

Thermodynamic Model of Charging the Gas/Water Interface

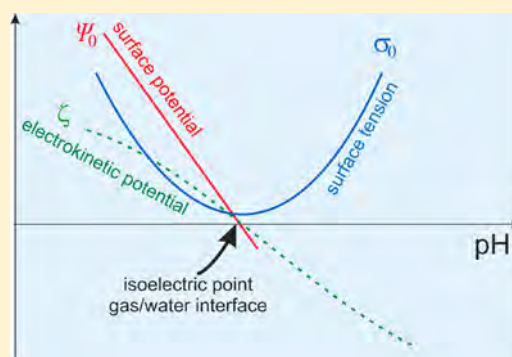
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ABSTRACT: In this work, charging of the water layer at the gas/water interface is analyzed experimentally and theoretically. Experimental data on the surface tension and surface potential in the acidic range are presented. Literature electrokinetic data indicate that the isoelectric point of the gas/water interface is pH 3.8. In the acidic region, a plot of the surface potential versus pH has a slope of 55% of the Nernstian value. The surface tension exhibits a minimum at pH 3.8. A thermodynamic model based on the distribution of ions between the bulk and the interface is developed. The interpretation of the surface and electrokinetic potential data provided equilibrium constants for the distribution of ions between the bulk and the interface and the ionization equilibrium constant of interfacial water. A significantly higher ionization of interfacial water with respect to the bulk phase was observed. The affinity of hydrogen and hydroxide ions to accumulate at the interface is higher than the affinity to accumulate in the bulk of the solution, especially for hydroxide ions. The minimum of the surface tension at the isoelectric point is presented and analyzed. The thermodynamic concept, in accordance with the Gibbs isotherm, takes into account the variation of the composition at the interface. The effect of electrolytes on the surface tension, that is, the Jones–Ray effect, is also discussed.



1. INTRODUCTION

The state of water at interfaces is an important subject, but there are still controversies between theory and experiment as to whether the water at gaseous interfaces is positively or negatively charged.¹ There are at least two open questions. The first question is whether the ions from the bulk of the solution are accumulated or depleted from the interfacial layer. If there is accumulation or depletion, the second question concerns the nature of the ions that can be accumulated or depleted and under which conditions these processes occur. In other words, the second question is related to the difference in affinities of ions to the bulk and to the interface. If ions tend to accumulate at the interface, a difference in the affinities of anions and cations can result in an interfacial electrical charge, which, in turn, depends on their bulk concentrations (activities). The same applies if ions are depleted from the interface and differences in depletion occur. For example, Tian et al.² found experimentally that iodide ions in solution tend to appear at the gas/water interface. In this case, the experimental result agrees with theory. However, with respect to hydrogen and hydroxide ions, the disagreement could not be more severe. For pure water, the predominance of hydroxide versus hydrogen ions, or vice versa, results in a very fundamental question of whether the pure water/gas interface is negatively or positively charged. According to theoretical simulations,^{3–10} interfacial water should be positively charged. For example, Pegram and Record⁵ concluded that the interfacial concentration of H^+

ions is 50% higher than that in the bulk, whereas the interfacial concentration of OH^- ions is about 60% of their bulk concentration. They further concluded that the ionization equilibrium constant of interfacial water is approximately equal to that in the bulk solution. On the basis of molecular dynamic simulations, Baer et al.¹¹ concluded that there is no significant preference for or aversion to H_3O^+ and OH^- ions at the interface. However, they found that the solvation shell of H_3O^+ was only slightly dependent on its position, in contrast to the OH^- ions whose solvation shells near the air–water interface changed, which caused a different interfacial propensity for water self-ions. However, most experimental findings have shown the opposite.^{12–18} There are exceptions in both approaches. For example, Vácha et al.¹⁹ suggested that the anisotropy of the water hydrogen-bond distribution at the interface results in a region of net negative charge at ~ 5 Å below the Gibbs dividing surface. The estimated potential was found to be -2 mV, which is still significantly lower than the experimental electrokinetic potential. Kudin and Car²⁰ explained the negative charge of hydrophobic surfaces in terms of simulations, whereas on the experimental side, Winter et al.,²¹ for example, did not find evidence for an enhanced hydroxide propensity. In general, experimental electrokinetic

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data suggest a negative interfacial charge in a broad pH region above the isoelectric point.^{12–18} Therefore, it could be expected that a negative surface charge should be observable through surface tension measurements because of a strong affinity of hydroxide ions for the surface.^{22,23} However, surface tension data for the gas/water interface, over a wide pH range, were not previously available, and only Lorenz²⁴ reported a Jones–Ray effect when changing the acid concentration at rather acidic conditions (i.e., pH < 3). In a previous article, Beattie et al.²³ reported surface tension data over the full pH range. Their experiments were performed in the absence and in the presence of 0.01 mol dm⁻³ salt solutions. In the absence of salt, the surface tension pH curve was found to be flat. However, a small local minimum was found around pH 4. Direct titration measurements on oil²⁵ showed that the uptake of hydroxide ions does stabilize the oil/water system by charging the interface. Several experimental techniques such as measurement of the surface potential²⁶ and disjoining pressure,²⁷ atomic force microscopy,^{28,29} and some spectroscopic methods³⁰ do suggest a negative surface charge, whereas other spectroscopic data³¹ exclude strong surface enhancement of hydroxide ions and the absence of changes in the surface propensity of hydroxide ions.³²

To analyze the issue of the interfacial charge of water, one should first consider and define the region carrying an excess of positive or negative charge. It is obvious that bulk water and interface water at equilibrium are overall uncharged. Regarding electrokinetic data,³³ one should be aware that the negative electrokinetic charge applies to the so-called “stagnant” electrokinetic layer. A negative electrokinetic potential and charge means that the stagnant layer, the thickness of which is assumed³⁴ to be 1–2 nm, bears a net negative charge. The thickness of the entire diffuse layer is a few Debye distances l_D , (e.g., for aqueous solutions at room temperature and an ionic strength of 10⁻² mol dm⁻³, $l_D \approx 3$ nm), so that the diffuse layer extends as far as 10 nm from the surface. The diffuse layer is divided by the shear or slip plane into a stagnant layer and a “mobile” part (where the term mobile is with respect to the surface plane dividing the two phases). The charge of the stagnant layer is compensated by the charge of the mobile layer. The orientation of water dipoles at the surface can cause charge separation, but this cannot directly affect the electrokinetic phenomena, as the shear plane simply cannot be located within water dipoles, dividing positive from negative sides of the water molecules. However, in principle, the local field caused by oriented dipoles could affect the distribution of other ions at the interface and cause charge separation within the entire electrical interfacial layer. This hypothesis can be analyzed by considering electrokinetic data for pure “neutral water” (pH \approx 7) exhibiting a negative electrokinetic charge. The only ions present in pure water are OH⁻ and H⁺ ions. If they were bound equally at the gas/water surface, the interface would be electroneutral. If H⁺ (H₃O⁺) ions were bound to surface H₂O molecules, the process could be simply considered as an accumulation of H⁺ ions at the surface. The same would apply to OH⁻ ions. Therefore, the electrokinetic data showing a generally negative surface charge (charge of the electrokinetic stagnant layer) for pH > 4 and a positive charge for pH < 3 could be interpreted as the unsymmetrical accumulation (or depletion) of OH⁻ and H⁺ ions in (or from) the stagnant part of the interfacial layer. Consequently, a thermodynamic treatment based on the distribution of these ions between the bulk and the interface can be applied. Such an approach is

correct if the fraction of these ions at the surface is low so that the fraction of neutral water molecules remains practically 1. The same applies for other ions present in the system. The effect of electrolytes on the surface tension, particularly at high electrolyte concentrations, is well-established, and several models exist. Also, the macroscopic data and the computational results are consistent for these conditions. At low concentrations (curiously at the millimolar concentration range), the Jones–Ray effect occurs,^{35–37} which has been hotly debated since the first publication about it but was recently confirmed^{38,39} by spectroscopic methods for the millimolar concentration range. It is obvious that the interpretation of surface tension requires consideration of the composition of the interfacial layer. It can be expected that the addition of acid or base, that is, a change in pH, would affect the surface tension in different ways so that one could expect different behavior in the isoelectric region around pH \approx 3–4.

