

chains cannot yet be answered. The formation of large rings is very improbable on theoretical grounds,⁹ and in the formation of polyesters ring formation is known not to occur—the hydroxyl or carboxyl groups still persist at the ends of the polyester chain.^{7b,c,d,5c} However, no certain evidence of the presence of terminal amino or carboxyl group in the molecule of the polyamide could be obtained. The polyamide dissolves readily in cold concentrated hydrochloric acid, but when the solution is diluted with water it separates unchanged and free from more than traces of halogen. It is not soluble in hot or cold aqueous sodium hydroxide nor does it form any sodium salt. It reacts with molten *m*-bromobenzoic anhydride and, in hot pyridine, with *p*-bromobenzene-sulfonyl chloride. The products contain bromine in amounts which correspond with derivatives of minimum molecular weights about 1100 and 1500, respectively, but in view of the failure of other reactions these cannot be accepted as evidence of the presence of free amino groups in the polyamide. At present we are inclined to assume that the amino and carboxyl groups which would normally be present at the ends of the polyamide chains are lost by pyrolysis. (The evolution of carbon dioxide during the formation of the polyamide could not be detected, but the vapors evolved had a strong amine odor.)

Summary

ϵ -Aminocaproic acid (or its ethyl ester) on being heated reacts with itself both intra- and intermolecularly and yields the 7-ring lactam (*ca.* 30%) and a polyamide (*ca.* 70%). The formation of a molecule of the latter probably involves at least ten molecules of the amino acid.

WILMINGTON, DELAWARE

NOTES

A Method for the Determination of Molecular Weights in Liquid Ammonia.—Very recently Schwarz¹ and Signer² have published a new method for the determination of molecular weights. This method makes use of the principle that two solutions in the same solvent confined with a common vapor phase will come to the same molecular concentration by diffusion of the vapor.

The advantages of the method are that it enables the molecular weights of substances of low solubility and large molecular weight to be determined accurately; it makes possible molecular weight determinations in the same solvent at different temperatures; and it is adaptable to micro-manipulation.

⁹ Carothers, *THIS JOURNAL*, **51**, 2556 (1929).

¹ Schwarz, *Monatsh.*, **53**, **54**, 926 (1929).

² Signer, *Ann.*, **478**, 246 (1930).

Before these publications appeared, we found, employing the same method, that the slow diffusion of organic solvents was a great disadvantage. To correct this fault we resorted to liquid ammonia as solvent and found that it gave excellent results.

Even with liquid ammonia the time required to reach equilibrium was about 150 hours. The rate of transfer varied from 0.1 to 1.0 cc. per day, depending on the differences in concentrations of the solutions.

Apparatus and Procedure.—The apparatus was made by joining two long calibrated test-tubes with a U-tube at their middle points. The tubing was 1 mm. thick and 8 mm. in internal diameter. Into the U was sealed a 4-mm. tube by which connection was made with the ammonia cylinder. Known quantities of solutes were placed in the calibrated tubes, ammonia introduced and the tubes sealed.³ The apparatus, with U-tube inverted, was rocked mechanically until equilibrium was attained. The final volumes of the solutions were then read and the molecular weight of the unknown calculated from the formula, $M_2 = (w_2v_1M_1)/(w_1v_2)$. The symbols M , v and w signify molecular weight, final volume and solute weight, respectively. The subscripts 1 and 2 refer in turn to the standard and unknown substances.

Data and Discussion.—The results obtained are summarized in Table I.

