

Excess interfacial energy change of solid/aqueous salt solution system with increasing salt concentration at a constant charge-determining ion activity based on the Gibbs equation and ionic components of charge

Research Article

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Received 27 February 2012; Accepted 29 July 2012

Abstract: A thermodynamic equation relating the change of interfacial excess (Gibbs) energy in the solid/aqueous salt solution system, caused by a variation of concentration of inorganic salt at a constant charge-determining ion activity, temperature and pressure, is derived. The equation is based on the Gibbs equation and ionic components of charge parameters. On the basis of literature experimental data for the AgI/aqueous KNO₃ and TiO₂/aqueous NaCl systems it was shown that the interfacial excess energy decreases with increasing salt concentration due to variation of the ionic components of charge of the interface.

Keywords: Gibbs equation • Adsorption • Surface tension • Surface charge • Jones-Ray effect

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1. Introduction

Interfacial properties play important roles in technological processes and environmental phenomena. The properties of the interfaces depend on different parameters including temperature, pressure and presence of different components such as potential determining ions, surfactants, organic and inorganic salts [1]. One of these interfacial parameters is interfacial energy, which changes in aqueous solutions of inorganic electrolytes. The change of interfacial tension of the air/aqueous solution interface in the presence of aqueous inorganic electrolytes can be positive (most salts), negative (HClO₄, HNO₃, KPF₆) or nearly neutral (CH₃NH₃Cl) [2,3]. However, at low electrolyte concentrations there is a dispute on the interfacial tension change. It was claimed by Jones and Ray (for instance [4]) that in very dilute aqueous electrolyte solutions, it decreases;

this is known as the Jones-Ray effect. It was refuted by other researchers [5,6] and is not considered in classical textbooks [2,7]. However, recent studies seems to confirm the existence of the Jones-Ray effect [8-10].

Other interfacial systems – such as aqueous phase in contact with either mercury [11,12] or oil [13] at a constant electrochemical potential – also show a reduction in the interfacial tension with the increase of the electrolyte concentration. It can be expected that a similar effect occurs at the solid/aqueous solution interface because in all cases, as interpreted by Manciu and Ruckenstein [10], the reason is adsorption of OH⁻ ions, which generate accumulation of cations in the vicinity of the surface. On the other hand, adsorption at the interfaces is governed by Gibbs thermodynamics, which, coupled with experimental data, should be able to predict the direction of change of the interfacial tension

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with electrolyte addition in the region of low electrolyte concentrations.

The basic formula for adsorption at interfaces is the Gibbs equation

$$d\gamma = (-\sum \Gamma_i d\mu_i)_{p,T}, \quad (1)$$

which relates the interfacial tension (interfacial excess energy) (γ , J m⁻²) to the surface excesses (Γ_i , mol m⁻²) and chemical potentials (μ_i , J mol⁻¹) at constant pressure p and temperature T for components i which are electroneutral [14]. The Gibbs equation is a starting point for derivation of different equations involving adsorption (e.g. Szyszkowski's equation), as well as spreading and wetting [15,16]. It was demonstrated by Lyklema [17] that the Gibbs equation can help in relating the Esin and Markov coefficient ($dpH/d \ln f_{\pm} c_s$) _{σ_0} , where σ_0 is the surface charge density, c_s electrolyte concentration, $f_{\pm}$ mean activity coefficient, pH negative logarithm of hydrogen ions activity, with ionic components of charge σ_+ and σ_- of the interface.

In this paper Lyklema's [17] analysis will be extended to show a formula relating changes of the interfacial excess (Gibbs) energy with salt addition at a constant charge-determining ion activity, temperature and pressure. The obtained relation can be useful for characterization of phenomena taking part at the solid/diluted aqueous inorganic salt solution interface.