Electrokinetic data⁴⁰ for water at inert surfaces, such as hydrocarbon/water interfaces^{25,41,42} (which are frequently termed oil/water interfaces), Teflon/water interfaces,^{43,44} ice/water interfaces,^{45,46} and some mineral and metal aqueous surfaces are similar to those for gas/water interfaces.⁴⁷ All of these interfaces exhibit low isoelectric points between pH 2 and pH 4, and it has been suggested that their interfacial charges are governed by similar mechanisms.^{45,48}

The goal of the present study was to contribute to the understanding of charging of gas/water interfaces. The pH dependency of the surface potential at the air/water interface was measured and compared to electrokinetic data from the literature. A thermodynamic interpretation was developed considering the distribution of ions between the bulk and the interface, as well as the ionization of the interfacial water. To explain the minimum in the surface tension around pH 4, as indicated in a previous report,²³ additional experiments were performed in this pH region. The thermodynamic equilibrium constants for the distribution of hydrogen (hydronium) and hydroxide ions between the bulk and interface provide insight into the state and processes at gas/water interfaces. Additionally, the proposed model enables the evaluation of the degree of ionization of interfacial water, which has been estimated to be higher at the interface than in the bulk of the solution.^{47,49} A thermodynamic model, in accordance with the well-known Gibbs equation, was developed on the basis of chemical potentials of ionic species in the bulk of the solution and at the interface. Such an approach enabled a consideration of complex and variable compositions at the interface.

This approach would yield thermodynamic equilibrium parameters and model inherent information on the composition of the interfacial layer. The thermodynamic treatment is necessarily limited with respect to the detailed molecular origin of the macroscopically observed behavior. However, beyond our simple thermodynamic approach, it is expected that a theoretical analysis of the new data will be helpful in elucidating the effects on the molecular level. Beyond the pH dependence, our thermodynamic model will be applied to demonstrate and elucidate the minimum of surface tension at the gas/aqueous electrolyte solution⁵⁰ in the vicinity of the interfacial electro-neutrality point, that is, the Jones–Ray effect.

1.1. Thermodynamic Basis. To compare the ionization of interfacial water with the ionization of bulk water, as well as to study the equilibrium at the gas/water interface, a straightforward thermodynamic model should be derived. The fact that the values of the thermodynamic equilibrium constants depend

on the definition and choice of the standard state should be taken into account.⁵¹ The chemical potential, that is, the partial molar Gibbs energy (μ_B), of any species B involved in a chemical reaction is generally, at standard pressure ($p^\circ = 1 \text{ bar}$), given by

$$\mu(B) = \mu^\circ(B) + RT \ln a(B) \quad (1)$$

where $a(B)$ is the relative activity of species B. For condensed systems (liquids and solids), the above relation holds for pressures not significantly different from the standard value, $p^\circ = 10^5 \text{ Pa}$. Relative activity depends on the arbitrary choice of the standard state. The (relative) activity depends on the composition of the system and interactions between species. For species B, the relative activity is given by

$$a(B) = y(B) r(B) \quad (2)$$

where $y(B)$ is the activity coefficient of species B describing the deviation from the assumed ideality and the respective interactions occurring in real systems.

The term $r(B)$ is the “relative content” of species B which depends on the composition of the system. Several quantities can be used to describe the composition of a system: (i) the relative content of the bulk solvent, (ii) the relative content of a solute dissolved in the bulk of the solution, and (iii) the relative content of interfacial species.

(i) *Relative Content of the Bulk Solvent.* The common practice, as recommended by IUPAC,³³ considers the solvent as a component of the mixture so that the “relative content” of solvent species is defined in terms of its amount (i.e., mole) fraction, x

$$r(B) = x(B) \quad (3)$$

where the standard state is the pure component, that is, $x^\circ = 1$.

(ii) *Relative Content of a Solute Dissolved in the Bulk of the Solution.* For solute species B dissolved in the bulk liquid solution, such as $\text{H}^+(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{K}^+(\text{aq})$, and $\text{NO}_3^-(\text{aq})$, the relative content is commonly defined in terms of molar concentration as

$$r(B) = \frac{c(B)}{c^\circ} = [B] \quad (4)$$

where $c^\circ = 1 \text{ mol dm}^{-3}$, so that the square brackets denote the numerical value of the concentration if it is expressed in moles per cubic decimeter. The relative activity for a solute species based on concentration is

$$a_c(B) = y(B) \frac{c(B)}{c^\circ} = y(B)[B] \quad (5)$$

However, the relative content of solute B can also be defined in terms of its amount (mole) fraction, as in eq 3. Accordingly, the relative activity for solute species B based on the amount (mole) fraction is

$$a_x(B) = y(B) x(B) \quad (6)$$

(iii) *Relative Content of Interfacial Species.* The quantity that is considered for the definition of the standard composition at the interface is either the amount fraction or surface concentration (amount divided by surface area). Accordingly, the relative content for interfacial species $\equiv B$ based on the amount fraction is

$$r_x(\equiv B) = x(\equiv B) \quad (7)$$

Consequently, the relative activity of an interfacial species on the basis of amount (mole) fraction is

$$a_x(\equiv B) = y(\equiv B) x(\equiv B) \quad (8)$$

In the interpretation of interfacial equilibrium, the effect of electrostatic potential on charged interfacial species should be taken into account. The difference between the chemical potential of interfacial species B in the real and ideal states is therefore given by the activity coefficient y , which is generally defined as

$$\mu^{\text{real}}(B) - \mu^{\text{ideal}}(B) = RT \ln y(B) \quad (9)$$

For the interfacial species $\equiv B$ of charge number $z(\equiv B)$ exposed to the electrostatic potential Ψ , the deviation from ideality is predominantly due to the electrostatic interactions, so that

$$\mu^{\text{real}}(\equiv B) - \mu^{\text{ideal}}(\equiv B) = RT \ln y(\equiv B) = z(\equiv B)F\Psi \quad (10)$$

where F denotes the Faraday constant. Accordingly, the activity coefficient of interfacial species $\equiv B$ of charge number $z(\equiv B)$ is given by

$$y(\equiv B) = \exp\left[\frac{z(\equiv B)F\Psi}{RT}\right] \quad (11)$$

For ions in solution, activity coefficients can be calculated using the Debye–Hückel or Davies equations within the appropriate ranges of ionic strength (i.e., at low salt content).

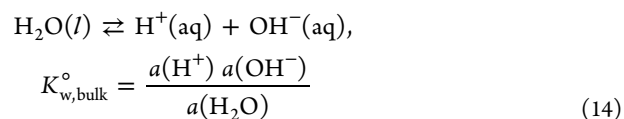
The reaction Gibbs energy $\Delta_r G$ is zero in the equilibrium state and is related to the chemical potentials of species involved in the reaction multiplied by their corresponding stoichiometric coefficients ν_i

$$\begin{aligned} \Delta_r G &= \sum_i \nu_i \mu_i = \sum_i \nu_i \mu_i^\circ + RT \ln \prod_i a_i^{\nu_i} \\ &= \Delta_r G^\circ + RT \ln \prod_i a_i^{\nu_i} = 0 \end{aligned} \quad (12)$$

Following eqs 1 and 12, the thermodynamic equilibrium constant is generally defined by

$$K^\circ = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \prod_i a_i^{\nu_i} \quad (13)$$

1.2. Ionization of Bulk and Interfacial Water. Ionization of bulk water is commonly represented by



where $K_{\text{w,bulk}}^\circ$ is the thermodynamic equilibrium constant for the ionization of bulk water. To simplify the notation, the bulk species in the equations will be denoted simply as H_2O , H^+ , and OH^- , for example. According to the convention, the activity of solvent molecules is defined in terms of the amount (mole) fraction, so that, for dilute solutions, $y_{\text{H}_2\text{O}} \rightarrow 1$ and $x_{\text{H}_2\text{O}} \rightarrow 1$, which results in $a_{\text{H}_2\text{O}} \rightarrow 1$ and the thermodynamic equilibrium constant as

$$K_{\text{w,bulk}}^\circ = a(\text{H}^+) a(\text{OH}^-) \quad (15)$$

Conventionally, the activities of solute species are defined on the concentration basis as in eq 8, so that the corresponding thermodynamic equilibrium constant for the ionization of bulk water is

$$K_{w,bulk,c}^{\circ} = y(H^+)[H^+] y(OH^-)[OH^-] \quad (16)$$

According to the literature,⁵² the value of the conventional thermodynamic equilibrium constant based on concentration for the ionization of bulk water at 25 °C, $K_{w,bulk,c}^{\circ}$ is equal to 1.006×10^{-14} .

