| | |
|---|---|
| Title | Thermodynamics of adsorption at the aqueous-air interface |
| Author(s) | Pajarre, Risto; Koukkari, Pertti |
| Citation | Journal of Colloid and Interface Science. Elsevier. Vol. 337 (2009) No: 1, Pages 39 - 45 |
| Date | 2009 |
| URL | http://dx.doi.org/10.1016/j.jcis.2009.05.023 |
| Rights | © 2016. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/ |

# Thermodynamics of adsorption at the aqueous-air interface

Risto Pajarre*, Pertti Koukkari

VTT Technical Research Centre of Finland, Biologinkuja 7, Espoo, P.O. Box 1000, FIN-02044 VTT, FINLAND

Risto.Pajarre@vtt.fi Tel: +358-20-722 6332, Fax: +358-20-722 7026

## Abstract

A thermodynamic model is presented for the aqueous-air interface. For common organic solutes a relationship between the activity coefficients in the bulk solution and on the surface layer is deduced by using the concept of a surface monolayer. This relation has enabled development of an equation expressing the air-water surface adsorption coefficient as a function of bulk activity coefficients, surface tensions, molar volumes and vapour pressures of the adsorbing species. The data for 51 compounds, including alkanes, cycloalkanes, aromatics, halogenated hydrocarbons, alcohols, ethers and esters, and ketones were used in the study.

## Keywords

adsorption; air-water interface; monolayer model; thermodynamic modeling; surface tension

## 1   Introduction

Air-water surface adsorption is an area of considerable interest both in physical and environmental sciences as the interfacial properties greatly affect distributions and mass transfer rates of chemicals in any systems where gaseous and aqueous phases coexist, whether they are of environmental, industrial or biological nature. A key parameter often determined by experimental methods or whose prediction is aimed for by various semi empirical models is the water surface adsorption coefficient ($K_{i/a}$) (e.g. [1-3]). Thermodynamic studies based on the idea that the surface properties can be predicted using models in which the topmost molecular layer of a liquid is modelled as a separate phase with its thermodynamic properties different but related to those of the bulk liquid have been found successful in describing adsorption behaviour in high temperature metallurgical systems [4-5]. The purpose of this study was to find a consistent relationship between the activity coefficients in the bulk and on the surface layer at the infinite dilution limit and consequently to predict values of adsorption coefficient based on other known thermodynamic data.

## 2   Theory

The water surface adsorption coefficient ($K_{i/a}$) is defined as

$$K_{i/a} = \frac{\Gamma_i}{C_a} \tag{1}$$

where $\Gamma_i$ is the adsorbed amount as moles/m$^2$ and $C_a$ the concentration in air as moles/m$^3$. The chemical process where the adsorbing species is transferred from gas to the aqueous solvent surface (while maintaining the original surface area) can be written as

$$Ads^g + \frac{A_{Ads}}{A_{Solv}} Solv^s \leftrightarrow Ads^s + \frac{A_{Ads}}{A_{Solv}} Solv^b \tag{I}$$

The factor $A_{Ads}/A_{Solv}$ is needed because in general the molar surface areas of the adsorbing substance and solvent are not equal. The equilibrium coefficient for the process can be written as

$$K_{eq} = \frac{a_{Ads}^s \left(a_{Solv}^b\right)^{\frac{A_{Ads}}{A_{Solv}}}}{a_{Ads}^g \left(a_{Solv}^s\right)^{\frac{A_{Ads}}{A_{Solv}}}} = \exp\left(-\frac{\Delta G_{Adsorption}^0}{RT}\right)$$

$$= \exp\left(\frac{\mu_{Ads}^{0,g} + \frac{A_{Ads}}{A_{Solv}}\mu_{Solv}^{0,s} - \mu_{Ads}^{0,s} - \frac{A_{Ads}}{A_{Solv}}\mu_{Solv}^{0,b}}{RT}\right) \tag{2}$$

If one makes the monolayer assumption [34] that the surface effects are restricted to the single molecular layer closest to the surface, the standard state chemical potential at the surface becomes

$$\mu_i^{0,s} = \mu_i^{0,b} + A_i \sigma_i \tag{3}$$

where $\sigma_i$ is the surface tension of the pure substance $i$. $K_{eq}$ can then be written as

$$K_{eq} = \exp\left(\frac{\Delta G_{Ads}^{0,vap} + A_{Ads}\left(\sigma_{Solv} - \sigma_{Ads}\right)}{RT}\right) = \frac{p^0}{p_{Ads}^{vap}}\exp\left(\frac{A_{Ads}\left(\sigma_{Solv} - \sigma_{Ads}\right)}{RT}\right) \tag{4}$$

