

Estimating the Change in Liquid Junction Potential on Glass Electrodes

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Abstract

Formal potential of combination glass electrodes, a necessary parameter commonly needed in the determination of stoichiometric equilibrium constants, has been calculated at several temperatures and ionic strength values. These data, together with the activity coefficient of the proton calculated with Pitzer equations, have been used to study the change in the liquid junction potential, E_j . Since the asymmetry potential is unknown, absolute values of E_j can not be calculated. However, it has been possible to determine the variation as a function of the ionic strength in KCl as background electrolyte. A linear relationship has been found for the three temperatures studied. Dependence with temperature of the term $-s \log m_{\text{H}^+_{\text{int}}}$ represents the most important influence on the temperature dependence of the formal potential of a combination glass electrode.

Keywords: Liquid junction, pH electrode, Activity coefficient, Formal potential, Potentiometry

1. Introduction

The determination of acid-base equilibrium constants in constant ionic media by potentiometry, the most used technique [1–4], entails in most cases a previous calibration of the electrode, normally a glass electrode. The calibration is obtained by using a logarithmic relationship between potential and proton concentration: E vs. $\log [\text{H}^+]$. The intercept of this fit, the formal potential, includes among other contributions, the liquid junction potential. The formal potential, $E^{0'}$, has an important effect on the final value of the equilibrium constant, so we have considerable interest to study the contribution of the liquid junction potential term to $E^{0'}$ when the ionic strength and temperature are changed as it happens in typical studies about chemical equilibria in saline media [5]. There are many different studies either very theoretical (i.e., [6–8]) or experimental (i.e., [9, 10] and references therein) about liquid junction potentials. However, work connecting this potential with the common practice of potentiometric determination of stability constants is really scarce [11]. This article tries to contribute to fill the gap in that area.

As is well known, the determination of the activity coefficients of a single ion and liquid junction potentials is impossible. However, conventional values can be ascribed to the activity coefficients, so the liquid junction potential can be calculated. A liquid junction potential calculated in that way will be conventional as well [4].

We have calculated the formal potential, $E^{0'}$, of combination glass electrodes as a function of the ionic strength and temperature. Different contributions to $E^{0'}$ will be analyzed, which will allow us to get information about the variation of E_j with the ionic strength and the temperature.

2. Theory

As a rule, the system consisting of the working solution and the glass electrode can be schematized as follows:

external reference electrode, KCl (satd) || solution | glass membrane | internal reference electrode
where || denotes the liquid junction.

The measured potential difference comprises various contributions. Two of them are due to the reference electrodes, of opposite sign and of usually comparable magnitude, and have a constant value. As both electrodes used are the same, viz. Ag|AgCl, we will assume that the reference electrode potentials cancel each other. There are also two potential differences due to the liquid junction and the glass membrane; the latter depends on the activity of proton in both sides of the membrane and the asymmetry potential, E_{as} . Hence, the potential can be described with the following equation [4]:

$$E = E_{\text{as}} + E_j - s \log(\text{H}^+)_{\text{int}} + s \log(\text{H}^+)_{\text{ext}} \quad (1)$$

where s is the electrode slope. $(\text{H}^+)_{\text{ext}}$ and $(\text{H}^+)_{\text{int}}$ are the activities of protons in the external and in the internal sides of the glass membrane, respectively. Using the definition of activity, Equation 1 can be rewritten as follows:

$$E = E_{\text{as}} + E_j - s \log(\text{H}^+)_{\text{int}} + s \log \gamma_{\text{H}^+_{\text{ext}}} + s \log m_{\text{H}^+_{\text{ext}}} \quad (2)$$

If the ionic strength of the medium is kept constant, the activity coefficient of the proton will be constant as well and can be encompassed in the formal potential $E^{0'}(\text{m})$:

$$E = E^{0'}(\text{m}) + s \log m_{\text{H}^+_{\text{ext}}} \quad (3)$$

where

$$E^{0'}(\text{m}) = E_{\text{as}} + E_j - s \log(\text{H}^+)_{\text{int}} + s \log \gamma_{\text{H}^+_{\text{ext}}} \quad (4)$$

