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Purification and Physical Properties of Organic Compounds. XII. The Lower Aliphatic Bromides[1]

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In the course of some rate of reaction work it became necessary to know the densities of certain bromides of the aliphatic series. The data in the literature showed considerable disagreement. Accordingly a number of these bromides were prepared in as pure a form as practicable and their boiling points, densities and freezing points were determined.

Preparation and Purification of the Bromides.—The bromides were all prepared by the action of constant boiling hydrobromic acid of high purity on the corresponding pure alcohols by the method of Norris[2] as modified by McCullough and Cortese.[3] The alcohols were carefully fractionated pure materials boiling over a range of not more than 0.1°. Their purity was checked by density determinations. For the sample of *n*-amyl bromide we are indebted to Dr. Richard H. F. Manske of the Canadian National Research Laboratories, Ottawa.

Each of the bromides was washed repeatedly with constant boiling hydrobromic acid and then dried over anhydrous sodium sulfate or calcium chloride and subjected to systematic fractional distillation through a 180-cm. spiral fractionating column electrically heated and supplied with a still-head for controlling the reflux. The boiling ranges and boiling points recorded in the accompanying table are the values obtained for the best fraction in this distillation. In the case of isopropyl bromide this sample was then fractionally crystallized from its own melt by means of an apparatus to be described in a later communication.

The final step in the purification always consisted of distilling the material in a high vacuum at low temperatures by immersing the receiver in liquid air. One portion of the middle fraction was collected in a freezing point tube and another, for use in the density determination, was collected in a special sample tube. Both were sealed off without admitting air.

Measurement of Physical Constants.—The boiling points except as noted were read by means of Anschütz thermometers totally immersed in the vapors. They were calibrated under the same conditions against standards of the same design certified by the U. S. Bureau of Standards and the Deutsches Reichsanstalt. In the cases of *n*-butyl, *s*-butyl and *n*-amyl bromide, a carefully calibrated copper–constantan thermocouple was used. Correction to 760 mm. was made by use of the temperature–pressure coefficients given in the "International Critical Tables."

The densities were determined by means of a 5-cc. Pyrex Sprengel pycnometer having the arms bent up at an angle of about 20° and provided with tightly fitting ground glass caps. The pycnometer after being rapidly filled from a freshly opened vacuum-sealed ampoule was capped and allowed to remain immersed in the thermostat for at least twenty minutes before the adjustment was made between two scratch marks. The temperature of the thermostat, which was maintained at 25.00 ± 0.01°, was checked by a standard certified Reichsanstalt thermometer which was in turn carefully checked against a platinum resistance thermometer at the ice-point and in a thermostat maintained at 30.000 ± 0.002°. The pycnometer was always allowed to stand inside the balance case for thirty minutes before being weighed with calibrated weights, making correction to vacuum.

The freezing points were determined from both cooling and heating curves,[4] an average being taken of the values obtained by the two methods.

Results and Discussion.—The results obtained are listed in Table I. For comparison with previous values in the literature only those of Timmermans, who with his co-workers has done the most extensive accurate work in this field, have been cited except where more recent accurate determinations have been made.

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[1] The experimental work for this paper was completed in 1928 during the tenure of a National Research Council Fellowship by the Senior Author.

[2] Norris, *Am. Chem. J.*, **38**, 640 (1907).

[3] McCullough and Cortese, THIS JOURNAL, **51**, 225 (1929).

[4] For a description of the freezing point apparatus, its uses in estimating the purity of the sample, and the establishment of the thermometric scale used, see the first two papers of this series: *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933), and *J. Phys. Chem.*, **37**, 609 (1933).

