by the contribution of the third term on the right of equation (2), and this variation from 0 to 0.01 molar amounts to about 0.5%, which is one-tenth of the variation of the thermodynamic term over the above concentration range. The difference between the values in the last columns of the table equals the contribution of the mobility term. In Fig. 1, the dashed curve is the plot of $\mathfrak{D}_M \times 10^5$. The solid curve appears to represent the actual results somewhat better than the dashed curve. However, it would be a mistake to conclude categorically that such evidence confirms the correctness of the mobility term.

Summary

1. The differential diffusion coefficient of potassium nitrate in water at 25° from 0.001 to 0.01 molar has been determined by the conductometric method.

2. The results are in agreement with theory within the experimental error.

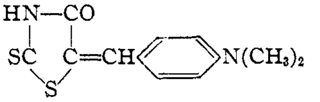
NEW HAVEN, CONN. RECEIVED JULY 5, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Ionization Constants of *p*-Diethylaminobenzylidenerhodanine

BY E. B. SANDELL AND J. J. NEUMAYER

Feigl[1] prepared *p*-dimethylaminobenzylidenerhodanine in 1928 and used it for the detection of silver.



Since that time this compound, or its ethyl analog, has become an important reagent for the photometric determination of gold, silver, mercury and, indirectly, of cyanide. A knowledge of the ionization constants of the compound would be helpful in establishing the most favorable conditions for these procedures. The constants of the ethyl compound are reported in the present work.

Two equilibria have been found to exist in aqueous solutions of *p*-diethylaminobenzylidenerhodanine (HR)

$$\underset{\text{almost colorless (very pale yellow)}}{HR{\cdot}H^+} \rightleftarrows \underset{\text{pink}}{HR} + H^+$$

$$HR \rightleftarrows H^+ + \underset{\text{(yellow)}}{R^-}$$

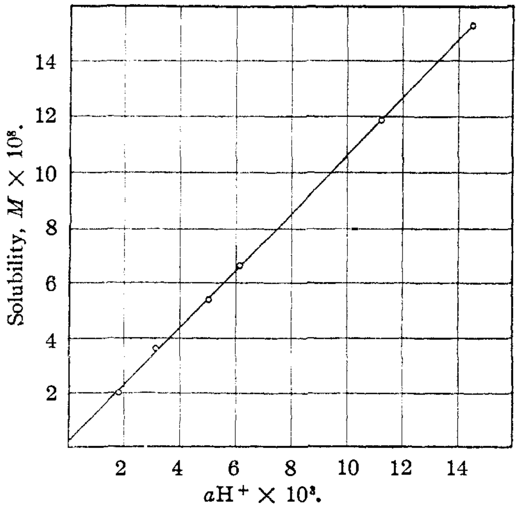


Fig. 1.—Solubility of *p*-diethylaminobenzylidenerhodanine in 20% ethyl alcohol solution on the acidic side of the isoelectric point.

The expressions for the respective ionization constants are

$$aH^+[HR]/[HR{\cdot}H^+] = K_1 \quad (1)$$

$$aH^+[R^-]/[HR] = K_2 \quad (2)$$

The values of these constants have been found by determining the solubility, S, of the substance as a function of the hydrogen-ion activity

$$S = [HR]_s + [HR{\cdot}H^+] + [R^-]$$
$$= [HR]_s + aH^+[HR]_s/K_1 + K_2[HR]_s/aH^+ \quad (3)$$

where $[HR]_s$ is the concentration of the un-ionized form in the saturated solution.

The value of $[HR]_s/K_1$ is given by the slope of the line representing the solubility in the acidic range (Fig. 1), where $[R^-]$ may be considered negligible; the value of $K_2[HR]_s$ is given by the slope of the line representing the solubility in the alkaline range (Fig. 2), where $[HR{\cdot}H^+]$ is negligible. It then remains to determine $[HR]_s$ to obtain K_1 and K_2. Evidently the most favorable acidity for determining $[HR]_s$ from equation (3) is at or near that corresponding to minimum solubility (isoelectric point), where the ionized forms make the smallest contribution to the total solubility. The hydrogen-ion activity at the isoelectric point is given by

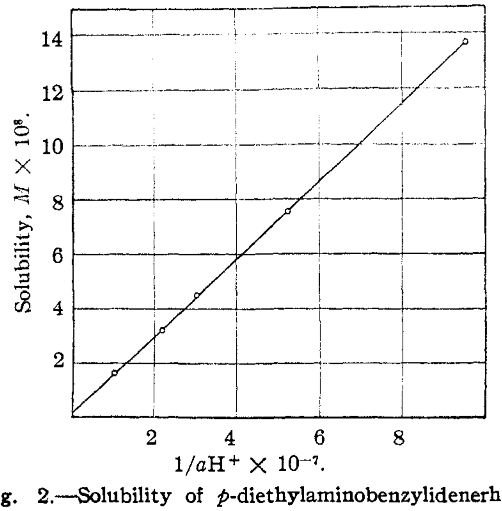


Fig. 2.—Solubility of *p*-diethylaminobenzylidenerhodanine in 20% ethyl alcohol solution on the basic side of the isoelectric point.