If the potential difference is measured in a solution of known proton concentration, s and $E^{0'}(\text{m})$ can be calculated, by means of Equation 3. The measurements are done at several ionic strength compositions and the relationship between $E^{0'}(\text{m})$ and I at working temperature is obtained. From Equation 4 it is clear that if the formal potential is obtained experimentally and the activity coefficient is calculated with Pitzer equations, only the asymmetry potential and the liquid junction potential will remain unknown. Rearranging Equation 4:

$$E_j + (E_{\text{as}} - s \log m_{\text{H}^+_{\text{int}}}) = E^{0'}(\text{m}) + s \log \frac{\gamma_{\text{H}^+_{\text{int}}}}{\gamma_{\text{H}^+_{\text{ext}}}} = E_{\text{rep}} \quad (5)$$

Assuming that the asymmetry potential is constant at a given temperature, the term between brackets in Equation 5 is constant, and it will be denoted as $C = E_{\text{as}} - s \log m_{\text{H}^+}$. E_{rep} encompasses all the known terms, since $E^{0'}(m)$ can be determined as described in Section 3, and the activity coefficients of the protons in both sides of the glass membrane can be calculated as described in the appendix (sec. 6). The internal reference electrode is immersed in a saturated potassium chloride solution, so the activity coefficient of the proton will be calculated using the concentration of a saturated KCl solution at the working temperature, assuming that the proton concentration can be neglected compared to KCl concentration. The dependence of E_{rep} with ionic strength and temperature allows one to study the dependence of the liquid junction potential with these parameters.

3. Experimental

Calibrations were done in an acid medium as described elsewhere [12]: variable volumes, v , of a strong acid of concentration c were successively added to an initial volume, V_0 , of inert electrolyte solution. Thus, the proton molar concentration was given by:

$$[\text{H}^+] = \frac{cv}{V_0 + v} \quad (6)$$

where $2.3 < -\log[\text{H}^+] < 2.9$ [13]. We used an initial volume $V_0 = 40.0$ mL to which 0.04 mL aliquots of $0.1000 \text{ mol L}^{-1}$ HCl were added successively.

We carried out experiments at several ionic strengths adjusted with KCl, Merck p.a. reagent. The water used to prepare every solution was purified by passage through a Millipore Milli-Q system. All experiments were performed in a dual-wall cell through which thermostated water at 15, 25 and 35 °C was circulated. 99.999% purity nitrogen, water saturated, was bubbled through the cell to remove CO_2 and stir the solution. A Crison microBU 2030 automatic burette furnished with a 2.5 mL syringe for dispensing the titrant was used. The burette was controlled via a computer that afforded reading the emf of a Crison microPH 2002 pH-meter connected to a Radiometer GK2401C electrode (electrodes A and B). This last was a glass electrode combined with a Ag|AgCl reference electrode where the liquid junction was established by a salt bridge consisting of a porous ceramic pin. Some of the experiments were performed using a combination Radiometer pHC2401 electrode, electrode C, which has an

annular porous ring as a salt bridge, with a Ag|AgCl reference electrode. Both junctions can be classified as indefinite junctions [4, 14], although the geometry is not exactly the same in both systems.

$E^{0'}(M)$ is determined from a linear plot of experimental E , $\log [\text{H}^+]$ pairs. As Pitzer equations are expressed in the molality scale, solution concentrations, initially in molarity, have to be change to that scale. The relationship between molarity and molality of protons in a solution where an inert electrolyte is present in a big ratio respect to the acid concentration is given by [15]:

$$m_{\text{H}^+} = \frac{[\text{H}^+]}{\rho_{\text{KCl}} - [\text{KCl}]MW_{\text{KCl}}} \quad (7)$$

where ρ_{KCl} is the solution density and MW_{KCl} is the molecular weight of KCl. The equation that relates $E^{0'}$ in molality and molarity can be obtained using Equations 3 and 7:

$$E^{0'}(m) = E^{0'}(M) + s \log(\rho_{\text{KCl}} - [\text{KCl}]MW_{\text{KCl}}) \quad (8)$$

The density of KCl solutions, as a function of temperature and concentration, has been taken from reference [16].