2. Theoretical details

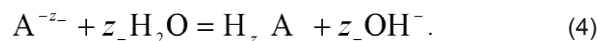
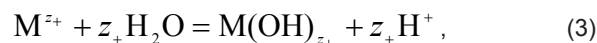
2.1. Derivation of the equation

Let us consider a system consisting of an inorganic solid particle (p) suspended in an aqueous solution (w) containing an inorganic salt (s). The general formula of the salt is $M_{\nu_+} A_{\nu_-}$, where M denotes the metal forming salt and A stands for anion. The symbols ν_+ and ν_- are the stoichiometry coefficients, and they are always positive numbers. Salts added to the solution in our consideration are strong electrolytes, and therefore dissociate according to the reaction:

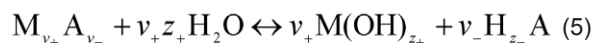


where z_+ and z_- stand for the valence of cation and anion, respectively. The values of z_+ and z_- are always positive numbers. For instance, for NaCl $\nu_+ = 1$, $\nu_- = 1$, $z_+ = 1$ and $z_- = 1$ while for Mg(NO₃)₂ $\nu_+ = 1$, $\nu_- = 2$, $z_+ = 2$ and $z_- = 1$.

The ions can partly hydrolyze to form acid $H_{z_-}A$ and base $M(OH)_{z_+}$:



The reactions, taking place in the solution, can also be written as:



where

$$\nu_+ z_+ = \nu_- z_-. \quad (6)$$

Equilibrium (Eqs. 2-5) takes place when salt $M_{\nu_+} A_{\nu_-}$, acid $H_{z_-}A$, and/or base $M(OH)_{z_+}$ are added to the aqueous solution.

Changing c_s or pH changes the chemical composition of the system. The Gibbs equation relates these changes to the change in the interfacial excess energy. In our case the Gibbs equation at constant temperature and pressure assumes the form:

$$d\gamma = -\Gamma_p d\mu_p - \Gamma_w d\mu_w - \Gamma_{H_{z_-}A} d\mu_{H_{z_-}A} - \Gamma_{M(OH)_{z_+}} d\mu_{M(OH)_{z_+}} - \Gamma_{M_{\nu_+} A_{\nu_-}} d\mu_{M_{\nu_+} A_{\nu_-}}. \quad (7)$$

It should be noted that because of electroneutrality, the system composition is fully determined by the concentrations of electroneutral electrolytes.

The Gibbs equation for the considered system can be simplified by taking into account that for particle and water in diluted aqueous solutions:

$$d\mu_p = 0, \quad d\mu_w = 0. \quad (8)$$

The chemical potentials of the system must obey the Gibbs-Duhem theorem for systems at equilibrium for which the sum of all thermodynamic potentials of all components is:

$$\sum_i k_i d\mu_i = 0, \quad (9)$$

where k_i denotes stoichiometry coefficients of the considered reaction. In our case for Reaction 5 in diluted solutions:

$$d\mu_s = \nu_+ d\mu_{M(OH)_{z_+}} + \nu_- d\mu_{H_{z_-}A}. \quad (10)$$

Using Eq. 10 we can eliminate either $d\mu_{H_{z_-}A}$ or $d\mu_{M(OH)_{z_+}}$ from Eq. 7. For the first case we obtain relation:

$$d\gamma = \left(\frac{\nu_+}{\nu_-} \Gamma_{\text{Hz}_-\text{A}} - \Gamma_{\text{M(OH)}z_+} \right) d\mu_{\text{M(OH)}z_+} - \left(\frac{1}{\nu_-} \Gamma_{\text{Hz}_-\text{A}} + \Gamma_s \right) d\mu_s, \quad (11)$$

in which we used the abbreviation

$$\Gamma_{\text{M}\nu_+\text{A}\nu_-} d\mu_{\text{M}\nu_+\text{A}\nu_-} = \Gamma_s d\mu_s. \quad (12)$$

