

TABLE I
DERIVATIVES OF α^1, α^3 -XYLENEDIOL

Substituents	Formula	% Yield, crude	M. p., ^b °C.	Analyses, % ^a			
				Calcd. Carbon	Found	Calcd. Hydrogen	Found
5-Ethyl-4-hydroxy- ^c	C ₁₀ H ₁₄ O ₂	82.4	92.0-92.5	65.92	65.68	7.74	7.69
4-Hydroxy-5-isopropyl- ^c	C ₁₁ H ₁₆ O ₂	89.6	89.6-90.0	67.32	67.36	8.22	8.33
5-s-Butyl-4-hydroxy- ^d	C ₁₂ H ₁₈ O ₂	82.3	79.0-79.3	68.54	68.60	8.63	8.90
5-s-Butyl-2-hydroxy- ^e	C ₁₂ H ₁₈ O ₂	95.4	75.4-76.3	68.54	68.39	8.63	8.93

^a Microanalyses were carried out by Miss L. E. May. ^b Melting points are corrected. ^c Recrystallized once from benzene and once from 1,2-dichloroethane. ^d Recrystallized once from carbon tetrachloride and once from benzene. ^e Reacted for forty-eight hours; recrystallized once from benzene.

quantitative bromination of phenols and phenol alcohols. It is the aim of this note to describe the preparation of these new compounds, and to comment briefly on the reaction employed.

Hydroxymethyl derivatives of phenols are most conveniently prepared by the reaction due to Lederer² and Manasse,³ according to which the phenol is treated with formaldehyde in the presence of an alkaline catalyst, at room or elevated temperature depending upon the strength of the catalyst. Since the reaction may proceed beyond the desired hydroxymethyl stage to produce condensed products such as dihydroxydiphenylmethanes^{4,5,6} and higher polymers, it is not uncommon in preparing a derivative to obtain a crystalline dimer or an oil which cannot be crystallized. The present work indicates that the experimental conditions are more critical than one might infer from the literature, so that the reaction should be carried out under carefully controlled, and hence reproducible, conditions if undesirable condensation is to be avoided. In this way, a procedure which is satisfactory for one phenol may often be successfully applied to a large number of other phenols. Moreover, should analysis indicate that a large yield of dimer has been obtained, the conditions can be accurately modified (the temperature, reaction time or catalyst concentration decreased; the mole ratio of formaldehyde to phenol increased) so that the desired hydroxymethyl derivative is obtained. It has also been found that when an oil is obtained upon acidification of the alkaline solution, it is far better to proceed to crystallize the oil *in situ* by intense refrigeration than to extract the oil with ether and to attempt to crystallize the ether extract. The procedure described below has given good results not only for the new compounds reported, but for other phenol alcohols.

Experimental

General Procedure.—One-quarter of a mole of the phenol was dissolved in 100 g. (0.25 mole) of a 10% aqueous sodium hydroxide solution, and the solution was

(2) L. Lederer, *J. prakt. Chem.*, **50**, 223 (1894); U. S. Patent 563,975 (1896).

(3) O. Manasse, *Ber.*, **27**, 2409 (1894); U. S. Patent 526,786 (1894); *ibid.*, **35**, 3844 (1902).

(4) K. Auwers, *ibid.*, **40**, 2524 (1907).

(5) F. S. Granger, *Ind. Eng. Chem.*, **24**, 442 (1932).

(6) A. Zinke, F. Hanus and E. Ziegler, *J. prakt. Chem.*, **152**, 126 (1939).

cooled to 25-30°. Forty-four and six-tenths grams (0.55 mole) of 37% formaldehyde was added, and the reaction mixture in a stoppered flask was placed in a constant temperature bath at 27° for twenty-four hours. When the solution was acidified with 5 *M* acetic acid, an oil separated out. Upon refrigeration of the mixture (oil plus watery layer) in a Dewar flask containing a freezing mixture of solid carbon dioxide and trichloroethylene, the oil crystallized. The solid mass was filtered off and dried *in vacuo*.

