

Studies on silver–silver carboxylate indicator electrodes: Part 1–The silver–silver acetate electrode

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MS received 10 December 1988; revised 18 May 1990

Abstract. Silver–silver acetate (Ag–Ag Acet) electrodes have been prepared and their electrochemical and thermodynamic behaviour studied in different media containing acetate ions. The linear relationship between electrode potential and $\log [\text{CH}_3\text{COO}^-]$ shows that this electrode can be used in the quantitative determination of CH_3COO^- in aqueous, aquo-alcoholic and alkaline media. The values of thermodynamic functions, viz. ΔG° , ΔH° and ΔS° for the electrode reaction have been determined. The standard free energy of formation (ΔG_f°) and solubility product constant (K_{sp}) of CH_3COOAg in aqueous medium at 25°C have also been determined.

Keywords. Silver–silver acetate electrode; acetate ions; thermodynamic behaviour.

1. Introduction

Larson and McDougall (1937) and Larson and Tomsicek (1939) prepared the mercury–mercurous acetate electrode in order to use the electrode in the quantitative determination of acetate ions. Nayak and Dash (1973) determined the standard potential of the silver–silver acetate electrode in formide medium. The importance of carboxylate ions such as acetate, citrate, lactate, malate and tartrate in the field of enology, and the lack of a convenient and rapid method for their determination, prompted us to undertake a project on the preparation of silver–silver carboxylate indicator electrodes responsive to various carboxylate ions and extend them to other similar systems. In this paper we report the results of our investigations on the electrochemical and thermodynamic behaviour of silver–silver acetate electrodes in solutions containing acetate ions.

2. Experimental

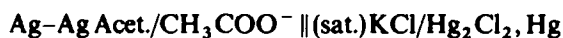
All the chemicals used were of analytical reagent grade and their stock solutions were prepared in conductivity water.

The silver–silver acetate (Ag–Ag Acet.) electrode was prepared by the deposition method. A platinum wire of 1.5 cm length and 0.5 mm diameter was fused in a pyrex tube keeping 1.2 cm of the wire outside. It was cleaned with chromic acid and washed repeatedly with distilled water. Silver was deposited electrolytically on to the platinum

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wire. For achieving uniform and stable deposition this was fully dipped into a 0.01 M solution of AgNO_3 . Another platinum wire was used as a counter electrode. A constant current of 10 milliamperes was passed for about 5 min. The silver electrode so prepared was washed with conductivity water and then kept immersed overnight in a saturated aqueous solution of sodium acetate so as to get a uniform coating of silver acetate on it. The electrode was then washed again and kept immersed in conductivity water for 24 hours to attain equilibrium potential. The electrode was preconditioned (Frieser 1980) in 0.1 M solution of CH_3COONa for one hour prior to use.

The potential of the electrode in solutions containing CH_3COO^- ions was measured under different experimental conditions by setting up a cell of the type:



The liquid junction potential contribution of the above cell should also be taken into consideration. However, according to Goates *et al* (1951) the uncertainty of the assumption of complete elimination of the liquid junction potential by a saturated KCl salt bridge (as in the present study) involves an error of 1–2 millivolts. In the present study, however, this error can be safely neglected in comparison to the magnitude of the cell e.m.f.

3. Results and discussion

3.1 Evaluation of the electrode

The potential of the Ag–Ag acetate electrode was measured in aqueous sodium acetate solution of different concentrations (2×10^{-5} – 1×10^{-3} M) at $25 \pm 0.1^\circ\text{C}$. It was found that the potential of the electrode becomes constant within three minutes of its immersion in well-stirred solutions. It is thus inferred that the electrode attains equilibrium potential fairly rapidly. The reproducibility of the electrode potential was ascertained by preparing the electrode five times under identical conditions and measuring its potential every time in well-stirred aqueous solutions of different concentrations (2×10^{-5} – 1×10^{-3} M) at $25 \pm 0.1^\circ\text{C}$. It was seen that variations in the values of electrode potential were within the limits of standard deviation (1.2×10^{-3}) which shows that the potential of the electrode is reproducible.

The stability of the electrode was ascertained by measuring its potential in aqueous solutions of sodium acetate at different concentrations (2×10^{-5} – 1×10^{-3} M) after intervals of one month at $25 \pm 0.1^\circ\text{C}$. It was found that the electrode remained steady upto six months. This study shows that the electrode is fairly stable if handled carefully and stored in conductivity water after use.

