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

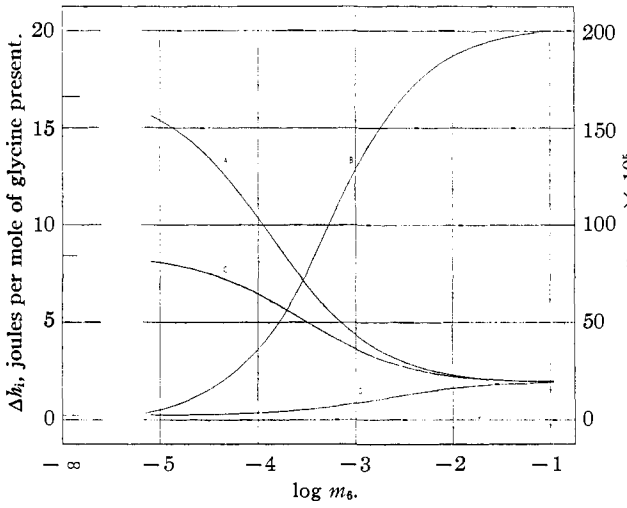

Fig. 1.—Curve A, n_2; curve B, Δh_i; curve C, n_3; curve D, n_1.

broken into the following steps

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

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.

most striking is that referred to by D. Deutsch.[2] He dissolved certain dyes in water and produced a color change by shaking this solution with equal volumes of benzene or another immiscible liquid. Deutsch explained the color change, which is reversible and can be repeated at will, by assuming that the dissociation of the dyestuff molecule changes according to the dielectric constant of the medium, *i. e.*, dissociation increases in a medium of high dielectric constant (water), and decreases in a medium of low dielectric constant (benzene). This theory has been opposed by Thiel,[3] who is of the opinion that this explanation does not hold for the cases of *thymolsulfonephthalein* and *tropaeoline OO*.

The purpose of my experiments was to repeat Deutsch's findings and to offer, if possible, a more general explanation of the phenomenon.

Various concentrations of every dyestuff were tried at a given *p*H, to determine the conditions of most pronounced color change. The following concentrations have been found to be the most effective ones.[4]

Malachite green base (C. I. 657) in 0.4 *N* HCl	0.0025%
Brilliant green base (C. I. 662) in 0.25 *N* HCl	.025–0.01%
Brom thymol blue in tap water	.001–0.0005%
Thymolsulfonephthalein (C. I. 764) in 0.0016 *N* HCl	.01–0.025%
Rhodamine O (C. I. 749) in benzene	.0005%

It should be mentioned here that the color changes do not reach their maximum stability in the first twelve hours, because the dissolution of the dye is not instantaneous. Since the color of the solution becomes increasingly deeper, final observations were made with specimens which had been stored for at least twelve hours. This change is particularly pronounced in the case of *thymolsulfonephthalein*.

It was also found that methyl violet (C. I. 680),[5] which so far has not been reported in connection with these experiments, gives a color change in 0.1 *N* hydrochloric acid. The color changes on shaking from blue to purple. I was unable to reproduce the color change of *tropaeoline OO* (C. I. 143), under the conditions given by Deutsch. However I did obtain a distinct color change in the foam at a *p*H of 2.28.

A general explanation of the entire phenomenon, on basis of the Hardy–Harkins rule of least abrupt change in the interfacial layer, seemed promising. However since the color changes of the sulfonephthaleins did not yield to explanation on this basis, a general explanation is still missing.

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(2) D. Deutsch, *Ber.*, **60**, 1036 (1927); D. Deutsch, *Z. physik. Chem.*, **136** 353 (1928).

(3) Thiel, *Z. Elektrochem.*, **35**, 266 (1929).

(4) Deutsch used in all cases 0.01% solutions.

(5) The *methyl violet* used and reported by Deutsch is actually *crystal violet* (C. I. 681).

4,4′-Diaminodiphenyl Sulfone

BY A. M. VANARENDONK AND E. C. KLEIDERER

4,4′-Diaminodiphenyl sulfone has recently[1] become of interest because of its potency in combatting experimental streptococcic infections in mice.

In our work we have been employing a method which differs from the published procedures.[2,3,4]

Thioaniline in an impure form may be obtained commercially and purified by means of its relatively insoluble disulfate. Subsequent acetylation with acetic anhydride and oxidation with hydrogen peroxide yields the 4,4′-diacetylaminodiphenyl sulfone, which may then be hydrolyzed to produce the free 4,4′-diaminodiphenylsulfone.

Purification of Thioaniline.—300 g. of crude thioaniline is dissolved in a solution of 300 g. of concentrated sulfuric acid in 6 liters of water, boiled for a few minutes and filtered. The filtrate is treated with 50 g. of decolorizing carbon, boiled, filtered, and concentrated without heat under vacuum until cold and filtered. The filtrate is then concentrated under vacuum to about 2 liters, cooled, and filtered. The two lots of precipitate are dissolved in 8 liters of boiling water, treated with Norit and filtered. While the filtrate is still warm, it is made alkaline with ammonia and cooled in the chill room overnight. The purified thioaniline weighs 95–105 g. and melts at 105–107° (uncor.). The product is a light tan in color.

4,4′-Diacetylaminodiphenyl Sulfone.—To 30 g. of thioaniline in a beaker is added a solution of 60 cc. of acetic anhydride in 120 cc. of glacial acetic acid. The solution is boiled gently for one hour on a hot plate, allowed to cool to room temperature, and 500 cc. of glacial acetic acid added; 50 cc. of superoxol is added with stirring, and the solution is allowed to stand without stirring for three hours. The temperature of the solution rises to about 40° during the first hour. At the end of the three hours, it is warmed to 50° and allowed to stand for two hours and then heated to boiling when practically all of the precipitate dissolves. The solution is allowed to cool until ebullition ceases and 30 cc. of superoxol added. The solution is allowed to come

(1) Buttle, Stephenson, Smith, Dewing and Foster, *Lancet*, **I**, 1331–1334 (1937).

(2) Fromm and Wittmann, *Ber.*, **41**, 2264–2273 (1908).

(3) British Patent 510,127.

(4) Sugasawa and Sakurai, *J. Pharm. Soc. Japan*, **60**, 22–24 (1940); *C. A.*, **34**, 3704 (1940).