The adsorbed amount (or relative surface excess [35]) in the monolayer model can be written as

$$\Gamma_{Ads} = \frac{n_{Ads}^s - n_{Solv}^s \frac{x_{Ads}^b}{x_{Solv}^b}}{A} \xrightarrow[n_{Ads}^s \to 0]{} \frac{n_{Ads}^s}{A} - \frac{x_{Ads}^b}{A_{Solv}} \tag{5}$$

Approaching the infinite dilution limit for the adsorbing species we have

$$K_{eq} \xrightarrow[x(ads)\to 0]{} \frac{x_{Ads}^s \gamma_{Ads}^{\infty,s}}{x_{Ads}^g \left(p/p_0\right)} = \frac{\frac{n_{Ads}^s}{A} A_{Solv}\gamma_{Ads}^{\infty,s}}{\frac{n_{Ads}^g}{V^g}\frac{RT}{p_0}} = K_{i/a}\frac{A_{Solv}\gamma_{Ads}^{\infty,s}p_0}{RT} + x_{Ads}^b\frac{\gamma_{Ads}^{\infty,s}p_0}{\frac{n_{Ads}^g}{V^g}RT} \tag{5}$$

Applying the thermodynamic equilibrium relationship between molar fractions in liquid solution and in ideal gas vapour

$$x_{Ads}^b = \frac{p \cdot x_{Ads}^g}{\gamma_{Ads}^b p_{Ads}^{vap}} \tag{6}$$

we get

$$K_{eq} = K_{i/a}\frac{A_{Solv}\gamma_{Ads}^{\infty,s}p_0}{RT} + \frac{\gamma_{Ads}^{\infty,s}p_0}{\gamma_{Ads}^{\infty,b}p_{Ads}^{vap}} \tag{7}$$

From equations (4) and (7) we finally obtain

$$\gamma_{Ads}^{\infty,s} = \left(\frac{A_{Solv}K_{i/a}}{RT} + \frac{1}{p_{Ads}^{vap}\gamma_{Ads}^{\infty,b}}\right)^{-1}\frac{1}{p_{Ads}^{vap}}\exp\left(\frac{A_{Ads}\left(\sigma_{Solv} - \sigma_{Ads}\right)}{RT}\right) \tag{8}$$

If the surface infinite dilution activity coefficients would be known, equation (8) could also be solved for $K_{i/a}$.

## *2.1 Molar surface areas*

Equation (8) requires knowledge of molar surface areas of the adsorbing species and the solvent. In this paper two different assumptions were experimented:

1) Direct estimation of molar surface areas based on molar volumes of the substances [36]:

$$A_i = 1.091 \cdot N_a^{1/3} V_i^{2/3} \tag{9}$$

2) Use of Paquette volumes from an anisotropic surface model [37] instead of molar volumes in the previous equation leading to

$$A_i = 1.091 \cdot N_a^{1/3} V_i^{4/15} \left(V_i^{crit}\right)^{6/15} \tag{10}$$

where $V_i^{crit}$ is the critical molar volume of substance *i*. It should be noted that both of the equations (9) and (10) effectively assume that the adsorbing molecules can be considered spherical in estimating the molar surface areas. Also, it is assumed that the molar surface areas are the same at infinite dilution as they would be for the pure organic liquid.

# 3 Correlation between surface and bulk activity coefficients

The thermodynamic data (at 25 °C) used is presented in Table 1. All the experimental adsorption coefficient values are from reference [1] and infinite dilution activity coefficient values from reference [38].

The surface activity coefficients calculated from equation (8) with the two surface area assumptions are presented in Fig. 1 and Fig. 2.