3.2 Electrochemical behaviour of silver–silver acetate electrode vis-a-vis its use in the quantitative determination of acetate ion

A series of aqueous solutions of sodium acetate at different concentrations ranging from 2×10^{-5} to 1×10^{-3} M were prepared. The potential of the electrode was measured as a function of $[\text{CH}_3\text{COO}^-]$ at $25 \pm 0.1^\circ\text{C}$. The plot of $E_{\text{Ag-Ag Acct.}}$ vs. $\log [\text{CH}_3\text{COO}^-]$ is linear (figure 1). The electrochemical equation to this linear plot can be obtained as under,

$$E_{\text{Ag-Ag Acct.}} = -0.430 - 0.057 \log [\text{CH}_3\text{COO}^-], \quad (1)$$

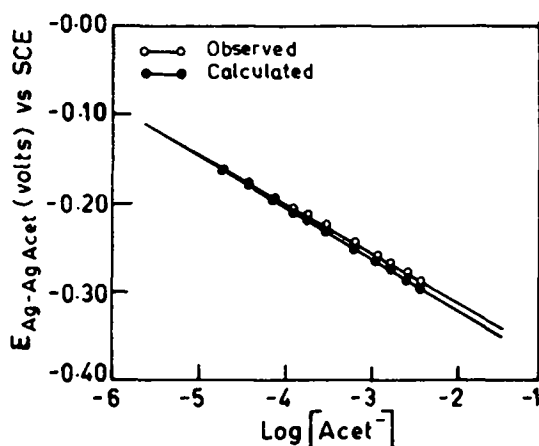
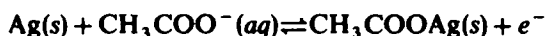


Figure 1. Plots of $E_{\text{Ag-Ag Acet.}}$ vs. $\log[\text{Acet}^-]$ in aqueous sodium acetate solutions at $25 \pm 0.1^\circ\text{C}$.

where the intercept potential value, -0.430 V at $\log[\text{CH}_3\text{COO}^-]$ is the algebraic sum of the standard electrode potential (E^0) of the Ag-Ag Acet. electrode and that of SCE from which the E^0 of the Ag-Ag Acet. electrode works out to be -0.671 V at $25 \pm 0.1^\circ\text{C}$. The experimental slope (0.057 V) is fairly close to the theoretical Nernstian value (0.0591 V). From the experimental slope value it is also concluded that one electron is involved in the electron reaction:



The validity of (1) has been further checked by obtaining from it the calculated values of the potential of the Ag-Ag Acet. electrode as a function of $[\text{CH}_3\text{COO}^-]$. In figure 1 the observed and calculated values of electrode potential have been plotted against $\log[\text{CH}_3\text{COO}^-]$. It is seen that the difference between the observed and the calculated value is 0.5% in the range investigated. Thus, the Ag-Ag Acet. electrode can be successfully used in the quantitative determinations of CH_3COO^- in given samples.

3.3 Effect of various experimental conditions on the working of the silver-silver acetate electrode

3.3a Effect of foreign ions: The effect of increasing the concentrations (1×10^{-5} – $1 \times 10^{-2}\text{ M}$) of some foreign ions, viz. F^- , Cl^- , Br^- , I^- , CO_3^{2-} , HCO_3^- and NO_2^- on the working of the Ag-Ag Acet. electrode in the presence of $1 \times 10^{-4}\text{ M}$ aqueous sodium acetate solution has been investigated and the results of this study indicate that there is hardly any difference between the potential of the electrode in the presence of F^- , Cl^- , Br^- , I^- and CO_3^{2-} . However, in the presence of HCO_3^- and NO_2^- , an appreciable change in the potential of the electrode occurs. Thus, the Ag-Ag Acet. electrode can be used in the quantitative determination of CH_3COO^- in the presence of impurities such as F^- , Cl^- , Br^- , I^- and CO_3^{2-} . The potential of the Ag-Ag Acet. electrode has also been measured as a function of $[\text{CH}_3\text{COO}^-]$ when this ion is present in saturated solutions of the above foreign ions. It is seen that the electrode shows a fairly Nernstian response to $\log[\text{CH}_3\text{COO}^-]$ when it is present in