4. Results and Discussion

4.1. Dependence of E_j with Ionic Strength

Figure 1 shows the plot of E_{rep} vs. I for KCl, Equation 5, using electrodes A (Fig. 1a) and C (Fig. 1b) at 25 °C. As has been mentioned above, E_{rep} has been calculated using Pitzer equations to determine the activity coefficients of proton and tabulated interaction parameters, see appendix (sec. 6), together with formal potentials. Experimental formal potentials listed in Table 1 have been changed to molality scale by means of Equation 8. Since $E_{\text{rep}} = E_j + C$, where C is a constant, Equation 5, a plot of E_{rep} vs. I will show the dependence of the liquid junction potential with the ionic strength of the solution. Two different behaviors can be seen:

- In electrode A a linear relationship is found. Table 2 lists the slopes obtained in a linear fit at 15, 25 and 35 °C and at 25 °C with a similar electrode, electrode B, taken from [17]. Slopes show a good agreement, taking into account the error obtained in the fitting, as could be expected when electrodes with a similar liquid junction connection, e.g., porous pin, are

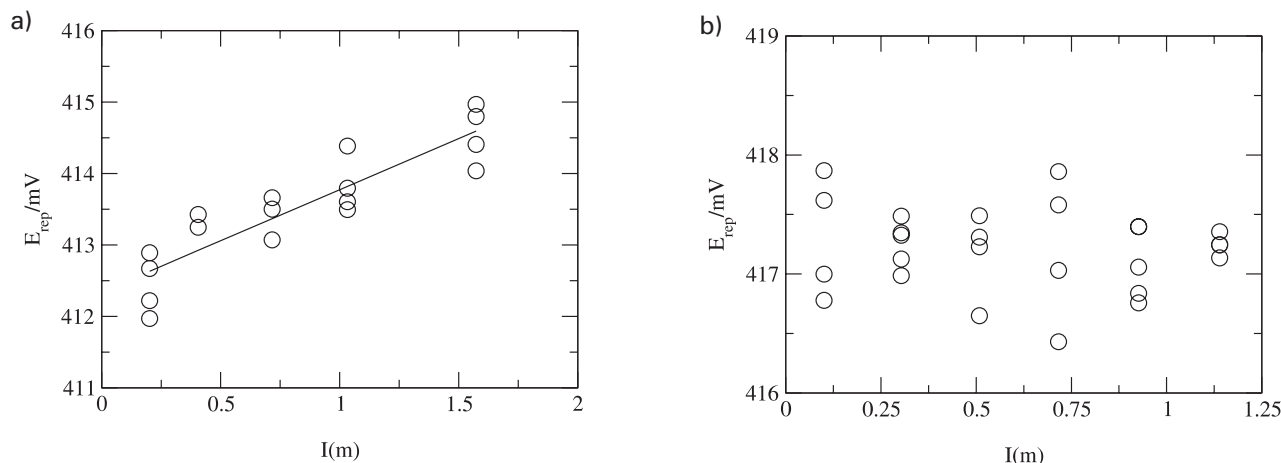


Fig. 1. Dependence of E_{rep} with ionic strength for two different electrodes; temperature 25 °C and KCl as background electrolyte.

Table 1. Formal potential data in molarity scale, $E^{0'}(M)$ for electrodes A and C.

