CLXX.— *α -Bromonaphthalene: its Physical Properties and its Application to the Determination of Water in Moist Alcohol.*

By MARIAN JONES and ARTHUR LAPWORTH.

α -BROMONAPHTHALENE is probably not at present to be purchased in anything but a decidedly impure condition; even the best specimens examined by us have contained quite considerable quantities of free naphthalene and of dibromonaphthalene.

As several hundred grains of α -bromonaphthalene were required in a highly purified state, several methods of preparation were examined, but none of these yielded even approximately pure samples, and we were therefore led to attempt the purification of the commercial material.

Fractional crystallisation of α -bromonaphthalene picrate had been used by Roux (*Ann. Chim. Phys.*, 1887, [vi], **12**, 343), and was fairly satisfactory, but it was finally found unnecessary to prepare the picrate when dealing with large quantities of material, and the following procedure led to excellent results.

Commercial α -bromonaphthalene is fractionally distilled in a current of steam as long as the odour of naphthalene is perceptible, or until the distillate no longer deposits crystals at laboratory temperatures. The residue is then separated from the water, dissolved in absolute alcohol, the whole thoroughly cooled, seeded, if necessary, with solid bromonaphthalene prepared by cooling a few

drops of the liquid, without solvent, in a test-tube immersed in the freezing mixture. The mass is then transferred to a Büchner funnel with a large filtering surface, and freed as rapidly as possible from the mother liquor with the aid of an efficient vacuum pump. When dealing with large quantities of bromonaphthalene there is no difficulty, even in warm weather, in securing most of the crystalline material before it melts, owing to the cooling effect of the mass of mother liquid on the funnel. By repeated cooling of the mother liquors, collection of the deposits, and recrystallisation from absolute alcohol, large fractions may finally be obtained, in which, even before removal of the last traces of alcohol, an immersed thermometer records a melting point of 6° or slightly higher, and these may be dealt with as follows:

To remove alcohol, the α -bromonaphthalene is subjected to the action of a current of steam for some time. To eliminate the last traces of water the liquid is shaken with calcium chloride, filtered, and finally a stream of dry air or carbon dioxide is passed through it at 100° .

It has also been found that in large quantities α -bromonaphthalene may be purified by repeated partial crystallisation without the use of any solvent, a Büchner funnel being employed as above. The moisture which accumulates by deposition from the atmosphere on the cold material causes little practical difficulty.

Physical Properties of α -Bromonaphthalene.

Melting Point.—(1) The most highly purified specimens always melted at 6.20 ± 0.02 when the solid consisted of the stable modification.

The melting point was invariably determined by immersing a standardised Jena-glass thermometer in a considerable bulk of the substance contained in a Dewar vacuum vessel, the very small corrections required for exposed portions of the scale, and for any appreciable changes in the ice points of the thermometers, being made after each observation.

(2) Under certain conditions, samples which normally melted at 6.20° gave on solidification a solid, which fused, usually somewhat indefinitely, between 0° and 2° ; we have not found it possible to obtain this form with a quite sharp melting point. The observations render it certain, however, that α -bromonaphthalene is dimorphous.

Density.—The densities of two specimens of α -bromonaphthalene purified in these laboratories and melting at $6.20 \pm 0.02^{\circ}$ have been determined, the one by Mr. J. I. Crabtree with a sample he had himself purified, and the other by one of us (M. J.). The results

were identical to the fifth significant figure, and were: (1) D_4^{20} 1.4834 and (2) D_4^{25} 1.4785.*

Refractive Indices at 20°.—These were determined with the aid of a Pulfrich refractometer, observing all the precautions recommended by Lowry in his valuable article in the Proceedings of the Optical Convention (1912, p. 292).

Line.	C.	D.	Hg (5461).	F.	Hg (4358).	G.
	1.6494	1.6582	1.6659	1.6819	1.7027	1.7037

These values for the C, D, F, and G lines are uniformly 2—2.5 units in the fourth decimal place lower than those given by Brühl (*Zeitsch. physikal. Chem.*, 1897, **22**, 388, 409). Values for the mercury lines do not appear to have been recorded hitherto. A sample of α -bromonaphthalene obtained from Kahlbaum, although melting several degrees too low, had almost precisely the refractive indices above given; the same was true of a number of our own specimens melting between 5.6° and 6.2°.