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[1] F. Feigl, *Z. anal. Chem.*, **74**, 380 (1928).

$\sqrt{K_1K_2}$ (since $dS/daH^+ = 0$), the value of which is found from the slopes of the two solubility lines (Figs. 1 and 2).

In the absence of a miscible organic solvent, $[HR]_s$ is so small that it cannot readily be determined. Therefore, a dilute ethyl alcohol solution has been used in the present work.

Experimental

All solubility determinations were made at 20 ± 1° in 20% by volume ethyl alcohol solutions, and the ionic strength was maintained constant at 0.05 by addition of sodium chloride. Clark and Lubs buffers were used and the *pa*H was determined, after solubility equilibrium had been attained, by means of a glass electrode.

In many of the experiments solubility equilibrium was approached from over- and under-saturation with identical results. Vigorous mechanical shaking for two hours after an initial 18-hour period of standing was found to be sufficient for attainment of equilibrium.

The total rhodanine concentration of the saturated solution was obtained by taking 5 to 20 ml. of the filtrate, treating with 1 ml. of 2 *N* sodium hydroxide to convert all forms to R^- and determining the transmittancy of the solution at about 470 mμ (filter photometer). The standard curve was established under similar conditions. The yellow solution shows no change in color intensity for at least 10 minutes under the above conditions.

The concentration of rhodanine in the saturated solution at the isoelectric point (*pa*H 4.93) is so small that it is necessary to extract the compound with a small volume of chloroform before the transmittancy can be measured. For this purpose, 100 ml. of the saturated 20% alcoholic solution buffered at *pa*H 4.93 was shaken with four successive 2.5-ml. portions of chloroform. The transmittancy of the combined portions was measured at about 415 mμ (filter photometer) and the concentration was found with the aid of a standard curve established under the same conditions.

Discussion

The limiting factor in the accuracy of determination of K_1 and K_2 is the error in determination of $[HR]_s$. The directly determined value of $[HR]_s$ is 2.1×10^{-7} *M* and this figure may perhaps be considered accurate to 10%. Confirmation of this value is obtained by extending the linear portion of the solubility curves until they cut the solubility axes; the intercepts are equal to $[HR]_s$. The straight lines in the figures were obtained by the method of least squares. The intercepts are, respectively, 2.3×10^{-7} *M* (Fig. 1) and 2.0×10^{-7} *M* (Fig. 2), and the extrapolated values thus agree satisfactorily with the directly determined figure. Calculation then gives $K_1 = 2 \times 10^{-4}$ and $K_2 = 7 \times 10^{-7}$.

The molar extinction coefficient of *p*-diethylaminobenzylidenerhodaninium ion at 370 mμ is 3.6×10^4, that of the anion is 4.1×10^4 at 470 mμ and that of the undissociated form is approximately 1.0×10^5 at 500 mμ, the latter value being calculated with the aid of the equilibrium constants of *p*-diethylaminobenzylidenerhodanine.

The transmission curves are shown in Fig. 3.

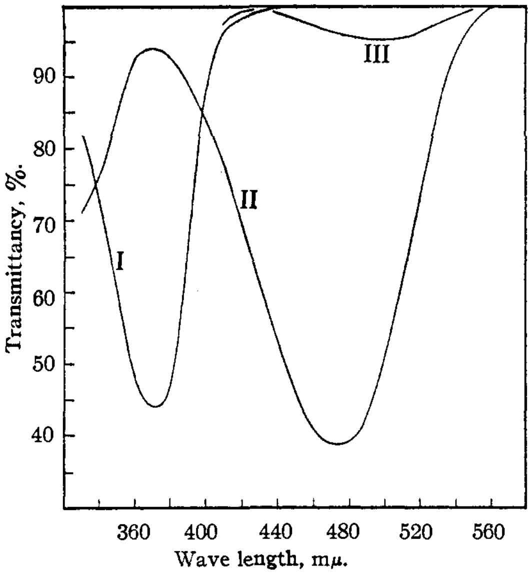

Fig. 3.—Transmission curves of the cationic, anionic and molecular forms of *p*-diethylaminobenzylidenerhodanine in 20% ethyl alcohol solution (obtained with Beckman model B spectrophotometer, 1 cm. cell): I, $HR \cdot H^+$ (10^{-5} *M*, 1 *N* HCl); II, R^- (10^{-5} *M*, 0.02 *N* NaOH); III, HR (1.6×10^{-7} *M* calculated; *p*H 3.1).

Summary

p-Diethylaminobenzylidenerhodanine is an ampholyte, with ionization constants $aH^+[HR]/[HR \cdot H^+] = 2 \times 10^{-4}$ and $aH^+[R^-]/[HR] = 7 \times 10^{-7}$, at 20° in 20% ethyl alcohol and at an ionic strength of 0.05.

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