

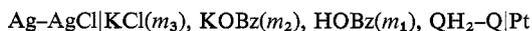
**Studies on the Application of the
Quinhydrone Electrode in Formamide. VI*
The Ionization Constant of Benzoic Acid and
Standard Potential of the Mercury-Mercurous
Benzoate Electrode from E.M.F. Measurements at 25°**

Upendra Nath Dash

Department of Chemistry, G. M. College,
Sambalpur (Orissa), India.

Abstract

The cells



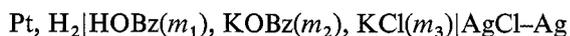
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have been used to redetermine the ionization constant of benzoic acid in formamide and the standard potential of the $\text{Hg-Hg}_2(\text{OBz})_2$ electrode in formamide at 25°. The ionization constant of benzoic acid is found to be 4.79×10^{-7} and is in good agreement with the value 4.37×10^{-7} obtained earlier. The value 0.2535 ± 0.0005 V for the standard potential of the $\text{Hg-Hg}_2(\text{OBz})_2$ electrode is in good agreement with the values 0.2541 ± 0.0003 and 0.2545 ± 0.0005 V obtained previously from two independent cells.

Introduction

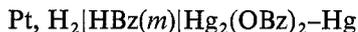
In previous communications^{1,2} we reported the ionization constant of benzoic acid from the e.m.f. measurements of the buffered cell



and the standard potential of the mercury-mercurous benzoate electrode from the study of the cells



and



at 25° in formamide.

It has been shown in the previous studies³⁻⁷ that quinhydrone behaves as a satisfactory electrode system in this solvent and can be used as a substitute for the

* Part V, *Aust. J. Chem.*, 1975, 28, 1649.

¹ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1972, 25, 941.

² Dash, U. N., *Electrochim. Acta*, 1975, 20, in press.

³ Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, 26, 111.

⁴ Nayak, B., and Dash, U. N., *Aust. J. Chem.*, 1973, 26, 115.

⁵ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, 28, 793.

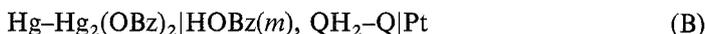
⁶ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, 28, 797.

⁷ Dash, U. N., and Nayak, B., *Aust. J. Chem.*, 1975, 28, 1649.

hydrogen electrode. In the present work, the quinhydrone electrode has been used for the redetermination of the ionization constant of benzoic acid and of the standard potential of the mercury-mercurous benzoate electrode, in formamide at 25°, with a view to having independent checks on the previous data, and accordingly the cells studied are



and



Experimental

The preparation of the electrodes has been described earlier.^{2,3} The cell vessel for the cell (A) was of the type recommended by Harned and Wright⁸ and for cell (B) the design of Nayak and Sahu⁹ was adopted.

The purification of materials needed for the e.m.f. measurements and preparation of various solutions was done as described in our earlier articles.^{1-3,10} E.m.f. measurements were made as described in previous studies.

After careful washing and drying, the cells were filled as follows. Saturated solutions of quinhydrone-formamide-HOBz-potassium salts and of quinhydrone-formamide-HOBz were prepared by shaking formamide-HOBz-potassium salts solution or formamide-HOBz solution with quinhydrone in a well stoppered bottle for a few minutes at 0° and were then transferred to the quinhydrone compartments in which the platinized platinum electrode was previously placed under dry nitrogen. In the case of cell (A), the Ag-AgCl electrode was placed in the appropriate cell compartment after filling of the compartment with HOBz-potassium salts-formamide solution and after thorough rinsing with the solution. In the case of the benzoate electrode, the electrode was prepared in the cell compartment before HOBz-formamide solution was added. After filling, the cells were kept in a thermostat maintained at 25°. Purified, deoxygenated and dried nitrogen was bubbled through for a few minutes. All outlets from the cells were fitted with CaCl₂ guard tubes during the passage of the gas.