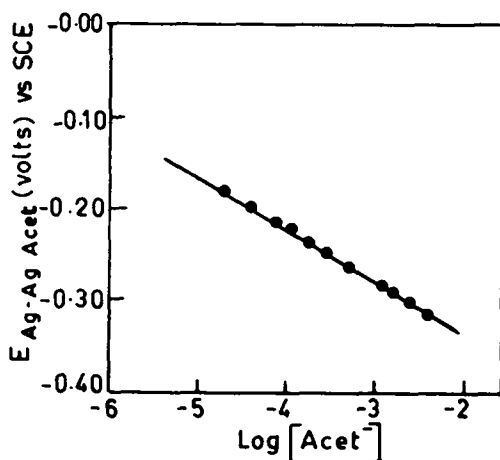


Figure 2. Plot of $E_{\text{Ag-Ag Acet.}}$ vs. $\log [\text{Acet.}^-]$ in 50% (v/v) aquo-alcoholic sodium acetate solutions at $25 \pm 0.1^\circ\text{C}$.

saturated solutions of the above ions. The linear relationship between the electrode potential and $\log [\text{CH}_3\text{COO}^-]$ shows that the Ag-Ag Acet. electrode can be used satisfactorily in the quantitative determination of acetate ion in the presence of saturated solutions of F^- , Cl^- , Br^- , I^- and CO_3^{2-} .

3.3b *Effect of medium:* The electrochemical behaviour of Ag-Ag Acet. electrode has been studied in alcoholic solutions of sodium acetate of varying concentrations (2×10^{-5} – 1×10^{-3} M). The potential of the electrode has been measured as a function of $[\text{CH}_3\text{COO}^-]$ in 50% (v/v) aquoalcoholic solution at $25 \pm 0.1^\circ\text{C}$. The plot of $E_{\text{Ag-Ag Acet.}}$ vs. $\log [\text{CH}_3\text{COO}^-]$ is linear (figure 2) thereby showing that the electrode can be successfully used in the quantitative determination of acetate ions in aquo-alcoholic media. The electrochemical equation to the linear plot can be represented as below

$$E_{\text{Ag-Ag Acet.}} = -0.450 - 0.058 \log [\text{CH}_3\text{COO}^-]. \quad (2)$$

The value of E^0 works out to be -0.691 V and the experimental slope value is 0.058 V. From this slope value it is evident that the response of the electrode to $\log [\text{CH}_3\text{COO}^-]$ in an aquoalcoholic solution is Nernstian.

3.3c *Effect of pH:* A series of sodium acetate solutions of varying concentrations ranging from 1.0×10^{-5} to 3.0×10^{-3} M were prepared in Britton-Robinson (BR) buffers (pH 7.96–11.98) and the potential of the electrode was measured as a function of $[\text{CH}_3\text{COO}^-]$ at fixed (controlled) pH values (7.96–11.98). The plots of $E_{\text{Ag-Ag Acet.}}$ vs. $\log [\text{CH}_3\text{COO}^-]$ are linear (figure 3). The electrochemical equations to these plots have been obtained as:

$$\begin{aligned} E_{\text{Ag-Ag Acet.}} &= -0.371 - 0.066 \log [\text{CH}_3\text{COO}^-], \quad \text{at pH 7.96,} \\ &= -0.414 - 0.055 \log [\text{CH}_3\text{COO}^-], \quad \text{at pH 8.69,} \\ &= -0.466 - 0.058 \log [\text{CH}_3\text{COO}^-], \quad \text{at pH 10.38,} \\ &= -0.510 - 0.058 \log [\text{CH}_3\text{COO}^-], \quad \text{at pH 11.98.} \end{aligned}$$

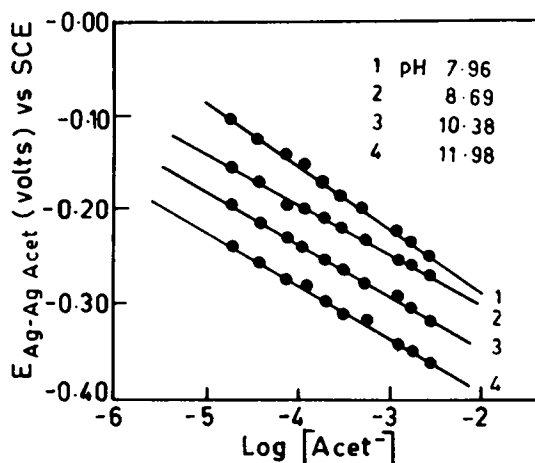


Figure 3. Plots of $E_{\text{Ag-AgAcet.}}$ vs. $\log[\text{Acet.}^-]$ at different (controlled) pH values at $25 \pm 0.1^\circ\text{C}$.

