First and Second Dissociation Constants of Deuterio-o-Phthalic Acid in D₂O from 5 to 50 °C

Yung Chi Wu and William F. Koch

Received September 19, 1985; Revised January 8, 1986

The first and second dissociation constants of deuterio-o-phthalic acid in deuterium oxide have been determined by the emf method over the temperature range of 5 to 50 °C. The pD values for potassium deuterium phthalate have been calculated from these two constants and experimentally verified. The thermodynamic properties for the dissociation of deuterio-o-phthalic acid have been evaluated. At 25 °C, these values in the molality scale are: \( pK_{1A} = 3.505, pK_{2A} = 5.890, \) and \( pD = 4.518. \) From \( K_{1A} \) and \( K_{2A}, \) respectively: \( \Delta G^0 = 20.003, 33.582 \text{ kJ-mol}^{-1}; \) \( \Delta H^0 = 2.851, 2.208 \text{ kJ-mol}^{-1}; \) \( \Delta S^0 = -76.7, -105.2 \text{ J-mol}^{-1} \cdot \text{K}^{-1}; \) and \( \Delta C_P^0 = -52.7, -315.6 \text{ J-mol}^{-1} \cdot \text{K}^{-1}. \) The isotope effect is discussed.

KEY WORDS: Activity coefficients; deuterio-o-phthalic acid; deuterium oxide; dissociation constants; electrochemical; emf; isotope; potassium hydrogen phthalate.

1. INTRODUCTION

Potassium hydrogen phthalate (KHph) has been internationally adopted as a pH standard in H₂O because it is a single salt, easy to purify, and neither hydroscopic nor deliquescent. For the same reasons, it is suitable as a pD standard for use in D₂O as the solvent.

In order to establish an accurate pD standard for KDph by the emf method, the following galvanic cell without liquid junction is used.

\[
Pd, D_2(g, 1 \text{ atm}) | KDph(m_1), KCl(m_2) | AgCl, Ag
\]  

where palladium black is used for the deuterium electrode to avoid the catalytic action by platinum black, and \( m \) is the molality in mol·kg⁻¹.

1Center for Analytical Chemistry, National Bureau of Standards, Gaithersburg, MD 20899.
The evaluation of pD is similar to that of pH.\textsuperscript{(2,3)} It requires a knowledge of the standard potential $E^\circ$ of the cell

$$\text{Pd, } D_2(g, 1 \text{ atm}) | DCl(m) | AgCl, Ag$$

(II)

and of the ionic strength of the cell solution in order to evaluate the activity coefficient of the ionic species involved. The $E^\circ$ of cell (II) has been reported previously,\textsuperscript{(4)} but the concentrations of the ionic species, $Dph^-$ and $ph^{2-}$, remain to be evaluated so that the total ionic strength can be calculated. The ionic equilibria for the solution in Cell I are related to two dissociation constants

$$Dph^- = D^+ + ph^{2-} \quad (1)$$

and

$$D_2ph = D^+ + Dph^- \quad (2)$$

where $\gamma_i$ is the ionic activity coefficient (the charges, + and -, for the ionic species in the subscript are dropped for convenience).

To calculate the ionic concentration of $Dph^-$ and $ph^{2-}$, it is necessary to determine these two constants experimentally. The following cell is employed to determine $K_{1A}$

$$\text{Pd, } D_2(g, 1 \text{ atm}) | D_2ph(m_1), K\text{Dph}(m_2), K\text{Cl}(m_3) | AgCl, Ag$$

(III)

$K_{2A}$ is determined using the knowledge gained from Cell III combined with the results from Cell I, as explained below.

2. EXPERIMENTAL

2.1. Materials

Standard Reference Material potassium hydrogen phthalate, KHph, (SRM 185f) was dried at 110°C for 24 h before use. The phthalic acid was prepared by adding 1\textit{m} HCl to a saturated KHph solution. The precipitate and the solution were cooled to 4°C for 16 h, filtered, and redissolved in boiling distilled water. The recrystallization process was repeated three times. The final filtered precipitate was in the form of fine white crystals, $H_2ph$. The filtered solution was tested