For the purpose of this study, to quantitatively compare the interface and bulk of the solution, it is suitable to use the equilibrium constant for bulk water ionization based on the amount fractions of solute species, which is given by

$$K_{w,bulk,x}^{\circ} = y(H^+) x(H^+) y(OH^-) x(OH^-) \quad (17)$$

The two equilibrium constants are related, and $K_{w,bulk,x}^{\circ}$ could be simply recalculated from $K_{w,bulk,c}^{\circ}$. In relatively dilute aqueous solutions, for solute species B, the relationship between the bulk concentration and the amount fraction is

$$x(B) = \frac{c(B) M(H_2O)}{\rho(H_2O)} = 1.8 \times 10^{-2} [B] \quad (18)$$

where M and ρ are the molar mass and ρ density, respectively, of water.

Consequently, the water ionization thermodynamic equilibrium constant based on the amount fraction is $K_{w,bulk,x}^{\circ} = 3.26 \times 10^{-18}$ at 25 °C, and the degree of the bulk water ionization in the neutral solutions at pH 7 is therefore

$$\alpha_{bulk} = (K_{w,bulk,x}^{\circ})^{1/2} = 1.8 \times 10^{-9} = 1.8 \times 10^{-3} \text{ ppm} \quad (19)$$

Because of the different physical and chemical properties of water at inert hydrophobic surfaces with respect to bulk water,^{53,54} the ionization of interfacial water is represented by

$$\begin{aligned} \equiv H_2O &\rightleftharpoons \equiv H^+ + \equiv OH^-, \\ K_{w,int}^{\circ} &= \frac{a(\equiv H^+) a(\equiv OH^-)}{a(\equiv H_2O)} \approx a(\equiv H^+) a(\equiv OH^-) \end{aligned} \quad (20)$$

Note that the activity of neutral water molecules is unity ($a_{\equiv H_2O} \rightarrow 1$) if the degree of ionization is sufficiently low ($x_{\equiv H_2O} \rightarrow 1$). At the interface, it is more suitable to introduce amount fractions of interfacial species (eq 8)

$$K_{w,int,x}^{\circ} = y(\equiv H^+) x(\equiv H^+) y(\equiv OH^-) x(\equiv OH^-) \quad (21)$$

Assuming that deviation from ideality for the above interfacial species is predominantly due to electrostatic interactions⁵⁵ and determined by the electrostatic potential at the plane dividing the gas phase from bulk water (surface potential Ψ_0), the activity coefficients of interfacial H^+ and OH^- species according to eq 10 are

$$y(\equiv H^+) = \exp(F\Psi_0/RT) \quad (22)$$

$$y(\equiv OH^-) = \exp(-F\Psi_0/RT) \quad (23)$$

Multiplying eqs 22 and 23 leads to $y(\equiv H^+) y(\equiv OH^-) = 1$, so that eq 21 is reduced to

$$K_{w,int,x}^{\circ} = x(\equiv H^+) x(\equiv OH^-) \quad (24)$$

The degree of interfacial water dissociation, α_{int} is related to the corresponding interfacial equilibrium constant based on amount fractions, $K_{w,int,x}^{\circ}$ by $\alpha_{int} = (K_{w,int,x}^{\circ})^{1/2}$.

The known values of amount fractions of hydronium and hydroxide ions enable the evaluation of the thermodynamic equilibrium constant and the degree of interfacial water ionization.

Note that the activity coefficients for bulk solution species change with the electrolyte concentration in an ion-specific way at concentrations higher than 0.5 mol dm^{-3} . The concentration limit for the surface species might be lower, if the occurrence of ion-specific behavior is taken as a threshold,^{34,56} but still higher than the concentration ranges treated in the present work.

1.3. Charging of Interfacial Water. Charging of the water layer at the gas/water interface could, in principle, be represented by several different stoichiometries (reaction equations). Assuming the presence of negative surface sites, Leroy et al.⁵⁷ applied a surface complexation model. In the present article, the distribution of H^+ and OH^- between bulk and interface is not considered in terms of a surface complexation (site-binding) model, but rather is described by a distribution equilibrium involving distribution equilibrium constants applicable for high fractions of neutral water molecules. Our simplified model of the interfacial water layer is presented in Figure 1.

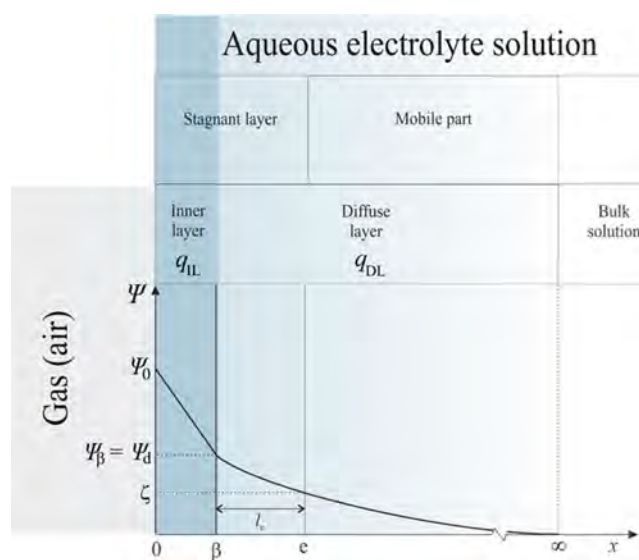
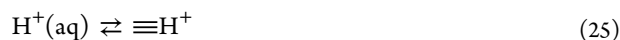


Figure 1. Interfacial water layer at the gas/aqueous electrolyte solution interface. Potentials within the interfacial layer are indicated. However, the distances between planes are not representative but rather are for illustration.

As it is common practice, to simplify the system, we consider the accumulation of ions in idealized planes. For thermodynamic considerations, only the states of reactants and products are relevant. To be able to compare equilibrium constants of different processes, one should be consistent in defining reaction stoichiometries and the corresponding equilibrium constants. The accumulation of hydrogen (hydronium) and hydroxide ions at the interface is represented as the distribution of H^+ ions between the bulk of the solution and the interfacial region



and the distribution of OH⁻ ions between the bulk of the solution and the interfacial region



The corresponding thermodynamic equilibrium constants can be defined depending on the choice of the standard state. The standard states are defined here in terms of concentration for bulk solution species (eq 8) and amount fractions for interfacial species (eq 7), whereas activity coefficients for interfacial species are given by eq 11. Accordingly, the thermodynamic equilibrium constants of reactions 25 and 26 are

$$K^\circ(\text{H}^+) = \frac{\exp(\Psi_0 F/RT) x(\equiv\text{H}^+)}{a_c(\text{H}^+)} \quad (27)$$

$$K^\circ(\text{OH}^-) = \frac{\exp(-\Psi_0 F/RT) x(\equiv\text{OH}^-)}{a_c(\text{OH}^-)} \quad (28)$$

where Ψ_0 denotes the surface potential, that is, the electrostatic potential affecting the state of interfacial H⁺ and OH⁻ ions. According to eqs 27 and 28, the surface potential Ψ_0 is related to the bulk pH by

$$\Psi_0 = \frac{RT}{2F} \ln \frac{K^\circ(\text{H}^+)}{K^\circ(\text{OH}^-)K_{\text{w,bulk,c}}^\circ} - \frac{RT}{2F} \ln \frac{x(\equiv\text{H}^+)}{x(\equiv\text{OH}^-)} - \frac{RT \ln 10}{F} \text{pH} \quad (29)$$

Equation 29 suggests that the slope of the $\Psi_0(\text{pH})$ function should be lower in magnitude than the Nernstian slope $[(RT \ln 10)/F]$ because of the pH dependency of the ratio of H⁺ and OH⁻ fractions at the interface.