The values of E^0 of the Ag–AgAcet. electrode work out to be -0.612 , -0.655 , -0.707 and -0.751 V at pH 7.96, 8.69, 10.38 and 11.98, respectively, and at $25 \pm 0.1^\circ\text{C}$. The experimental slope values are 0.066 , 0.055 , 0.058 and 0.058 V, respectively, under the same conditions, which are very close to the Nernstian value. From this study it is inferred that the Ag–AgAcet. electrode can be used for the quantitative determination of CH_3COO^- in alkaline solutions of sodium acetate.

3.3d Potential pH relationship: The response of the Ag–AgAcet. electrode to changes in pH in the presence of fixed $[\text{CH}_3\text{COO}^-]$ has been studied. The plots of $E_{\text{Ag-AgAcet.}}$ vs. pH are linear (figure 4). The electrochemical equations to the linear plots can be represented as:

$$\begin{aligned}
 E_{\text{Ag-AgAcet.}} &= 0.344 - 0.056 \text{ pH} \quad ([\text{CH}_3\text{COO}^-] = 1.99 \times 10^{-5} \text{ M}) \\
 &= 0.303 - 0.056 \text{ pH} \quad ([\text{CH}_3\text{COO}^-] = 1.18 \times 10^{-4} \text{ M}) \\
 &= 0.246 - 0.056 \text{ pH} \quad ([\text{CH}_3\text{COO}^-] = 5.66 \times 10^{-4} \text{ M}) \\
 &= 0.195 - 0.056 \text{ pH} \quad ([\text{CH}_3\text{COO}^-] = 2.85 \times 10^{-3} \text{ M})
 \end{aligned}$$

Thus, Ag–AgAcet. electrode can be used for the measurement of the pH in the range 7.96–11.98 in the presence of acetate ions. It is relevant to mention here that this electrode gives erratic readings in acidic media.

3.3e Effect of temperature on standard electrode potentials (E^0) of silver–silver acetate electrodes in aqueous, aquo-alcoholic and alkaline solutions of sodium acetate and determination of thermodynamic functions (ΔG^0 , ΔH^0 and ΔS^0): The potential of the electrode has been measured as a function of $[\text{CH}_3\text{COO}^-]$ at different temperatures ranging from 5 to 25°C , in aqueous, alcoholic (50% v/v) and alkaline media. From the plots of $E_{\text{Ag-AgAcet.}}$ vs. $\log[\text{CH}_3\text{COO}^-]$ at different temperatures in various media, the values of E^0 of the electrode have been obtained at different temperatures and are listed in table 1. The temperature coefficient ($\partial E^0/\partial T$) of E^0 has also been determined

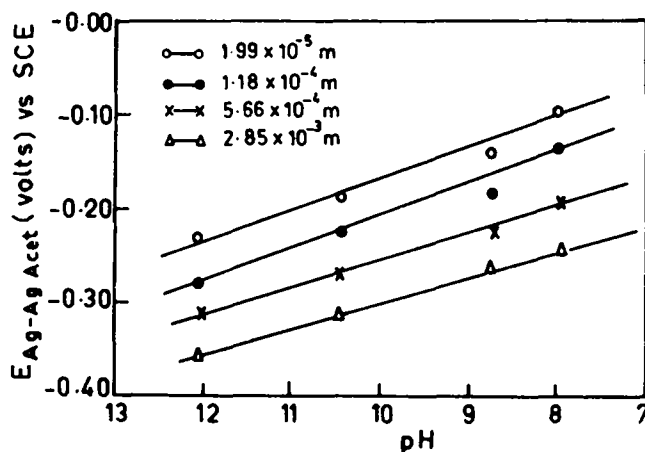


Figure 4. Plots of $E_{Ag-Ag Acet.}$ vs. pH at constant $[Acet.^-]$ at $25 \pm 0.1^\circ C$.