Electrode A						Electrode C					
15 °C			25 °C			35 °C			25 °C		
<i>I/M</i>	$E^{0'}(M)/mV$	<i>s/mV</i>	<i>I/M</i>	$E^{0'}(M)/mV$	<i>s/mV</i>	<i>I/M</i>	$E^{0'}(M)/mV$	<i>s/mV</i>	<i>I/M</i>	$E^{0'}(M)/mV$	<i>s/mV</i>
0.2	375.52	57.16	0.2	384.81	58.95	0.2	394.93	60.98	0.1	390.21	58.74
0.2	375.16	56.87	0.2	385.48	59.45	0.2	394.67	61.47	0.1	390.43	58.79
0.2	375.81	57.14	0.2	385.26	59.31	0.2	395.52	61.11	0.1	391.30	58.91
0.2	375.62	56.76	0.2	384.56	59.25	1.0	398.67	61.00	0.1	391.05	58.76
0.2	376.11	57.25	0.4	385.69	59.43	1.0	399.45	61.04	0.3	389.50	58.95
1.0	378.66	56.75	0.4	385.87	58.83	1.0	400.03	60.97	0.3	389.72	59.07
1.0	379.48	57.07	0.7	386.53	59.07	1.0	399.31	61.31	0.3	389.86	59.03
1.0	379.49	56.61	0.7	386.96	59.17	1.5	403.27	61.28	0.3	389.70	58.76
1.0	379.18	56.65	0.7	387.12	59.38	1.5	403.09	61.23	0.3	389.36	58.70
1.0	378.44	56.69	1.0	388.57	58.86	1.5	404.68	61.37	0.5	389.33	58.62
1.5	382.95	56.95	1.0	388.87	59.03				0.5	389.91	58.93
1.5	382.20	56.63	1.0	388.68	58.94				0.5	389.99	58.72
1.5	383.64	57.31	1.0	389.46	59.18				0.5	390.17	58.90
1.5	383.55	57.31	1.5	393.25	59.32				0.7	389.89	58.72
1.5	383.72	57.35	1.5	392.86	59.24				0.7	391.04	59.10
			1.5	393.42	59.42				0.7	390.49	58.87
			1.5	392.49	59.09				0.7	391.32	59.03
									0.9	391.25	58.94
									0.9	391.33	58.94
									0.9	391.55	58.78
									0.9	391.89	58.88
									0.9	391.89	58.99
									1.1	393.05	58.83
									1.1	392.94	58.89
									1.1	392.83	59.02
									1.1	392.94	58.81

Table 2. Slopes obtained from the fitting of $E_j + C$ vs. I of KCl for electrodes A and B (data from [17]) at three different temperatures.

	Temperature		
	15 °C	25 °C	35 °C
Electrode A	1.1 ± 0.2	1.43 ± 0.18	2.2 ± 0.5
Electrode B	–	1.53 ± 0.40	–

compared. Although a linear relationship is found, the variation of E_j with the ionic strength of solution is not very big, as would be expected taking into account that a saturated KCl salt bridge was used [14] and the ionic strength of the solution was adjusted using an excess of KCl.

- In electrode C, the liquid junction potential remains constant, as can be seen in Figure 1b. However, it is not possible to calculate its magnitude because the constant C includes the asymmetry potential. Since for this electrode E_j is constant, the variation of the formal potential with ionic strength must be due to a variation of the activity coefficient of the proton in the solution where the electrode is dipped, Equation 5. Figure 2 shows the experimental plot of $E^{0'}(M)$ vs. I (M) together with the calculated curve of $s \log \gamma_{H^+}$ vs. I (M), where γ is the activity coefficient in the molarity scale [17]. The curve has been shifted 396.4 mV along the vertical axes, which corresponds to the constants that appear in Equation 5, viz. E_{as} , E_j and $s \log(H^+)_{int}$. The similarity between the curve and the experimental points is excellent, especially if we consider that it is assumed that the real activity coefficient can be precisely calculated with Pitzer equations.

