From 1-pentene: b. p., cc.: 27–34 (most at 29–32, which is 1-pentene), 27.5; 34–37 which is 2-pentene, 1.5; residue, 3.0.

From 2-pentene: 27–34, 2.9; 34–37, 45; residue 11.5.

The precision of this distillation method makes it evident that rearrangement of 1- to 2-pentene and *vice versa* has occurred.

The residues from the six runs were combined and fractionated: (b. p., cc.) 77–85, 1.0; 85–105, 1.0; 105–115, 1.5; 115–130, 2.0; 130–150, 3.0; residue, 2.0. The refractive index of the 77–85° fraction was 1.448, which is too low for benzene (1.501); yet, sufficient benzene was present to make a satisfactory derivative of *m*-dinitrobenzene. Cyclohexene was probably the other product. The fraction was definitely unsaturated toward bromine in carbon tetrachloride solution. The 105–115° fraction was unsaturated similarly, $n^{20}D$ 1.4670. The low refractive index was evidence for the presence of a mixture of methylcyclohexene and toluene. Actually, a dinitrotoluene derivative could not be obtained, which pointed to the low concentration of toluene if any.

Liquid Products from the Pure Synthetic Pentenes.—The synthetic 1-pentene, which had been carefully freed of isopropylethylene, and the synthetic 2-pentene were both subjected to pyrolysis at 550 and 580° with contact times of eight to twenty-two seconds. The same apparatus was used as before. The amount of hydrocarbon taken for each of four runs was 30–39 g. Only the liquid product of these runs was studied. The condensed material was distilled through the Davis column and a reflux ratio of at least 20:1 was maintained. The adapter between the condenser and the receiving bulb was kept ice cold. The tip of the adapter was drawn out to long, capillary dimensions so that it could pass into the slightly larger, long, capillary neck of the tared receiving bulbs, which were also kept at 0° to avoid possible evaporation losses. The fractionation data from one run each of the two pentenes will be cited.

From 1-pentene: (b. p., g.): 0–18 (dissolved butenes) 1.1; 18–26, 0.03; 26–29.8, 0.14; 29.8–32 (1-pentene), 18.4; 32–34, 1.20; 34–36, 0.92; residue, 2.20.

From 2-pentene: (b. p., g.): 10–18, 0.13; 18–26, 0.13; 26–34, 0.94; 34–36.5, 21.4; residue, 1.5.

No constant boiling portion appeared at 18–26° in either case, indicating an absence of isopropylethylene. The few drops which accrued represented merely the distillation lag. A definite distillation plateau was noticed, however, for 2-pentene from 1-pentene, and for 1-pentene from 2-pentene. Distillation of the combined residues from the 2-pentene runs revealed a sharp rise to 80° and a definite plateau at 82–84°, indicative of cyclohexene; and another at 97–101°, indicative of methylcyclohexene.

Summary

1-Pentene undergoes pyrolytic rearrangement to a small extent into 2-pentene and *vice versa*. This is a high temperature process, occurring at temperatures above 580°. No branched chain isomers are formed from pure 1-pentene or pure 2-pentene. Methane, 1-butene, propylene, ethane and ethylene in molar quantities respectively of 6:2:2:2:1 accounted for over nine-tenths of the gas. Some 2-butene, butadiene and hydrogen were identified also. Evidence was obtained for both aromatics and unsaturates (presumably cycloalkenes) in the liquid products.

EVANSTON, ILLINOIS RECEIVED AUGUST 20, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TEXAS CHRISTIAN UNIVERSITY]

Densities and Refractive Indices of Bromoform–Benzene Mixtures[1]

BY J. L. WHITMAN AND LEROY CLARDY

Mixtures of bromoform and benzene, because of their wide variation in density, have been used for the separation of minerals of different specific gravities.[2] To facilitate such use we have now determined the densities and indices of refraction of these mixtures over the entire composition range.[3]

The benzene and bromoform were redistilled, the latter *in vacuo*, until fractions were obtained with a density of 0.8679 for benzene, and an index of refraction of 1.5911 for the bromoform, at 30°. The best values in the literature are respectively, 0.8681 and 1.5980 (at 19°).[4]

The densities were measured with a pycnometer of 2.5 ml. capacity, using a thermostat maintained at 30 ± 0.005°. All values are the mean of six independent measurements with a maximum deviation of 0.00057 and average deviation of 0.00014. The estimated accuracy is 0.02%. The mixtures were made up by weight and were always used within five hours of the time of preparation.

The measurements of the index of refraction were made at 30 ± 0.1° using an Abbe–Spencer

(1) Abstract of a thesis submitted by LeRoy Clardy in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Texas Christian University.