Incorporating Eq. 6 into Eq. 11 gives:

$$d\gamma = \left(\frac{z_-}{z_+} \Gamma_{\text{Hz}_-\text{A}} - \Gamma_{\text{M(OH)}z_+} \right) d\mu_{\text{M(OH)}z_+} - \left(\frac{1}{\nu_-} \Gamma_{\text{Hz}_-\text{A}} + \Gamma_s \right) d\mu_s. \quad (13)$$

The next step in the derivation is substitution of the surface concentrations Γ_i with the ionic components of charge σ_+ and σ_- providing surface charge σ_0 . Their definitions, based on Lyklema works [14,17], and modified to cover 1:1 and other types of salts are:

$$\sigma_- = -z_- F (\Gamma_{\text{Hz}_-\text{A}} + \nu_- \Gamma_s), \quad (14)$$

$$\sigma_+ = z_+ F (\Gamma_{\text{M(OH)}z_+} + \nu_+ \Gamma_s), \quad (15)$$

$$\sigma_0 = F (z_- \Gamma_{\text{Hz}_-\text{A}} - z_+ \Gamma_{\text{M(OH)}z_+}) \quad (16)$$

thus

$$\sigma_0 = -(\sigma_+ + \sigma_-), \quad (17)$$

where σ_0 , σ_+ and σ_- can be zero, negative or positive [18] due to possible positive or negative sorption. Substitution of Eqs. 14 and 16 in Eq. 13 leads to:

$$d\gamma = \frac{\sigma_0}{z_+ F} d\mu_{\text{M(OH)}z_+} + \frac{\sigma_-}{\nu_- z_- F} d\mu_s. \quad (18)$$

For practical use it is necessary to replace the chemical potentials with concentrations. For equilibrium (Eq. 2) the change of the chemical potential of the salt is:

$$d\mu_s = \nu_+ d\mu_{\text{M}} + \nu_- d\mu_{\text{A}}. \quad (19)$$

According to Eq. 2, activity a_{M} of the metal ion, when the salt is completely dissolved and dissociated, is equal to $\nu_+ a_s$ while for the anion $a_{\text{A}} = \nu_- a_s$. Since

$$\mu_{\text{M}} = \mu_{\text{M}}^o + RT \ln(\nu_+ a_s) \quad (20)$$

and because

$$\mu_{\text{A}} = \mu_{\text{A}}^o + RT \ln(\nu_- a_s) \quad (21)$$

then

$$d\mu_{\text{M}} = d\mu_{\text{A}} = 2.303RT d \log a_s. \quad (22)$$

Inserting twice Eq. 22 into Eq. 19 and introducing:

$$a_s = c_s f_{\pm} \quad (23)$$

one gets

$$d\mu_s = \nu_+ d\mu_{\text{M}} + \nu_- d\mu_{\text{A}} = 2.303RT d \log c_s^{\nu_+ + \nu_-} f_{\pm}^{\nu_+ + \nu_-}, \quad (24)$$

where c_s is the molar concentration of the salt and $f_{\pm}$ stands for the mean activity coefficient.

For Reaction 3 we can write:

$$d\mu_{\text{M(OH)}z_+} = d\mu_{\text{M}} - z_+ d\mu_{\text{H}^+}. \quad (25)$$

Since $d\mu_{\text{H}^+} = -2.303RT dpH$, we get:

$$d\mu_{\text{M(OH)}z_+} = d\mu_{\text{M}} + 2.303z_+ RT dpH, \quad (26)$$

where $pH = -\log c_{\text{H}^+} f_{\pm}$. Substituting Eqs. 22, 24 and 26 into Eq. 18 gives

$$d\gamma = \frac{2.303RT\sigma_0}{F} dpH + \frac{2.303RT\sigma_0}{z_+ F} d \log(c_s f_{\pm}) + \frac{2.303RT(\nu_- + \nu_+)\sigma_-}{z_- \nu_- F} d \log(c_s f_{\pm}). \quad (27)$$

