The method should be applicable to the preparation of other 6-dialkylamino-1-aminohexanes.

Procedure.—Crude ϵ-bromocaproic acid[3] (165 g., 0.85 mole) was heated on a steam-bath for one hour with 100 ml. of thionyl chloride. The excess thionyl chloride was removed under reduced pressure and the residue was added drop by drop to 1 liter of concentrated ammonium hydroxide with vigorous stirring, keeping the temperature below 10°. The solid amide was filtered, washed with ice-water and air dried; yield, 104 g. (64%).

The crude amide was heated on a steam-bath for two hours with 100 ml. of thionyl chloride, a vigorous reaction ensuing. The excess thionyl chloride was removed under reduced pressure and the residue distilled through a 15-cm. Vigreux column. ϵ-Bromocapronitrile was obtained as a pale yellow liquid, b. p. 115–117° at 6 mm., yield, 72.5 g. (76%).

The ϵ-bromocapronitrile (0.41 mole) was stirred and heated under reflux for eighteen hours with 87.5 g. (1.2 moles) of diethylamine. The reaction mixture was cooled, 100 ml. of ether was added and the diethylamine hydrobromide filtered off. The precipitate was washed thoroughly with ether, the combined ether solutions distilled and the residue distilled through a 15-cm. Vigreux column. The ϵ-diethylaminocapronitrile was obtained as a colorless liquid, b. p. 102–102.5° at 4 mm.; yield, 62 g. (90%). The picrate melted at 62–62.5°; a mixed melting point with the picrate of the aminonitrile prepared by another method[2] was the same.

ϵ-Diethylaminocapronitrile was reduced with Raney nickel in the usual manner in 70% yield. The 6-diethylamino-1-aminohexane boiled at 103–105° at 10 mm. and formed a chloraurate salt melting at 118–120° (reported,[2] 120–122°).

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The Partial Specific Volumes of Zein and Gliadin

BY JOSEPH F. FOSTER AND DEXTER FRENCH

In order to evaluate molecular weight and shape from sedimentation and diffusion data it is necessary to know rather accurately the partial specific volume of the solute in the solvent used. In the case of the prolamines the usual solvent is aqueous alcohol, the optimum concentration being about 70% alcohol in the case of zein and somewhat lower in the case of gliadin. To the authors' knowledge no experimental values of the partial specific volumes of any of the prolamines in aqueous alcohol have been reported. This is largely due to the difficulty in making sufficiently accurate measurements of partial specific volumes in mixed volatile solvents. For example, an error of only 0.03% in solvent composition in the case of a measurement on a 1% protein solution in 70% alcohol will cause an error of 1% in the measured partial specific volume. It is very difficult if not impossible to control the alcohol composition to the necessary accuracy in the usual pycnometric method.

Krejci and Svedberg[1] have reported a partial specific volume for gliadin in dilute hydrochloric acid of about 0.72, the value varying somewhat with concentration. In the absence of any experimental value for zein, values anywhere from 0.71 to 0.75 have been assumed by various investigators.

To eliminate these uncertainties the authors have evolved a dilatometric technique which is especially applicable to the prolamines. This technique reduces evaporation errors to a minimum and appears capable of a high degree of reproducibility. The results show that the partial specific volumes of zein and gliadin are far from being the same, as sometimes assumed.

Experimental

Apparatus.—A Pyrex dilatometer was constructed from a bulb of approximately 100 ml. capacity and a capillary of 1 ml. capacity with 0.01-ml. graduations. The top of the capillary was enlarged and fitted with a glass stopper to minimize solvent evaporation. For equilibration the bulb and stem of the dilatometer were immersed in a water-bath at 25.00 ± 0.01°. The capillary stem was calibrated by filling the dilatometer to the lowest mark on the stem, equilibrating at 25° and noting the increase in volume on the addition of weighed amounts of mercury or lead shot.