The surface is electrically neutral if the amounts of H⁺ and OH⁻ at the surface are equal, that is, $x(\equiv\text{H}^+) = x(\equiv\text{OH}^-)$, and consequently, the surface potential is zero ($\Psi_0 = 0$). According to eq 29, the electroneutrality point pH_{eln} is related to the equilibrium constants describing positive and negative charging, that is, to the values of the thermodynamic constants for the accumulation of positive H⁺ ions and negative OH⁻ ions, respectively

$$\text{pH}_{\text{eln}} = \frac{1}{2} \log \frac{K^\circ(\text{H}^+)}{K^\circ(\text{OH}^-)K_{\text{w,bulk,c}}^\circ} \quad (30)$$

In the case of symmetrical, or lack of, counterion association, the electroneutrality point coincides with the isoelectric point: $\text{pH}_{\text{eln}} = \text{pH}_{\text{iep}}$.⁵⁸ According to eq 29, the pH dependence of the surface potential can be expressed as

$$\Psi_0 = \alpha_N \frac{RT \ln 10}{F} (\text{pH}_{\text{eln}} - \text{pH}) \quad (31)$$

where α_N is the deviation of the actual $\Psi_0(\text{pH})$ slope from the Nernstian slope defined as

$$\begin{aligned} \alpha_N &= -\frac{F}{RT \ln 10} \left[\frac{d\Psi_0}{d(\text{pH})} \right] \\ &= \frac{1}{\ln 10} \frac{d\{\ln[x(\equiv\text{H}^+)/x(\equiv\text{OH}^-)]\}}{d(\text{pH})} + 1 \end{aligned} \quad (32)$$

Because, in principle, the increase in pH lowers the fraction of interfacial H⁺ ions and increases the fraction of OH⁻ ions, the derivative of the logarithm of their ratio with respect to pH

is negative, causing α_N to be positive and less than 1. However, if both fractions were high, α_N would be close to 1.

The distribution of counterions (cations C⁺ and anions A⁻) between the bulk and the interface should also be considered. The corresponding reactions are



and



In our interfacial model, counterions within the interfacial layer are affected by the interfacial electrostatic potential Ψ_β , which lies between Ψ_0 and the ζ potential. The corresponding equilibrium constants, based on concentrations in the bulk of the solution and amount fractions at the interface, are

$$K^\circ(\text{C}^+) = \frac{\exp(\Psi_\beta F/RT) x(\equiv\text{C}^+)}{a_c(\text{C}^+)} \quad (35)$$

$$K^\circ(\text{A}^-) = \frac{\exp(-\Psi_\beta F/RT) x(\equiv\text{A}^-)}{a_c(\text{A}^-)} \quad (36)$$

The surface charge density at the gas/water interface (q_0) is related to the surface concentrations of the ions in the interfacial region

$$q_0 = F[\Gamma(\equiv\text{H}^+) - \Gamma(\equiv\text{OH}^-)] \quad (37)$$

The surface concentrations of interfacial species are related to the corresponding amount fractions

$$\Gamma(\equiv\text{B}) = \frac{x(\equiv\text{B})}{Ls} \approx \frac{x(\equiv\text{B})}{L \left[\frac{M_r(\text{H}_2\text{O})u}{\rho(\text{H}_2\text{O})} \right]^{2/3}} \quad (38)$$

where s is the surface area occupied by one H₂O molecule, L is Avogadro's number, $M_r(\text{H}_2\text{O})$ is the relative molar mass of water, and u is the unified atomic mass constant.

The counterions ($\equiv\text{C}^+$ and $\equiv\text{A}^-$) are also distributed within the interfacial water layer, and it is assumed that they are exposed to the surface potential Ψ_β . The surface charge density at the β plane (q_β) is given by the surface concentration of associated counterions

$$q_\beta = F[\Gamma(\equiv\text{C}^+) - \Gamma(\equiv\text{A}^-)] \quad (39)$$

A net surface charge density of the inner layer (q_{IL}) can be acquired by the unequal adsorption of positively and negatively charged ions and is related to the surface concentration of the interfacial species

$$\begin{aligned} q_{\text{IL}} &= q_0 + q_\beta = F[\Gamma(\equiv\text{H}^+) - \Gamma(\equiv\text{OH}^-) + \Gamma(\equiv\text{C}^+) \\ &\quad - \Gamma(\equiv\text{A}^-)] \end{aligned} \quad (40)$$

Because of the overall charge neutrality of the interfacial water layer, the net surface charge density of the inner layer (q_{IL}) is compensated by the charge of the diffuse layer (q_{DL}). The Gouy–Chapman theory provides the relationship between the potential at the onset of the diffuse layer Ψ_β and the net surface charge density for 1:1 electrolytes at sufficiently low concentrations

$$q_{\text{DL}} = -q_{\text{IL}} = \sqrt{8RT\varepsilon I_c} \sinh\left(-\frac{\Psi_\beta F}{RT}\right) \quad (41)$$

The same theory enables the calculation of Ψ_β from the measured electrokinetic potentials ζ

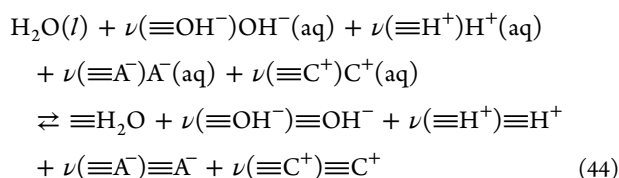
$$\Psi_\beta = \frac{2RT}{F} \ln \left[\frac{\exp(-l_e \kappa) + \tan(F\zeta/4RT)}{\exp(-l_e \kappa) - \tan(F\zeta/4RT)} \right] \quad (42)$$

where l_e is the electrokinetic slip- (shear-) plane separation and κ is the reciprocal Debye distance determined by the ionic strength (I_e)

$$\kappa = \frac{1}{l_D} = \sqrt{\frac{2F^2 I_e}{\epsilon RT}} \quad (43)$$

1.4. Surface Tension of a Gas in Contact with an Aqueous Electrolyte Solution. The change in the composition of the interface in the presence of an acid or base, or even a neutral electrolyte, should, in principle, affect the surface (interfacial) tension. This problem cannot be analyzed by the commonly used simple form of the Gibbs adsorption isotherm⁵⁹ because the change in bulk composition changes the composition of the interface involving different kinds of ionic species. Nevertheless, the analysis employed in this study is in accordance with the Gibbs concept.⁶⁰

Therefore, the problem is considered on the basis of a (chemical) equation describing the transfer of one water molecule from the bulk of the solution to the interface, taking into account the transfer of accompanying ions



In this equation, ν represents the number of species (H^+ , OH^- , C^+ , and A^-) that accompany one water molecule in the process. If the values of ν are low, specifically below or around 10^{-3} , the fraction of neutral water molecules at the surface is very close to 1 and nearly constant, so that the coefficients ν in eq 43 are equal to the amount (mole) fraction of relevant species at the surface, x . Stoichiometric coefficients (ν) for species involved in the process are negative for reactants, $-x(\text{OH}^-)$, $-x(\text{H}^+)$, $-x(\text{A}^-)$, and $-x(\text{C}^+)$, and positive for product species, $x(\equiv\text{OH}^-)$, $x(\equiv\text{H}^+)$, $x(\equiv\text{A}^-)$, and $x(\equiv\text{C}^+)$.

