

Determination of Hydrogen Single Ion Activity Coefficients in Aqueous HCl Solutions at 25°C

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The single ion activity coefficients of hydrogen and chloride ions in aqueous HCl solutions have been estimated at 25°C at concentrations up to 1 mol·kg⁻¹, using potentiometric measurements with ion-selective electrodes and appropriate calibration procedures. Two methods are described for an internal calibration of the electrodes in the extended Debye–Hückel concentration range. The results are compared to the conventional pH calibration with external buffer solutions. Since the latter calibration method does not account for the liquid junction potential E_J which arises at the reference electrode, the resulting activity coefficients are quite different in HCl solutions of higher concentration. These differences between internal and external calibration decrease significantly, when a correction for E_J is introduced into the conventional pH calibration. Hence, in solutions of higher ionic strength the accuracy of the conventional pH electrode calibration using buffer solutions is very limited, when exact H⁺ activities are required. The consistency of the results indicates that the liquid junction potentials in the examined systems calculated by the Henderson/Bates approximation are of reasonable precision.

KEY WORDS: Ions; activity coefficients; single ion activity coefficients; pH measurement; liquid junction potential; diffusion potential; ion-selective electrodes.

SYMBOLS

A_m (kg ^{1/2} ·mol ^{-1/2})	Debye–Hückel constant
a_i	activity of the ion i
c_+ , c_- (mol·L ⁻¹)	molarity of the cation or anion
E (V)	ISE potential
E^0 (V)	ISE standard potential
E_J (V)	diffusion potential (reference electrode)

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E_J^H (V)	diffusion potential of the Henderson/Bates equation
F (C·mol ⁻¹)	Faraday constant, $F = 96484.56$ C·mol ⁻¹
I_m (mol·kg ⁻¹ solvent)	ionic strength, $I_m = 1/2 \sum_i z_i^2 m_i$
m (mol·kg ⁻¹ solvent)	molality
m_+, m_- (mol·kg ⁻¹ solvent)	molality of the cation or anion
R (J·mol ⁻¹ ·K ⁻¹)	gas constant, $R = 8.3143$ J·mol ⁻¹ ·K ⁻¹
S, S_+, S_- (V)	electrode slope
T (K)	temperature
z_+, z_-	valency of the cation or anion
Λ_+^0, Λ_-^0 (m ² = Ω ⁻¹ ·mol ⁻¹)	electrical conductivity at infinite dilution of the cation or anion
γ_+, γ_-	rational activity coefficient of the cation or anion, based on the hypothetical state of an ideally diluted solution of 1 mol·kg ⁻¹

1. INTRODUCTION

The knowledge of ion activities instead of concentrations is very important in manifold cases involving electrolyte systems. Of course, physical and chemical equilibria can be calculated using mean activity coefficients; but for the characterization of transport phenomena as well as (re)activities of single species in electrolyte systems, individual ion activity coefficients are necessary. While mean ionic activities are accessible by various measuring methods, the single ion activity coefficients can be estimated experimentally using ion-selective electrodes (ISE).

The best known application of ion-selective electrodes is the measurement of the pH value, *i.e.* the hydrogen ion activity.

The precision of the potentiometric measurement of ion activities is limited by the occurrence of the liquid junction potential, which arises at the diaphragm of the reference electrode due to diffusion. This junction potential can neither be exactly calculated nor experimentally measured. In principle, an exact determination of single ion activity coefficients is not possible. However, the mean ionic activity coefficients of a dissolved electrolyte, which are calculated from the individual ion activities of the cations and anions, are independent of the liquid junction potential. In this case the diffusion potential is eliminated during the calculation, as explained later.

By the introduction of simplifying assumptions, the magnitude of the liquid junction potential E_J can be estimated theoretically. These values are subsequently used for the estimation of reasonable single ion activity coefficients.

The present paper continues a previous work, where the determination of Na⁺, K⁺, Ca²⁺, and Cl⁻ single ion activity coefficients in aqueous solutions of NaCl, KCl, and CaCl₂ was described.⁽¹⁾

In this work, aqueous HCl solutions in the concentration range between 0.002 and 1 mol·kg⁻¹ are investigated. The principle of the experimental determination, the analysis of the data and the results will be presented, including a comparison with conventionally measured pH values by external calibration with buffer solutions. Additionally, the influence of the background electrolyte CaCl₂ (constant concentration of 1 mol·kg⁻¹) on the pH value of the HCl solutions is examined.

2. EXPERIMENTAL

The experimental setup consisted of a chloride ion-selective electrode and a glass membrane pH electrode, which were immersed into aqueous HCl solutions of different concentrations, starting with 0.002 mol·kg⁻¹ up to 1 mol·kg⁻¹. These individual solutions were diluted from standard HCl concentrates (0.01 and 1.0 mol·kg⁻¹, Riedel-de Haën). The particular potentials against a Ag/AgCl reference electrode were recorded.

The electrodes were purchased from Metrohm (solid-state chloride ISE and Ag/AgCl reference electrode with ceramic diaphragm and 3 mol·L⁻¹ KCl as reference electrolyte) and WTW (glass membrane pH electrode, SenTix 81), respectively. The potential differences were measured with an ion meter pH340/ION with a resolution of 0.1 mV delivered by WTW. The temperature of all solutions was kept at 25.0°C using a constant temperature bath (Haake V26-DC10). The ultrapure water used for the dilution of the HCl standards and for the preparation of the KCl and buffer solutions was processed with a Milli-Q RG purification system (Millipore) from deionized water. The specific electrical resistance was always proven to be larger than $18 \times 10^6 \Omega\text{-cm}$. All chemicals were purchased from Fluka ("puriss. p.a."). KCl for preparation of the reference electrolyte was oven-dried at 105°C for 48 h and cooled in a desiccator prior to use. CaCl₂ hexahydrate was taken from freshly opened packages without further treatment, and the stoichiometric crystal water content of this salt was verified by ion chromatography and was taken into account for calculation of the total water content of the prepared HCl solution.

