

Initial Thermoelectric Powers of the Silver-Silver Ion Electrode in Acetonitrile-Water and Ethanol-Water Mixtures

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Initial thermoelectric powers of the silver-silver nitrate couple were measured in solvent mixtures of acetonitrile-water and ethanol-water at different concentrations of silver nitrate. It was found that the solvent composition has a great influence on the initial thermoelectric power. In the acetonitrile-water system the sign is changed from negative in water to positive in acetonitrile. Small additions of acetonitrile to water increases the initial thermoelectric power markedly before the curve is flattening out towards acetonitrile, indicating the strong interactions between the silver ion and acetonitrile.

In the ethanol-water system the initial thermoelectric power reaches its minimum at about 20 wt. % of ethanol. This confirms the fact that the solvent system reaches its maximum structure ordering at this composition.

In a previous paper¹ results from measurements of initial thermoelectric powers (ε_0) in ethanol-water and acetonitrile-water mixtures were presented using the quinhydrone (Q-QH₂) electrode. The electrolytes were HCl and HClO₄ and it was found that ε_0 got more positive in the solutions rich in acetonitrile. At about 65 wt. % of acetonitrile it even changed its sign from negative to positive. The quinhydrone electrode, however, is not quite satisfactory in the solutions with high contents of acetonitrile. We now report the results of some work done with the silver-silver nitrate electrode in acetonitrile-water and ethanol-water mixtures.

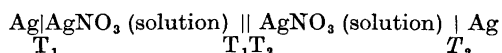
ε_0 measurements may reveal interesting information concerning the structure of the solution and the transport properties of solvated ions in a temperature gradient. Work on initial thermoelectric powers in nonaqueous solutions have only been carried out in a few systems.¹⁻⁴

Measurements of ε_0 requires a stable and reversible electrode. In nonaqueous solvents many of the usual reference electrodes in water are not satisfactory. Butler⁵ has recently reviewed works reported on reference electrodes in aprotic solvents, but still much work has to be done in finding suitable electrodes in

nonaqueous solvents. The silver-silver ion couple is stable and reversible in acetonitrile. This has been confirmed by potentiometric technique by several authors.⁶⁻⁹ Measurements of ε_0 with this electrode are not reported in nonaqueous solvents, but in aqueous solutions the method has been applied by several authors.¹⁰⁻¹⁵

The general equation for the initial thermoelectric power of an electrolytic thermocell is developed by Holtan¹⁶ on the basis of the thermodynamics of irreversible processes by applying Onsagers reciprocal relations.

For the thermocell



the solvent being a mixture of acetonitrile-water or ethanol-water, ε_0 is given as

$$F \varepsilon_0 = t_{\text{NO}_3^-} S_{\text{NO}_3^-}^* - t_{\text{Ag}^+} S_{\text{Ag}^+}^* - S_{e1}^* + S_{\text{Ag}} - t_{\text{NO}_3^-} S_{\text{AgNO}_3^-} + \Delta N_{\text{H}_2\text{O}} S_{\text{H}_2\text{O}} + \Delta N_2 S_2 \quad (1)$$

where

F = the Faraday;

ε_0 = the initial thermoelectric power;

t = the true ionic transport number;

S^* = the transported entropies of the solvated ions and the electrons, respectively;

S = the partial molar entropy;

ΔN = the number of moles of solvent transported from the anode to the cathode compartment, when on Faraday of electricity has passed through the solution

The number 2 is referring to the nonaqueous solvent.

Expressions similar to the general equation of Holtan are given by Haase,¹⁷ Agar,¹⁸ and Tyrell.¹⁹ The advantage of Holtan's equation is that the thermo-static part (the part that does not contain any transported entropies) of the equations will not contain any ionic entropies, but only partial molar entropies of the neutral components. These can in principle be measured separately. Holtan has also taken into account the solvent transport due to the fact that the solvation shell round the ions will be transported in an electric field. By using the Hittorf reference system the terms containing transport of solvent fall out, according to Haase.¹⁷ Some questions can, however, be put forward using the Hittorf reference system in a system with a temperature gradient. These questions will be discussed in a later paper.

EXPERIMENTAL

The cell used for measuring the initial thermoelectric power in this work is the same as in the previous paper.¹ It is earlier described by Tyrell and Hollis¹⁹ and Haase and Schönert.²⁰

The reagents were of Merck preparations of *p.a.* quality and distilled and deionised water. Acetonitrile and ethanol were redistilled.