Since we are interested in the change of the interfacial excess energy with changing salt concentration at a constant pH ($dpH = 0$), Eq. 27 can be rewritten to:

$$\left(\frac{d\gamma}{d \log(c_s f_{\pm})} \right)_{pH} = \frac{2.303RT}{F} \left(\sigma_0 \frac{1}{z_+} + \sigma_- \frac{\nu_- + \nu_+}{z_- \nu_-} \right). \quad (28)$$

Taking into account Eqs. 6 and 17 we obtain:

$$\left(\frac{d\gamma}{d \log(c_s f_{\pm})} \right)_{pH} = -\frac{2.303RT}{F} \left(\frac{\sigma_+}{z_+} - \frac{\sigma_-}{z_-} \right). \quad (29)$$

Eq. 29 shows that the change of the interfacial excess energy with the salt concentration at a constant pH, temperature and pressure depends on the ionic components of charge and the valence of ions.

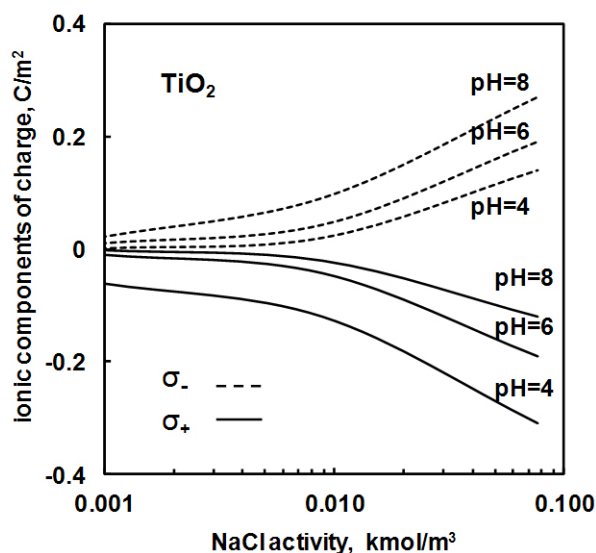


Figure 1. Influence of NaCl activity on ionic components of charge for TiO_2 at selected pH values. Numerical values taken from Sprycha *et al.* [19]. Due to lack of σ_- for 0.001 M NaCl solutions in the paper, values of σ_- were assumed to be the same as $-\sigma_+$ for pH equally distant from the pzc. In the original paper σ_- values were plotted as negative numbers without marking them as negative on the y axis.

A more general form of Eq. 29 is

$$\left(\frac{d\gamma}{d \log(c_s f_{\pm})} \right)_{\text{pP}} = - \frac{2.303RT}{F} \left(\frac{\sigma_+}{z_+} - \frac{\sigma_-}{z_-} \right), \quad (30)$$

where pP is the negative decimal logarithm of activity of potential determining ions.

2.2. Calculation of interfacial excess energy change caused by increasing concentration of salt at a constant activity of potential determining ions using ionic components of charge

Eqs. 28-30 can be used for calculation of the change of the interfacial excess energy caused by addition of salt at a constant concentration of charge-determining ions and temperature. It can be easily accomplished provided that the ionic components of the charge, that is σ_- and σ_+ , at the considered concentrations of salt are known. In this work, calculations were performed utilizing experimental data on ionic components of charge of Sprycha *et al.* [19] for the TiO_2 /aqueous NaCl system and for the AgI/aqueous KNO_3 system using numerical values taken from Lyklema [18]. Lyklema plotted his results as ionic components vs. surface potential. For the purpose of this work, potentials was recalculated back to activity of the potential determining ions (Ag^+) by means of the Nernst equation $\psi_0 = 59.1 (\text{pAg} - \text{pzc})$ (mV) taking into account that the pzc is at