3. CALCULATION OF ACTIVITY COEFFICIENTS

For the calculation of individual ion activity coefficients from electrical potential measurements, a generalized form of the Nernst equation for the ionic species, *i*, is used:

$$E_i = E_i^0 + S \ln a_i + E_J \quad (1)$$

with E_i^0 as the standard potential, $a_i = m_i \gamma_i$ as the activity, and E_J as the liquid junction potential, which arises at the diaphragm of the reference electrode due to unequal diffusion velocities and activities of the ionic species. According to

Nernst, the slope S of an ideal electrode is given by

$$S = \frac{RT}{zF} \quad (2)$$

The value of the liquid junction potential, E_J , is estimated with the Henderson approximation, modified by Bates.⁽²⁾ The approximation neglects the activity coefficients and assumes linear concentration gradients within the diaphragm. The required diffusion coefficients of the involved ions are substituted by the equivalent conductances at infinite dilution, Λ^0 , disregarding the concentration dependence. This substitution has been proven before as being reasonable.⁽³⁾ With these assumptions the liquid junction potential between solutions 1 and 2 can be estimated by

$$\begin{aligned} E_J^H &= E_2^H - E_1^H \\ &= \frac{RT}{F} \frac{(\sum \Lambda_+^0 c_+ - \Lambda_-^0 c_-)_1 - (\sum \Lambda_+^0 c_+ - \Lambda_-^0 c_-)_2}{(\sum \Lambda_+^0 z_+ c_+ + \sum \Lambda_-^0 |z_-| c_-)_1 - (\sum \Lambda_+^0 z_+ c_+ + \sum \Lambda_-^0 |z_-| c_-)_2} \\ &\quad \times \ln \frac{(\sum \Lambda_+^0 z_+ c_+ + \sum \Lambda_-^0 |z_-| c_-)_1}{(\sum \Lambda_+^0 z_+ c_+ + \sum \Lambda_-^0 |z_-| c_-)_2} \end{aligned} \quad (3)$$

Following the common convention, index 1 refers to the measurement solution and index 2 to the reference solution.

The determination of the standard potential and, if required, of the slope of the ion-selective electrodes is performed by an internal calibration within the range of validity of the extended Debye–Hückel equation (up to 0.01 mol·kg⁻¹). In this range the ion activity coefficients can be estimated with sufficient precision by

$$\log \gamma_i = -\frac{A_m z_i^2 \sqrt{I_m}}{1 + \sqrt{I_m}} \quad (4)$$

The internal calibration can be performed in two different ways. In the bi-parametric adjustment, the slope, S , and the standard potential, E^0 , are adjusted to the measured potential data of the extended Debye–Hückel range by linear regression. This adjustment is done similar to the method of Koshkbarchi and Vera,⁽⁴⁾ but without the described “dimensionless” calculation to reduce the data, since this step does not change the results at all. At this point it should be mentioned that the paper of Koshkbarchi and Vera,⁽⁴⁾ as well as several follow-up articles of Vera’s work group, contains an error in the sign of the calculated liquid junction potential. Arising from different sign conventions for electrode potentials, this error resulted in incorrect single ion activity coefficients. The false values of E_J and the single ion activity coefficients are now corrected in a revised version.⁽⁵⁾ The other possibility of internal calibration is the single parametric adjustment

according to Harned and Ehlers,^(6,7) where the electrodes are expected to show Nernstian behavior. The slope is therefore set to $S = R \cdot T \cdot (z \cdot F)^{-1}$, and the standard potential, E^0 , is calculated by linear regression of the measured potentials in the extended Debye–Hückel range.⁽⁸⁾

According to Eq. (1), in the case of a 1:1 electrolyte with univalent ions ($z_+ = 1$ and $z_- = -1$) the ion activity coefficients—related to the standard state of an ideally diluted solution of $1 \text{ mol}\cdot\text{kg}^{-1}$ —are calculated by

$$\ln \gamma_+ = \frac{1}{|S_+|} (E_+ - E_+^0 - E_J) - \ln m \quad (5)$$

$$\ln \gamma_- = -\frac{1}{|S_-|} (E_- - E_-^0 - E_J) - \ln m \quad (6)$$

with $m = m_+ = m_-$ as the molality of the dissolved electrolyte.

To show that E_J is eliminated during the calculation of the mean activity coefficients, γ_{\pm} , one can assume that the result of the Henderson/Bates approximation for the liquid junction potential may noticeably differ from the actual value of E_J . In this case an error, ΔE_J , may occur, which in turn causes an error $\Delta \ln \gamma$ of the calculated single ion activity coefficients:

$$E_J = E_J^H + \Delta E_J \quad (7)$$

Considering this, the individual ion activity coefficients can be expressed by

$$\ln \gamma_+^H = \frac{1}{|S_+|} (E_+ - E_+^0 - E_J + \Delta E_J) - \ln m = \ln \gamma_+^{\text{exact}} + \Delta \ln \gamma_+ \quad (8)$$

$$\ln \gamma_-^H = -\frac{1}{|S_-|} (E_- - E_-^0 - E_J - \Delta E_J) - \ln m = \ln \gamma_-^{\text{exact}} - \Delta \ln \gamma_- \quad (9)$$

with

$$\Delta \ln \gamma_+ = \frac{\Delta E_J}{|S_+|}, \quad \Delta \ln \gamma_- = \frac{\Delta E_J}{|S_-|} \quad (10)$$

The internal calibration with single parametric adjustment assumes that both slopes S_+ and S_- of the ion-selective electrodes are of equal magnitude of opposite sign. In this case, an error, $\Delta \ln \gamma_+ = \Delta \ln \gamma_- = \Delta \ln \gamma$, of the single ion activity coefficients is completely eliminated in the calculation of the mean activity coefficients, γ_{\pm} :

$$\begin{aligned} \ln \gamma_{\pm} &= \frac{1}{2} (\ln \gamma_+ + \ln \gamma_-) = \frac{1}{2} (\ln \gamma_+^{\text{exact}} \\ &\quad + \Delta \ln \gamma_+ + \ln \gamma_-^{\text{exact}} - \Delta \ln \gamma_-) = \ln \gamma_{\pm}^{\text{exact}} \end{aligned} \quad (11)$$

In the case of the bi-parametric adjustment, a minor influence of the liquid junction potential is left in the calculation of the mean activity coefficients, since both slopes S_+ and S_- usually differ a little when determined by internal calibration.