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On the Distribution of Water in Cellulose and Other Materials*

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The distribution of water molecules in cellulose and similar textile materials is of theoretical and industrial importance. However, the mechanism of their interaction is not completely understood. It is a well known fact that the water content of these systems increases in a characteristic way dependent upon the vapor pressure, as shown for the case of cellulose in Fig. 1. This familiar sigmoid curve is characteristic of a large variety of systems: *e. g.*, protein-water,¹ titanium dioxide-water² and sulfuric acid-water.³ These systems differ in structure and chemical properties and it would therefore be surprising if the same mechanism of sorption were operating in each. The question then arises, does the distribution of water in cellulose lead to a system more akin to a solution or is it indeed a system more nearly like the one involved in the adsorption of water by titanium dioxide?

One might speculate that in the limit of low vapor pressure the combination of the polymer with water is more nearly an adsorption phenomenon. Actually the shape of the pertinent curves and the amounts involved correspond to what has been observed in adsorption. In the opposite limit of high vapor pressure the process might be more appropriately considered as a "solution" phenomenon.

* This material formed part of a paper presented at the 113th meeting of the American Chemical Society, held at Chicago, Illinois April, 1948.

(1) H. B. Bull, *THIS JOURNAL*, **66**, 1499 (1944).

(2) G. E. Boyd and H. K. Livingston, *ibid.*, **64**, 2383 (1942).

(3) E. I. Valko, "Cellulose and Cellulose Derivatives," edited by E. Ott, Interscience Publishers Inc., New York, N. Y., 1943.

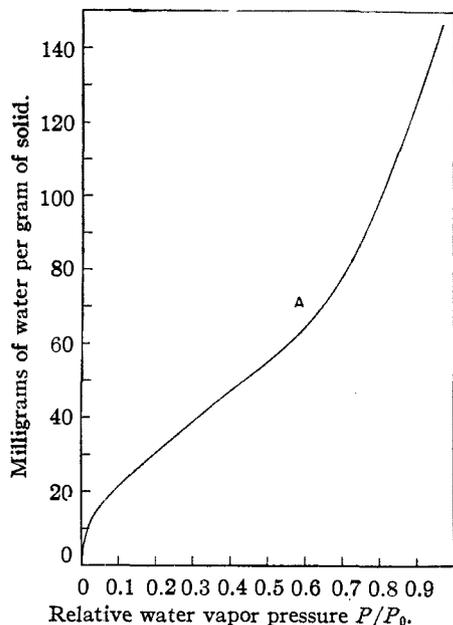


Fig. 1.—Sorption of water vapor by cellulose at 25°.

Such a concept has been advanced⁴ in order to account for the upward curvature at higher pressures (beyond A in Fig. 1).

There is no complete theory at present of the mixing of a partially crystalline polymer such as cellulose with a liquid. Nevertheless it appears of interest to apply current statistical treatments^{5,6,7} of polymer-liquid mixtures to the cellulose-water and similar systems. The results of such an analysis may then be compared with the results obtained from the application of modern adsorption theory⁸ to the same system. In this note such a comparison is made based on experimental data obtained in this laboratory.⁹

Using the notation of references (5) and (6), we may write

$$\ln a_1 \doteq \ln (P/P_0) = \ln v_1 + v_2 + \mu(v_2)^2 \quad (1)$$

where a_1 is the activity, P/P_0 the relative pressure, v_1 the volume fraction of water and v_2 the volume fraction of polymer. A term of the order of the reciprocal of the chain length has been omitted in (1). μ is the well-known semi-empirical interaction parameter appearing in these theories.

The relationship resulting from the Brunauer-Emmett-Teller treatment is

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_0} \quad (2)$$

where V is the volume of water adsorbed, V_m is the fixed volume of water adsorbed when a uni-

(4) P. H. Hermans, "Monographs on the Progress of Research in Holland, Contribution to the Physics of Cellulose Fibers," Appendix I by J. J. Hermans, Elsevier Publishing Co., Inc., Amsterdam, Brussels, 1946.

(5) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(6) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(7) E. A. Guggenheim, *Proc. Roy. Soc. (London)* **183A**, 213 (1944).

(8) Brunauer, Emmett and Teller, *THIS JOURNAL*, **60**, 309 (1938).

(9) J. W. Rowen and R. L. Blaine, *Ind. Eng. Chem.*, **39** (1947).

molecular layer completely covers the surface, and C is a constant which is related to the energy of binding between the gas molecules in the first layer and the absorbent. According to this theory, a plot of $P/V(P_0 - P)$ against P/P_0 should be a straight line with $1/V_m C$ as the intercept and $C - 1/V_m C$ as its slope.