The silver electrodes were prepared by heating freshly prepared silver oxide on a silver plate in an electric furnace at about 400°C for 30 min. The silver oxide was precipitated from a solution of silver nitrate and sodium hydroxide and washed several times by deionised water. The silver oxide decomposes at this temperature yielding a silver surface of high reactivity. Silver electrodes prepared in this way are extremely reproducible, and isothermal emf's above 20 μ V were a scarceness in both water and the nonaqueous solvents.

Measurements of emf were made using a digital voltmeter of type Solartron LM 1604.2. The isothermal emf was measured before and after the experiment. The thermopotential was measured at a mean temperature of 298 K and the temperature difference between the electrodes was 10 K. The halfcells were kept at the desired temperature by circulating water from the two thermostats for one hour to obtain thermal equilibrium before the measurement. The emf was then measured and the process was repeated, but now the electrode being the warm in the first case was the cold one. The mean value of the two thermopotentials is divided by the temperature difference giving the initial thermoelectric power, assuming that ε_0 is temperature-independent or a linear function of the temperature in the interval.

RESULTS AND DISCUSSION

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

Acetonitrile-water mixtures. The initial thermoelectric powers were measured as a function of the concentration of silver nitrate and the solvent composition. The results are presented in Table 1.

Table 1. Initial thermoelectric powers in mV/deg. as function of the concentration of AgNO₃ and the solvent composition in acetonitrile-water mixtures.

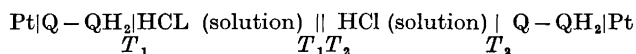
Mol % CH ₃ CN	1.0 N	0.5 N	0.1 N	0.05 N	0.01 N	0.001 N
0	-0.271	-0.323	-0.445	-0.500	-0.622	-0.798
1.8	-0.225	-0.170	-0.045	-0.082	-0.147	-0.318
3.7	-0.121	+0.024	+0.124	+0.090	-0.001	-0.167
5.7	+0.016	+0.179	+0.209	+0.160	+0.078	-0.090
7.9	+0.142	+0.268	+0.248	+0.202	+0.124	-0.040
10.3	+0.246	+0.324	+0.272	+0.224	+0.149	-0.009
12.9	+0.301	+0.366	+0.298	+0.245	+0.166	+0.011
18.7	+0.358	+0.393	+0.323	+0.271	+0.194	+0.038
25.6	+0.385	+0.412	+0.361	+0.293	+0.214	+0.058
34.0	+0.419	+0.430	+0.384	+0.310	+0.229	+0.074
44.6	+0.458	+0.471	+0.414	+0.343	+0.258	+0.098
58.0	+0.500	+0.501	+0.460	+0.391	+0.325	+0.172
75.6	+0.558	+0.542	+0.520	+0.468	+0.394	+0.266
99.0	+0.591	+0.578	+0.559	+0.508	+0.450	+0.358

ε_0 is much more positive in acetonitrile than in water. ε_0 is directly related to the entropy of electrochemical transport involved in the reduction of silver ion to silver metal. The solvent ordering in acetonitrile solutions is therefore greater than in aqueous solutions. Several factors may cause this difference. One is that there are strong interactions between the silver ion and acetonitrile

as indicated by the fact that the standard reduction potential is 0.57 V lower in acetonitrile than in water²¹ and as is shown by the formation of silver-acetonitrile complexes.²² Another factor is that solvation of small ions decreases the high degree of structure normally present. The solvent ordering would be opposed by initial structure breaking effects, making the overall entropy change smaller. Liquid acetonitrile is relatively nonstructured compared to water.²³ Thus the structure breaking effects of ions would be smaller in acetonitrile than in water. The stronger interactions and the smaller structure breaking effects should predict a more positive entropy change in acetonitrile and therefore a more positive ε_0 .

Small additions of acetonitrile have a great influence on ε_0 . At a concentration of 0.1 N AgNO_3 ε_0 increases 0.653 mV/deg. with an addition of 5.7 mol % of acetonitrile to pure water. An addition of 23.4 mol % of water to 99 % acetonitrile, however, only decreases ε_0 by 0.039 mV/deg.