The elimination of the liquid junction potential, shown here for a 1:1 electrolyte, is valid in general for all types of electrolytes.

To compare the internal calibration with the commonly used external calibration, the pH electrode is also calibrated conventionally with standard buffer solutions, using the same experimental setup for the potential measurement. For this purpose a two-point calibration with buffer solutions prepared according to NIST is used. Buffer solution 1 (pH = 4.01 at 25.0°C) is a 0.05 mol·kg⁻¹ potassium hydrogen phthalate solution. Buffer solution 2 contains 0.025 mol·kg⁻¹ KH₂PO₄ and 0.025 mol·kg⁻¹ Na₂HPO₄ (pH = 6.87 at 25.0°C). To control the validity of the calibration, the pH of a standard solution (pH = 1.01 at 25.0°C, Merck) is tested.

The diffusion potentials are estimated according to Henderson/Bates using the concentrations and equivalent conductances at infinite dilution of all ions present in the solutions.

The concentrations of the different ionic species in the equilibrated buffer solutions (pH 4.01 and pH 6.87) are calculated from the weighed portions of salts with a FORTRAN program for the minimization of the Gibbs energy.⁽⁹⁾ Most standard values of the Gibbs energy of formation in aqueous solution, $\Delta_f G^0$, are taken from the literature.⁽¹⁰⁾ Since published values for the phthalic acid species could not be found, and since only the difference between the Gibbs energies of formation of the species is required for the calculation of concentrations in equilibrium, $\Delta_f G^0$ of phthalic acid in aqueous solution was arbitrarily set to -700 kJ·mol⁻¹. The difference is then calculated by using the tabulated acid dissociation constants.

Tables I and II show the results of these calculations for both buffer solutions.

The hydrogen phthalate equivalent conductance at infinite dilution is estimated to be approximately 30×10^{-4} m²·S·mol⁻¹, as the result of a comparison

Table I. Thermodynamic Data: Potassium Hydrogen Phthalate Buffer^{a(11)}

	$\Delta_f G^0$ (kJ·mol ⁻¹)	m (mol·kg ⁻¹)	Λ^0 (10 ⁻⁴ m ² ·S·mol ⁻¹)
K ⁺	-283.27	0.05	73.541
HPh ⁻	-683.16 ^b	0.04378	30 (estimated)
Ph ²⁻	-652.17 ^b	0.00317	52.3
H ₂ Ph	-700 (set)	0.00305	—
H ⁺	0	0.000119	349.81

^aIonic strength $I_m = 0.05329$ mol·kg⁻¹, pH (set point) = 4.01, and pH (calculated for control) = 4.016.

^bCalculated from $\Delta_r G = -\ln(K) \cdot RT$ with $pK_1 = 2.89$ and $pK_2 = 5.51$.⁽¹²⁾

Table II. Thermodynamic Data: Potassium Dihydrogen Phosphate + Sodium Hydrogen Phosphate Buffer^{a(11)}

	$\Delta_f G^0$ (kJ·mol ⁻¹)	m (mol·kg ⁻¹)	Λ^0 (10 ⁻⁴ m ² ·S·mol ⁻¹)
K ⁺	-283.27	0.025	73.541
Na ⁺	-261.905	0.050	50.092
PO ₄ ³⁻	-1018.70	<10 ⁻⁶	Negligible concentration, not required
HPO ₄ ²⁻	-1089.15	0.025	
H ₂ PO ₄ ⁻	-1130.28	0.025	33.0
H ₃ PO ₄	-1142.54	<10 ⁻⁶	—
H ⁺	0	<10 ⁻⁶	349.81

^aIonic strength $I_m = 0.1000$ mol·kg⁻¹, pH (set point) = 6.87, and pH (calculated for control) = 6.858.

with the value for phthalate (52.3), and the relation between oxalate (74.11) and bioxalate (40.2). A variation of this roughly estimated value between 25×10^{-4} and 35×10^{-4} m²·S·mol⁻¹ results only in a minor deviation of the calculated E_J , (± 0.08 mV) and of the pH value (± 0.001), which is smaller than the resolution of the potentiometer (± 0.1 mV) or the accuracy of the ion-selective electrodes. Hence, a moderate error of the estimation is tolerable.