Materials Examined.—"Standard Zein" is a commercial product[2] containing about 0.4% ash and a small amount of insoluble organic matter. "Washed Zein" is commercial zein which has been washed exhaustively with water at 0°. "Fractionated Zein" is commercial zein from which the most and least soluble components have been removed by alcohol–water fractionation. "Laboratory Zein"[3] was prepared in this Laboratory from white corn at 0°. The gliadin sample had been dialyzed against 70% alcohol and precipitated in acetone, and contained only about 0.2% ash.[4]

Method.—The powdered sample (of known moisture content) is compressed into small rod-shaped pellets which will readily slide down the dilatometer capillary. The dilatometer bulb and lower part of the stem are filled with solvent, equilibrated at 25°, and the meniscus estimated to 0.001 ml. The dilatometer bulb is then cooled[5] to −5°, and a weighed portion of the pellets added. The dilatometer is twirled to facilitate solution of the pellets, allowed to stand with occasional shaking until the pellets are completely dissolved (usually twelve to twenty-four hours), and the solution thoroughly mixed and re-equilibrated at 25°. The increase in volume is read and the volume increment per gram of (anhydrous) protein ($\Delta V/\Delta g$) is calculated as follows:

$$\frac{\Delta V}{\Delta g} = \frac{\Delta v - (\bar{V}_w)(\alpha)(W)}{W(1 - \alpha)}$$

where Δv is the observed increase in volume, $\bar{V}_w$ is the partial specific volume of H_2O in the solvent, W is the weight and α the moisture content of the sample. In general the pellets were added in increments of about 0.7 to 1.0 g. The dependence of the volume increment on the protein concentration was investigated by starting with a protein solution of given concentration rather than the pure solvent. No hysteresis effects after cooling the dilatometer to −5° and warming to 25° have been noted.

Discussion

The experimental results are presented in the table. The increment quotient ($\Delta V/\Delta g$) actually

(1) L. Krejci and T. Svedberg, THIS JOURNAL, 57, 946 (1935).

(2) Supplied by the Corn Products Refining Company, Argo, Illinois.

(3) This preparation was made by C. C. Jensen and C. R. Harmison.

(4) The authors are indebted to Dr. H. B. Vickery of the Connecticut Agricultural Experiment Station for this gliadin sample.

(5) This step serves the double purpose of emptying the capillary by contraction of the solvent and of minimizing evaporation during the addition of the sample.

measured is equal to the partial specific volume (dV/dg) provided these quantities are independent of concentration. This appears to be true, at least in the case of zein. Less precision was obtained with gliadin than with zein, due in part to the greater fragility of the gliadin pellets and possibly in part to the fact that pressing into pellets caused a partial denaturation and insolubilization of gliadin[6] (of the order of a few tenths of one per cent.).

TABLE I

SUMMARY OF RESULTS

Preparation[a]	Initial concn.	Final concn.	$\Delta V/\Delta g$[b]
Standard Zein (commercial zein not further purified)	0.00	0.41	0.770
	.00	.71	.766
	.00	1.15	.773
	1.15	2.21	.772
	2.21	3.20	.773
			Av. = 0.771 ± 0.002
Washed Standard Zein (commercial zein repeatedly washed by suspension in H_2O)	0.00	0.83	0.773
	.83	1.59	.771
	1.59	2.49	.771
			Av. = 0.772 ± 0.001
Fractionated Standard Zein (main component of commercial sample after removal of the most and least soluble material)	0.00	0.50	0.778
	.00	.81	.776
	.81	1.81	.776
	1.81	2.81	.776
			Av. = 0.776 ± 0.001
Fractionated Standard Zein in 52% ethanol ($\bar{V}_w$ = 0.959)	0.00	0.67	0.778
	.67	1.54	.773
			Av. = 0.776 ± 0.003
Laboratory Zein (prepared by low temperature extraction of white corn)	0.00	0.80	0.775
	.80	1.72	.777
			Av. = 0.776 ± 0.001
Gliadin (Connecticut Agricultural Experiment Station preparation)	0.00	0.63	0.723
	.63	1.31	.723
	1.31	2.03	.733
	2.33	3.11	.718
			Av. = 0.724 ± 0.004

[a] The measurements on zein, except in the two cases indicated, were in 73% aqueous alcohol ($\bar{V}_w$ = 0.927). In the case of gliadin the solvent was 62% alcohol ($\bar{V}_w$ = 0.944). [b] The precision of the measurements is indicated in terms of mean deviations.