Table 1. Thermodynamic data used in the modelling

| | Log($K_{i/a}$) (experimental) | ln($\gamma_{Ads}^{\infty,b}$) | $V_i$ (m³/mol) | Ref | $V_i^{crit}$ (m³/mol) | Ref | $\sigma_i$ (N/m) | Ref | $P_{Ads}^{vap}$ (bar) | Ref | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|
| n-pentane | -7.22 | 11.487 | 1.175E-04 | [6] | 3.110E-04 | [15] | 0.0155 | [21] | 6.84E-01 | [24] | a |
| n-hexane | -6.9 | 12.941 | 1.316E-04 | [6] | 3.680E-04 | [15] | 0.0179 | [21] | 2.02E-01 | [24] | a |
| n-heptane | -6.6 | 14.565 | 1.475E-04 | [6] | 4.280E-04 | [15] | 0.0197 | [21] | 6.10E-02 | [24] | a |
| n-octane | -6.23 | 16.051 | 1.635E-04 | [6] | 4.920E-04 | [15] | 0.0211 | [21] | 1.87E-02 | [24] | a |
| n-nonane | -5.91 | 17.632 | 1.797E-04 | [6] | 5.550E-04 | [16] | 0.0224 | [21] | 5.81E-03 | [24] | a |
| n-decane | -5.58 | 19.198 | 1.959E-04 | [7] | 6.240E-04 | [16] | 0.0234 | [21] | 1.82E-03 | [24] | a |
| 2,2,4-trimethylpentane | -6.47 | 14.820 | 1.661E-04 | [8] | 4.680E-04 | [15] | 0.0202 | [21] | 6.57E-02 | [25] | a |
| 1-nonene | -5.72 | 15.654 | 1.741E-04 | [6] | 5.260E-04 | [16] | 0.0226 | [21] | 7.24E-03 | [6] | a |
| cyclohexane | -6.97 | 11.306 | 1.080E-04 | [6] | 3.080E-04 | [15] | 0.0247 | [21] | 1.30E-01 | [6] | a |
| cyclooctane | -6.25 | 13.579 | 1.348E-04 | [6] | 4.100E-04 | [17] | 0.0293 | [21] | 7.52E-03 | [6] | a |
| benzene | -6.32 | 7.832 | 8.940E-05 | [6] | 2.560E-04 | [15] | 0.0282 | [21] | 1.27E-01 | [6] | a |
| toluene | -5.93 | 9.165 | 1.069E-04 | [6] | 3.160E-04 | [15] | 0.0279 | [21] | 3.84E-02 | [6] | a |
| p-xylene | -5.57 | 10.497 | 1.238E-04 | [6] | 3.780E-04 | [15] | 0.0280 | [21] | 1.18E-02 | [6] | a |
| ethylbenzene | -5.58 | 10.471 | 1.230E-04 | [6] | 3.740E-04 | [16] | 0.0287 | [21] | 1.27E-02 | [6] | a |
| isoprpylbenzene | -5.39 | 11.629 | 1.401E-04 | [6] | 4.270E-04 | [18] | 0.0277 | [21] | 6.17E-03 | [6] | a |
| styrene | -5.56 | 9.798 | 1.156E-04 | [6] | 3.520E-04 | [18] | 0.0315 | [22] | 8.64E-03 | [6] | a |
| biphenyl | -4.1 | 13.042 | 1.496E-04 | [9] | 5.020E-04 | [18] | 0.0392 | [21] | 1.30E-05 | [26] | a, b |
| naphtalene | -4.69 | 11.101 | 1.185E-04 | [10] | 4.070E-04 | [15] | 0.0401 | [21] | 1.12E-04 | [27] | a, b |
| nitrobenzene | -3.99 | 8.169 | 1.027E-04 | [11] | 3.490E-04 | [18] | 0.0434 | [21] | 3.77E-04 | [28] | a, d |
| thiophene | -6.43 | 7.346 | 7.950E-05 | [12] | 2.190E-04 | [19] | 0.0321 | [12] | 1.08E-01 | [29] | a |
| ethanol | -4.15 | 1.329 | 5.869E-05 | [6] | 1.680E-04 | [15] | 0.0220 | [21] | 7.87E-02 | [6] | |
| 1-propanol | -3.83 | 2.613 | 7.515E-05 | [6] | 2.180E-04 | [16] | 0.0233 | [21] | 2.81E-02 | [6] | |
| 2-propanol | -3.85 | 2.063 | 7.690E-05 | [6] | 2.220E-04 | [16] | 0.0209 | [21] | 5.77E-02 | [6] | |
| 2-methyl-1-propanol | -3.61 | 3.886 | 9.295E-05 | [6] | 2.740E-04 | [16] | 0.0225 | [21] | 1.54E-02 | [6] | |
| acetone | -4.78 | 2.000 | 7.400E-05 | [6] | 2.090E-04 | [15] | 0.0240 | [21] | 3.08E-01 | [30] | |