With 3 mol·L⁻¹ KCl as the reference electrolyte, the diffusion potential at the liquid junction with the buffer solutions yields

$$\text{buffer pH 4.01: } E_J = -2.78 \text{ mV}$$

$$\text{buffer pH 6.87: } E_J = -2.72 \text{ mV}$$

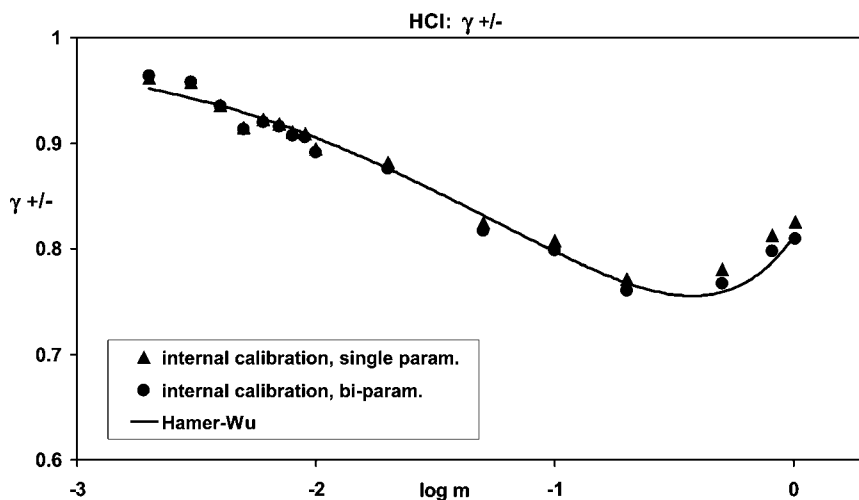


Fig. 1. Mean ion activity coefficients $\gamma_{\text{HCl}}^{\pm}$.

Table III. Activity Coefficients of HCl Obtained From ISE Measurements (Concentration Range for the Parameter Adjustments up to $m = 0.01 \text{ mol}\cdot\text{kg}^{-1}$)^a

$m_{\text{HCl}} (\text{mol}\cdot\text{kg}^{-1})$	$\gamma_{\pm} (1\text{p})$	$\gamma_{\pm} (2\text{p})$	$\gamma_{\pm} (\text{Hamer-Wu})$	$\gamma_{+} (1\text{p})$	$\gamma_{+} (2\text{p})$	$\gamma_{-} (1\text{p})$	$\gamma_{-} (2\text{p})$
0.002	0.962	0.963	0.952	0.970	0.976	0.954	0.952
0.003	0.958	0.958	—	0.950	0.956	0.966	0.960
0.004	0.936	0.935	—	0.933	0.939	0.939	0.931
0.005	0.915	0.913	0.929	0.905	0.911	0.925	0.915
0.006	0.923	0.920	—	0.915	0.921	0.930	0.919
0.007	0.918	0.916	—	0.916	0.922	0.921	0.909
0.008	0.910	0.907	—	0.901	0.907	0.920	0.907
0.009	0.909	0.906	—	0.900	0.906	0.919	0.905
0.010	0.895	0.891	0.905	0.876	0.881	0.915	0.901
0.020	0.882	0.876	0.876	0.888	0.894	0.877	0.859
0.050	0.825	0.817	0.832	0.860	0.866	0.792	0.770
0.101	0.808	0.798	0.797	0.906	0.913	0.720	0.697
0.201	0.771	0.760	0.768	0.910	0.918	0.653	0.629
0.506	0.780	0.767	0.759	1.043	1.053	0.583	0.559
0.814	0.813	0.798	0.785	1.164	1.175	0.567	0.541
1.022	0.825	0.809	0.811	1.201	1.213	0.567	0.540

^a1p: internal calibration, single parametric adjustment; 2p: = internal calibration, bi-parametric adjustment; and γ_{\pm} : mean activity coefficient.

4. RESULTS AND DISCUSSION

Figure 1 shows the mean ion activity coefficients of HCl ($\gamma_{\pm\text{HCl}}$), calculated from γ_{+} and γ_{-} .

The values in Table III are the average of four measurement series. The reference data for the mean ion activity coefficients are taken from Hamer and Wu.⁽¹³⁾

It can be seen that the values for γ_{\pm} obtained after bi-parametric adjustment are in slightly better agreement with the reference data from Hamer and Wu, compared to the data from a single parametric adjustment, particularly in the medium and high concentration range. The average deviation of the results from the literature data in the given concentration range is 0.5% in case of the bi-parametric adjustment, compared to 1.5% in case of the single parametric method.

Figures 2 and 3 present the determined individual ion activity coefficients of H_3O^{+} (γ_{+}) and chloride (γ_{-}) as a function of the common logarithm of HCl molality.

In the case of internal calibration, the results for single and bi-parametric adjustment are depicted. The concentration region for the internal calibration procedure equals the extended Debye–Hückel range between $\log m = -3$ and $\log m = -2$.

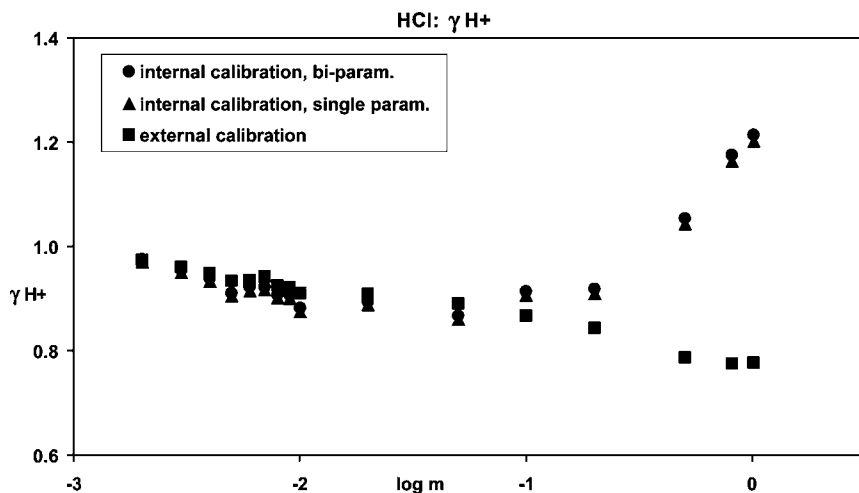


Fig. 2. Individual ion activity coefficients γ_{H^+} as a function HCl molality.

The pH values obtained from the conventional external buffer calibration are converted into γ_{+}^H by the equation (see Table IV):

$$\gamma_{+}^H = \frac{10^{-pH}}{m} \tag{12}$$

These activity coefficients are also plotted in Fig. 2 (squares).