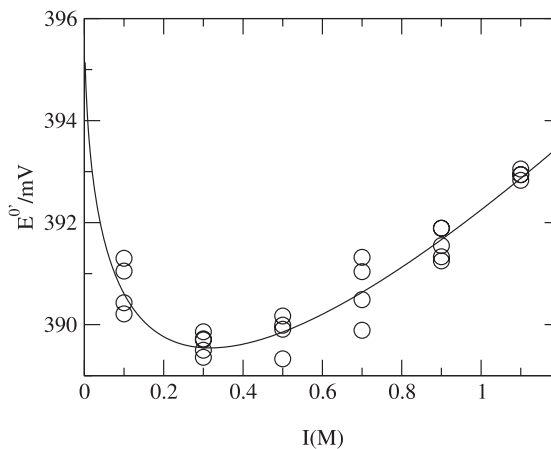


Fig. 2. Dependence of formal potential, $E^{0'}$, with ionic strength at 25 °C and KCl as background electrolyte. Solid line represents $s \log \gamma_{H^+}$, where the proton activity coefficient has been calculated using Pitzer equations.

The activity coefficient of the proton in the internal solution has been used to calculate E_{rep} . Two comments must be mentioned:

- Pitzer equations describe the activity coefficient of species at high ionic strength ($I > 2$ m) when the mixing parameters are included. Although it is possible to use Pitzer equations at 25 °C, double and triple interaction parameter for mixtures, θ and ψ , are not tabulated either at 15 °C or at 35 °C and they can not be calculated, because their temperature dependence is not known. Since the saturated KCl concentration is about 4 m, the mixing parameters could have a big influence. In

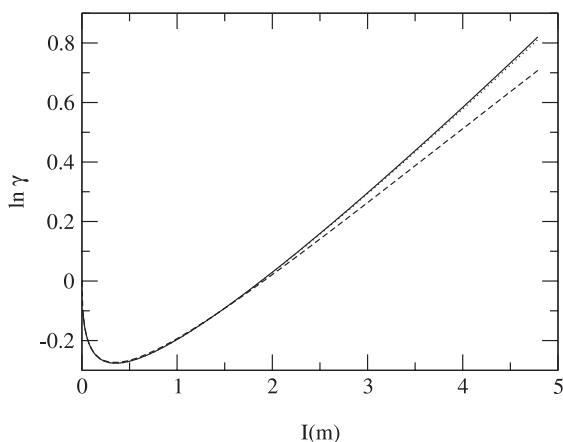


Fig. 3. ----) Full Pitzer equation for proton activity coefficient, including the terms C^ϕ , θ and ψ . —) Pitzer equation for proton activity coefficient, including the term C^ϕ but not θ and ψ Pitzer equation for proton activity coefficient without including the terms C^ϕ , θ and ψ . In all cases KCl is the background electrolyte.

Figure 3 activity coefficients are compared when the above-mentioned Pitzer parameters at 25 °C have been and have not been included. Figure 3 clearly shows that curves have an increasing different trend as ionic strength increases.

- A glass membrane is not expected to show a perfect Nernstian response in a medium with such a high alkaline ion concentration.

However, at a constant temperature, $\gamma_{\text{H}^+_{\text{int}}}$ is going to be a constant because the concentration of the internal solution remains unchanged. Therefore, none of the two problems mentioned above will affect the slope listed in Table 2 (it could affect the intercept of the $E^{0'}$ vs. I plot). As will be explained below, the dependence of $\log \gamma_{\text{H}^+_{\text{int}}}$ vs. temperature has to be taken into account in order to explain the E_{rep} vs. temperature dependence.