For the thermocell



where $\text{Q} - \text{QH}_2$ is the quinhydrone electrode and the solvent is a mixture of acetonitrile and water, the opposite effect was found.¹ A small addition of acetonitrile to water did not increase the thermoelectric power. ε_0 on the contrary slightly decreased in the solutions rich in water to about 10 mol % of acetonitrile where it reached its minimum. In the solutions rich in acetonitrile addition of water markedly decreased ε_0 . This is due to the strong interactions between water and the hydrogen ion, which is dominating in the solutions rich in water. The smaller structure breaking effects in acetonitrile compared to water are only coming into account in the solutions rich in acetonitrile making ε_0 increase.

Strehlow and Koepp²⁴ have measured the selective solvation in the system $\text{AgNO}_3 - \text{H}_2\text{O} - \text{CH}_3\text{CN}$ by a transference method. They found that the silver ion is selective solvated by acetonitrile and the nitrate ion by water. IR, NMR and Raman spectra^{25,26} of this solution have shown similar results. The curvature of ε_0 as function of mol % of acetonitrile is indicating the same. Oliver and Janz²⁶ have found that the silver ion is solvated by acetonitrile in a solution with an acetonitrile content as low as 4.7 mol %. This is the point where the curve of ε_0 as function of the solvent composition is flattening out. ε_0 measurements may therefore give information of the solvation of ions in solvent mixtures.

The thermostatic part (ε_0') of eqn. 1 reads in pure acetonitrile,

$$F\varepsilon_0' = S_{\text{Ag}} - t_{\text{NO}_3} (S_{\text{AgNO}_3}^\circ - 2R \ln C - 2R \ln \gamma_{\pm}) - 2RT \ln \gamma_{\pm} / dT + \Delta N_{\text{CH}_3\text{CN}} S_{\text{CH}_3\text{CN}} \quad (2)$$

where

$$\begin{aligned} S_{\text{AgNO}_3}^\circ &= \text{the hypothetical standard partial molar entropy of } \text{AgNO}_3; \\ C &= \text{the concentration;} \\ \gamma_{\pm} &= \text{the mean ionic activity coefficient of } \text{AgNO}_3. \end{aligned}$$

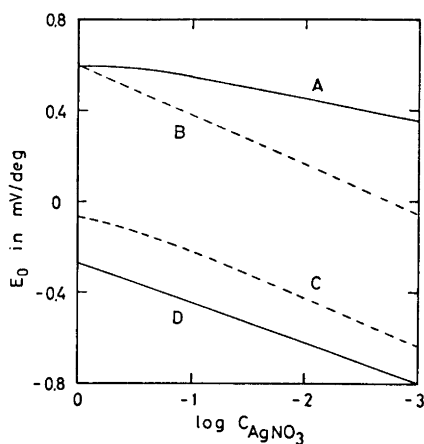


Fig. 1. ε_0 as function of the concentration of AgNO_3 in: A, CH_3CN and D, H_2O . The stippled lines are: C the term $t_{\text{NO}_3^-} \times 2RF^{-1} \ln C\gamma_{\pm}$ in H_2O , and B the term $\varepsilon_0(1) + t_{\text{NO}_3^-} 2RF^{-1} \ln C$ in CH_3CN .

In Fig. 1 ε_0 is presented as function of the concentration of AgNO_3 in pure acetonitrile and water. In Fig. 1 is also presented the term (stippled line C)

$$t_{\text{NO}_3^-} 2RF^{-1} \ln C\gamma_{\pm}$$

in pure water. The transport numbers are taken from McInnes and Longworth²⁷ and the activity coefficients are taken from McInnes and Brown²⁸ and Robinson and Tait.²⁹ The stippled line B is the term

$$\varepsilon_0(1 \text{ N}) + t_{\text{NO}_3^-} 2RF^{-1} \ln C$$

in pure acetonitrile. The transport numbers are taken from Strehlow and Koepp.²⁴

In the water solutions ε_0 are close to the ideal slope when corrected for the activity coefficients, indicating that the other terms of eqn. 1 are not influenced by concentration changes or have the same concentration dependence. In pure acetonitrile ε_0 as function of the concentration is far from the ideal slope. The activity coefficients of AgNO_3 in acetonitrile are therefore markedly lower than one, which is earlier noticed by Pleskov.⁷ This may be due to partial association of AgNO_3 in acetonitrile. This is earlier demonstrated by conductance³⁰ and potentiometric⁹ measurements even in dilute solutions.

Ethanol-water mixtures. The ε_0 measurements in ethanol-water solutions are presented in Table 2. In the solutions rich in ethanol measurements of ε_0 could not be carried out in concentrated solutions of AgNO_3 because of the smaller solubility of AgNO_3 .

