CCCCLI.—*The Purification and Some Physical Constants of Formamide.*

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IN the course of a study of the mutarotation of the sugars, it appeared desirable to investigate the reaction in formamide as solvent. In view of the marked effect on the velocity of mutarotation of minute traces of catalytically active substances, it was essential for this purpose to obtain formamide of the highest possible degree of purity. It was apparent, however, that the usual methods of purification do not yield a completely pure product, and more efficient processes were therefore sought. Further, in view of the importance of this solvent, and of the paucity of trustworthy data relating to its physical properties, it also appeared desirable to determine or redetermine certain of these constants.

The most usual method of purification previously employed has been that of fractional distillation under reduced pressure. English and Turner (J., 1914, **105**, 1656), using this method, obtained formamide of m. p. 2·20°, and Davis and Putnam (*Carnegie Inst. Pub.*, 1915, 230, p. 17) and Brann (*J. Amer. Chem. Soc.*, 1918, **40**, 793), employing the same method, both give the slightly higher m. p. of 2·25°. These results were confirmed. An impure specimen of formamide (m. p. *ca.* — 12°), after repeated distillation under 1—2 mm., gave finally a product of m. p. 2·25—2·30°, which was not raised by further distillation. Although the solid melted fairly sharply at this temperature, it seemed doubtful whether it was absolutely pure, for it often smelt faintly, but distinctly, of hydrogen cyanide, presumably formed by thermal decomposition (see Frier and Sherman, *Amer. Chem. J.*, 1898, **20**, 223). This decomposition could not be obviated by distillation under a lower pressure, since during the process it is essential to bubble a fairly rapid stream of dry air through the boiling liquid in order to prevent violent bumping.

Fractional freezing has similarly proved unsatisfactory. Merry and Turner (J., 1914, **105**, 748) record that six successive freezings raised the m. p. by only 0·08° (from 0·60° to 0·68°), and English and Turner (*loc. cit.*) by twenty successive freezings raised it by only 0·4° (from 0·60° to 1·0°); they therefore considered the method to be of little use. In view, however, of the very hygroscopic nature of formamide, it appeared probable that the failure of the method was due to the neglect of this factor, since moisture would be absorbed from the atmosphere during the operations of freezing and draining. Experiments were therefore carried out in which the formamide was frozen and drained under conditions which prevented the ingress of water from the atmosphere; the process was then entirely satisfactory, since formamide was eventually obtained of f. p. 2·55°, which is 0·3° higher than any previously recorded.

The apparatus is represented diagrammatically in Fig. 1. The formamide was frozen, by means of an ice–salt mixture, in a large, wide-mouthed hard-glass bottle (A) of about 1000-c.c. capacity. The bottle was fitted with a rubber bung carrying a thermometer and three glass tubes, two of which reached almost to the bottom; one of these served to remove from the crystals the mother-liquor remaining after freezing, and convey it to any of the five attached bottles (only two of which are shown) by means of suitable branched tubes and glass taps; the other was connected to a conductivity cell of the pipette type, and to a tube from which the pure formamide could be collected when required. The liquid formamide was conveyed from one bottle to another by applying an air pressure or suction to the short tube B. All the tubes having access to the air were protected by means of tubes containing calcium chloride and phosphoric oxide.

The usual procedure was to freeze the formamide successively four or five times, the mother-liquor from each freezing (10—15% of the whole) being conveyed to a separate bottle. It was then necessary to refreeze the poorer fractions and combine them in a suitable manner. In general, except when the formamide was almost pure, the freezing point was raised by about 0·2—0·3° after each freezing. The conductivity continued to decrease after the f. p. had reached its maximum : the lowest conductivity recorded when the experiments had to be discontinued was $1{\cdot}98 \times 10^{-6}$ at 20°. The best previous value was $2{\cdot}8 \times 10^{-6}$, obtained by Davis, Putnam, and Jones (*J. Franklin Inst.*, 1915, **180**, 567). In Table I are shown the alteration of f. p. during purification of several samples of formamide, and also the change in specific conductance (κ) during the series for the last sample.

TABLE I.

	F. p. of formamide after *n*th freezing.				
Sample.	$n = 1.$	$n = 2.$	$n = 3.$	$n = 4.$	$n = 5.$
1	0·60°	1·20°	1·60°	1·80°	2·00°
2	1·35	1·60	1·80	2·10	
3	2·25	2·35	2·45		
4	2·30	2·45	2·55		
5	2·55	2·55	2·55		
6	2·55	2·55	2·55	2·55	2·55
$\kappa \times 10^6$	26	13·2	6·84	2·57	1·98

The experiments show that 2·55° is the f. p. of pure formamide, but no estimate can be given of the specific conductance, which is probably considerably lower than 1×10^{-6}.

