with the modification that one activated acetate unit initiates the condensation of seven malonate units to form the anthraquinone in an over-all reaction.


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An Attempt to Evaluate a Proton Activity Function from the 
\( H^* \) Function

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Recently a method was developed for the evaluation of ion activity functions with the aid of the Hammett acidity function, \( H_0 \). It was found by Wyatt \(^1\), that \( H_0 \), i.e. the proton activity function, is a unique function of the water activity in several strong acids. It was now of interest to learn if other acidity functions give analogous results. The most intensively studied function besides \( H_0 \) is \( H_R \) defined by the reaction:

\[
\text{ROH} + H^+ \leftrightarrow \text{R}^+ + H_2O \tag{1}
\]

\[
H_R = -pK_1 - \log \left( \frac{[\text{R}^+][\text{ROH}]}{[\text{ROH}]} \right) = -\log \left( y_{\text{ROH}} y_{\text{R}^+} a_{H^+} + a_{H_2O} \right) \tag{2}
\]

where \( K_1 \) is the thermodynamic equilibrium constant of reaction (1) and \( y_{\text{ROH}} \) and \( y_{\text{R}^+} \) are the activity coefficients of ROH and R\(^+\). ROH is an alcohol of the triphenylecarbinol type and R\(^+\) the corresponding substituted triphenylmethyl cation. For the sake of simplicity of notation we define:

\[
y_{\text{ROH}} y_{\text{R}^+} = \varphi_R \tag{3}
\]

From (2) and (3):

\[
\log \varphi_R \cdot a_{H^+} = -H_R + \log a_{H_2O} \tag{4}
\]

If \( \varphi_R a_{H^+} \) can be used as a measure of the proton activity it should be a unique function of the water activity as found for \( \varphi_0 a_{H^+} \) where \( \varphi_0 \) is defined by:

\[
\varphi_0 = y_B y_{BH^+} \tag{5}
\]

i.e., the ratio of the activity coefficients of the base and acid forms of the indicators used in the evaluation of \( H_0 \). According to definition:

\[
\log \varphi_0 a_{H^+} = -H_0 \tag{6}
\]

(From preceding papers \(^2\), \(^3\), \( \varphi_0 \) has been denoted by \( \varphi \). By calling it \( \varphi_0 \), the relation to \( H_0 \) is indicated in the same manner as with \( \varphi_R \) and \( H_R \). The indicators used in the evaluation of \( H_0 \) are mostly substituted anilines.

\( H_R \) has recently been measured in the systems \( H_2SO_4 - H_2O \), \( HClO_4 - H_2O \) and \( HNO_3 - H_2O \) by Deno and coworkers \(^4\). \(^5\).

![log \( \varphi_R a_{H^+} \) plotted against log \( a_{H_2O} \) for the three systems:](image)

- O \( HClO_4 - H_2O \)
- □ \( H_2SO_4 - H_2O \)
- ● \( HNO_3 - H_2O \)

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Using these data and the water and acid activities discussed in Ref. 1, the function \( q_R a_{H^+} \) has been computed according to (4). In Fig. 1 \( q_R a_{H^+} \) is plotted against \( \log a_{H_2O} \) for the three acids. As seen \( q_R a_{H^+} \) is not a unique function of the water activity. This indicates individual variations in \( q_R \) and therefore \( H_R \) cannot be used for defining a unique proton activity function. However in concentrated sulfuric acid the situation is more hopeful. In Table 1 \( \log q_R a_{H^+} \) obtained by elimination of \( \log a_{H^+} \) from (4) and (6) is given from 10.0 - 18.3 M \( H_2SO_4 \). In the range 13.0 - 18.3 M \( H_2SO_4 \) \( \log q_R a_{H^+} \) is practically constant; the average value is:

\[
\log q_R a_{H^+} = 4.85 \pm 0.07 \tag{7}
\]

This is about the same concentration range where it was found that \( q_0 \) could be regarded as practically constant. In this concentration range the following relation holds between \( H_R \) and \( H_0 \):

\[
H_R = H_0 + \log a_{H_2O} - 4.85 \tag{8}
\]

Any mechanism that correlates with \( H_R \) will also correlate with \( H_0 + \log a_{H_2O} \) in the range 13.0 - 18.3 M \( H_2SO_4 \) and one is as good as the other.

On the other hand for the equilibrium:

\[
HNO_3 + H^+ \rightleftharpoons NO^+ + H_2O \tag{9}
\]

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