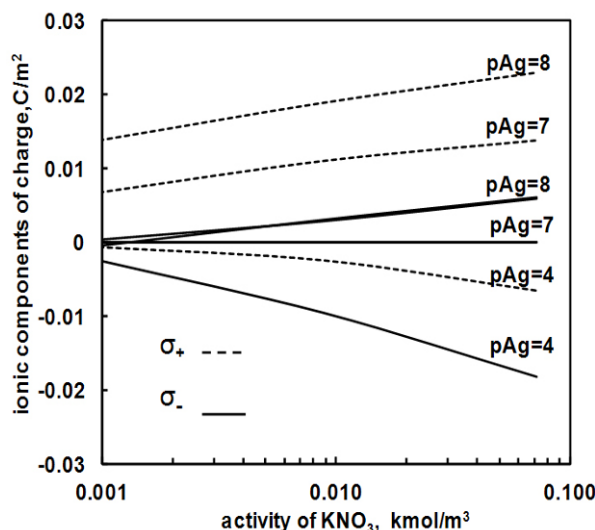


Figure 2. Influence of KNO_3 activity on ionic components of charge for AgI at selected pAg values (data taken from Lyklema [18]).

pAg = 5.2. The ionic components of charge as a function of salt activity for the considered systems are plotted in Figs. 1 and 2.

To calculate the changes of the interfacial excess energy, it is convenient to write Eq. 29 in another form, taking into account that $d \log a_s = \frac{1}{\ln 10} \cdot \frac{1}{a_s} da_s$:

$$d\gamma = - \frac{RT}{F} \left(\frac{\sigma_+}{z_+} - \frac{\sigma_-}{z_-} \right) \frac{1}{a_s} da_s \quad (\text{at constant pP}). \quad (31)$$

The integral form of Eq. 31, knowing that σ_+ and σ_- are functions of a_s , is:

$$\int_{\gamma_{a_{s1}}}^{\gamma_{a_{s2}}} d\gamma = - \frac{RT}{F} \int_{a_{s1}}^{a_{s2}} \left(\frac{\sigma_+(a_s)}{z_+} \frac{1}{a_s} da_s \right) + \frac{RT}{F} \int_{a_{s1}}^{a_{s2}} \left(\frac{\sigma_-(a_s)}{z_-} \frac{1}{a_s} da_s \right) \quad (\text{at constant pP}), \quad (32)$$

and

$$\Delta\gamma = \gamma_{a_{s1}} - \gamma_{a_{s2}} = - \frac{RT}{F} \int_{a_{s1}}^{a_{s2}} \left(\frac{\sigma_+(a_s)}{z_+} \frac{1}{a_s} da_s \right) + \frac{RT}{F} \int_{a_{s1}}^{a_{s2}} \left(\frac{\sigma_-(a_s)}{z_-} \frac{1}{a_s} da_s \right) \quad (\text{at constant pP}) \quad (33)$$

where $\Delta\gamma$ denotes the change of interfacial excess energy when the salt activity is increased from a_{s1} to a_{s2} .

For calculation of $\Delta\gamma$, the data on σ_+ and σ_- from Figs. 1 and 2 were expressed as polynomials for a given pP, inserted into Eq. 33, and integrated with a computer software. To recalculate concentration into activity we used the known relation $a_s = c_s f_{\pm}$ using activity

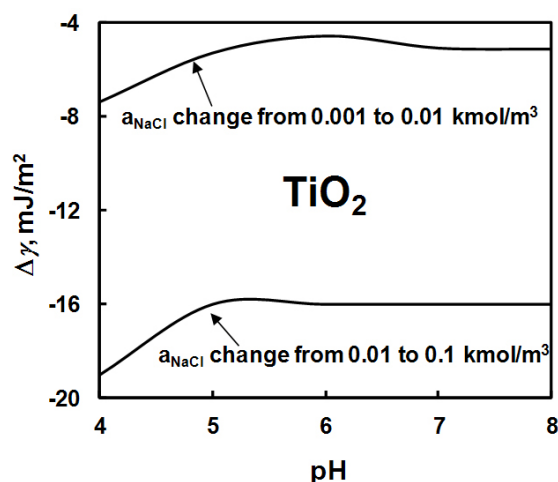


Figure 3. Change of interfacial excess energy of TiO_2 due to NaCl activity change at a constant pH. $\text{pH}_{\text{pzc}} = 6.0$.