(2) Sullivan, "Heavy Liquids for Mineralogical Analyses," Dept. of Commerce, Bureau of Mines, Tech. Paper 381, 1927.

(3) But one reference to density data for this system could be found: "I. C. T.," Vol. III, p. 146, with no values given, and the notation that "the reliable data cover less than three values." Öholm, *Medd. Vetenskapsakad. Nobelinst.*, **2**, No. 26, 1913.

(4) "I. C. T.," Vol. III, p. 29, and Vol. VII, p. 34.

refractometer. The data given represent the mean of three concordant readings for each sample. The estimated accuracy is 0.05%.

TABLE I

DENSITY AND REFRACTION DATA FOR MIXTURES OF BROMOFORM AND BENZENE

C_w	C_v	d^{30}_{30} (expt.)	d(calcd.)	Diff.	$n^{30}D$	r
0.000	0.000	0.8679	0.8679	0.0000	1.4952	0.3361
9.979	3.260	.9326	.9327	.0001	1.4982	.3144
19.988	7.059	1.0079	1.0082	.0003	1.5018	.2917
29.956	11.505	1.0963	1.0965	.0002	1.5061	.2710
40.001	16.852	1.2024	1.2028	.0004	1.5111	.2492
49.993	23.308	1.3307	1.3311	.0004	1.5181	.2278
58.703	30.174	1.4670	1.4675	.0005	1.5247	.2080
69.891	41.373	1.6890	1.6900	.0010	1.5356	.1845
80.007	54.883	1.9567	1.9585	.0018	1.5484	.1624
90.866	75.150	2.3608	2.3612	.0004	1.5694	.1386
100.000	100.000	2.8550	2.8550	.0000	1.5911	.1184

In the discussion given below, and in Table I, the following notation is used:

C_w, weight % of component B (bromoform)
C_v, volume % of component B
d_A, density of component A (benzene)
d_B, density of component B
d_s, density of solution
V_A, volume of component A in 100 g. of solution
V_B, volume of component B in 100 g. of solution
Δd, difference in densities of A and B
n, index of refraction
r, specific refraction

Discussion

If we assume that two liquids A and B form an ideal solution with respect to volume composition, *i. e.*, that there is no change of volume on mixing, then the density–volume composition curve must be a straight line or "average" relationship, the equation of which is

$$d_s = aC_v + b \qquad (1)$$

where a is the slope of the line and b is the intercept on the d_s axis. But

$$a = (d_B - d_A)/100; \text{ and, } b = d_A$$

Substituting these values in equation (1)

$$\left.\begin{aligned} d_s &= (d_B - d_A)C_v/100 + d_A \text{ or} \\ d_s &= 0.01\ \Delta d C_v + d_A \end{aligned}\right\} (2)$$

Equation (2) is the *straight line* relationship between density and volume % for an *ideal* liquid pair. The density–weight % equation may also be derived by the use of the following obvious relations

$$\left.\begin{aligned} C_v &= 100V_B/(V_A + V_B) \\ V_A &= (100 - C_w)d_A \\ V_B &= C_w/d_B \end{aligned}\right\} (3)$$

Substituting these values in (2) and simplifying

$$d_s = d_A d_B/(d_B - 0.01\ \Delta d C_w) \qquad (4)$$

which is the relationship between density and weight % for an *ideal* solution. This equation is of the general form

$$y = a/(b - cx)$$

which is the equation of an hyperbola, yet it describes a property–composition relationship for an *ideal* solution.

Equation (4) is a theoretical equation based on the assumption of an ideal system. If experimental values from Table I are substituted in (4) the theoretical densities of the various mixtures may be calculated. These values are given in Column 4, Table I, and are found to be in good agreement with the experimental values given in Column 3 showing that at least with respect to density relationships the pair bromoform–benzene is nearly ideal. Because of the great difference in chemical nature between these two compounds this might not have been expected, although Linebarger[5] found that the vapor pressure of the system chloroform–benzene conformed quite closely to the ideal system. The greatest difference between the experimental and calculated values (Column 5) is 0.0018 and occurs at about 80 weight per cent. of bromoform.

Equating (2) and (4), reducing and substituting numerical values

$$C_v = 0.3040C_w/(1 - 0.006960C_w) \qquad (5)$$

Values of C_v calculated from (5) are given in Column 2. Solving equations (2) and (4) for C_v and C_w, respectively, we have

$$C_v = (d_s - d_A)/0.01\ \Delta d, \text{ and} \qquad (6)$$
$$C_w = d_B(d_s - d_A)/0.01\ \Delta d\ d_s \qquad (7)$$

Substituting numerical values in (6) and (7) and simplifying

$$C_v = d_s/0.01987 - 43.675, \text{ and} \qquad (6a)$$
$$C_w = 143.67 - 124.69/d_s \qquad (7a)$$

These are the practical working equations by which either C_v or C_w may be calculated from a single density measurement.

