$C_{31}H_{48}O_7$: C, 69.89; H, 9.08; CH_3CO, 16.12. Found by Haslewood for hepatol diacetate: C, 71.2; H, 9.2. Found in this work for hepatol diacetate: C, 70.1, 70.2; H, 9.1, 9.2. Found for digitogenin diacetate: CH_3CO, 16.25.

In view of the evidence presented above it is suggested that the hepatols are decomposition products of digitonin. No further work has been done to determine the nature of the second hepatol, which has the properties of a more contaminated digitogenin. There also seems to be room for some doubt whether 7-hydroxycholesterol is a natural constituent of liver, or rather an autoxidation product of cholesterol.

I wish to thank Dr. E. Fernholz for his interest and advice during this investigation.

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Preparation of "Siliconoyl Alcohol"

BY EDMUND L. NIEDZIELSKI

In the course of an investigation it was found necessary to have larger amounts of pure "siliconoyl alcohol" at our disposal. The literature reports only one vague and cumbersome description[1] for its preparation which does not contain either the analysis of the substance in question or data on yields. In order to justify the continued inclusion of this compound in the literature, the following procedure for its successful preparation may be suggested.

As starting material tetraethylsilane[2] was used which was transformed into triethyl-chloroethyl-monosilane according to Friedel and Crafts. Ten grams of the chloro compound was refluxed for three hours with 5 g. of fused potassium acetate and 1.5 g. of acetic acid. The reaction product was poured into excess of water, separated, dried and submitted to fractionation, yielding 3.2 g. of a fraction boiling between 208 and 214° which consisted of triethyl-acetoxyethyl-monosilane (yield 28%). Three and two-tenths grams of triethyl-acetoxyethyl-monosilane was refluxed with 10 cc. of a 22% solution of alcoholic potassium hydroxide. After three hours the product was transferred into excess of water and the isolation procedure given above for the acetate was applied. One and two-tenths grams of siliconoyl alcohol (b. p. 190° (uncor.)) was obtained amounting to a yield of 48%. Calcd. for $C_8H_{20}OSi$: C, 60.00; H, 12.50. Found: C, 58.26; H, 11.72.

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(1) C. Friedel and J. M. Crafts, *Ann.*, **138**, 19 (1866).
(2) S. Sugden and H. Wilkins, *J. Chem. Soc.*, 128 (1931).

Effect of Aging Cottonseed Meal on the Solubility of the Proteins

BY H. S. OLCOTT AND T. D. FONTAINE

A sample of ethyl ether-extracted cottonseed meal[1] was stored in a closed glass container at room temperature (75–92°F.). At three to five week intervals separate portions were extracted with water and 0.5 *N* sodium chloride solution according to the method previously described[2] for determining relative protein solubilities. Over a period of fifteen months, during which the meal, originally light yellow, acquired a brownish cast, there were no significant changes in solubility. The average percentage of the total nitrogen soluble in water was 26.5 ± 0.3; that soluble in 0.5 *N* sodium chloride solution was 79.1 ± 0.4. These findings are in marked contrast to the decrease in solubility described for the proteins of soy bean meal during storage.[3,4]

(1) The meal used contained 9.8% H_2O, 9.15% N (dry basis), and 1.9% residual oil (by chloroform extraction).
(2) H. S. Olcott and T. D. Fontaine, THIS JOURNAL, **61**, 2037 (1939); **62**, 1334 (1940).
(3) D. B. Jones and C. E. F. Gersdorff, *ibid.*, **60**, 723 (1938).
(4) A. K. Smith and S. J. Circle, *Ind. Eng. Chem.*, **30**, 1414 (1938).

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Note on the Heats of Dilution of Amino Acids

BY JULIAN M. STURTEVANT

Doehlemann and Lange[1] have pointed out that appreciable heat effects arising from disturbance of the water equilibrium may be encountered at very low concentrations in the dilution of various types of electrolytes. It is important to note that analogous effects should be encountered with amphoteric electrolytes, particularly amino acids.

An aliphatic amino acid at its isoelectric point in aqueous solution is almost entirely in the form of zwitter ions, $Z^{\pm}$. In the case of glycine, for example, only about 0.04% is present as positive and negative amino acid ions.[2] A solution of a pure amino acid in pure water is in general not isoelectric, though it becomes very nearly so at sufficiently high concentrations. At infinite dilution the solution is necessarily at *p*H 7, so that in the dilution of a concentrated solution,

(1) Doehlemann and Lange, *Z. physik. Chem.*, **170**, 391 (1934).
(2) Edsall and Blanchard [THIS JOURNAL, **55**, 2337 (1933)] have shown that an entirely negligible fraction of the amino acid is in the form NH_2RCOOH.

some of the zwitter ions will be changed to positive and negative ions, and at the same time some water molecules will have to dissociate to maintain the water equilibrium. The heat effects accompanying these ionization processes must be subtracted from the observed heat of dilution to obtain the true heat of dilution of zwitter ions.

