

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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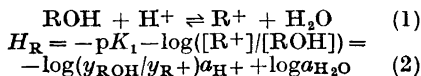
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## An Attempt to Evaluate a Proton Activity Function from the $H_R$ -Function

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Recently a method was developed for the evaluation of ion activity functions with the aid of the Hammett acidity function,  $H_0$ <sup>1</sup>. It was found by Wyatt<sup>2</sup>, 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:



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  $\text{R}^+$ . ROH is an alcohol of the

triphenylcarbinol type and  $\text{R}^+$  the corresponding substituted triphenylmethyl cation. For the sake of simplicity of notation we define:

$$y_{\text{ROH}}/y_{\text{R}^+} = \varphi_R \quad (3)$$

From (2) and (3):

$$\log \varphi_R \cdot a_{\text{H}^+} = -H_R + \log a_{\text{H}_2\text{O}} \quad (4)$$

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

$$\varphi_0 = y_{\text{B}}/y_{\text{BH}^+} \quad (5)$$

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:

$$\log \varphi_0 a_{\text{H}^+} = -H_0 \quad (6)$$

(In preceding papers<sup>1,3</sup>  $\varphi_0$  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  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ ,  $\text{HClO}_4\text{--H}_2\text{O}$  and  $\text{HNO}_3\text{--H}_2\text{O}$  by Deno and coworkers<sup>4,5</sup>.

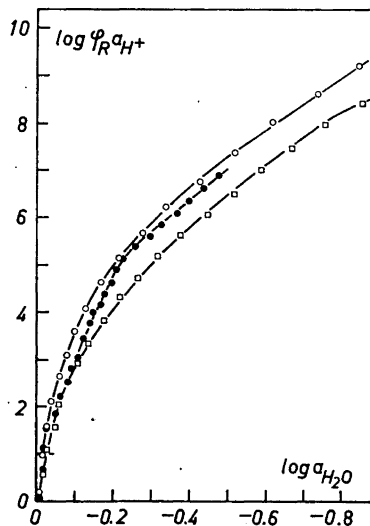


Fig. 1.  $\log \varphi_R a_{\text{H}^+}$  plotted against  $\log a_{\text{H}_2\text{O}}$  for the three systems:

- $\text{HClO}_4\text{--H}_2\text{O}$
- $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$
- $\text{HNO}_3\text{--H}_2\text{O}$

Table 1.  $\log \varphi_R \varphi_0^{-1}$  in the system  $H_2SO_4-H_2O$ .

$[H_2SO_4]$ M	$\log \varphi_R \varphi_0^{-1}$
10.0	3.99
10.5	4.19
11.0	4.35
11.5	4.53
12.0	4.62
12.5	4.70
13.0	4.78
13.5	4.81
14.0	4.85
14.5	4.89
15.0	4.92
15.5	4.92
16.0	4.98
16.5	4.88
17.0	4.85
17.5	4.74
18.0	4.77
18.1	4.78
18.2	4.86
18.3	4.82

Using these data and the water and acid activities discussed in Ref<sup>1</sup>, the function  $\varphi_R a_{H^+}$  has been computed according to (4). In Fig. 1  $\log \varphi_R a_{H^+}$  is plotted against  $\log a_{H_2O}$  for the three acids. As seen  $\varphi_R a_{H^+}$  is not a unique function of the water activity. This indicates individual variations in  $\varphi_R$  and therefore  $H_R$  cannot be used for defining a unique proton activity function. However in concentrated sulfuric acid the situation is more hopeful<sup>6</sup>. In Table 1  $\log \varphi_R \varphi_0^{-1}$  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  $H_2SO_4$   $\log \varphi_R \varphi_0^{-1}$  is practically constant; the average value is:

$$\log \varphi_R \varphi_0^{-1} = 4.85 \pm 0.07 \quad (7)$$

This is about the same concentration range where it was found that  $\varphi_0$  could be regarded as practically constant<sup>1</sup>. In this concentration range the following relation holds between  $H_R$  and  $H_0$ :

$$H_R = H_0 + \log a_{H_2O} - 4.85 \quad (8)$$

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:



$H_R$  is found to correlate better than  $H_0 + \log a_{H_2O}$  in concentrated perchloric acid solutions<sup>5</sup>. This is reasonable in view of the possibility that the activity coefficient ratio  $\gamma_{HNO_2} \gamma_{NO^+}^{-1}$  may be subject to the same individual variations as  $\varphi_R$ .

The present state of our knowledge of these systems allows us only to guess the reason for the different behavior of  $\varphi_R$  in the three acids. The measurements by Cigén<sup>7-9</sup> on the proton equilibria of various triphenylmethane dyes show that reaction (1) is only one of several possible reactions. It has been found to hold in concentrated sulfuric acid for the  $H_R$  indicators but in dilute aqueous solutions some of the other reactions found by Cigén might interfere.

Recently Deno *et al.*<sup>10</sup> have proposed that  $H_R'$  defined by

$$H_R' = H_R - \log a_{H_2O} = -\log \varphi_R a_{H^+} \quad (10)$$

is a better measure of the proton activity than  $H_0$ , because the large triphenyl cations are likely to be practically unhydrated and behave more ideally than the substituted anilines used in the evaluation of  $H_0$ . The finding in this paper does not support such a view.

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