649
0.1862	0.2208	0.84296	1.43945	1.01797
0.2216	0.2607	0.83923	1.43914	1.01952
0.3003	0.3471	0.83108	1.43838	1.02284
0.4564	0.5099	0.81596	1.43691	1.02893
0.4930	0.5464	0.81256	1.43661	1.03033
0.4970	0.5504	0.81220	1.43653	1.03043
0.5030	0.5563	0.81164	1.43654	1.03072
0.5038	0.5570	0.81155	1.43654	1.03076
0.5553	0.6073	0.80698	1.43606	1.03257
0.6988	0.7418	0.79454	1.43494	1.03767
0.8222	0.8514	0.78444	1.43405	1.04183
0.8423	0.8687	0.78276	1.43394	1.04256
0.8458	0.8717	0.78254	1.43386	1.04259
0.8918	0.9108	0.77905	1.43359	1.04406
		n-Hexadecane–1-Chlorotetradecane		
0.1514	0.1625	0.84696	1.44280	1.01932
0.3014	0.3193	0.83260	1.44091	1.02461
0.4365	0.4572	0.82002	1.43919	1.02918
0.4391	0.4598	0.81978	1.43916	1.02927
0.5484	0.5690	0.80991	1.43788	1.03292
0.6928	0.7103	0.79706	1.43624	1.03771
0.8300	0.8415	0.78520	1.43471	1.04221
0.8527	0.8629	0.78324	1.43440	1.04278
0.8764	0.8852	0.78129	1.43419	1.04354
		n-Hexadecane–1-Chlorohexadecane		
0.1550	0.1509	0.84704	1.44581	1.02229
0.2969	0.2903	0.83451	1.44371	1.02645
0.4487	0.4409	0.82092	1.44133	1.03087
0.5536	0.5458	0.81154	1.43983	1.03406
0.7085	0.7020	0.79752	1.43739	1.03863
0.8447	0.8405	0.78519	1.43532	1.04272
0.8532	0.8492	0.78437	1.43517	1.04298
		n-Hexadecane–1-Chlorooctadecane		
0.1535	0.1368	0.84754	1.44822	1.02445
0.2941	0.2669	0.83594	1.44585	1.02788
0.4551	0.4219	0.82211	1.44314	1.03208
0.5450	0.5114	0.81432	1.44155	1.03439
0.6982	0.6691	0.80024	1.43876	1.03864
0.8554	0.8379	0.78523	1.43577	1.04315

all *n*-alkanes. The refractivity intercepts of the 1-chloroalkanes increase with chain length, reaching 1.0358 for 1-chlorotetracontane (supercooled liquid). Assuming that the above noted uncertainties of ±0.00003 in each of density and refractive index are propagated to the refractivity intercept, an uncertainty of ±0.00004 in the last-named is obtained. Thus for the refractivity intercept, the uncertainty corresponds to, respectively, 0.05, 0.2, and 0.4% of the difference of that property between the *n*-alkane and the halides of 4, 18, and 40 carbons. The behavior of the refractive index and the refractivity intercept in these systems shows that for the most effective use of refractometric measurements in the analysis of the type of system considered here, for a given *n*-alkane of the longer chain lengths it may be necessary to shift from the one to the other property as the halide chain length is varied.

Densities, refractive indices, and refractivity intercepts of the mixtures in the nine *n*-hexadecane–1-chloroalkane systems are given in Table II in order of increasing halide chain length. All three properties show a monotonic change with composition in each system. Departure of the properties from additivity may be expressed through

$$p = f_1p_1 + f_2p_2 + f_1f_2[A + B(f_1 - f_2) + C(f_1 - f_2)^2 + \cdots] \quad (1)$$

where f_i is a composition variable, and p and p_i are, respectively, the physical property of the mixture and the pure component i. If the composition variable in Equation 1 is volume fraction, the first two terms on the right side represent ideal density and refractometric behavior, and the remaining term represents departure therefrom. Constants for Equation 1 on that basis are listed in Table III, together with the resulting errors in those properties. The constants were obtained by least-squares procedures. For all systems, mixing causes expansion, with the effect decreasing as the halide chain length increases. The density data are well fitted by Equation 1, with a typical standard error of ±0.00005 gram per ml. in a system.