According to eq 12, the reaction Gibbs energy is the sum of the products of the chemical potentials and corresponding stoichiometric coefficients of all species involved in a chemical reaction. To calculate the Gibbs energy of reaction 44, the chemical potentials of all species in aqueous solution and all interfacial species should be taken into account.

Chemical potentials for solute species, as well as for interfacial species, do not depend on the choice of the standard state, eqs 1–11. However, their standard values depend on the choice of the standard state. In the analysis of the pH dependency of the surface tension, the standard values of the chemical potentials and relative activities for solute species are based on molar concentrations, whereas for interfacial species, amount fractions are introduced. For interfacial species $\equiv\text{B}$, the standard chemical potential can be separated into the chemical contribution $\mu^\ominus(\equiv\text{B})$ and the contribution associated with the interfacial tension $\mu^\sigma(\equiv\text{B})$

$$\mu^\circ(\equiv\text{B}) = \mu^\ominus(\equiv\text{B}) + \mu^\sigma(\equiv\text{B}) \quad (45)$$

Upon introducing this formalism into eqs 1, 7, and 10, the chemical potentials of the interfacial species become

$$\begin{aligned} \mu(\equiv\text{OH}^-) &= \mu^\ominus(\equiv\text{OH}^-) + \mu^\sigma(\equiv\text{OH}^-) \\ &+ RT \ln x(\equiv\text{OH}^-) - \Psi_0 F \\ \mu(\equiv\text{H}^+) &= \mu^\ominus(\equiv\text{H}^+) + \mu^\sigma(\equiv\text{H}^+) + RT \ln x(\equiv\text{H}^+) \\ &+ \Psi_0 F \\ \mu(\equiv\text{A}^-) &= \mu^\ominus(\equiv\text{A}^-) + \mu^\sigma(\equiv\text{A}^-) + RT \ln x(\equiv\text{A}^-) \\ &- \Psi_\beta F \\ \mu(\equiv\text{C}^+) &= \mu^\ominus(\equiv\text{C}^+) + \mu^\sigma(\equiv\text{C}^+) + RT \ln x(\equiv\text{C}^+) \\ &+ \Psi_\beta F \\ \mu(\equiv\text{H}_2\text{O}) &= \mu^\ominus(\equiv\text{H}_2\text{O}) + \mu^\sigma(\equiv\text{H}_2\text{O}) \\ &+ RT \ln x(\equiv\text{H}_2\text{O}) \end{aligned} \quad (46)$$

Note that, at the surface, H^+ and OH^- ions are exposed to surface potential Ψ_0 , whereas counterions distributed within the diffuse part of the interfacial layer are exposed to the (average) potential Ψ_β . Consequently, the surface tension (σ) is the sum of contributions of all interfacial species involved in the reaction

$$\sigma = -\frac{1}{sL} \sum_{\equiv\text{B}} [\nu(\equiv\text{B}) \mu^\sigma(\equiv\text{B})] \quad (47)$$

where s denotes the area occupied by one water molecule at the surface and $\nu(\equiv\text{B})$ represents the stoichiometric coefficients, that is, the mole fractions (x), of interfacial species B. Accordingly, the surface tension is given by

$$\begin{aligned} \sigma &= -\frac{1}{sL} [x(\equiv\text{OH}^-) \mu^\sigma(\equiv\text{OH}^-) + x(\equiv\text{H}^+) \mu^\sigma(\equiv\text{H}^+) \\ &+ x(\equiv\text{C}^+) \mu^\sigma(\equiv\text{C}^+) + x(\equiv\text{A}^-) \mu^\sigma(\equiv\text{A}^-) \\ &+ x(\equiv\text{H}_2\text{O}) \mu^\sigma(\equiv\text{H}_2\text{O})] \end{aligned} \quad (48)$$

where the mole fractions x of interfacial species are determined by interfacial equilibrium constants, surface potentials, and bulk concentrations (eqs 27, 28, 35, and 36). Note that $x(\equiv\text{H}_2\text{O}) \approx x[\text{H}_2\text{O}(l)] \approx 1$.

2. EXPERIMENTAL SECTION

2.1. Surface Potential Measurements. Surface potentials were measured at 25 °C using an ionizing ²⁴¹Am electrode positioned at a certain level above the gas/solution interface and a reference electrode immersed in an identical solution. The experimental procedure and setup were described in detail previously.⁶¹ The pH was adjusted by addition of sodium hydroxide solution to the initial solution of hydrochloric acid (1×10^{-2} mol dm⁻³) so that the ionic strength in the acidic region was kept constant at $I_e = 1 \times 10^{-2}$ mol dm⁻³. The measurements provide surface potential data on a relative scale. The absolute values of the surface potential data were obtained by setting them to zero (electroneutrality point) at the isoelectric point, $\text{pH}_{\text{eln}} = \text{pH}_{\text{iep}} = 3.8$. In the acidic pH range ($\text{pH} < 3$), surface potential is then positive and decreases with increasing pH with the slope of the $\Psi_0(\text{pH})$ function being lower than the Nernstian slope ($\alpha_N \approx 0.55$). Electrokinetic potential data of gas bubbles were taken from the literature.^{16,17} In calculations, the smoothed curve and the value of the isoelectric point $\text{pH}_{\text{iep}} = 3.8$ were used. The electrokinetic

measurements of gas bubbles in aqueous solutions are tedious, and measured electrokinetic potentials are affected by the instability of bubbles, by additional bubble movement due to buoyancy, and by the model used for the calculation of electrokinetic potentials from the measured mobilities.⁶²

2.2. Surface Tension Measurements. Surface tensions of aqueous solutions of hydrochloric acid were measured on a KRÜSS Processor tensiometer K100 at 25.0 ± 0.1 °C. Water was deionized and boiled prior to use. During experiments, the measuring system was under an argon atmosphere to avoid dissolution and the influence of carbon dioxide. Special care was taken to avoid any traces of surfactants. For all interfacial surface tension measurements, the following procedure was applied: Chrome–sulfuric acid was used to remove organic matter from the glassware. Glassware was soaked in chrome–sulfuric acid and left overnight. After that, the chrome–sulfuric acid was removed by intense washing with regular distilled and deionized water. Before each measurement, the ring was immersed for 10 min in chrome–sulfuric acid. Then, it was extensively washed with distilled and deionized water. After being washed, it was exposed to the reduction flame of a Bunsen burner to remove impurities from the ring.

In the experiments, HCl was gradually added to (a) pure water up to a concentration of 1×10^{-2} mol dm⁻³ (to pH ≈ 2), in which case the ionic strength was increased, and (b) 1×10^{-3} mol dm⁻³ NaCl solution up to a concentration of 1×10^{-3} mol dm⁻³ (to pH ≈ 3), also resulting in an increase in ionic strength. It was found that the surface tension exhibits a minimum in the isoelectric region around pH ≈ 4 .

3. RESULTS AND INTERPRETATION OF DATA

3.1. Evaluation of Equilibrium Constants from Interfacial Potentials. Two different interfacial electrostatic potentials characterizing the gas/water interface are experimentally available. The first is the surface potential Ψ_0 , measured in the present work with an ionizing ²⁴¹Am electrode, whereas the second is the electrokinetic ζ potential measured by electrophoresis of gas bubbles.^{16,17} The data are shown in Figure 2.