The solid formamide undergoes a change in appearance during the purification. When impure, it freezes as a white mass of interlacing crystals, but as the purity increases, the solid formed on freezing gradually becomes less opaque, until finally, when the substance is pure, the solid mass is almost transparent.

The method of purification described has the disadvantage that it is rather slow, especially if the formamide is initially very impure, since it is then necessary to work up a large number of poorer fractions. The most rapid method would appear to be a preliminary purification by distillation under reduced pressure, whereby formamide of f. p. 2·25° is obtained, followed by a final purification as described.

Determination of Physical Constants.—The hygroscopic nature of formamide necessitated special precautions to avoid contamination with water vapour during the filling of the vessels, as well as during the actual determinations. The following method of filling vessels was adopted. The narrow glass tube used to convey the formamide from the container bottle was surrounded for the last 4 or 5 cm. of its length by a wider tube of 2—3 cm. diameter and about 7 cm. in length (see Fig. 1). The latter was provided with a side tube through which a rapid stream of dry air was blown, thus surrounding the formamide running from the inner tube with a jacket of dry air. The vessel to be filled was inserted well into the wide outer tube.

FIG. 1.

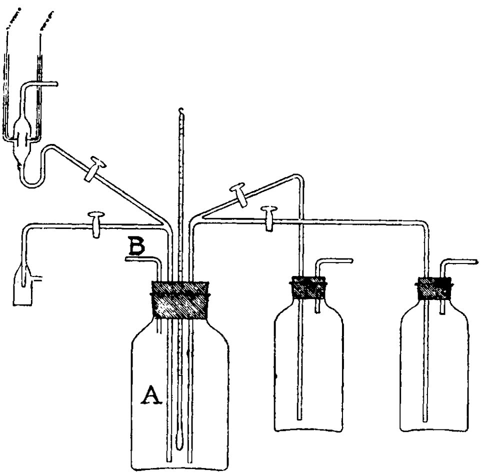
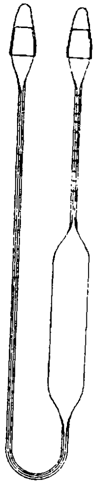


FIG. 2.



The values of the density, viscosity, and surface tension were determined at 18°, 20°, 25°, and, in addition, measurements of density and surface tension were made at 35° and 50°.

(1) *Density.* An ordinary pyknometer could not be used for the determination of density, since considerable exposure of the liquid to atmospheric moisture would inevitably take place during the filling and the adjustment of volume. A pyknometer of the type shown in Fig. 2 was therefore employed. It consisted of a bulb of about 23-c.c. capacity, provided with two capillary limbs of about 1 mm. internal diameter. On one limb was etched a single mark,

while the other limb was graduated in mm. Both limbs were provided with ground-glass caps. The pyknometer was calibrated at 18°, 20°, 25°, and 35°, water being used as the standard substance. A suitable volume of water having been introduced into the pyknometer and the weight determined, the procedure was to adjust the liquid level (by means of a slight air pressure) to the single etched mark, the scale reading on the other limb then being noted. A series of determinations was carried out at each temperature, and a calibration curve constructed. The volume of a given weight of formamide could then be determined from the corresponding scale-reading and the appropriate calibration curve.

A somewhat less accurate value of the density was also determined at 50°; this was required for the calculation of the surface tension at this temperature. The pyknometer was not calibrated directly at 50°, but the volume of the vessel at 50° was calculated from that at 25° and the coefficient of expansion of the glass, which was obtained from the calibration curves at 18°, 25°, and 35°.

The results are given below. The samples of formamide used in the determinations all had the same f. p., *viz.*, 2·55°, but the specific conductance varied from 3 to 5 gemmhos.

Density of formamide.

Temp.	18°	20°	25°	35°	50°
$d_{4^\circ}^{t^\circ}$	1·13510	1·13339	1·12918	1·12068	1·1078
	$\pm 2 \times 10^{-5}$	$\pm 1 \times 10^{-5}$	$\pm 1 \times 10^{-5}$	$\pm 2 \times 10^{-5}$	$\pm 2 \times 10^{-4}$

As already noted by Röhler (*Z. Elektrochem.*, 1910, **16**, 419), the relation between the density of formamide and temperature is strictly linear. From the figures given above, it is

$$d_{4^\circ}^{t^\circ} = 1{\cdot}13510 - 0{\cdot}00084756(t^\circ - 18).$$

Previously recorded values of the density are somewhat discordant. At 20° they range from 1·1340 to 1·1358 (Röhler, *loc. cit.*; Turner and Merry, J., 1910, **97**, 2076; Brühl, *Z. physikal. Chem.*, 1895, **16**, 193), and at 25° from 1·1280 to 1·1318 (Walden, *ibid.*, 1906, **55**, 230; Röhler, *loc. cit.*). No great reliance can be placed on these figures, however, since the formamide employed was generally of low m. p.