The differences between the various zein preparations are slight and probably due in large part to inorganic impurities which would be expected to cause a decrease in specific volume by electrostriction. The higher value, 0.776, obtained on the more purified preparations is probably closest to the true value for zein. To the authors' knowledge this is the highest value yet reported for any unconjugated protein (most values range from 0.73 to 0.75) and reflects the unusually high proportion of non-polar amino acids in zein. The results also indicate the partial specific volume of zein to be independent of alcohol concentration over the range 52–73%.

The large difference in partial specific volume between zein and gliadin is not unexpected on the basis of their amino acid compositions. Thus using the corrected molal volumes of the amino acid residues as given by Cohn and Edsall[7] together with the amino acid compositions collected by them, one calculates the values 0.75_2 and 0.70_5 for zein and gliadin, respectively, both of which are lower by 3% than the values found experimentally. This might be interpreted as indicating deficiencies in the present amino acid analyses of these proteins.

The dilatometric technique is most applicable to systems involving organic solvents (a large temperature coefficient of expansion and good drainage qualities are essential). Experiments involving water as solvent have proved quite unsatisfactory.

(6) This denaturing effect of pressing into pellets was also observed in an experiment with serum albumin.

(7) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Chaps. 15 and 16, Reinhold Publishing Corporation, New York, N. Y., 1943.

DEPARTMENT OF PHYSICAL CHEMISTRY
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Preparation of Chloroacetaldehyde Hydrate

BY LEWIS F. HATCH AND HAROLD E. ALEXANDER[1]

Recently a method has been described[2] for the preparation of alkoxyacetaldehydes by the oxidation of the α-alkyl ethers of glycerol using periodic acid as the oxidizing agent. This method for the preparation of substituted acetaldehydes has been extended to the preparation of chloroacetaldehyde hydrate by the oxidation of glycerol α-monochlorohydrin with periodic acid.

Experimental

One-half mole of Eastman Kodak Co., "practical" grade glycerol α-monochlorohydrin was oxidized by 0.50 mole of periodic acid under the same conditions as used for the oxidation of the α-alkyl ethers of glycerol.[2] Eighteen ml. (25.2 g.) of material boiling at 84° (742 mm.) was obtained. Chloroacetaldehyde and its hydrate are both reported[3] to boil at 85–85.5°.

Refluxing two 3-g. samples of the product for three hours with 20% alcoholic potassium hydroxide gave 35.6% saponifiable chlorine. The theoretical chlorine for $CH_2ClCHO \cdot H_2O$ is 36.8%. This would indicate a purity of 97% and a yield of 50%. This yield can be increased to about 60% by redistilling the material boiling between 84–98° obtained after removal of the material boiling at 84°.

The semicarbazone melted at 133–134° (literature 134°[4]) and decomposed in hot aqueous solutions.

(1) At present on active duty with the U. S. N. R.
(2) Hatch and Nesbitt, THIS JOURNAL, 67, 39 (1945).
(3) Natterer, *Monatsh.*, 3, 442 (1882).
(4) Kling, *Compt. rend.*, 148, 568 (1909).

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Derivatives of Ipral, Neonal, Nostal and Sandoptal: an Optical Crystallographic Study

BY MARTIN E. HULTQUIST, CHARLES F. POE AND NORMAN F. WITT

In previous studies, the optical properties of ten substituted benzyl esters of barbital and