According to eqs 29 and 31, the deviation of the surface potential values from the Nernst equation provides the ratio of the surface amount (mole) fractions of positive and negative surface groups. This ratio is equal to the ratio of their amounts and, consequently, to the ratio of their surface concentrations. The electrokinetic ζ potential is related to the net charge of the surface within the shear plane, that is, to the difference in the surface concentrations of positive and negative interfacial species, and is influenced by the ionic strength. To calculate the difference between the Ψ_β and ζ potentials, the Gouy–Chapman theory was applied (eqs 39–43). At first, a certain value of the shear-plane separation l_e was assumed, and the potential at the onset of the diffuse layer Ψ_β was calculated using eq 42. The choice of shear-plane separation in the range of $0.5 \text{ nm} < l_e < 2.5 \text{ nm}$ does not significantly affect the final result of the calculations. In the second step, the surface charge density of the diffuse layer (q_{DL}), which is equal in magnitude but opposite in sign to the net surface charge density ($q_{IL} = -q_{DL}$), was calculated using eq 41. To calculate the difference in surface concentrations and fractions of positive (H^+) and negative (OH^-) ions at the surface from the net surface charge density (q_{IL}), the surface concentrations of associated counterions A^- and C^+ should be known (eq 39). These concentrations were calculated from the corresponding

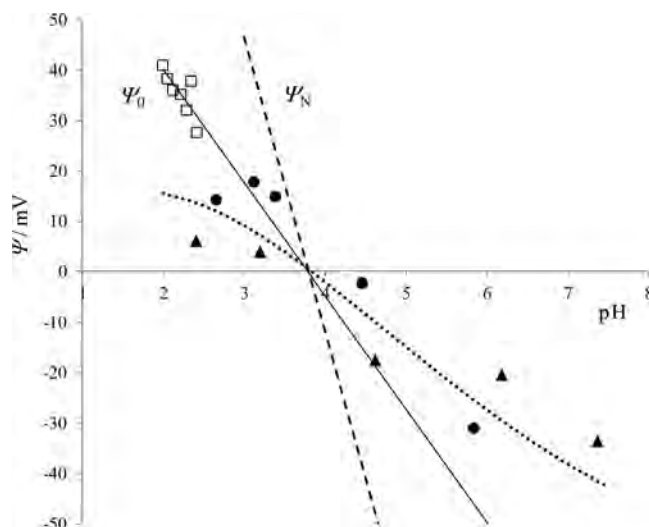


Figure 2. Dependency of the surface potential (\square) at the gas/water interface on pH at $\vartheta = 25$ °C and $I_c = 1 \times 10^{-2}$ mol dm⁻³; $pH_{iep} = pH_{eln} = 3.8$. The results are compared with the values of the zeta potential of gas bubbles in aqueous solution published by (\blacktriangle) Yang and co-workers¹⁶ ($I_c = 1 \times 10^{-2}$ mol dm⁻³) and by (\bullet) Takahashi¹⁷ (variable ionic strength). The Nernstian slope is presented as a dashed line, whereas the solid line represents the surface potential function corresponding to a reduced slope, $\alpha_N = 0.55$. A smoothed zeta potential function used in the interpretation is presented as a dotted line (\dots).

thermodynamic equilibrium constants, which were treated as adjustable parameters.

Once the difference (eqs 39 and 40) and ratio (eq 29) of surface concentrations of interfacial water species OH^- and H^+ are known, their individual values can be calculated. The individual values of surface concentrations can be transformed into the mole fractions of interfacial species using eq 38.

With values for the potentials Ψ_0 and Ψ_β , as well as the mole fractions of interfacial species, the thermodynamic equilibrium constants for the distribution of positive H^+ and negative OH^- ions between the bulk of the solution and the interface were evaluated by means of eqs 27, 28, 35, and 36. The thermodynamic equilibrium constants $K^\circ(H^+)$ and $K^\circ(OH^-)$ for the distribution of H^+ and OH^- ions between the bulk and the interface, based on the bulk concentrations and interfacial mole fractions, were calculated for the examined pH values and are presented in Figure 3. The values of thermodynamic equilibrium constants should not depend on pH, so that the constancy of the obtained values of $K^\circ(H^+)$ and $K^\circ(OH^-)$ was used as a criterion while adjusting values of equilibrium constants for the distributions of Na^+ and Cl^- counterions $K^\circ(Na^+)$ and $K^\circ(Cl^-)$.

The values of counterion distribution equilibrium constants were adjusted to obtain constant $K^\circ(H^+)$ and $K^\circ(OH^-)$ values. However, as can be concluded from Figure 3, these values depend on the choice of l_e . An increase of l_e by 1 nm results in an increase of the logarithms of the $K^\circ(H^+)$ and $K^\circ(OH^-)$ values by approximately 0.2. For $l_e = 1 \pm 0.5$ nm, the following values were obtained: $\log K^\circ(H^+) = 1.31 \pm 0.1$, $\log K^\circ(OH^-) = 7.63 \pm 0.1$. The adjusted distribution equilibrium constants for counterions did not depend on the choice of l_e , and the final values were $\log K^\circ(Na^+) = \log K^\circ(Cl^-) = -0.74$. These values of distribution equilibrium constants are based on amount fractions of interfacial species and their concentrations in the

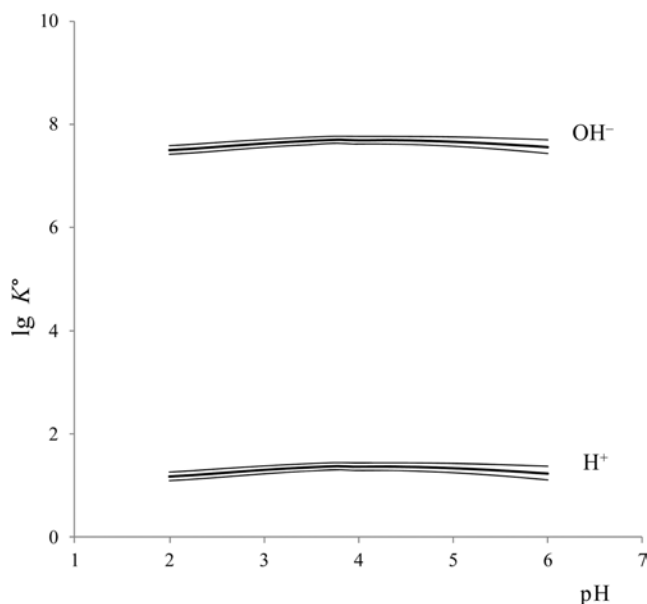


Figure 3. Calculated equilibrium constants $\log K^\circ(\text{H}^+)$ and $\log K^\circ(\text{OH}^-)$ for the distribution of H^+ and OH^- ions between the bulk and interface, characterizing the charging of the gas/water interface as a function of pH at $\vartheta = 25^\circ\text{C}$, $I_c = 10^{-2} \text{ mol dm}^{-3}$ (NaCl). $\text{pH}_{\text{eln}} = \text{pH}_{\text{iep}} = 3.8$ and $\log K^\circ(\text{Na}^+) = \log K^\circ(\text{Cl}^-) = -0.74$ for slip-plane separation. $l_e = 1 \text{ nm}$ (heavy line), $l_e = 0.5 \text{ nm}$ (lower thin line), and $l_e = 1.5 \text{ nm}$ (upper thin line).

bulk of the solution. According to eq 18, the introduction of the amount (mole) fraction basis for both solute and interfacial species results in the following values of distribution equilibrium constants: $\log K_{x,x}^\circ(\text{H}^+) = 3.06 \pm 0.1$, $\log K_{x,x}^\circ(\text{OH}^-) = 9.38 \pm 0.1$. Regardless of the uncertainty connected to the choice of l_e , the values of the distribution equilibrium constants are high, indicating the preference of H^+ and OH^- ions for the surface, with this preference being markedly more pronounced for OH^- ions.

According to the above results, the equilibrium constant of interfacial water ionization based on amount fractions (eqs 24, 27, and 28) is equal to $\log K_{w,\text{int},x}^\circ = \log-[K^\circ(\text{H}^+) K^\circ(\text{OH}^-) K_{w,\text{bulk},x}^\circ] = 5.06 \pm 0.2$. Consequently, the degree of interfacial water dissociation is evaluated as $\alpha_{\text{int}} = (2.95 \pm 0.1) \times 10^{-3}$, which is approximately 10^6 times higher than in the bulk of the solution.