The e.m.f. of the cells (A) and (B) were found to decrease slowly with time,^{3,9} with a varying rate, possibly due to the slow thermal decomposition of the solvent. The e.m.f. of both the cells (A) and (B) were consequently measured at intervals of 0.5 h up to 4-5 h and then the values obtained were extrapolated to zero time to yield the true e.m.f. of the cell corresponding to zero decomposition of the solvent.^{2,9,11,12}

Results and Discussion

As usual, values of K'_a were calculated with the help of equation (1), and the ionization constant of benzoic acid K_a was found by the method^{1,3,4} of extrapolating the auxiliary function K'_a given by^{1,3}

$$\begin{aligned} -\log K'_a &= [E - E^0(\text{Ag-AgCl}) + E^0(\text{QH}_2\text{-Q})]F/2 \cdot 303RT + \log(m_1 m_3 / m_2) \\ &= -\log K_a - \log[\gamma(\text{Cl}^-) \cdot \gamma(\text{HOBz}) / \gamma(\text{OBz}^-)] \end{aligned} \quad (1)$$

to $\mu = 0$, as $\log[\gamma(\text{Cl}^-) \cdot \gamma(\text{HOBz}) / \gamma(\text{OBz}^-)]$ tends to zero, the symbols having their usual significance. The values of $E^0(\text{Ag-AgCl})$ and $E^0(\text{QH}_2\text{-Q})$ at 25° needed for the calculations were obtained from the literature.^{9,12}

⁸ Harned, H. S., and Wright, D. D., *J. Amer. Chem. Soc.*, 1933, **55**, 4849.

⁹ Nayak, B., and Sahu, D. K., *Electrochim. Acta*, 1973, **18**, 271.

¹⁰ Dash, U. N., and Nayak, B., *Indian J. Chem.*, 1970, **8**(7), 659.

¹¹ Nayak, B., and Dash, U. N., *J. Electroanal. Chem.*, 1973, **41**, 323.

¹² Agarwal, R. K., and Nayak, B., *J. Phys. Chem.*, 1966, **70**, 2568.

The pK_a value at 25° is found to be 6.32 ± 0.02 and is in good agreement with the value 6.36 ± 0.01 reported earlier.¹

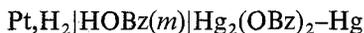
For the cell (B), the e.m.f. E is given by the expression^{13,14}

$$E = E^0 - 2.3026(RT/F) \log[K_a m(1-\alpha)\gamma_u] \quad (2)$$

where K_a is the thermodynamic ionization constant (expressed on the molality scale) of benzoic acid; γ_u , the activity coefficient of the undissociated acid, is taken as unity; and α , the degree of ionization, is considered equal to $(K_a/m)^{1/2}$.

From the K_a value obtained in the present study, the values of E^0 were determined from equation (2) for every molality. These values, as expected, did not remain constant with change of molality and have been tabulated as E' . The true E_m^0 value was obtained¹¹ by plotting the E' values against the ionic strength, μ (here, $\mu = m\alpha$) and extrapolating to zero ionic strength. Extrapolation of the E' values to zero ionic strength by the method of least squares gives 0.2535 ± 0.0005 V for the E_m^0 of the Hg-Hg₂(OBz)₂ electrode in formamide. The straight line of best fit has a slope of 1.36×10^2 V mol⁻¹ kg.

The standard potential of the Hg-Hg₂(OBz)₂ electrode obtained in the present work compares well with the values, 0.2541 ± 0.0003 and 0.2545 ± 0.0005 V, respectively, obtained earlier² from the study of the cells



and



These results suggest that the Hg-Hg₂(OBz)₂ electrode behaves as a satisfactory electrode system in formamide.

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¹³ Larson, W. D., *J. Phys. Chem.*, 1963, **67**, 937.

¹⁴ Larson, W. D., and MacDougall, F. H., *J. Phys. Chem.*, 1937, **41**, 493.