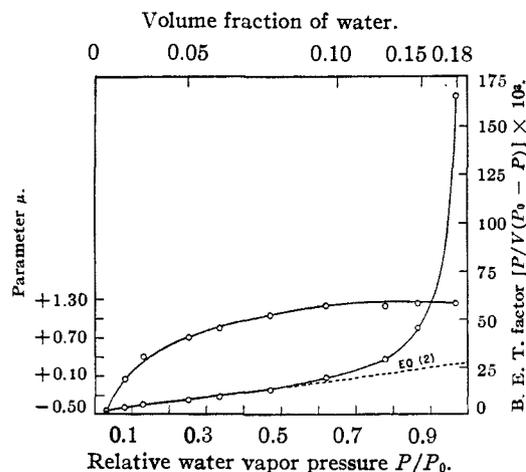


Fig. 2.—Application of equations (1) and (2) to the cellulose-water system. Dotted line indicates plot of equation (2).

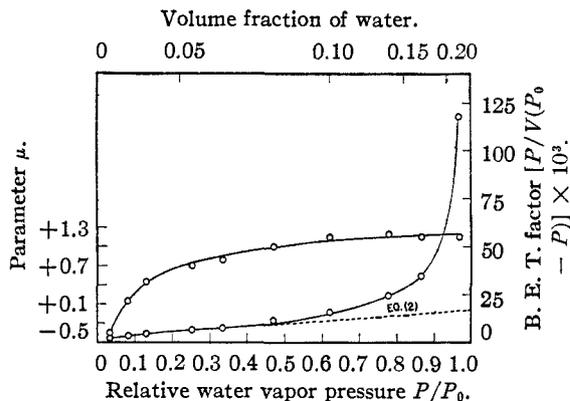


Fig. 3.—Application of equations (1) and (2) to the silk-water system. Dotted line indicates plot of equation (2).

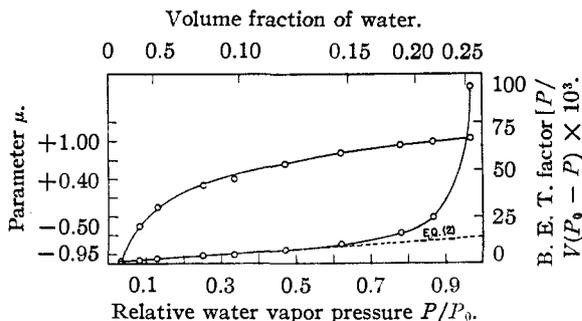


Fig. 4.—Application of equations (1) and (2) to the wool-water system. Dotted line indicates plot of equation (2).

The data⁹ obtained on cellulose, silk and wool-water systems are plotted for comparison in Figs. 2, 3 and 4, according to equation (1) and equation (2), respectively. It is noted that for $P/P_0 < 0.5$, the data follow the straight line relationship called for by equation (2). Thereafter a more rapid increase is observed. The agreement over such a wide range is remarkable although unexpected on the basis of the assumptions underlying the derivation of equation (2). On the other hand it will be seen that the parameter μ starts out with a negative value, increases slowly and then assumes a fairly constant positive value of about 1.0–1.25 for $P/P_0 > 0.6$. In terms of the volume fraction v_1 of water the total range of measurements corresponds to $0.01 < v_1 < 0.26$. In the region of $0.10 < v_1 < 0.26$, equation (1) is obeyed by cellulose and silk. In wool μ varies approximately from 0.93 to 1.05 over the range $0.18 < v_1 < 0.26$. The various energy and entropy contributions to the quantity μ are different at high and low polymer concentrations.¹⁰ These changes can lead to a variation of the "constant" μ . For rubber-benzene mixtures, the only system so far studied over the whole concentration range,^{11,12} no significant change of μ was observed. In any case the deviations from equation (1) obtained by us over a relatively narrow range of volume fractions are too large to be caused by the above-mentioned effect. The limiting values obtainable from these data are $\mu = 1.25, 1.15$, and 1.05 for cellulose, silk and wool, respectively. If the polymer is regarded effectively as a network, allowance must be made for the free energy change accompanying elastic distortion during sorption. The model of a Hookean isotropic medium, subject to a deformation dependent on the concentration, leads merely to a slight reduction in the μ -values reported. These are larger than those usually found by means of solution or swelling measurements for other polymers.^{13,14} Also, an examination of the temperature coefficients of μ leads to negative values of the heat term and reduced entropies which indicate that mixing is not a random process. In view of the nature of the systems considered here this is not surprising.