3.2. Surface Tension. The measured surface tension data for hydrochloric acid added to pure water and to $10^{-3} \text{ mol dm}^{-3}$ sodium chloride solution as a function of pH are presented in Figure 4. The dependency of surface tension on pH was calculated on the basis of the developed thermodynamic model. The individual values of mole fractions of the interfacial species were calculated, using eq 48, from the thermodynamic equilibrium constant (evaluated by the procedure described in the previous section), bulk concentrations of ions, and corresponding surface potentials. The electroneutrality point was taken to be at the isoelectric point of $\text{pH}_{\text{eln}} = \text{pH}_{\text{iep}} = 3.8$, and the slip-plane separation was assumed to be $l_e = 1 \text{ nm}$.

The values of $\mu^\sigma(\equiv\text{B})$ for all interfacial species were adjusted to fit the experimental surface tension data (Figure 4) as follows: $\mu^\sigma(\equiv\text{H}^+) = -5.8 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{OH}^-) = -5.0 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{Na}^+) = -4.5 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{Cl}^-) = -4.1 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{H}_2\text{O}) = -4.2 \text{ kJ mol}^{-1}$.

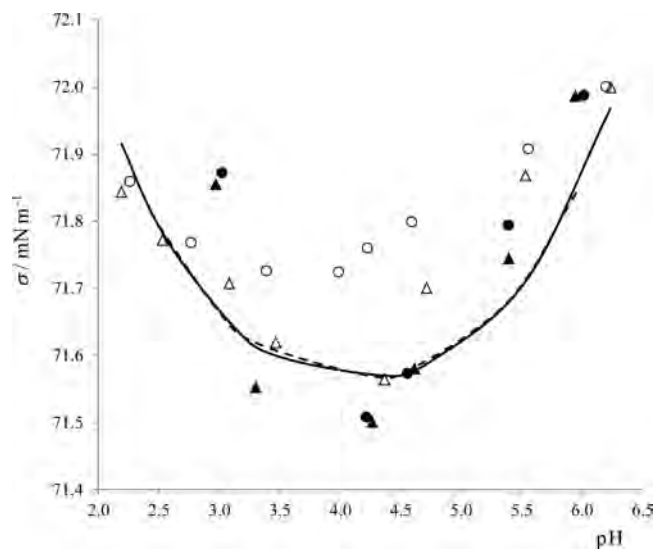


Figure 4. Surface tension of the gas/water interface as a function of pH: addition of hydrochloric acid to pure water (two runs are presented, Δ, \circ) and addition of hydrochloric acid to sodium chloride $c = 10^{-3} \text{ mol dm}^{-3}$ (two runs are presented, \blacktriangle, \bullet). The lines were calculated from equilibrium parameters obtained from the interpretation of electrokinetic and surface potential data by means of eq 48. The solid line corresponds to the addition of hydrochloric acid to pure water, whereas the dashed line corresponds to the addition of hydrochloric acid to sodium chloride $c = 10^{-3} \text{ mol dm}^{-3}$. In the calculations, the following parameters were used: $\text{pH}_{\text{eln}} = \text{pH}_{\text{iep}} = 3.8$, $\vartheta = 25.0^\circ\text{C}$, $l_e = 1 \text{ nm}$, $\log K^\circ(\text{H}^+) = 1.31$, $\log K^\circ(\text{OH}^-) = 7.63$, $\log K^\circ(\text{C}^+) = \log K^\circ(\text{A}^-) = -0.74$. Adjusted values of contributions to surface tension were as follows: $\mu^\sigma(\equiv\text{H}^+) = -5.8 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{OH}^-) = -5.0 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{Na}^+) = -4.5 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{Cl}^-) = -4.1 \text{ kJ mol}^{-1}$, $\mu^\sigma(\equiv\text{H}_2\text{O}) = -4.2 \text{ kJ mol}^{-1}$.

The presence of sodium chloride ($10^{-3} \text{ mol dm}^{-3}$) did not significantly affect the calculated surface tension function.

4. DISCUSSION AND CONCLUSIONS

In the first step of the interpretation, the values of the distribution equilibrium constants for the accumulation of H^+ and OH^- , as well as counterions Na^+ and Cl^- , were obtained from experimental surface and electrokinetic potentials. The thermodynamic model used in this work involves approximations related to the electrostatic potentials affecting the states of ionic species at the interface. As will be shown, these approximations do not affect the main conclusion that H^+ and OH^- ions exhibit a preference for the interfacial layer and that the ionization of interfacial water is markedly more pronounced compared to that of bulk water.

At the electroneutrality point, where $\Psi_0 = 0$, the fraction of interfacial hydronium ions is more than 10^3 times higher than the amount of hydronium ions in the bulk of the solution. At the same time, the fraction of interfacial hydroxide ions is 10^9 times higher. From these data, it is obvious that the affinity of hydroxide ions toward the interface is much more pronounced than the affinity of hydronium ions.

Electrostatic potentials Ψ_0 affecting the state of interfacial OH^- and H^+ ions are determined by the electroneutrality point pH_{eln} ($\Psi_0 = 0$) and the deviation from the Nernstian potential, α_N . Both parameters pH_{eln} and α_N affect the values of the equilibrium distribution constants of OH^- and H^+ ions. However, calculations performed involving deviations from the experimental values still result in markedly higher degrees

of ionization for interfacial water and markedly higher affinities of OH⁻ ions for the interfacial region with respect to H⁺ ions.

Electrostatic potentials affecting the state of counterions distributed within the diffuse part of the interfacial layer Ψ_β cannot be directly measured and should be between the ζ and Ψ_0 potentials. The best approximation is to use experimentally available electrokinetic ζ potentials (Figure 2) and to apply Gouy–Chapman theory (eq 42) assuming reasonable values of the slip-plane separation, for example, $l_e = 1$ nm. The minimum possible value of l_e is zero. In such a case, the counterions would be located in the electrokinetic slip plane (i.e., in the e plane, $\Psi_\beta = \zeta$). Consequently, the logarithm of the distribution equilibrium constants for H⁺ and OH⁻ ions would be lower by 0.2 with respect to the values calculated for $l_e = 1$ nm. The maximum possible l_e value could be estimated by comparing experimental Ψ_0 and ζ electrokinetic potentials. Equation 42 provides the distance between the e and 0 planes. The maximum l_e value corresponds to the assumption that 0 the and β planes are identical. In that case, the counterions would be distributed in the same layer as the H⁺ and OH⁻ ions, that is, in the 0 plane, $\Psi_\beta = \Psi_0$. According to the experimental data presented in Figure 3, the maximum possible l_e value would be 2.5 nm, leading to values of the logarithm of the distribution equilibrium constants for H⁺ and OH⁻ ions that are higher by 0.3 with respect to the values calculated for $l_e = 1$ nm. The value of the slip-plane separation was considered as representative because it agrees with findings for metal oxide surfaces.⁶³

The equilibrium constants for the distributions of OH⁻ and H⁺ ions between the bulk and the interface were obtained by applying the criterion of their constancy as a function of pH. The variation of l_e did not affect the constancy of the $K^\circ(\text{H}^+)$ and $K^\circ(\text{OH}^-)$ values. However, the variation of the counterion distribution equilibrium constants results in a pH dependency of the $K^\circ(\text{H}^+)$ and $K^\circ(\text{OH}^-)$ values. The values of $K^\circ(\text{Na}^+)$ and $K^\circ(\text{Cl}^-)$ were treated as adjustable parameters and were finally found to be approximately equal, which is in accordance with published electrokinetic data, suggesting that the isoelectric point does not significantly depend on the electrolyte concentration. In principle, one should consider the possible change in water density at the interface. Introducing a value of 0.5 g cm⁻³, the values for the logarithms of the distribution equilibrium constants for H⁺ and OH⁻ would be higher by 0.24, which would not affect the conclusions.

The available electrokinetic data as taken from the literature (Figure 2) showed significant discrepancies, and a smoothed $\zeta(\text{pH})$ function was used in the calculations. The error in ζ potential values did not significantly affect the results.