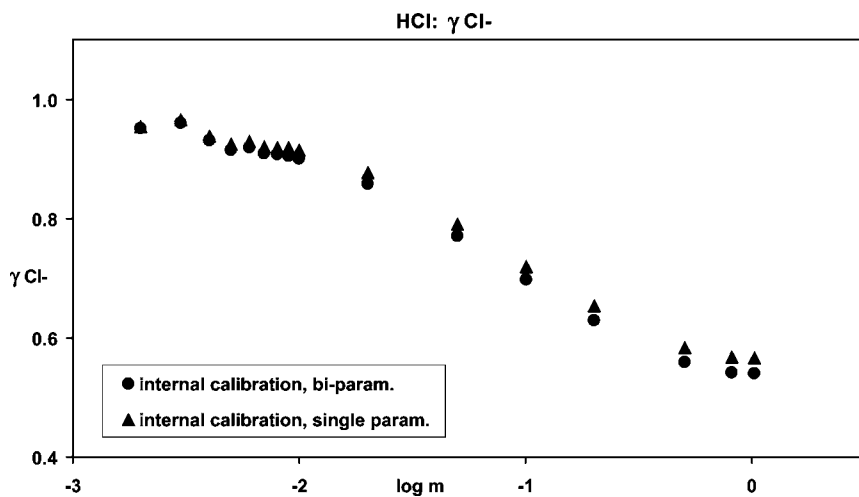


Fig. 3. Individual ion activity coefficients γ_{Cl^-} as a function of HCl molality.

Table IV. Comparison of pH Values Obtained From Internal Calibration (Single Parametric Adjustment, 1p) and From External Buffer Calibration (bc)^a

m_{HCl} (mol·kg ⁻¹)	γ_+ (1p)	pH (1p)	γ_+ (bc)	pH (bc)
0.002	0.970	2.71	0.973	2.71
0.003	0.950	2.54	0.960	2.54
0.004	0.933	2.43	0.949	2.42
0.005	0.905	2.34	0.934	2.33
0.006	0.915	2.26	0.936	2.25
0.007	0.916	2.19	0.942	2.18
0.008	0.901	2.14	0.925	2.13
0.009	0.900	2.09	0.922	2.08
0.010	0.876	2.06	0.910	2.04
0.020	0.888	1.75	0.908	1.74
0.050	0.860	1.37	0.890	1.35
0.101	0.906	1.04	0.867	1.06
0.201	0.910	0.74	0.844	0.77
0.506	1.043	0.28	0.786	0.40
0.814	1.164	0.02	0.775	0.20
1.022	1.201	-0.09	0.777	0.10

^a 1p: single parametric adjustment; bc: buffer calibration; pH (1p): calculated from γ_+ (1p); and γ_+ (bc): calculated from measured pH (bc).

The results for γ_+ and γ_- from the two internal calibration methods are similar, but not identical. The deviation between the individual activity coefficients of both adjustment methods is smaller in the case of H⁺. The differences can be attributed to a non-Nernstian behavior of the ion-selective electrodes. The single parametric fit neglects possible deviations of the actual electrode slope from Nernstian behavior. In contrast, the slope is the second adjustable parameter of the bi-parametric method. Consequently, experimental deviations from the Nernstian behavior are taken into account here.

A comparison of these data with the activity coefficients obtained from the conventional pH measurement after external calibration with buffer solutions (see Fig. 2) is of particular interest.

The values for γ_+^{H} from internal and external calibration methods agree well at low and medium ionic strength, but starting from a molality of 0.1 mol·kg⁻¹ the differences increase. These differences arise from the diffusion potential.

In the conventional determination of pH values, using external buffers for calibration of the electrode, the change in the liquid junction potential when changing from buffer solutions to the sample solution is not taken into account. This can surely be neglected at lower ionic strengths, as the liquid junction potential between the inner electrolyte of the reference electrode and the sample solution (diluted to approximately 0.1 mol·kg⁻¹ HCl) does not change much with

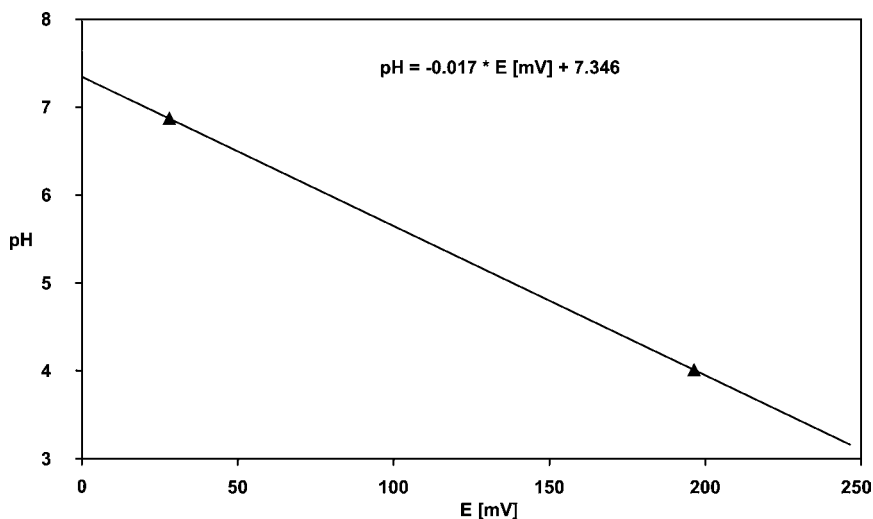


Fig. 4. E_J corrected calibration equation for the measurement of pH values (conventional two-point buffer calibration).

increasing concentration of the sample. With an inner electrolyte of 3 mol-L^{-1} KCl, the values for E_J vary between -3 and -4 mV when the sample molality increases from 0.001 to 0.1 mol-kg^{-1} . This is still close to the liquid junction potential of the reference electrode in the buffer solutions (*ca.* -2.8 mV). Yet, when higher concentrations are reached, the diffusion potential drops to -16 mV in 1 mol-kg^{-1} HCl. The difference between -2.8 and -16 mV is too large to be neglected, as is done during external calibration. In the case of the internal calibration methods, the error is corrected calculating E_J with the Henderson/Bates approximation. As a consequence, the calculated single ion activity coefficients from both calibrations are significantly different at higher concentrations. The difference in the pH values seems to be small, which is only a result in the logarithmic scale (see Fig. 4): Small differences in the pH value ($\Delta\text{pH} \approx 0.15$) are related to large differences of the ion activity coefficients ($\Delta\gamma_+^{\text{H}} \approx 0.4$), which can be read from Table IV.

