Densities of Some Organic Substances

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The densities in air of ethyl acetate, 1,4-dioxane, isoamyl alcohol, and benzyl alcohol were measured at 25° C and between 30–70° C at 10° intervals with a modified Robertson pycnometer. Research grade benzene was used as the calibrating standard. The accuracy of the density measurements was estimated to be ±0.0005 g-cm^{-3} or better. A second-order polynomial was fitted to each set of experimental data. The agreement with the available literature values is satisfactory except for isoamyl alcohol for which compound our values and the Thermodynamics Research Center (TRC) Data Project selected values cross at 40° C.

In the literature, density values for many organic substances, as functions of temperature, are old and in many cases unreliable. Recent investigations achieve accurate redeterminations of the density data with purer samples and more accurate measurement techniques. In the present investigation the density values in air of ethyl acetate, 1,4-dioxane, isoamyl alcohol, and benzyl alcohol were measured from 25–70° C using a modified Robertson pycnometer as described by Thomas and McAllister (*11*). The calibrating standard used was research grade benzene supplied by the British Drug House Laboratory (BDH) with a purity of at least 99.97 mol %. The temperature-density data for benzene were taken from the American Petroleum Institute Research Project 44 (*10*).

SUBSTANCES USED

Ethyl acetate and 1,4-dioxane were research grade samples supplied by the BDH with stated purity of 99.5 mol % used without further purification. The laboratory reagent samples of isoamyl alcohol and of benzyl alcohol were purified by fractionally distilling in a spinning band column. The middle cut (boiling point 131.9° C/754 mm Hg for isoamyl alcohol and 205.2° C/754 mm Hg for benzyl alcohol) was used for the density measurement. The purity of each sample was checked by vapor phase chromatography using a 10 ft × ¼ in. carbowax column. Each alcohol was more than 99.5 mol % pure.

APPARATUS

The constant temperature bath had commercial ethylene glycol as bath fluid controlled to ±0.01° C by a thermoregulator. Each temperature was checked during the investigation with an L&N platinum resistance thermometer and a G-1 Mueller bridge. An Ainsworth-type 24*N* balance capable of measuring weights up to ±0.00005 gram was used for all weighings. For 25° C measurements, a Fisher constant temperature bath (0–150° C) was used with a Sargent thermometer capable of controlling temperatures to ±0.01° C. The level in the pycnometer was measured by a cathetometer with an accuracy of 0.05 mm.

RESULTS

Each observation was duplicated satisfactorily by two pycnometers of the type mentioned above. Air buoyancy corrections were applied to all the density measurements. The following correction procedure was followed (*1*):

The true density, d, in air is given by

$$d = d' + c$$

where d′ is the measured density and c is the correction factor given by

$$c = D(1 - d'/d_0)$$

where d_0 = density of the calibrating liquid and D is the density of air calculated by

$$D = 0.001293\,(P - k)/(1 + 0.00367\,t)760$$

$k = 0.0038\,(H)(P'_{H_2O})$

P = atmospheric pressure in balance room, mm Hg

t = temperature of balance room, ° C

H = relative humidity, %

P'_{H_2O} = vapor pressure of water at t ° C, mm Hg

In almost all cases these corrections amounted to two units in the fifth place. The accuracy of the density measurements was estimated to be ±0.0005 g-cm^{-3} or better. Factors such as temperature control, sample purity, weighings, and adjustment of sample level in the pycnometer were taken into consideration. The results are compared with the existing literature values in Tables I through IV. The calculated values came from the empirical equation in Table V.

Table I. Temperature vs. Density for Ethyl Acetate

	Density of ethyl acetate, g-cm^{-3}				
Temp, ° C	Wade-Merriman (*12*)	Biron (*3*)	Mumford-Phillips (*7*)	This work	Calcd values
0.00	0.92454	0.92425	...	...	0.9243
20.00	0.90056	0.90030	0.9007	...	0.9004
25.00	0.89446	...	0.8946	0.8939	0.8943
30.00	0.88830	...	...	0.8876	0.8881
40.00	0.87598	0.87555	...	0.8755	0.8756
50.00	...	...	...	0.8630	0.8628
60.00	...	...	...	0.8499	0.8498
70.00	...	...	...	0.8364	0.8365