Table III. Constants of Equation 1[a]

	Density, Volume Fraction			10^5 Error, G. per Ml.		Refractive Index, Volume Fraction		10^5 Error, Refractive Index		Refractivity Intercept, Weight Fraction		10^5 Error, Refractivity Intercept	
	10^5A	10^5B	10^5C	Stand.[b]	Max.	10^5A	10^5B	Stand.[b]	Max.	10^5A	10^5B	Stand.[b]	Max.
n-Hexadecane–1-chlorobutane	−790	−198	−69	4	6	−462	−147	9	15	1113	−94	4	7
n-Hexadecane–1-chloropentane	−681	−68	−273	6	10	−373		20	38	960		16	31
n-Hexadecane–1-chlorohexane	−578	−122	−261	5	10	−250		18	30	890		17	27
n-Hexadecane–1-chlorooctane	−417	−108		3	5	−198		17	23	637		15	19
n-Hexadecane–1-chlorodecane	−320	−56		7	14	−167		8	16	670		4	7
n-Hexadecane–1-chlorododecane	−156			6	14	−72		3	4	434		4	7
n-Hexadecane–1-chlorotetradecane	−103			3	4	−47		4	4	379		5	10
n-Hexadecane–1-chlorohexadecane	−52			3	5	−6		4	6	344		3	4
n-Hexadecane–1-chlorooctadecane	−16			5	8	14		3	5	304		3	4

[a] Component 1 is hexadecane. [b] Standard error calculated as $\{\Sigma[\text{exptl.} - \text{calcd.}]^2/\text{number of observations}\}^{1/2}$.

The fitting of Equation 1 to the refractive indices is less satisfactory than for the density. The reason was not established, but it may be related to the volatility of the shorter halides. Nevertheless, for both properties the constants clearly show a systematic trend with varying chain length, with the departure of refractive index from ideality passing through a sign change in the range of halide homologs.

Refractivity intercepts have the intended physical significance only when applied to *n*-alkane systems, although their practical application to analysis involving other components has been clearly shown (*6*). The standard errors in the fitted densities and refractive indices, and the corresponding uncertainties of the constants in Table III for fitting those properties, indicate a doubtful statistical significance for the significantly smaller constants obtainable by fitting the refractivity intercepts *vs.* volume fraction with Equation 1. An assumption of linear dependence appears to be indicated within the precision of the data.

Heric and Coursey (*4*) have reported refractivity intercept behavior in the system 1-chlorobutane–1-chlorooctadecane. With more precise refractive index measurements than those reported here, they found a clearly positive deviation from linearity of refractivity intercept with variation in the volume fractions. The maximum deviation, approximately at equimolarity, was only 0.0001 in refractivity intercept, however, so the effect is small. A somewhat larger deviation from linearity, about 0.0004, was found in each of the systems *n*-hexane–*n*-hexadecane and *n*-hexane–*n*-tetradecane (*3*). The convenience of this near linearity in application to analysis is significant.

The dependence of the refractivity intercepts on both volume and weight fraction has also been considered (*7*), and the behavior in terms of weight fraction is useful in showing the systematic behavior here. Again using Equation 1, with p as the refractivity intercept and f as the weight fraction, the constants obtained are listed in Table III. Within the standard errors stated here, there is a monotonic decrease in the constants.

NOMENCLATURE

- A, B, C = constants of Equation 1
- d = density, g. per ml.
- f = composition variable, Equation 1
- n_D = refractive index, sodium-D line
- n_D-d/2 = refractivity intercept
- p = physical property, Equation 1

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