4.2. Dependence of E_{rep} with Temperature

Figure 4 shows a E_{rep} vs. t (°C) plot at 0.2, 1.0 and 1.6 ionic strengths. A linear relationship is held in the temperature and

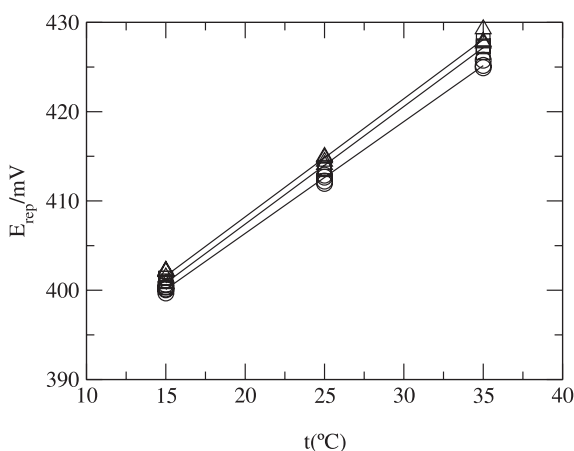


Fig. 4. E_{rep} vs. t for electrode A. ○) $I=0.2$ m, □) $I=1.0$ m, Δ) $I=1.6$ m.

Table 3. Slopes obtained from the fitting of $E_j + C$ vs. t for electrode A at several ionic strengths of KCl.

	Ionic strength		
	0.2 m	1.0 m	1.6 m
Slope	1.25 ± 0.01	1.32 ± 0.02	1.32 ± 0.02
y axes intercept	381.3 ± 0.4	381.1 ± 0.4	381.7 ± 0.6

ionic strength ranges studied. Slopes of the linear fit, listed in Table 3, match up within fitting error.

Going back to Equation 5, E_{rep} is equal to $E_j + E_{\text{as}} - s \log m_{\text{H}^+_{\text{int}}}$; hence, the temperature dependence observed in Figure 4 can be ascribed to two different factors:

- 1) a possible temperature dependence of E_j , which is unknown;
- 2) temperature dependence of the $-s \log m_{\text{H}^+_{\text{int}}}$ term. $s = RT \ln 10/F$ therefore a linear relationship with temperature is held, with a slope equal to $-\log m_{\text{H}^+_{\text{int}}} R \ln 10/F$. If the concentration of protons in the inner solution is known, the contribution to E_{rep} of the last term could be calculated. An approximation to that concentration can be done calculating the concentration that makes $E=0$ (see Equations 2 and 3) for calibration straight lines of Table 1. When $E=0$ proton the activities at both sides of the glass membrane are approximately the same (neglecting E_{as} and E_j). Activity coefficients have already been calculated with Pitzer equations thus the proton concentration in the inner solution can be solved. $-\log m_{\text{H}^+_{\text{int}}} = 7.00$ has been obtained using this approximation. Using this value, the contribution of $-s \log m_{\text{H}^+_{\text{int}}}$ to the E_{rep} temperature dependence will be:

$$-\frac{\log m_{\text{H}^+_{\text{int}}} RT \ln 10}{F} = 1.39T \quad (9)$$

As an example, if $E_{\text{as}} + E_j = 10$ then the slope of the E_{rep} vs. t plot would be 1.42 mV/degree while if $E_{\text{as}} + E_j = -10$ then the slope would be 1.36 mV/degree.

Since linear relationship observed in the E_{rep} vs. t plot has a slope value close to 1.3 (Table 3), the variation with temperature of the formal potential appears to be due to the term $-\log m_{\text{H}^+_{\text{int}}} RT \ln 10/F$. This term is non-ionic-strength dependent and it will be the same for the three series of data shown in Figure 4. The small shift observed in Figure 4 for the fitting lines can be ascribed to the variation of E_j with ionic strength obtained for the electrode (see section 4.1).

As is stated elsewhere [18], the dependence of E_j upon temperature has not received too much study. It is expected that E_j would change with temperature owing to the modification of the activity coefficients and the mobility of ions. However, calculations of such changes [18] show that the temperature dependence of E_j , -0.16 mV degree $^{-1}$ or less, would be at least one order of magnitude smaller than the dependence obtained for the $-\log m_{\text{H}^+_{\text{int}}} RT \ln 10/F$ term.