(2) *Viscosity.* Determinations of viscosity were made by means of a comparative viscometer of the usual type. It was filled by means of a special pipette designed to prevent exposure of the liquid to atmospheric moisture. As standards for calibrating the viscometer, solutions of sucrose appeared to be the most suitable (Bingham and Jackson, *Bull. Bur. Standards*, Vol. 14, No. 1, p. 59), since their viscosities are known accurately and the substance itself

is easily obtained pure. The sucrose was of two grades, (1) B.D.H. "A.R.," (2) B.D.H. "analytical standard," but no appreciable difference in the viscosities of the two could be detected; hence it was considered that either sample was of sufficient purity for the present purpose. The viscosity of formamide lies between those of 20% and 40% sucrose solutions, and over this viscosity range the viscometer obeyed Poiseuille's law within the experimental error of about ± 0·1%.

In Table II are given the times of flow at 18°, 20°, and 25° for three samples of formamide and for the 40% sucrose solution which was taken as standard. The viscosities of the formamide are given in the last column.

TABLE II.

Viscosity of formamide.

	Time of flow (secs.) for		Viscosity (c.g.s. units) of	
Temp.	formamide.	40% sucrose.	40% sucrose.	formamide.
18°	152·0	246·4	0·06675*	0·03970
20	144·1	228·7	0·06200	0·03764
25	127·0	191·85	0·05187	0·03302

* The viscosity of 40% sucrose solution at 18° is not recorded by Bingham and Jackson, but was obtained by interpolation, the relation between fluidity and temperature which they give for such a solution being

$$t = (\phi + 20) \times 0{\cdot}597 - \frac{1438{\cdot}6}{\phi + 20} + 38{\cdot}24$$

where ϕ is the fluidity at temperature t. This gives the value for η at 18° of 0·06675.

The viscosity at 25° given above is in good agreement with the determinations of English and Turner (*loc. cit.*), who record the two values, 0·03299 and 0·03302, at this temperature.

(3) *Surface tension.* It has been shown by Richards and Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1656) that the capillary-rise method gives accurate values for the surface tension, provided the proper precautions are taken. The most important of these is that the outer vessel containing the liquid in which the capillary is immersed shall be of sufficiently large diameter for the liquid surface to be perfectly flat. This was ensured in the present experiments by containing the liquid in a wide-mouthed bottle of about 6 cm. diameter; this also allowed of precautions being taken rigidly to exclude atmospheric moisture. The radius of the capillary tube was determined by weighing a mercury thread of measured length, the necessary correction being applied for the protrusion of the two mercury meniscuses. The mean radius was $0{\cdot}01179 \pm 0{\cdot}0_41$ cm.

A further check on the radius of the tube was obtained by using it to determine the surface tension of benzene, which had been purified by the usual methods and finally frozen until its f. p. was constant. The mean capillary height at 20° was 5·69 cm., which gives for the surface tension $\gamma = 28{\cdot}91$, as compared with 28·88 given by Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) and by Harkins and Brown (*ibid.*, 1919, **41**, 499). The results obtained were :

Surface tension of formamide.

Temp.	18°	20°	25°	35°	50°
Capillary height, cm. (± 0·01)	8·91	8·90	8·885	8·805	8·70
γ, dynes/cm.	58·53	58·35	57·91	57·11	55·72

These values appear to be appreciably higher than those obtained previously : Turner and Merry (*loc. cit.*) record $\gamma = 57{\cdot}35$ for 20° as compared with 58·35 given above.

The Ramsay–Shields constant calculated on the basis of the values of γ and d at 18° and 50° has the value 0·69, instead of the standard value 2·12. This abnormality had been attributed by Turner and Merry to association.

The values of the parachor between 18° and 50° are given in Table III.

TABLE III.

Temp.	γ.	d.	P (obs.).	P (calc.).
18°	58·53	1·13510	109·6	111·8
20	58·35	1·13339	109·8	
25	57·91	1·12918	110·0	
35	57·11	1·12068	110·4	
50	55·72	1·1078	111·0	

It is to be noted that the observed values of the parachor are all less than the calculated, the maximum divergence being of the order of 2%. A similar discrepancy was noted by Sugden (*J.*, 1924, **125**, 1177) in the case of acetamide, for which the observed value of P is 148·0, as compared with the calculated value of 150·8. In the case of formamide the parachor apparently increases steadily with rise of temperature, and would appear to approach quite closely to the calculated value at a sufficiently high temperature. A drift of this nature might possibly be explained on the assumption that at the lower temperatures the formamide exists to an appreciable extent in the associated condition.

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