Consider the dilution of a solution of one mole of amino acid which is sufficiently concentrated so that the amino acid is practically all in the form of zwitter ions. The dilution process can be

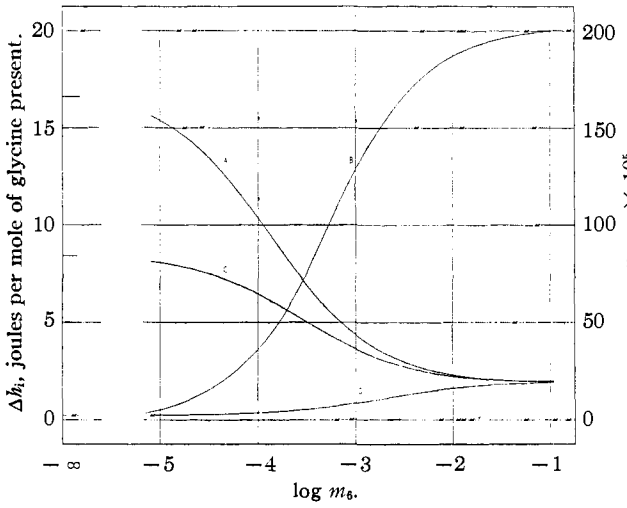

Fig. 1.—Curve A, n_2; curve B, Δh_i; curve C, n_3; curve D, n_1.

broken into the following steps

$$Z^{\pm}(m_i) = Z^{\pm}(m_f); \quad \Delta H_D \qquad (1)$$
$$n_1Z^{\pm} + n_1H^+ = n_1ZH^+; \quad -n_1\Delta H_A \qquad (2)$$
$$n_2Z^{\pm} + n_2OH^- = n_2ZOH^-; \quad -n_2\Delta H_B \qquad (3)$$
$$n_3H_2O = n_3H^+ + n_3OH^-; \quad n_3\Delta H_W \qquad (4)$$
$$\Delta H_{obs.} = \Delta H_D - n_1\Delta H_A - n_2\Delta H_B + n_3\Delta H_W$$

If we make the approximation of setting activities equal to molalities, we obtain the following expressions for n_1, n_2, n_3

$$n_1^2 = \frac{K_W(K_B + m_f)}{K_AK_B(K_A + m_f)}$$
$$n_2^2 = \frac{K_W(K_A + m_f)}{K_AK_B(K_B + m_f)}$$
$$n_3^2m_f^2 = \frac{K_W}{K_AK_B}\left[(K_A + m_f)^{1/2}(K_B + m_f)^{1/2} - K_A^{1/2}K_B^{1/2})\right]^2$$

Here K_A, K_B are the ionization constants[3] for the reverse of reactions (2) and (3), respectively, and K_W is the ionization constant of water. For $m_f = 0$, we have

$$n_1^0 = \frac{K_W^{1/2}}{K_A} \qquad n_2^0 = \frac{K_W^{1/2}}{K_B} \qquad n_3^0 = \frac{1}{2}(n_1^0 + n_2^0)$$

(3) The alternative scheme of ionization in which ZH^+ is considered as a dibasic acid could equally well be used.

With the numerical constants[4] for glycine at 25°, $K_A = 4.47 \times 10^{-3}$, $K_B = 6.04 \times 10^{-5}$, $K_W = 1.01 \times 10^{-14}$, we calculate the values of n_1, n_2, n_3 plotted in Fig. 1, curves D, A and C, respectively.

It is evident that $[\Phi_H - \Phi_H^0]^{\pm}$, the hypothetical relative apparent molal heat content of the amino acid zwitter ion, is given by

$$[\Phi_H - \Phi_H^0]^{\pm} = [\Phi_H - \Phi_H^0]^{obs.} + \Delta h_i$$

where

$$\Delta h_i = (n_1 - n_1^0)\Delta H_A + (n_2 - n_2^0)\Delta H_B - (n_3 - n_3^0)\Delta H_W$$

the assumption being made that the ionization heats are independent of concentration. If we take the values[5] $\Delta H_A = 3891$ joules per mole, $\Delta H_B = 11{,}590$ joules per mole, and the value[6] $\Delta H_W = 56{,}050$ joules per mole, we obtain for glycine at 25° the values of Δh_i shown in curve B, Fig. 1. The total effect for glycine amounts to some 20 joules per mole, of which about 15 joules per mole is accounted for by changes occurring between 10^{-2} and 10^{-4} m.

It would appear to be possible to detect these ionization heat effects in a calorimeter of sufficient sensitivity. However, in the measurements[7] which appear in the literature the effects to be expected are beyond the sensitivity of the apparatus used. It should be noted that the presence of carbon dioxide in the diluting water could mask the ionization effects even in a sensitive apparatus by holding the pH close to 6.1, the isoelectric pH of glycine.

(4) Owen, THIS JOURNAL, **56**, 24 (1934).
(5) Sturtevant, unpublished work.
(6) Lambert and Gillespie, THIS JOURNAL, **53**, 2632 (1931).
(7) Naude, *Z. physik Chem.*, **125**, 219 (1928); Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935); Sturtevant, THIS JOURNAL, **62**, 1879 (1940). See also the recalculation by Borsook and Huffman of the data of Zittle and Schmidt, in Schmidt, "The Chemistry of the Amino Acids and Proteins," Charles C. Thomas Co., 1938, p. 839.

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Changes in Chemical Equilibria in Liquid Interfaces[1]

BY GEORGE J. SZASZ

From the classical thermodynamic work of J. W. Gibbs and J. J. Thomson it is well known that the equilibrium constant in interfaces differs from that of the bulk phase. Many experiments have been undertaken to prove this point. One of the

(1) This Note is the result of work done in the Laboratories of Dr. Ernst A. Hauser, at the Massachusetts Institute of Technology, Cambridge, Mass., in the summer of 1939.