To take the different liquid junction potentials into account, the electrical potentials of the pH electrode recorded in the buffer solutions of $\text{pH} = 6.87$ and 4.01 (with 3 mol-L^{-1} KCl as the reference electrolyte) are corrected with the respective E_J according to Henderson/Bates. The pH set points of the buffer solutions are then plotted against these recalculated potentials to give a corrected equation for the external calibration (see Fig. 4). The equation allows for calculation of pH values in the sample solutions, where the potentials have been corrected with the respective E_J values. These results are referred to as “external buffer calibration, E_J corrected.”

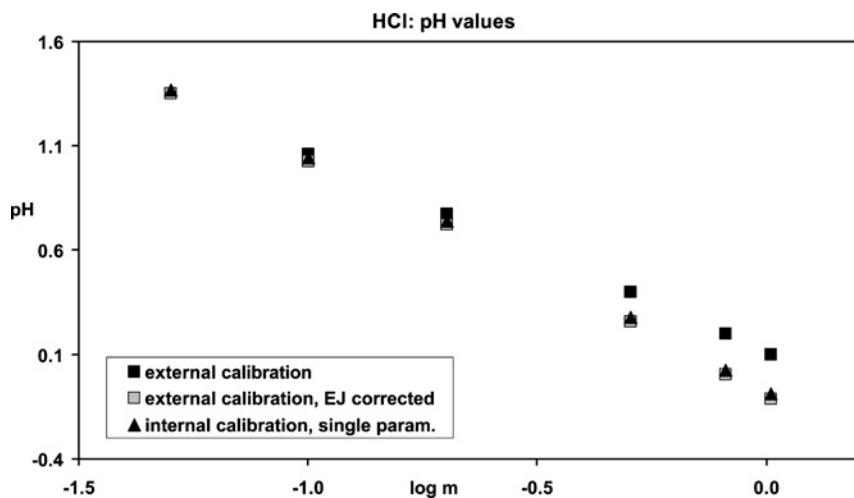


Fig. 5. Conventionally measured pH values (with and without correction of E_J) and pH values calculated from γ_{H^+} (1p) as a function of HCl molality.

If the liquid junction potentials of the buffer and sample solutions are taken into consideration during external calibration, the resulting H^+ ion activity coefficients and pH values show almost no difference to those obtained from internal calibration (see Table V and Figs. 5 and 6). As already explained, the differences between both calibration methods start to increase at a concentration of about

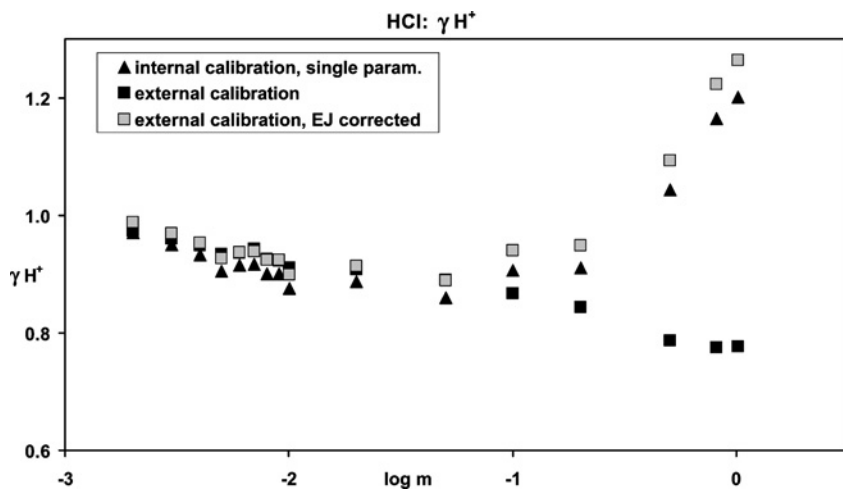


Fig. 6. H^+ individual ion activity coefficients from ISE measurements after internal and external calibration (latter with and without correction of E_J) as a function of HCl molality.

Table V. pH Values and H^+ Activity Coefficients Obtained From Single Parametric Adjustment (1p) and From Buffer Calibration (bc), Corrected with E_J^a

m_{HCl} (mol·kg ⁻¹)	pH (1p)	pH (bc)	pH (bc, E_J) corrected
0.050	1.37	1.35	1.35
0.101	1.04	1.06	1.02
0.201	0.74	0.77	0.72
0.506	0.28	0.40	0.26
0.814	0.02	0.20	0.00
1.022	-0.09	0.10	-0.11

^apH (1p): calculated from $\gamma+$ (1p), internal calibration, single parametric adjustment; pH (bc): pH from external buffer calibration; and pH (bc, E_J): pH from external buffer calibration, corrected with E_J .

0.05 mol·kg⁻¹ HCl. Hence, only concentrations of 0.05 mol·kg⁻¹ and higher are shown in Table V.

