

## Initial Thermoelectric Powers of the Quinhydrone-Electrode in Ethanol-Water and Acetonitrile-Water Mixtures

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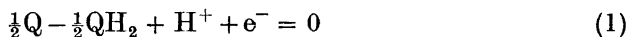
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Initial thermoelectric powers of the quinhydrone-electrode were measured in solvent mixtures of ethanol-water and acetonitrile-water. Two different acids, 0.1 M HCl and 0.1 M HClO<sub>4</sub>, were used as electrolytes. The results show the great influence of the solvent on the initial thermoelectric power. In the acetonitrile-water system the initial thermoelectric power even changes its sign at about 65 wt. % of acetonitrile.

The measurement of the thermoelectric power ( $\epsilon_0$ ) in an electrolytic thermocell when the Soret effect is hindered is relatively simple and has been carried out for a number of systems. The quinhydrone-electrode has been used by several authors with aqueous solutions of strong acids.<sup>1-5</sup> Measurements in nonaqueous solvents, however, have only been carried out in a few systems. Haase and Jansen<sup>6</sup> have used the silver-silverhalide electrode in pure methanol and *N*-methylformamid, Lin and de Haven<sup>7</sup> have used the hydrogen electrode in ethanol-water mixtures, and Lin<sup>5</sup> has used the quinhydrone-electrode in ethanol-water mixtures.

Studies of the solvent effects on the thermoelectric properties of thermocells may reveal interesting information concerning the structure of the solvent system and the mechanism of hydrogen ion transfer across a temperature-gradient. Lin<sup>5</sup> has suggested that thermoelectric studies on electrolytes in the mixed solvent system should be useful in elucidating such phenomena as ion-ion, ion-solvent, and solvent-solvent interaction. In this connection the initial thermoelectric power was measured using the quinhydrone-electrode with the strong acids HCl and HClO<sub>4</sub> in ethanol-water and acetonitrile-water mixtures.

The quinone-hydroquinone (Q-QH<sub>2</sub>) system has been considered as the classical organic reversible redox reaction:

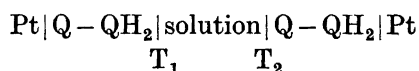


The general equation for the initial thermoelectric power for an electrolytic thermocell containing two kinds of charged particles is given by Holtan.<sup>8</sup>

$$F \varepsilon_0 = -\frac{t_-}{z} S_a^* - \frac{t_+}{z^+} S_c^* - S_{e1}^* - \Delta S + \frac{t_+}{z^+} S_c + \frac{t_-}{z} S_a + \Delta N S_{\text{solv}} + S_{e1} \quad (2)$$

where  $F$  is the Faraday,  $\varepsilon_0$  the initial thermoelectric power,  $t$  the ionic transport number,  $z$  the charge,  $S_a^*$  and  $S_c^*$  are the entropy of transport of the solvated anion and cation, respectively,  $S_{e1}^*$  and  $S_{e1}$  the entropy of transport and the molar entropy for the electron,  $S_c$  and  $S_a$  the partial molar entropy of the cation and anion,  $\Delta S$  is the entropy change for the electrode reaction,  $\Delta N$  the number of moles of solvent carried from anode to cathode compartment when one Faraday of electricity has passed through the solution, and  $S_{\text{solv}}$  is the partial molar entropy of the solvent.

For the thermocell



the solution being a mixture of ethanol-water or acetonitrile-water containing 0.1 m HCl or 0.1 M HClO<sub>4</sub>, the initial thermoelectric power is given, using eqn. (2), as:

$$F \varepsilon_0 = \frac{1}{2} (S_{\text{QH}_2} - S_{\text{Q}}) - t_{\text{A}} S_{\text{HA}} - S_{e1}^* - t_{\text{H}^+} S_{\text{H}^+}^* + t_{\text{Cl}^-} S_{\text{Cl}^-}^* + \Delta N_{\text{H}_2\text{O}} S_{\text{H}_2\text{O}} + \Delta N_2 S_2 \quad (3)$$

the number 2 referring to the nonaqueous solvent.

Expressions similar to (2) are given by Haase,<sup>9</sup> Agar<sup>10</sup> and Tyrell.<sup>11</sup> Haase<sup>9</sup> has discussed transport numbers and found that using water as frame of reference, the term containing transport of solvent falls out.

## EXPERIMENTAL

The cell used for measuring the initial thermoelectric power in this work is earlier described by Tyrell and Hollis<sup>12</sup> and Haase and Schönert.<sup>13</sup>

The reagents used were Merck preparations of *p.a.* quality, distilled water and commercial, redistilled ethanol.