Dispersion of Pure α -Bromonaphthalene at 20°.—Separate determinations of the dispersions of the compound were made, and are given to the fifth place (compare Lowry, *loc. cit.*).

Differences of Indices of the Sodium Line and the Lines:

C.	Hg (5461)	F.	Hg (4358).	G.
−0.00892	0.00769	0.02363	0.04453	0.04552

Application of α -Bromonaphthalene to the Determination of Water in Moist Alcohol.

The usual method of determining the compositions of mixtures of water and alcohol is by observations of their densities. Other methods, more or less successful, have been devised (compare, for example, Wiley, *J. Amer. Chem. Soc.*, 1896, **18**, 1063; Gaunt, *Zeitsch. anal. Chem.*, 1905, **44**, 106; and Wagner, *ibid.*, 1907, **46**, 508), including some depending on observations of clearing or clouding points of mixtures with other liquids. Thus Curtis tried toluene (*J. Physical Chem.*, 1898, **2**, 371), Siderski used ether (*Bull. Assoc. chim. Sucr. Dist.*, 1909, **27**, 562), whilst petroleum has also been suggested and applied successfully.

Certain investigations which one of the present authors had in view necessitated the working out of a method for estimating the composition of small quantities of moist alcohol (95—100 per cent.),

* Confirmation of the substantial accuracy of this number has kindly been supplied us by Mr. W. J. Jones, who determined the density of two samples of α -bromonaphthalene melting a few hundredths of a degree too low. His result was: D_4^{25} 1.47827—1.47837.

and a method based on the clouding points of mixtures with a pure third component appeared likely to prove most suitable. All materials previously employed were found unsatisfactory in practice, and finally α -bromonaphthalene was selected for the purpose, as it may readily be obtained in a state of sufficient purity, whilst the clearing points of its mixtures with 90—99 per cent. alcohol are easy to determine with an accuracy which corresponds with an error in the estimated percentage of water of less than 0.03.

The alcohol used in these experiments was prepared from ordinary absolute alcohol dried by calcium with the precautions described by Lapworth and Partington (T., 1910, 97, 24), and its purity checked by determination of its density.

Mixtures of weighed quantities of alcohol and water were prepared, all weighings being reduced to a vacuum. The liquids were stored in special flasks, from which they could be withdrawn and replaced by dry air.

The vessel employed had the form indicated in the figure, and was made of thin Jena glass; the length was 8 cm., and diameter of the tubular portion 2 cm. The opening *A* was used to introduce the bromonaphthalene, whilst *B* admitted the thermometer, secured by a rubber stopper, through which it passes to the lower section *D*. The bulb *C* prevents splashing of the liquid on to the corks during the gentle shaking necessary. The thermometer was one divided into 1/5ths of a degree, and could be read with accuracy to 0.05°, and all readings were corrected.

In working, about 6 c.c. of the alcohol-water mixture were introduced into *D*, the thermometer and rubber stoppers *B* and *A* fitted into the vessel, and the whole was weighed. A small amount of bromonaphthalene from a weighed burette was then introduced through *A* and the burette re-weighed. The vessel was given a rotatory motion to ensure admixture.

If the bromonaphthalene so added formed a homogeneous solution, the vessel was placed in a beaker containing water at room temperature. By the addition of ice-cold water the temperature was slowly lowered, whilst the apparatus was gently shaken until the liquid in *D* clouded.

Just above the critical point the liquid gradually assumes an opalescence, especially when large proportions of bromonaphthalene are present, but this appearance is easily distinguished from that

at the true critical point, when the liquid suddenly becomes opaque. The exact temperature at which this opacity appeared was noted, with a second thermometer in the cooling vessel, care being taken that at the clouding point the temperatures registered on the two thermometers did not differ by more than a fraction of a degree.