It can be seen in Figs. 5 and 6 that the differences of the ion activity coefficients and pH values of the external buffer calibration from the E_J corrected values increase with increasing HCl molality. This indicates that the prevailing liquid junction potential must not be neglected in this electrolyte system. As a second result, the correction of the measured potentials with E_J leads to similar ion activity coefficients and pH values, compared with the internal calibration of the ion-selective electrode without using buffer solutions. Both the single parametric adjustment in the extended Debye–Hückel range and the external buffer calibration give almost identical results for the pH, if E_J is accounted for. Since both methods use independent calibration procedures as described in the Experimental section, the present examination can therefore be considered as strong evidence that the Henderson/Bates approximation delivers sufficiently precise values for the liquid junction potentials in the observed systems “KCl – HCl” and “buffer – HCl.”

Additionally, the results allow a statement to be made on the quality of the commonly used external calibration with dilute buffer solutions. This method produces quite accurate pH values of dilute sample solutions with correspondingly low liquid junction potentials, which may be neglected to a certain degree. However, when external calibration is used for pH determination of higher concentrated solutions, the values are significantly different from those obtained by internal calibration. On the other hand, results of internal and external calibration are very similar, as long as E_J is accounted for in both methods. Hence, the precision of conventional pH measurements in higher concentrated sample solutions is often in sufficient, inasmuch as absolute pH values are desired.

Table VI. Comparison of pH Values of HCl Solutions with 1 mol·kg⁻¹CaCl₂ Obtained from Single Parametric Adjustment (1p) and from Buffer Calibration (bc) with E_J Correction (bc, E_J)^a

m_{HCl} (mol·kg ⁻¹)	γ_+^{H} (1p)	pH (1p)	γ_+^{H} (bc)	pH (bc)	γ_+^{H} (bc, E_J)	pH (bc, E_J)
0.002	1.109	2.70	1.539	2.56	1.039	2.73
0.003	1.181	2.50	1.664	2.35	1.105	2.53
0.004	1.258	2.35	1.723	2.21	1.177	2.38
0.004	1.273	2.24	1.775	2.10	1.190	2.27
0.005	1.290	2.16	1.820	2.01	1.205	2.19
0.006	1.344	2.07	1.876	1.93	1.256	2.10
0.007	1.323	2.02	1.884	1.87	1.236	2.05
0.008	1.323	1.97	1.879	1.82	1.235	2.00
0.009	1.339	1.92	1.898	1.77	1.251	1.95
0.018	1.415	1.60	1.982	1.45	1.320	1.63
0.045	1.422	1.20	1.945	1.06	1.325	1.23
0.090	1.491	0.87	1.939	0.76	1.388	0.91
0.180	1.554	0.55	1.931	0.46	1.445	0.59
0.452	1.810	0.09	1.885	0.07	1.681	0.12
0.727	2.059	-0.18	1.856	-0.13	1.910	-0.14
0.912	2.239	-0.31	1.820	-0.22	2.076	-0.28

^a 1p: single parametric adjustment; bc: buffer calibration; bc, E_J : buffer calibration, E_J corrected; pH (1p): calculated from γ_+^{H} (1p); and γ_+^{H} (bc): calculated from measured pH (bc).

5. EXAMINATION OF AQUEOUS HCl SOLUTIONS WITH CaCl₂ AS BACKGROUND ELECTROLYTE

In the presence of a background electrolyte, the single ion activities cannot be calculated using the extended Debye–Hückel equation for internal calibration, due to the high ionic strength. In this case, E^0 was taken from the measurements without a background electrolyte as an approximation and the electrode slope, S , is considered to follow Nernstian behavior. Therefore, the bi-parametric adjustment is not applicable here.

When a constant background concentration of CaCl₂ is present in the HCl solutions, the differences between the previously described calibration methods are even larger. The deviation of the H⁺ activity coefficients after internal calibration from the values of the conventional buffer calibration already appears at low HCl concentrations (see Table VI and Fig. 7). In the higher concentration range, even a reverse trend of the ion activity coefficients is noticeable (column 4): whereas in the case of internal calibration these values increase, a slight decrease is found for the other method.

Even at low HCl molality, the background electrolyte causes a high liquid junction potential, which is very different from E_J in the buffer solutions. With 1 mol·kg⁻¹ calcium chloride as background electrolyte, the values of E_J according to Henderson/Bates cover a range between +6.4 and -7.8 mV against

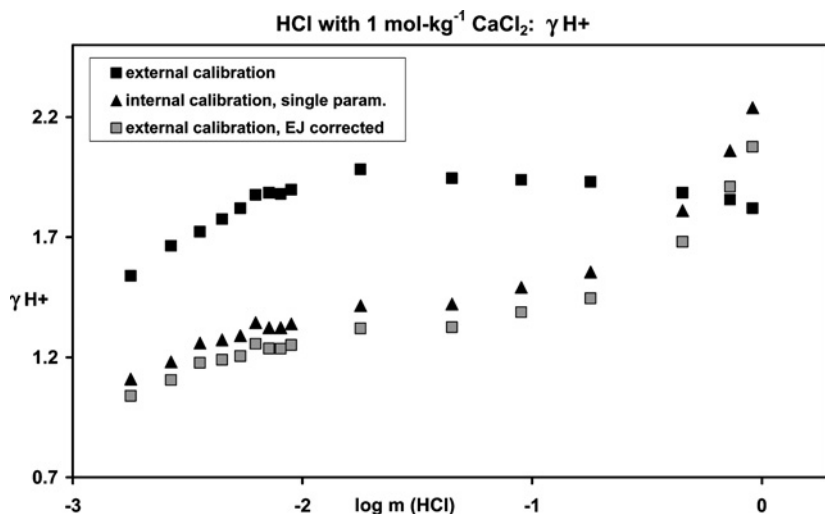


Fig. 7. H^+ individual ion activity coefficients from ISE measurements after internal and external calibration (latter with and without correction of E_J) as a function of HCl molality. Background electrolyte: $1 \text{ mol}\cdot\text{kg}^{-1} \text{ CaCl}_2$.