Table 1. Values of standard electrode potential (E^0) and temperature coefficient of Ag-Ag Acet. electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.96-11.98, BR buffer) solutions of $Acet.^-$

Medium	E^0 (volts) at different temperatures					Temperature coefficient ($\partial E^0/\partial T$) _p (V/K)
	278	283	288	293	298	
Aqueous	-0.641	-0.647	-0.651	-0.658	-0.667	-1.6×10^{-3}
Aquo-alcoholic (50% v/v)	-0.668	-0.673	-0.680	-0.686	-0.691	-1.5×10^{-3}
Alkaline (pH)						
7.96	-0.601	-0.606	-0.612	-0.617	-0.620	-1.3×10^{-3}
8.69	-0.619	-0.625	-0.631	-0.637	-0.648	-1.2×10^{-3}
10.38	-0.689	-0.694	-0.698	-0.703	-0.708	-1.33×10^{-3}
11.98	-0.728	-0.734	-0.739	-0.747	-0.758	-1.4×10^{-3}

from the linear plots of E^0 vs. T in various media and these values are also listed in table 1.

The thermodynamic functions ΔH^0 , ΔG^0 and ΔS^0 for the Ag-Ag Acet. electrode in different media containing CH_3COO^- , have been calculated and the values are listed in table 2.

3.4 The standard free energy of formation (ΔG_f^0) of silver acetate

The standard free energy of formation, ΔG_f^0 , of silver acetate can be calculated following the method of Goates *et al* (1951). The value of ΔG^0 for the reaction, $Ag(s) + CH_3COO^-(aq) \rightleftharpoons CH_3COOAg(s) + e^-$, works out to be $15.38 \text{ kcal. mol}^{-1}$ (vide table 2) at $25 \pm 0.1^\circ C$ in aqueous media. Thus we have,

$$15.38 = \Delta G_f^0[CH_3COOAg(s)] - \{ \Delta G_f^0[Ag(s)] + \Delta G_f^0[CH_3COO^-(aq)] \}.$$

As ΔG_f^0 of $Ag(s)$ (element) is zero and taking (Meites 1963) ΔG_f^0 for $CH_3COO^-(aq)$ as

Table 2. Values of various thermodynamic functions (ΔG^0 , ΔH^0 and ΔS^0) for Ag-AgAcet. electrodes in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.96-11.98) solutions of Acet. at $25 \pm 0.1^\circ\text{C}$.

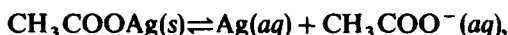
Medium	ΔG^0 kcal. mol ⁻¹	ΔH^0 kcal. mol ⁻¹	ΔS^0 (e.u.)
Aqueous	15.38	4.38	-39.90
Aquo-alcoholic (50% v/v)	15.93	5.62	-34.59
Alkaline (pH)			
7.96	14.29	5.35	-29.98
8.69	14.94	6.69	-27.67
10.38	16.32	7.18	-30.67
11.98	17.48	7.86	-32.28

*e.u. (entropy unit) i.e., cal. deg⁻¹ mol⁻¹

-88.29 kcal. mol⁻¹ (at 25°C), the value of ΔG_f^0 of silver acetate works out to be -72.91 kcal. mol⁻¹. This value is in agreement, within experimental error, with the literature value (Dean 1979) of -73.56 kcal. mol⁻¹.

3.5 Solubility product constant (K_{sp}) of silver acetate

This can be calculated from the standard free energy change of the reaction,



by means of the expression (Goates *et al* 1951b; Alberty and Daniels 1984)

$$\ln K_{sp} = -\Delta G^0/RT.$$

Since the value of ΔG_f^0 for silver acetate has already been calculated as -72.91 kcal. mol⁻¹ and using the literature values (Dean 1984; Alberty and Daniels 1984) of ΔG_f^0 for CH_3COO^- and Ag^+ as -88.29 kcal. mol⁻¹ and 18.433 kcal. mol⁻¹, respectively, the value of K_{sp} can be obtained from the above expression. This works out to be 5.86×10^{-3} at $25 \pm 0.1^\circ\text{C}$. This value compares fairly well with the literature value (4.4×10^{-3} , Meites 1965).

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