The result was checked, and the process repeated for each alcohol-water solution until a whole series of checked observations was obtained.

For temperatures below 0° a freezing mixture of ice and salt was used, and for temperatures above 15° , warm water. The percentage of water present in the alcohol varied from 1 to 10, and some twenty solutions were prepared, for each of which a series of temperatures of clouding points was obtained.

From our own results the appended table has been prepared, showing the temperatures of clouding of various mixtures.

Logs., to base 10, of Concentrations * of α -Bromonaphthalene.

	1.5.	1.6.	1.7.	1.8.	1.9.	0.0.	0.1.	0.2
	Percentages of water in the moist alcohol.							
Temp.								
30°	—	—	9.04	7.56	6.40	5.48	4.81	4.42
28	—	—	8.76	7.30	6.15	5.23	4.58	4.19
26	—	10.26	8.48	7.05	5.90	5.00	4.35	3.98
24	—	9.96	8.22	6.81	5.67	4.77	4.14	3.77
22	—	9.68	7.97	6.58	5.44	4.54	3.93	3.57
20	—	9.41	7.73	6.35	5.22	4.34	3.74	3.39
18	—	9.17	7.51	6.14	5.01	4.14	3.55	3.20
16	—	8.92	7.29	5.93	4.81	3.95	3.39	3.02
14	—	8.69	7.08	5.73	4.61	3.77	3.20	2.86
12	10.36	8.47	6.88	5.55	4.43	3.60	3.04	2.70
10	10.12	8.27	6.70	5.37	4.27	3.45	2.87	2.55
8	9.89	8.05	6.51	5.19	4.11	3.30	2.74	2.41
6	9.68	7.86	6.33	5.03	3.96	3.16	2.60	2.27
4	9.48	7.68	6.16	4.88	3.82	3.03	2.47	2.14
2	9.28	7.51	6.00	4.73	3.69	2.90	2.34	2.02
0	9.09	7.34	5.85	4.59	3.56	2.78	2.23	1.91
-2	8.91	7.18	5.71	4.46	3.45	2.67	2.13	1.80
-4	8.73	7.03	5.58	4.33	3.34	2.57	2.03	1.70
-6	8.58	6.88	5.45	4.23	3.24	2.48	1.94	1.61
-8	8.42	6.75	5.33	4.13	3.15	2.40	1.86	1.53
-10	8.29	6.64	5.22	4.04	3.07	2.32	1.78	1.46

* The term "concentration" is here used for

$$\frac{\text{Parts by weight of } \alpha\text{-bromonaphthalene}}{\text{Parts by weight of moist alcohol}}$$

A very careful correlation of the numbers throughout the table leads us to believe that the error of any single number in this table is not greater than 0.03 in the "percentage of water," and additional experiments have been carried out as a further test, with results confirming this conclusion.

In practice it will probably be found that with quantities of a few c.c. of moist alcohol it is desirable (1) to make several observations of clearing points to the nearest tenth of a degree with successive additions of known quantities of α -bromonaphthalene; (2) to read off the percentage of water for each from a graph prepared from the numbers given in the table; and finally (3) to adopt the mean of the values so obtained. This mean value is probably correct to 0.02 per cent. of water.

It has finally been found that the use of quite pure α -bromonaphthalene is not essential, as all fractions melting above 4.5° gave results identical within 0.1° ; hence it is safe to assume that any samples of α -bromonaphthalene prepared in the usual way, and purified by one of the methods already described, may be used in conjunction with the table, providing that their melting points are not lower than 5.0° .

Our thanks are due to Mr. R. M. Lingford, who was good enough to open the investigation by making a comprehensive and careful series of preliminary measurements with partly purified bromonaphthalene, which has proved of great assistance to us.

The cost incurred in the investigation was partly defrayed by a grant from the Government Grant Research Fund, and we have pleasure in expressing our indebtedness for this assistance.

CHEMICAL LABORATORIES,
THE UNIVERSITY, MANCHESTER.