The electrodes consisted of a platinum net dipping into the solution containing 3 g of quinhydrone per liter. This gives an unsaturated solution in water at 298 K and in the solvent mixtures. According to Breck,<sup>3</sup> solutions unsaturated with respect to quinhydrone are the most desirable. The solutions were made by mixing proper amounts of the concentrated acids (HCl and HClO<sub>4</sub>) with distilled water and acetonitrile or ethanol.

Oxygen was removed by bubbling pure nitrogen through the solution. The quinhydrone was washed with the acidic solution before its addition to the cell.

After filling the cell with the solution there was always a small isothermal emf due to some slight difference in the solutions or electrodes. If the isothermal emf was greater than 50  $\mu\text{V}$  the solution was replaced by a new solution with an isothermal emf lower than 50  $\mu\text{V}$ .

Measurements of emf were made using a potentiometer with a sensitive galvanometer of high resistance. The mean temperature was 298 K and the temperature difference was 10 K.

## RESULTS AND DISCUSSION

The cell emf is considered positive when the hot electrode is positive.

*Ethanol-water mixtures.* The measured initial thermoelectric powers  $\varepsilon_0$  are given in Fig. 1.  $\varepsilon_0$  is plotted against the weight percent of ethanol. The results are compared with the results previously obtained<sup>5</sup> in 0.01 N HCl.

It has been reported<sup>14</sup> that hydrochloric acid has a tendency to chlorinate quinone and give less reproducible results. In nonaqueous solvents the chlorination should be more prominent. In the present study, however, we have found that the electrode systems are quite stable and that reproducible results are obtained. This has also been noticed by several authors.<sup>5,15</sup>

The entropy of mixing in the water-ethanol system given by Franks and Ives<sup>16</sup> shows a minimum value at about 20 wt. % of ethanol. Lin<sup>5</sup> has compared his results with the entropy of mixing and found a maximum value for the transport number  $t_{H^+}$  at about 20 wt. %. The initial thermoelectric power shows no minimum at 20 wt. % but at about 40 wt. %. Other factors than mixing effects must therefore be considered.

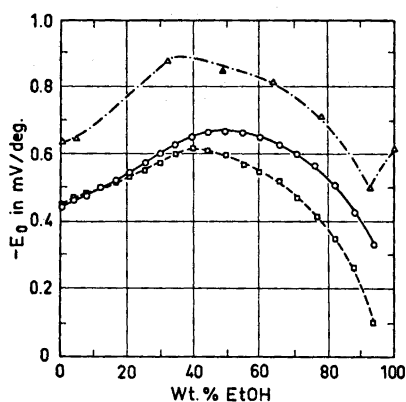


Fig. 1. Initial thermoelectric powers of the quinhydrone-electrode in the ethanol-water system.  $\circ$ , 0.1 M HCl.  $\square$ , 0.1 M  $\text{HClO}_4$ .  $\triangle$ , 0.01 M HCl taken from Ref. 5.

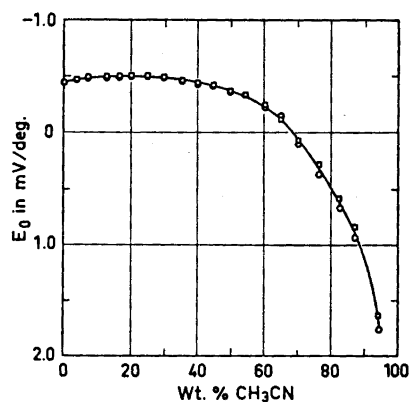


Fig. 2. Initial thermoelectric powers of the quinhydrone-electrode in the acetonitrile-water system.  $\circ$ , 0.01 M HCl.  $\square$ , 0.1 M  $\text{HClO}_4$ .

Wear *et al.*<sup>17</sup> have measured the number of grams of solvent transported from the anode to the cathode compartment per Faraday in the ethanol-water system with 0.2 N HCl, using the method first described by Buchböck.<sup>18</sup> The results are unfortunately not of high accuracy but they found that larger increasing amounts of solvent were transported with increasing concentration of ethanol.

*Acetonitrile-water mixtures.* This system is more complicated than the ethanol-water system. Polarographic investigations of the quinhydrone-electrode<sup>19-20</sup> in pure acetonitrile have showed that the electrode is not reversible. A small addition of water, however, arises the reversibility.<sup>20</sup>

It was therefore surprising to see how reproducible the results were. The measured thermoelectric powers are given in Fig. 2.  $\epsilon_0$  is plotted against wt. % of acetonitrile. The continuous curve is very interesting showing that the initial thermoelectric power changed the sign at about 65 wt. % of acetonitrile.

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