$3 \text{ mol}\cdot\text{L}^{-1} \text{ KCl}$, while the buffer solutions have a liquid junction potential of about -2.7 mV .

The correction of the external buffer calibration by taking the liquid junction potential into account leads again to significantly reduced differences of the H^+ ion activity coefficients between the internal and external calibration methods. By applying this correction, the previously reversed trends of the plotted lines are now in agreement.

In this case, the differences between internal and external calibration with E_J correction are slightly larger compared to those for pure HCl solutions. The reason for this may be found in the value of E^0 , which cannot be adjusted during the calibration due to the presence of a background electrolyte, as explained before. Hence, an additional error is introduced into the internal calibration by taking E^0 for pure HCl solutions.

With regard to the resulting pH values, the differences seem small, again on account of the logarithmic scale as already mentioned (see Fig. 8).

The measurements with CaCl_2 as a background electrolyte also show that in this instance the Henderson/Bates approximation is suitable for the calculation of reasonable and sufficiently accurate values of the liquid junction potential, E_J .

6. CONCLUSION

A method is introduced to estimate individual ion activity coefficients of H^+ and Cl^- in aqueous HCl solutions up to $1 \text{ mol}\cdot\text{kg}^{-1}$ based upon potentiometric

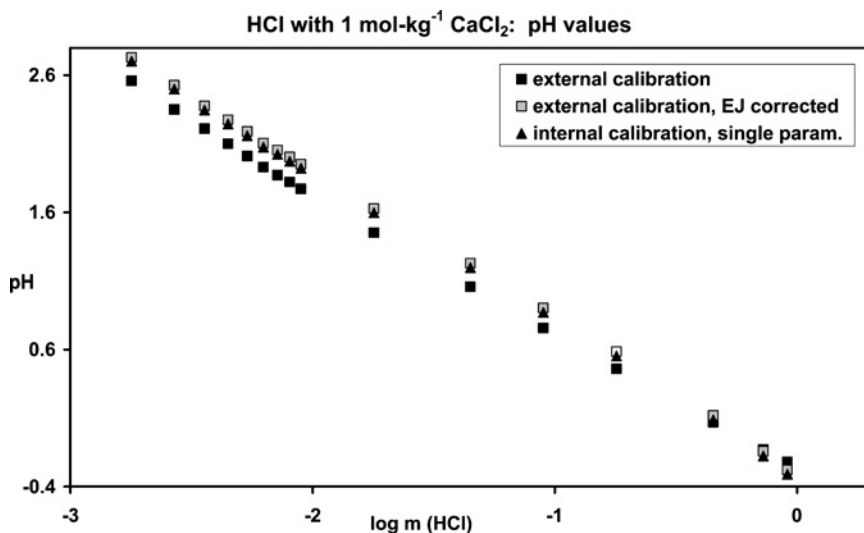


Fig. 8. pH values of HCl solutions with 1 mol·kg⁻¹ CaCl₂ background concentration, calculated from internal and external calibration methods (also E_J corrected).

measurements. During the measurement procedure, the ion-selective electrodes are internally calibrated without using external standard buffer solutions.

The present results show good agreement of the mean ion activity coefficients with reference values. In the case of H⁺, an increasing difference of the ion activity coefficients is observed at concentrations above 0.05 mol·kg⁻¹, when compared to the results of the conventional external calibration method with buffer solutions. This can be attributed to the fact that the change in the resulting liquid junction potential is neglected in usual pH measurements. This error can be corrected by considering the respective E_J values calculated according to the Henderson/Bates approximation. Using this correction of the external calibration, hydrogen ion activity coefficients and pH values are in satisfactory agreement with those obtained from internal calibration.

Since both methods are independent from each other, the present work indicates that the Henderson/Bates approximation gives access to reasonable values of the diffusion potential, E_J , which arises at the liquid junction of the reference electrolyte, KCl, with the aqueous HCl solutions. The validity of this statement for other electrolyte systems might be investigated in future work.

Additional measurements of HCl solutions containing a constant concentration of 1 mol·kg⁻¹ CaCl₂ as a background electrolyte substantiate the previous statement. Accordingly, when the measured potentials are corrected with E_J , the results of internal and external calibration are in satisfactory agreement.

As a final result, the accuracy of conventionally measured pH values using buffer solutions for calibration is significantly improved at higher ionic strengths, when the liquid junction potential is taken into account.

REFERENCES

1. A. C. Schneider, C. Pasel, M. Luckas, K. G. Schmidt, and J.-D. Herbell, *Chem. Ing. Techn.* **75**, 244 (2003).
2. R. G. Bates, *Determination of pH* (Wiley, New York, 1973).
3. A. Shatky and A. Lerman, *Anal. Chem.* **41**, 514 (1969).
4. M. K. Koshkbarchi and J. H. Vera, *AIChE J.* **42**, 249 (1996).
5. G. Wilczek-Vera, E. Rodil and J. H. Vera, *AIChE J.* **50**(2), 445 (2004).
6. H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **54**, 1350 (1932).
7. H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **55**(6), 2179 (1933).
8. M. Luckas and J. Krissmann, *Thermodynamik der Elektrolytlösungen* (Springer-Verlag, Berlin, 2001).
9. M. Luckas, *Chem. Ing. Techn.* **68**, 390–398 (1996).
10. D. D. Wagmann, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11**(Suppl. 2) (1982).
11. *CRC Handbook of Chemistry and Physics*, Vol. 5 (CRC Press, Boca Raton, FL, 1999), p. 96.
12. *CRC Handbook of Chemistry and Physics*, Vol. 8 (CRC Press, Boca Raton, FL, 1999), p. 53.
13. W. J. Hamer and Y.-C. Wu, *J. Phys. Chem. Ref. Data* **1**(4), 1047 (1972).