5. Conclusions

It can be concluded that although it would be expected that the liquid junction potential would change with the temperature, the big change of $E^{0'}$ vs. t (approximately 1 mV per degree) can be ascribed to the term $-s \log m_{\text{H}^+_{\text{int}}}$ and the variation of E_j with

temperature is within the experimental error in the experimental conditions.

6. Appendix

The relationship of $\log \gamma_{\text{H}^+}$ with I was studied in the light of the Pitzer equations [15], which have frequently been used to describe the influence of ionic strength on the activity coefficients for strong electrolytes at moderate to high concentrations. Based on Pitzer's formalism, the activity coefficient for the H^+ ion in the presence of excess electrolyte 1:1, KCl, is given by:

$$\ln \gamma_{\text{H}^+} = f^\gamma + 2I(B_{\text{ClH}} + IC_{\text{ClH}}) + I^2(B'_{\text{ClK}} + C_{\text{ClK}}) + I(2\theta_{\text{HK}} + I\psi_{\text{HClK}}) \quad (\text{A.1})$$

where the ionic strength is determined from the salt concentration since the salt is in a large excess relative to the proton. f^γ , B and B' are functions depending on the ionic strength and they have the usual meaning given in Pitzer equations [15, 17]; C , θ and ψ are interaction parameters for different ions. Substituting B and B' in the expression for the logarithm of the activity coefficient of H^+ ion yields:

$$\ln \gamma_{\text{H}^+} = f^\gamma + PI + QI^2 + RIe^{-2\sqrt{I}} + T[1 - (1 + 2\sqrt{I})e^{-2\sqrt{I}}] \quad (\text{A.2})$$

where

$$\begin{aligned} P &= 2(\beta_{\text{HCl}}^{(0)} + \theta_{\text{HK}}) = 0.3650 \\ Q &= C_{\text{HCl}}^\phi + \frac{C_{\text{KCl}}^\phi}{2} + \psi_{\text{HClK}} = -0.00662 \\ R &= \beta_{\text{KCl}}^{(1)} = 0.2122 \\ T &= \beta_{\text{HCl}}^{(1)} - \frac{\beta_{\text{KCl}}^{(1)}}{2} = 0.1884 \end{aligned} \quad (\text{A.3})$$

P , Q , R and T are thus constants that depend on the particular inert electrolyte [15]. The values in the above equations have been calculated using interaction parameters of KCl at 25 °C. But in the present work some experiences have been done at other temperatures than 25 °C, viz. 15 and 35 °C, thus it has been necessary to calculate the parameter values at these temperatures. If the temperature derivative, $\partial\beta^{(0)}/\partial T$, of a parameter is known together with the value of the parameter at a certain temperature, $\beta^{(0)}(T_0)$, then the value at another temperature T_1 , will be given by:

$$\beta_{\text{KCl}}^{(0)}(T_1) = \beta_{\text{KCl}}^{(0)}(T_0) + \frac{\partial\beta_{\text{KCl}}^{(0)}(T)}{\partial T}(T_1 - T_0) \quad (\text{A.4})$$

Temperature derivatives of parameters of single electrolytes are listed in reference [15]. Although parameters of mixtures of electrolytes, θ and ψ , are tabulated, the temperature derivatives are not. However, if the experimental ionic strength is not very

high (less than 2 m), the influence of these parameters can be neglected.

The activity coefficient of proton in the solution where the inner reference electrode is dipped corresponds to the activity coefficient of proton in a solution of saturated KCl. Interpolating the solubility data from [16], the solubility at working temperature can be calculated. The activity coefficient of protons is obtained solving Equation A.2 at that concentration of the inert electrolyte. Mixing interaction parameters have not been used because their temperature dependence is unknown.

A_ϕ is tabulated at several temperatures in reference [15]; values at the desired temperatures have been interpolated from those data.

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