dropwise with stirring, maintaining the temperature at 60–70°. After one hour, the excess sodium hypochlorite was removed by the addition of 14 g. of sodium bisulfite in 60 cc. of water, the mixture cooled and acidified with hydrochloric acid. The precipitated acid was recrystallized from water after charcoal clarification; yield 18 g. (72%), m. p. 78–79.5°, m. p. lit.[7] 76°.

Gentisic Acid.—Fifteen grams of 2,5-dimethoxybenzoic acid was demethylated by refluxing with 25 cc. of 48% hydrobromic acid and 25 cc. of glacial acetic acid for eighteen hours. The gentisic acid was isolated as in Method A; yield 7.5 g. (60%).

Purification of Gentisic Acid.—The gentisic acid, obtained from several demethylation experiments, was combined and sublimed at 1 mm. pressure at a bath temperature of 120–140°. The sublimed product was recrystallized from ether–petroleum ether giving white crystalline gentisic acid melting at 204.5–205°.

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[7] Tiemann and Muller, *Ber.*, **14**, 1993 (1881).

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An Initial Increase in Capillary Rise Shown by Aging Aqueous Solutions of 4-*n*-Hexylresorcinol

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During an investigation of the changes in surface tension which accompany the aging of these solutions, an unexpected increase in capillary rise was sometimes observed at the start of the study. Since no published explanation was found which seemed to account for the phenomenon, a careful study of it was undertaken.

The 4-*n*-hexylresorcinol, m. p. 68.3°, was supplied by the Sharpe and Dohme Company. The redistilled water used in preparing the solutions contained no surface active impurities.

The capillarimeter and cathetometer and the general procedure for locating the large meniscus have been described by Transue.[1] The measurements were made at 25.00°.

Solutions of 0.00025 and 0.00250 molarity were investigated many times with carefully observed and controlled procedures. The results may be summarized as follows. Whenever a certain procedure, which we refer to as the ordinary procedure, was used, the capillary rise was observed to decrease continuously from the start, rapidly at first and then more slowly, until an equilibrium value was reached. For example a 0.0025 *m* solution showed an initial rise of 4.11 cm., after 27 min. 3.98 cm., and after 227 min. 3.67 cm. After 20 hours the capillary rise was 3.17 cm.

In this ordinary procedure the liquid was forced nearly to the top of the capillary, and allowed to drain down, several times before the initial characteristic position was located.

When the procedure was modified either by taking care never to wet the capillary tube more than a very small distance above the characteristic position or by making certain that it was not wet for more than a very short time before taking the first reading, a different behavior was noted on aging. In place of the continuous fall from the start, an initial rise to a maximum was observed. The usual fall then took place. Typical results observed with a 0.00250 molar solution are presented in Table I.

TABLE I

Age, min.	Cap. rise, cm.	Age, min.	Cap. rise, cm.	Age, min.	Cap. rise, cm.
1	4.20	13	4.76	40	4.41
2	4.25	15	4.78	50	4.30
3	4.30	17	4.78	60	4.23
5	4.36	19	4.78	70	4.16
7	4.41	21	4.73	90	4.07
9	4.55	25	4.64	110	3.99
11	4.68	30	4.55	1408	3.11

It seems improbable that ionization of the solute, which has been suggested for what may be a similar case,[2] offers an explanation for this case.

Because of the low volatility of the solute it seems improbable that differences in the rates of its evaporation and diffusion[3] are responsible for the increase in this case.

An important difference in the two procedures of determining the initial characteristic position of the meniscus is that in the ordinary procedure opportunity is given for the glass surface in the vicinity of the characteristic position to become covered or saturated with the surface-active solute before the position is located. In the modified procedure no such opportunity is provided. Adsorption at the liquid–glass interface in the vicinity of the meniscus may remove solute from the liquid–air surface layer more rapidly than it can be replaced by diffusion to and absorption within this layer.

The solution making up this layer of the meniscus thus becomes more dilute and therefore rises in the capillary tube above its initial characteristic position.

However, the adsorption of the solute at the liquid–air interface is continually going on and its effect is to lower the surface tension of this interface. Eventually, this effect plus the action of gravity equals and then predominates over the tendency to increase the surface tension of the liquid–air interface due to adsorption of the solute at the liquid–glass interface. The slowing down of the rate of adsorption at the liquid–glass due to increased distance for diffusion and to a decrease in proportion of active spots available for adsorption makes it possible for the adsorption at the liquid–air interface to equal and then surpass that for the liquid–solid interface. The capillary rise then decreases as the solution ages.

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[1] L. F. Transue, E. R. Washburn and F. H. Kahler, THIS JOURNAL, **64**, 272 (1942).

[2] J. M. Andreas, E. A. Hauser and W. B. Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

[3] E. R. Washburn and C. H. Shildneck, THIS JOURNAL, **55**, 2354 (1933).