coefficient data for KNO_3 and NaCl for molal (mole kg^{-1}) concentrations taken from Zaytsev and Aseyev [20] and assuming solutions densities as 1 kg dm^{-3} . One of the equations for calculations involving TiO_2 was

$$\Delta\gamma_{|pH=4} = -\frac{RT}{F} \left[\int_{a_{s1}}^{a_{s2}} \frac{0.0316 \ln(a_s) + 0.2037}{a_s} da_s \right] + \frac{RT}{F} \left[\int_{a_{s1}}^{a_{s2}} \frac{-0.057 \ln(a_s) - 0.4335}{a_s} da_s \right]. \quad (34)$$

The results of integration over salts activity from $a_{s1} = 0.001 \text{ M}$ to $a_{s2} = 0.01 \text{ M}$ and separately from $a_{s1} = 0.01 \text{ M}$ to $a_{s2} = 0.1 \text{ M}$, providing changes of the interfacial excess energy vs. salt concentration at a constant pP (pH for TiO_2 and pAg for AgI), are given in Figs. 3 and 4.

The calculations indicate that at constant pP the interfacial excess energy at the solid/salt aqueous solution of both TiO_2 and AgI decreases with increasing activity of inorganic salt as a result of increasing adsorption of ions at the interface. This effect was observed up to about 0.1 M salt solutions. Such effects have been observed for other systems including oil/aqueous NaCl interface [13], mercury/aqueous KBr interface [12] and for the air/aqueous solution system, known as the Jones–Ray effect. It can be also expected that the derived formula will be useful for interpretation of other phenomena, including diminished flotation of hydrophobic materials

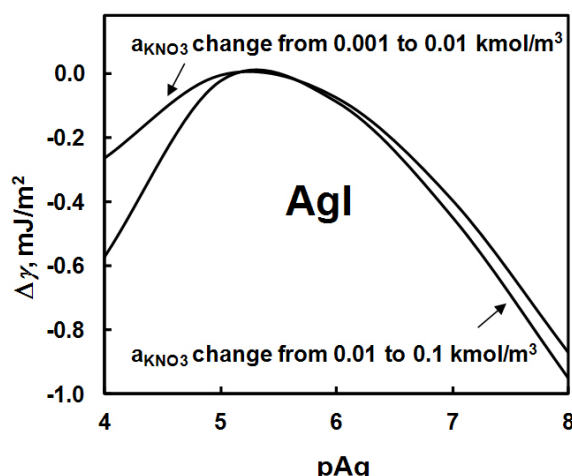


Figure 4. Change of interfacial excess energy of AgI due to KNO_3 activity change at a constant activity of Ag^+ ions (pAg). $\text{pAg}_{\text{pzc}} = 5.2$

in inorganic electrolytes at low concentrations [21], even though the mechanism of interfacial charging in the mentioned systems is different.

3. Conclusions

The Gibbs equation and ionic components of charge of the solid/aqueous solution interface can be used for derivation of a thermodynamic equation, being a derivative of the interfacial excess energy with respect to the logarithm of the salt activity at a constant charge-determining ion activity, temperature and pressure of the aqueous solution. The equation and experimental data indicate that the interfacial excess energy in the solid/aqueous solution system decreases with increasing activity of salt up to the investigated concentrations of about 0.1 M . The results of calculations are similar to the effects observed in other systems, such as oil/air, mercury/aqueous solution and aqueous solution/air (the Jones–Ray effect at very low salts concentrations).

Acknowledgements

The authors thank Prof. J. Lyklema for his valuable advice and criticism during the writing of this paper. Financial support by the Polish Statutory Research Grant S10088 is highly appreciated.

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