| 3-Methylbutan-2-one | -4.42 | 4.431 | 1.069E-04 | [6] | 3.080E-04 | [16] | 0.0246 | [23] | 6.72E-02 | [6] | |
| 2-butanone | -4.6 | 3.275 | 9.016E-05 | [6] | 2.670E-04 | [15] | 0.0240 | [21] | 1.21E-01 | [6] | |
| pentanal | -4.68 | 5.395 | 1.052E-04 | [13] | 3.130E-04 | [16] | 0.0254 | [21] | 4.87E-02 | [31] | e |
| cyclopentanone | -3.77 | 3.374 | 8.912E-05 | [6] | 2.580E-04 | [18] | 0.0328 | [21] | 1.51E-02 | [6] | |
| diethyl ether | -5.3 | 4.496 | 1.047E-04 | [13] | 2.800E-04 | [15] | 0.0167 | [21] | 7.16E-01 | [25] | |
| diisopropyl ether | -4.83 | 6.469 | 1.409E-04 | [13] | 3.860E-04 | [16] | 0.0173 | [21] | 2.01E-01 | [25] | |
| di-n-propyl ether | -4.81 | 7.275 | 1.373E-04 | [13] | 3.820E-04 | [18] | 0.0200 | [21] | 8.37E-02 | [25] | a |
| methylphenyl ether | -4.89 | 8.326 | 1.092E-04 | [13] | 3.410E-04 | [20] | 0.0351 | [21] | 4.56E-03 | [22] | e |
| 1,4-dioxane | -3.88 | 1.693 | 8.571E-05 | [14] | 2.380E-04 | [15] | 0.0328 | [21] | 4.98E-02 | [22] | |
| methyl formate | -5.55 | 2.741 | 6.165E-05 | [13] | 1.720E-04 | [15] | 0.0244 | [21] | 8.34E-01 | [22] | |
| ethyl formate | -6.08 | 3.857 | 8.026E-05 | [13] | 2.290E-04 | [15] | 0.0232 | [21] | 3.25E-01 | [22] | |
| methyl acetate | -5.06 | 3.118 | 8.017E-05 | [13] | 2.280E-04 | [15] | 0.0247 | [21] | 2.88E-01 | [22] | |
| ethyl acetate | -4.59 | 4.168 | 9.779E-05 | [13] | 2.860E-04 | [15] | 0.0234 | [21] | 1.26E-01 | [22] | |
| isobutyl acetate | -4.16 | 6.739 | 1.334E-04 | [13] | 4.010E-04 | [16] | 0.0231 | [21] | 2.34E-02 | [32] | |
| dichloromethane | -6.63 | 5.448 | 6.358E-05 | [13] | 1.770E-04 | [18] | 0.0272 | [21] | 5.80E-01 | [6] | c |
| chloroform | -6.4 | 6.678 | 8.069E-05 | [6] | 2.390E-04 | [15] | 0.0267 | [21] | 2.63E-01 | [6] | |
| 1-chlorobutane | -6.35 | 8.939 | 1.044E-04 | [13] | 3.000E-04 | [18] | 0.0216 | [21] | 1.36E-01 | [22] | |
| 1-bromobutane | -6.07 | 9.435 | 1.073E-04 | [13] | 3.190E-04 | [18] | 0.0259 | [21] | 5.26E-02 | [22] | |
| 1,1,2,2-tetarachloroethane | -5.22 | 8.095 | 1.058E-04 | [6] | 3.250E-04 | [18] | 0.0356 | [21] | 5.58E-03 | [6] | a |
| 1,1,1-trichloroethane | -6.54 | 8.656 | 1.004E-04 | [6] | 2.810E-04 | [18] | 0.0251 | [21] | 1.66E-01 | [6] | a |
| 1,2-dichloroethane | -6.08 | 6.450 | 7.943E-05 | [6] | 2.200E-04 | [18] | 0.0319 | [22] | 1.05E-01 | [6] | a |
| chlorobenzene | -5.9 | 9.499 | 1.017E-04 | [13] | 3.080E-04 | [15] | 0.0330 | [21] | 1.60E-02 | [22] | e |
| iodobenzene | -4.71 | 10.893 | 1.118E-04 | [13] | 3.510E-04 | [15] | 0.0387 | [21] | 1.32E-03 | [22] | |
| bromobenzene | -5.73 | 9.984 | 1.050E-04 | [13] | 3.240E-04 | [15] | 0.0352 | [21] | 5.52E-03 | [22] | e |
| 1,3-dichlorobenzene | -5.57 | 11.100 | 1.141E-04 | [13] | 3.510E-04 | [18] | 0.0354 | [21] | 2.65E-03 | [22] | a, e |
| 1,4-dichlorobenzene | -5.57 | 11.533 | 1.008E-04 | [13] | 3.510E-04 | [18] | 0.0325 | [22] | 2.41E-03 | [22] | a, e |
| water | | | 1.807E-05 | [22] | 5.600E-05 | [15] | 0.0720 | [39] | | | |