TABLE I

SOME PHYSICAL PROPERTIES OF THE LOWER ALIPHATIC BROMIDES

	Total b. p. range, °C.	B. p., °C. 760 mm.	B. p., °C., lit.	d^{25}_4	d^{25}_4 lit.[h]	F. p., °C.	F. p., °C., lit.
Ethyl bromide	0.04	38.34	38.40[a]	1.4512	1.45048[a]	−118.9	−119.0[a]
n-Propyl bromide	.05	70.97	71.00[a]	1.3455	1.34305[a]	−109.8	−110.0[a]
Isopropyl bromide	.03	59.41	59.35[b]	1.3063	1.30555[b]	− 90.0	− 89.0[b]
			59.45 ± 0.02[e]				− 88.6, −89.1[e]
n-Butyl bromide	.00	101.26	101.60[a]	1.2686	1.26840[a]	−112.3	−112.4[a,e]
			101.2 ± 0.1[e]		1.2689[f]		−112.7[f]
					1.2685[g]		
Isobutyl bromide	.06	(91.72)	91.40[b]	(1.2480)	1.25715[b]	(−118)	−118.05[e]
			91.1 ± 0.2[e]				
s-Butyl bromide	.04	91.24	91.20[c]	1.2530	1.25363[c]	−112.1	−111.9[c]
							−112.7[f]
n-Amyl bromide	.09	129.6	129.70 ± 0.02[d]	1.2121	1.21091[d]	− 87.9 (stable)	− 95.25[d]
					1.2114[f]	− 94.6 (unstable)	− 88.0[f]

[a] Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926). [b] Timmermans and Martin, *ibid.*, **25**, 411 (1928). [c] Timmermans and Delcourt, *ibid.*, **31**, 85 (1934). [d] Simon, *Bull. soc. chim. Belg.*, **38**, 47 (1929). [e] Timmermans, *ibid.*, **30**, 62 (1921). Deese, THIS JOURNAL, **53**, 3673 (1931). [g] Bridgman, *Proc. Am. Acad. Arts Sci.*, **68**, 1 (1933). [h] Calculated from the values given for 0, 15 and 30° values except for ref. (*f*).

The boiling point values agree very closely with those of Timmermans and others except in the case of isobutyl bromide which differed by 0.3 to 0.6°.

The density values are slightly higher than those previously reported except in the case of isobutyl and secondary butyl bromides. It was found that the final high vacuum distillation to which all the samples were subjected always raised the density. It should also be pointed out that the method of preparation and purification used avoided the formation of traces of unsaturated compounds and ethers[3] which might be difficult to remove and which would tend to lower the density. The largest discrepancy in density is in the case of isobutyl bromide. This was probably due to the presence of impurities as mentioned below.

The shape of the heating curves indicates that all of the compounds studied were of a high degree of purity[4] with the exception of the secondary butyl bromide, which contained a slight trace of impurity, and the isobutyl bromide. The latter gave very unsatisfactory cooling curves due to sluggish crystallization, and the heating curves indicated the presence of considerable impurity. The actual freezing point obtained was −118.1°, showing acceptable agreement with the best value previously reported, −118.05°, but it is probable that it would be at least 0.5° higher for the pure compound. It seems probable, on the other hand, that the other freezing points do not differ by more than a few tenths of a degree from the correct values for the pure bromides.

There are two solid forms of *n*-amyl bromide, an unstable form, melting at −94.6, and a stable form, melting at −87.9°. The unstable form always appeared when cooling curves were run in the usual way. When kept for some time at a temperature 10 to 20° below its melting point or when suddenly cooled in liquid air the unstable form transformed in the solid state to the stable form with an evolution of heat. It was found possible to get a heating curve on the unstable form immediately after a cooling curve even though the temperature of the sample fell to −102° meanwhile and remained there some twenty minutes. A cooling curve on the stable form was finally obtained on a sample which had been completely transformed in the solid state and then partially melted. This behavior proves that *n*-amyl bromide is dimorphous and further that it is monotropic. It also explains why Simon obtained a freezing point of −95.25° for this compound while Deese[5] obtained −88.0° (see Table I). The former obtained his value by freezing point measurements and the latter by heat content measurements which involved preliminary cooling to much lower temperatures.

An inspection of Table I shows that our freezing points agree acceptably with previous values except in the case of isopropyl bromide and the unstable form of *n*-amyl bromide.

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[5] Deese [THIS JOURNAL, **53**, 3673 (1931)] states that "a transition phenomenon was found to occur at about −113°" but heat content measurements failed to verify the existence of a second solid form.