In the second step of the interpretation, the surface tension data are analyzed. An appropriate form of the Gibbs isotherm is derived that considers the process in which solute ionic species (i.e., hydronium and hydroxide ions as well as counterions) and solvent molecules (i.e., water) are distributed between the bulk solution phase and the gas/water interface (the water surface). The applied thermodynamic approach is in accordance with the original Gibbs isotherm. It is based on chemical potentials (i.e., partial molar Gibbs energies) and takes into account the distributions of several species and their variable concentrations at the interface. Equations 46 and 47 can easily be reduced to the classical Gibbs equation. For example, the effect of a surfactant on the interfacial tension could be considered by eq 46 by equating the chemical potentials of interfacial and bulk species and introducing a concentration dependence of the latter. In the case of constant composition of the surface, the

term including the amount (mole) fraction of interfacial species is constant. Also, at constant composition of the interface, the surface potential is constant, causing the electrostatic term to be constant and independent of the bulk concentration. In the case of uncharged species, this term simply diminishes. By introducing the obtained μ^σ value into eq 47 and taking the derivative with respect to the logarithm of the bulk concentration, the common form of the Gibbs adsorption isotherm can be easily obtained.

The developed model was used to interpret the surface tension of an aqueous electrolyte solution as a function of pH and as a function of the concentration of electrolyte ions. As shown in Figure 4, the model agrees with the experimentally obtained minimum in the surface tension at the isoelectric point. In the analysis, the equilibrium parameters obtained by interpretation of surface and electrokinetic data were used. The contributions of chemical potentials of different interacting species, μ^σ , were used as adjustable parameters for the evaluation of surface tension. The obtained values of chemical potentials depend on the nature of the interfacial species and are in the range from -4 to -6 kJ/mol.

The above analysis of the experimental data suggests that the negative charge at the gas/water interface in a broad pH region (pH > 4) is due to preferential accumulation of OH⁻ ions at the surface compared to H⁺ ions. Both ions exhibit a pronounced affinity for the surface, but the affinity is markedly more pronounced for OH⁻ ions. Accordingly, the ionization of the surface layer of water is approximately 10⁶ times higher than that of the bulk of the solution, which agrees with the theoretical predictions of Colussi and co-workers.^{64,65} However, the majority of the surface water molecules still remain uncharged. In the analysis, a thermodynamic model based on the distribution of OH⁻ and H⁺ ions between the interface and the bulk phase was applied. The approach assumes that the amount (mole) fraction of neutral water molecules at the surface remains close to 1, which was shown to be the case because the fractions of interfacial OH⁻ and H⁺ ionic species were found to be sufficiently low. Despite the relatively low accuracy of the obtained values, one can definitely conclude that both OH⁻ and H⁺ show a tendency to be transferred to the surface. However, this tendency is significantly more pronounced for OH⁻ ions. The fact that some theoretical analyses suggest opposite conclusions might be explained as follows: First, the results of this study suggest that whole interfacial layer, from the electrokinetic slip plane to the surface plane, is negatively charged above pH 4, whereas theoretical studies deal with a defined plane or thin layer within the interfacial layer. The problem is most easily analyzed by considering the negative electrokinetic charge of the gas/pure water interface, that is, at pH 7. The only ions present in pure water are H⁺ and OH⁻, so that a negative interfacial charge could only be due to the preferential accumulation of OH⁻ ions at the surface. Because their bulk concentrations are equal, one can conclude that H⁺ ions exhibit a lesser affinity to the interface than OH⁻ ions.

A shallow minimum in surface tension was observed in the isoelectric pH region (Figure 4). The theoretical analysis predicts such a minimum and thus explains the experimental finding. The obtained values of the parameters are not accurate, but it is clear that the decrease in chemical potential related to the transfer of OH⁻ and H⁺ ions from the bulk to the interface should produce a minimum in the surface tension in the isoelectric region. The values obtained by interpreting the

electrokinetic and surface potential data therefore agree with the surface tension data.

The proposed procedure could also be applied to the effect of neutral electrolytes (which are not surface-active agents) on the surface tension. Such an analysis requires surface potential and electrokinetic data of gas/aqueous electrolyte solution for different concentrations of electrolytes. Measured surface tension data⁵⁰ of sodium chloride aqueous solutions are compared to our model calculations in Figure 5. For the

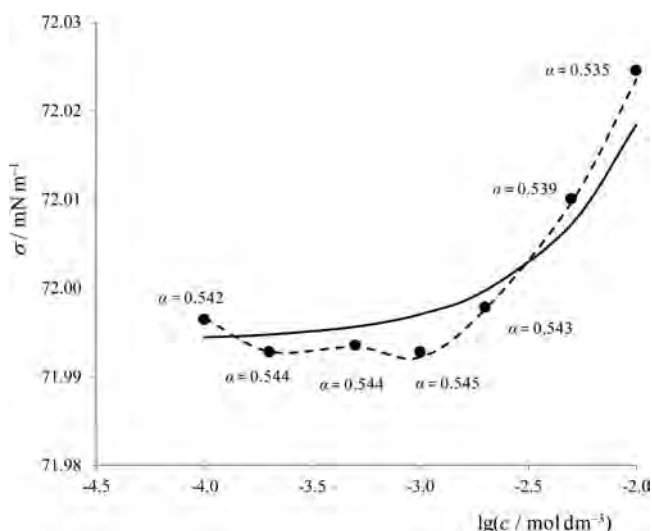


Figure 5. Surface tension of sodium chloride aqueous solution at pH 6. Jones–Ray effect: (●) literature data⁶⁶ and surface tension calculated using constant deviation from the Nernstian potential ($\alpha_N = 0.55$, solid line) and adjustable deviation from the Nernstian potential (values are given near corresponding experimental points, dashed line). Other parameters used in the calculations were as follows: $\text{pH}_{\text{eln}} = \text{pH}_{\text{rep}} = 3.8$, $\vartheta = 25.0$ °C, $l_c = 1$ nm, $I_c = 10^{-2}$ mol dm^{-3} , $\log K^\circ(\text{H}^+) = 1.31$, $\log K^\circ(\text{OH}^-) = 7.64$, $\log K^\circ(\text{C}^+) = -0.74$, $\log K^\circ(\text{A}^-) = -0.74$, $\mu^\sigma(\equiv\text{H}^+) = -5.8$ kJ mol^{-1} , $\mu^\sigma(\equiv\text{OH}^-) = -5.0$ kJ mol^{-1} , $\mu^\sigma(\equiv\text{Na}^+) = -4.5$ kJ mol^{-1} , $\mu^\sigma(\equiv\text{Cl}^-) = -4.1$ kJ mol^{-1} , $\mu^\sigma(\equiv\text{H}_2\text{O}) = -4.2$ kJ mol^{-1} .

calculation of surface tension, the available literature data for electrokinetic potentials,¹⁶ estimated surface potential values, and calculated thermodynamic equilibrium parameters were used. The calculated values were found to depend strongly on the choice of the parameter α_N (deviation from the Nernstian slope). Using a constant α_N value, good agreement with experimental data was found only for NaCl concentrations above 10^{-3} mol dm^{-3} . With the value given above, the observed minimum was not obtained in the simulations. However, by slightly changing the parameter α_N (± 0.01) for calculating surface potential the model follows the experimentally obtained⁴⁶ Jones–Ray effect. It can be concluded that the above analysis does not contradict to the observed Jones–Ray effect but cannot be used for its prediction because of the uncertain dependency of α_N value.

In conclusion, one can state that the controversies between the phenomenological (macroscopic) and theoretical approaches on the molecular scale still exist, which means that further research is necessary. Additional experimental methods should be developed and applied. The final goal will be achieved when the theoretical predictions match the experimental findings. This is important because the phenomono-

logical approach, as presented in this study, does not provide reasons for the behavior of the system on the molecular scale.

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Author Contributions

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Notes

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