A further interesting relationship may be obtained by dividing (6) by (7), from which

$$C_v/C_w = d_s/d_B \text{ or } d_s = d_B C_v/C_w \qquad (8)$$

The density of any ideal liquid mixture is equal to the density of one of the components multiplied by the ratio of the volume per cent. to the weight per cent. for the same component.

Similar reasoning may be applied to the refractive index–composition relationships, and equations similar to although somewhat more complicated than, those derived above may be obtained. They are, however, much less useful than the density equations since where the factor $(d_s - d_A)$ enters into (6) and (7), the factor $(n_s - n_A)$ occurs in the index of refraction equations. The numeri-

(5) Linebarger, THIS JOURNAL, 17, 695 (1895).

cal value of this latter factor is relatively so small that the resulting errors of calculation are much too great to be of use unless the values of n can be measured with reasonable precision to the fifth decimal place. These equations are therefore omitted, and if it is desired to use refractive data for determining composition it should be done either by using a large scale graph or from calculations involving the specific refractivity (Column 7) as given by the equation $r_s = xr_B + (1 - x)r_A$, where $100x$ is the weight per cent. of the component B in the solution.

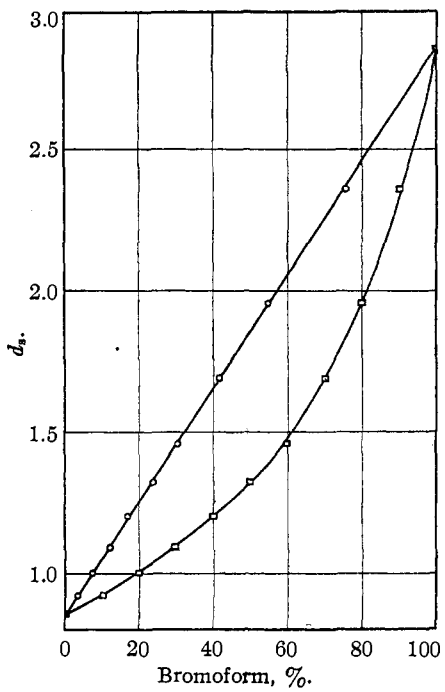

Fig. 1.—Density-composition curves for bromoform–benzene mixtures: ○, % by vol.; □, % by wt.

Density–composition and index of refraction–composition data are represented in Figs. 1 and 2, respectively, which emphasize the dependence of the type of curve obtained upon the method of expressing composition, although in all cases an ideal solution is being described. Specific refractions (Column 7), calculated from the Lorenz–Lorentz formula, $r = (n^2 - 1)/d(n^2 + 2)$, were found to give a straight line when plotted against weight per cent. composition.

From the data and equations given above, it is evident that the frequent tendency to associate straight line functions with ideal liquid systems is a dangerous practice and one which is likely to lead to false conclusions. Before such a simple functional relationship may be assumed, the particular properties to be related must be examined with care.

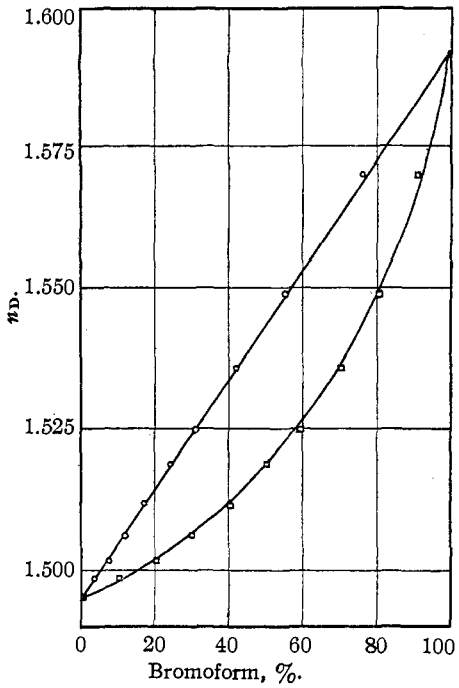

Fig. 2.—Index of refraction–composition curves for bromoform–benzene mixtures: ○, % by vol.; □, % by wt.

Summary

Experimental data are given for the densities and indices of refraction of a series of mixtures of bromoform and benzene.

Equations are derived for certain property–composition relations and are examined with respect to the ideality of the solution. It is shown that this system conforms very closely to an ideal system with respect to the density–composition relation.

Numerical equations are given which may be used in the calculation of either weight per cent. or volume per cent. from a single density measurement at 30°.

The necessity of using great caution in applying straight line functions to ideal systems is emphasized.

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