These results provide some support for the concept mentioned earlier. They suggest that the combination of water with these textile materials in the limit of low vapor pressures can be described in terms of adsorption theory. However, as one approaches the limit of high vapor pressures the system can be analyzed in terms of a theory of polymer-liquid mixtures. In the intermediate region between the two extremes a gradual transition occurs. It will be of interest to study the

- (10) P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).
- (11) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).
- (12) G. Gee and W. J. C. Orr, *ibid.*, **42**, 507 (1946).
- (13) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).
- (14) R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1947).

effect of variation in the nature of the liquid upon the properties of these systems.

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p-Aminosalicylic Acid (4-Amino-2-hydroxybenzoic Acid)

BY JOHN T. SHEEHAN

When *m*-aminophenol and ammonium carbonate react under pressure an acid is obtained which melts at 148°. In the original publication no identification is made beyond that of *m*-aminophenolcarboxylic acid. To determine whether the acid formed is *p*-aminosalicylic acid (4-amino-2-hydroxybenzoic acid) which is of current interest in the chemotherapy of tuberculosis,^{2,3} the preparation was repeated in this Laboratory.

It was found that the acid could be isolated directly from the reaction mixture rather than as the hydrochloride as originally described. It could also be precipitated as the barium salt, from which the acid can be readily obtained in purer form. The identity of the acid was established as *p*-aminosalicylic acid by converting it through the diazonium salt into 4-chlorosalicylic acid and comparing this with a sample of the same compound prepared by reacting 2,4-dichlorobenzoic acid with barium hydroxide. Finally a comparison of antibacterial activity⁴ disclosed no difference between the acid prepared by the present method and another sample of *p*-aminosalicylic acid.⁵

Experimental

***p*-Aminosalicylic Acid.**—A mixture of 150 g. (1.37 moles) of *m*-aminophenol, 600 g. of ammonium carbonate (6.25 moles) and 750 ml. of water was heated in a rocker-type autoclave at 110° for twelve hours. The mixture was filtered and the filtrate concentrated *in vacuo* to a volume of 450 ml. The solution was then acidified to pH 5 and extracted with three 250-ml. portions of ether, from which 75 g. of *m*-aminophenol was recovered. The aqueous solution from the extraction was adjusted to pH 2–3 and the *p*-aminosalicylic acid filtered off and washed with water. The product weighed 47 g. and was crystallized from warm alcohol. Alternatively, it can be purified through the barium salt. A 22% yield of product melting at 146–147°⁶ was obtained. *Anal.* Calcd. for C₇H₇NO₂: C, 54.90; H, 4.57; N, 9.15. Found: C, 55.03; H, 4.91; N, 9.13.

4-Chlorosalicylic Acid.—Fifteen and three-tenths grams (0.1 mole) of the above acid were diazotized and con-

- (1) German Patent 50,835; *Friedlander*, **2**, 139 (1887–90).
- (2) Lehman, *Lancet*, **250**, 15 (1946).
- (3) Youmans, *Quart. Bull. Northwestern Univ. Med. School*, **20**, 420 (1946); *C. A.*, **41**, 1011 (1947).
- (4) The chemotherapeutic investigation was made under the direction of Dr. G. W. Rake in the Division of Microbiology of this Institute.
- (5) Supplied by Calco Chemical Division, American Cyanamid Co., Bound Brook, New Jersey.
- (6) The reported melting point of *p*-aminosalicylic acid is 220° (dec.); Seidel, *Ber.*, **34**, 4351 (1901); Seidel and Bittner, *Monatsh.*, **23**, 415 (1902). Since the acid was prepared by reducing *p*-nitrosalicylic acid with tin and hydrochloric acid it seems likely that the melting point of the hydrochloride, which we found decomposes about this temperature, is recorded despite the fact that the empirical formula and analyses given are for the free acid.