The results are not so striking as those of the acetonitrile-water solutions. AgNO_3 has stronger interactions with water than with ethanol. When ethanol is added to water ε_0 decreases slightly until the composition reaches a value

Table 2. Initial thermoelectric powers in mV/deg. as function of the concentration of AgNO_3 and the solvent composition in ethanol-water mixtures.

Mol % EtOH	1.0 N	0.1 N	0.01 N	0.001 N
0	-0.270	-0.445	-0.622	-0.799
3.2	-0.302	-0.478	-0.653	-0.830
6.8	-0.320	-0.503	-0.680	-0.858
11.1	-0.329	-0.514	-0.687	-0.867
16.2	-0.314	-0.490	-0.662	-0.835
22.2	-0.299	-0.470	-0.639	-0.809
29.5	—	-0.433	-0.594	-0.759
38.8	—	-0.393	-0.558	-0.718
50.8	—	-0.363	-0.526	-0.687
66.3	—	-0.307	-0.438	-0.592
76.2	—	—	-0.296	-0.428
99.4	—	—	-0.062	-0.157

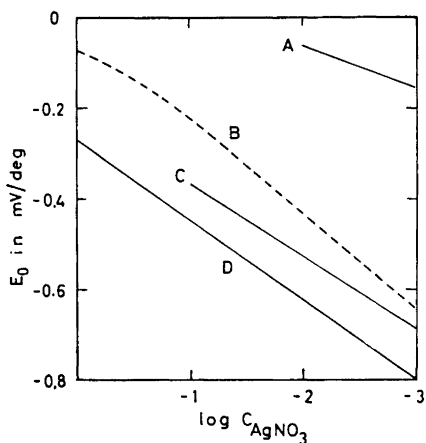


Fig. 2. ε_0 as function of the concentration of AgNO_3 in: A, EtOH, C, 50.8 mol % EtOH, and D, H_2O . The stippled line B is the term $t_{\text{NO}_3^-} - 2RF^{-1} \ln C\gamma_{\pm}$ in H_2O .

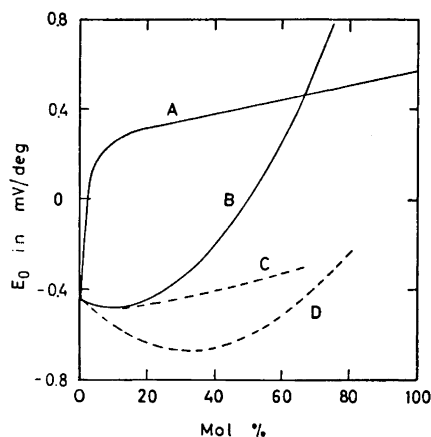


Fig. 3. ε_0 as function of the solvent composition. The mol % is mol % nonaqueous solvent. Electrolyte concentration is 0.1 N. A, $\text{Ag}|\text{AgNO}_3$ in CH_3CN ; B, $\text{Q-QH}_2|\text{HCl}$ in CH_3CN ; C, $\text{Ag}|\text{AgNO}_3$ in EtOH; and D, $\text{Q-QH}_2|\text{HCl}$ in EtOH. B and D from Ref. 1.

of about 20 wt. % of ethanol. ε_0 is then increasing when the composition changes towards pure ethanol, but ε_0 is negative at all concentrations. Other measurements³¹ have indicated that small additions of ethanol to water increase the order in the structure of the solvent. The maximum structural order is found to be at about 20 wt. % of ethanol. The structure breaking of the solvation of ions are therefore greatest at this solvent composition, explaining that ε_0 reaches its minimum at this point. For the HCl solutions using the quinhydrone electrode the minimum of ε_0 was found to be at about

40 wt. % of ethanol. Other effects than the structure of the solvent must influence ϵ_0 in this case.

The measurements are also showing that the activity coefficients of AgNO_3 are smaller in ethanol than in water. In Fig. 2, ϵ_0 is presented as function of the concentration of AgNO_3 in pure water, 50.8 mol % ethanol, and absolute ethanol. The slopes are indicating more non-ideality going from pure water to pure ethanol.

In Fig. 3, ϵ_0 measurements in 0.1 N electrolytes as function of the solvent composition are presented together. This figure shows the interesting influence of different solvents on ϵ_0 . Because of the lack of thermodynamic data, the explanation can not be given.

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