TABLE I
MOLECULAR WEIGHTS IN LIQUID AMMONIA

| Expt. | Unknown | Wt., g. | Volume | | Standard | Wt. | Volume | | Mol. wt. | |
|-------|-------------------|---------|---------|-------|-------------------|-------|---------|-------|----------|--------|
| | | | Initial | Final | | | Initial | Final | Obs. | Calcd. |
| 1 | Resorcinol | 0.495 | 8.67 | 8.52 | Resorcinol | 0.450 | 7.50 | 7.64 | 108 | 110 |
| 2 | Resorcinol | .495 | 10.95 | 8.68 | Resorcinol | .450 | 6.23 | 7.52 | 105 | 110 |
| 3 | Mannitol | .231 | 10.33 | 8.53 | Mannitol | .300 | 9.57 | 11.33 | 186 | 182 |
| 4 | Mannitol | .231 | 6.91 | 8.57 | Mannitol | .300 | 12.91 | 11.33 | 185 | 182 |
| 5 | Valeramide | .386 | 9.20 | 8.55 | Valeramide | .429 | 8.77 | 9.28 | 99 | 101 |
| 6 | Ammonium chloride | .386 | 11.11 | 12.22 | Ammonium chloride | .384 | 14.52 | 13.42 | 59 | 53.5 |
| 7* | Thymol | .125 | 6.48 | 6.18 | Thymol | .141 | 6.34 | 6.62 | 142 | 150 |
| 8* | Thymol | .193 | 8.23 | 5.39 | Resorcinol | .264 | 7.65 | 10.46 | 156 | 150 |
| 9 | Thymol | .268 | 7.79 | 4.85 | Resorcinol | .340 | 4.43 | 7.37 | 132 | 150 |
| 10 | Thymol | .231 | 6.82 | 5.14 | Resorcinol | .209 | 6.40 | 8.09 | 191 | 150 |
| 11 | Diphenylamine | .390 | 8.43 | 5.83 | Resorcinol | .360 | 7.72 | 10.28 | 210 | 169 |
| 12 | Ammonium chloride | .263 | 7.32 | 5.91 | Resorcinol | .500 | 8.05 | 9.40 | 92 | 53.5 |
| 13* | Ammonium chloride | .325 | 8.18 | 9.15 | Resorcinol | .307 | 8.30 | 7.38 | 94 | 53.5 |
| 14 | Valeramide | .457 | 5.63 | 7.73 | Diphenylamine | .468 | 6.40 | 4.35 | 93 | 101 |
| 15 | Thymol | .169 | 8.27 | 8.47 | Diphenylamine | .142 | 7.88 | 7.63 | 181 | 150 |

³ Franklin has described the technique used for handling the liquid ammonia, *J. Phys. Chem.*, 15, 509 (1911).

TABLE I (Concluded)

| Expt. | Unknown | Wt., g. | Volume | | Standard | Wt. | Volume | | Mol. wt. | |
|-------|----------------------------|---------|---------|-------|----------|-------|---------|-------|----------|--------|
| | | | Initial | Final | | | Initial | Final | Obs. | Calcd. |
| 16 | Diphenyl-amine | 0.156 | 8.58 | 7.82 | Mannitol | 0.240 | 8.18 | 8.78 | 133 | 169 |
| 17 | Resorcinol | .353 | 7.44 | 8.48 | Mannitol | .498 | 7.81 | 6.75 | 103 | 110 |
| 18* | Thymol | .148 | 7.81 | 5.54 | Mannitol | .288 | 7.56 | 9.72 | 164 | 150 |
| 19* | Naphthalene | .180 | 6.00 | 6.49 | Mannitol | .177 | 5.54 | 4.90 | 140 | 128 |
| 20* | Sorbitol | .209 | 6.10 | 5.69 | Mannitol | .276 | 6.05 | 6.46 | 157 | 182 |
| 21* | Mannose | .191 | 11.16 | 10.00 | Mannitol | .301 | 11.44 | 12.44 | 144 | 180 |
| 22* | Fructose | .348 | 11.38 | 15.31 | Mannitol | .299 | 10.67 | 6.61 | 92 | 180 |
| 23* | α -Methyl glucoside | .228 | 8.04 | 7.68 | Mannitol | .188 | 7.19 | 7.44 | 214 | 212 |

The data in the table show what accuracy may be expected by the use of this method. Undoubtedly more accurate results can be obtained if the tubes be put in a constant temperature bath, for better results were obtained in a room where the temperature variation was not more than 2° (starred experiments) than in the laboratory where the variations were much greater (unstarred experiments).

That the method is correct in principle is shown by the results recorded in Expts. 1-7. Here the solutions contained the same solute and reached the same molecular concentrations.

A surprising result was discovered in the case of ammonium chloride. Experiments 12 and 13 indicate that this substance exists in the dimolecular form in liquid ammonia.

The low value obtained for fructose (Expt. 22) is probably due to its reaction with the solvent. That such reaction is likely follows directly from Strain's⁴ results obtained with other ketones.

Should a micro method for molecular weight determinations in liquid ammonia be desirable, this method can probably be micrified, because Schwarz¹ has shown that this type of method is adaptable to micro-manipulation.

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DIVISION OF PLANT BIOLOGY
 CARNEGIE INSTITUTION OF WASHINGTON
 STANFORD UNIVERSITY, CALIFORNIA
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HAROLD H. STRAIN
 JAMES H. C. SMITH

⁴ Strain, THIS JOURNAL, 52, 820 (1930); *ibid.*, 52, 1216 (1930).