Table II. Temperature vs. Density for Isoamyl Alcohol

	Density of isoamyl alcohol, g-cm^{-3}		
Temp, ° C	Ref. *9*	This work	Calcd values
25.00	0.8071	0.8088	0.8079
30.00	0.8037	0.8046	0.8042
40.00	0.7969	0.7968	0.7969
50.00	0.7897	0.7892	0.7894
60.00	0.7823	0.7814	0.7818
70.00	0.7746	0.7736	0.7741

DISCUSSION

Except for isoamyl alcohol, the values agree with the literature. There the maximum difference is 0.0017 g-cm^{-3} from the TRC values. That both curves actually cross at 40° C might be explained by slight impurities in the sample of isoamyl alcohol. All the available density values

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as functions of temperature were fitted to a second-order polynomial, and the pertinent constants were computed by regression analysis using an IBM 7044 computer. The constants are reported in Table V.

For each compound, density measurements from 70–100° C were done using toluene as the calibrating standard. The densities of toluene used at these temperatures were taken from reference *10* reported to four significant figures. The two sets of measurements for each compound did not overlap smoothly between 70–80° C. The deviation in this temperature range (Figure 1) is probably due to the uncertainties in the toluene densities, but, as suggested by Antonoff (*2*) could also be explained by changes in the liquid structure. As this question is not yet resolved by us, densities at these higher temperatures are not reported.

Table III. Temperature vs. Density for Benzyl Alcohol

	Density of benzyl alcohol, g-cm^{-3}		
Temp, ° C	Perkin (*8*)	This work	Calcd values
0.00	1.061	...	
20.00	1.045	...	
25.00	1.041	1.0424	1.0423
30.00	1.038	1.0383	1.0386
40.00	1.030	1.0313	1.0310
50.00	1.021	1.0232	1.0233
60.00	1.013	1.0153	1.0154
70.00	1.005	1.0075	1.0074

Table IV. Temperature vs. Density for 1,4-Dioxane

	Density of 1,4-dioxane, g-cm^{-3}				
Temp, ° C	Ketelaar-Van Meurs (*6*)	Hammond-Stokes (*5*)	Griffiths (*4*)	This work	Calcd values
14.60	1.0394	...	...	...	1.0396
23.80	1.0297	...	...	...	1.0293
25.00	...	1.02797	1.02808	1.0280	1.0280
30.00	...	...	...	1.0221	1.0223
31.35	1.0208	...	...	...	1.0208
40.00	...	...	...	1.0110	1.0110
50.00	...	...	...	0.9994	0.9997
60.00	...	...	...	0.9886	0.9882
70.00	...	...	...	0.9766	0.9767

Table V. Values of Constants for the Equation, $d = A_0 + B_0T + C_0T^2$ (d in g-cm^{-3}; T in ° K)

Compound	A_0	$B_0 \times 10^3$	$C_0 \times 10^6$	Av dev
Ethyl acetate	1.15421	−0.513149	−1.20242	0.0002
Isoamyl alcohol	0.96907	−0.358821	−0.610029	0.0004
Benzyl alcohol	1.20061	−0.319040	−0.710885	0.0002
1,4-Dioxane	1.32842	−0.893913	−0.381851	0.0002

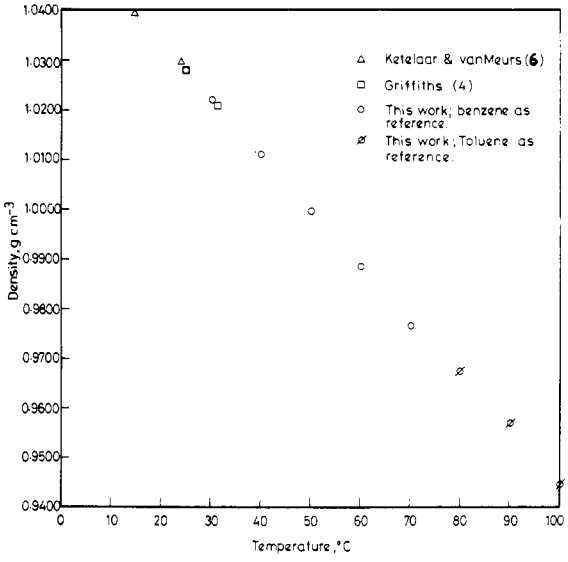

Figure 1. Density of 1,4-dioxane vs. temperature

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