[a] Activity coefficient based on solubility measurements

[b] Solid at 25 °C. Liquid surface tension and molar volumes extrapolated to 25 °C. Tabulated vapour pressure values (over solid) have been adjusted for calculations to correspond to those over supercooled liquid based on melting point temperature and heat of fusion (references [33] and [27] )

[c] Critical volume predicted based on the Marrero-Gani group contribution method [40]

[d] Surface tension value extrapolated to 25 °C

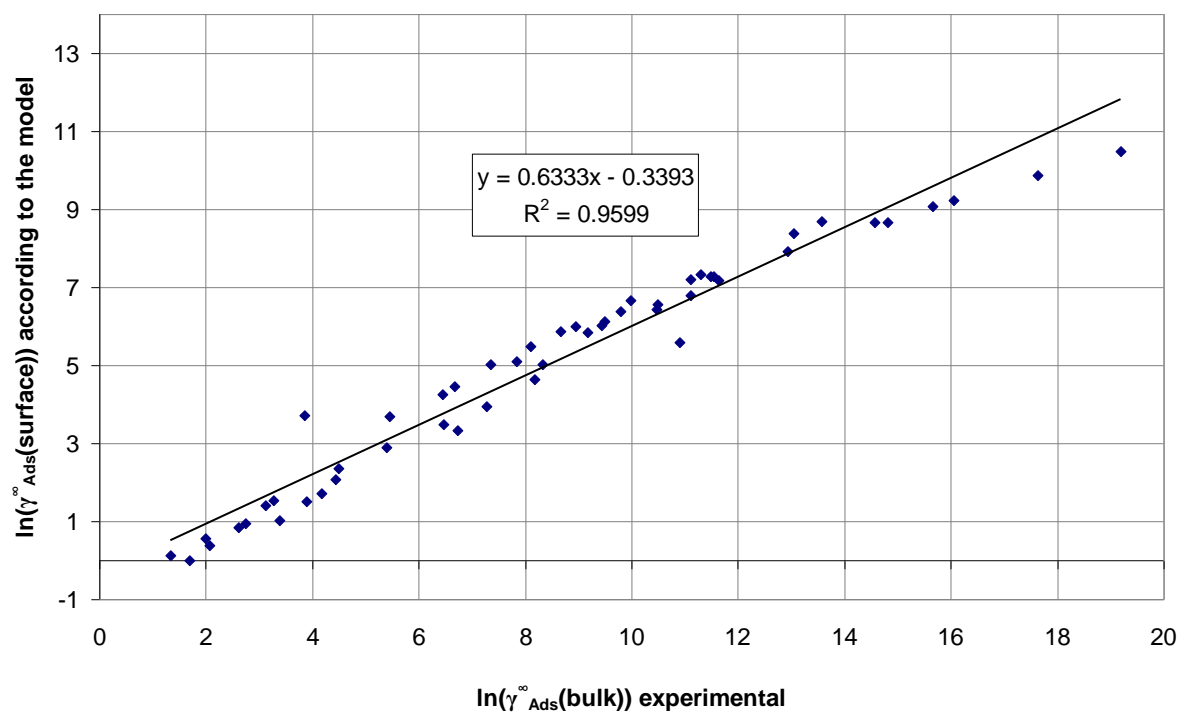[e] Vapour pressure extrapolated to 25 °C

Fig. 1. Activity coefficients for surface areas derived directly from molar surface areas using equation
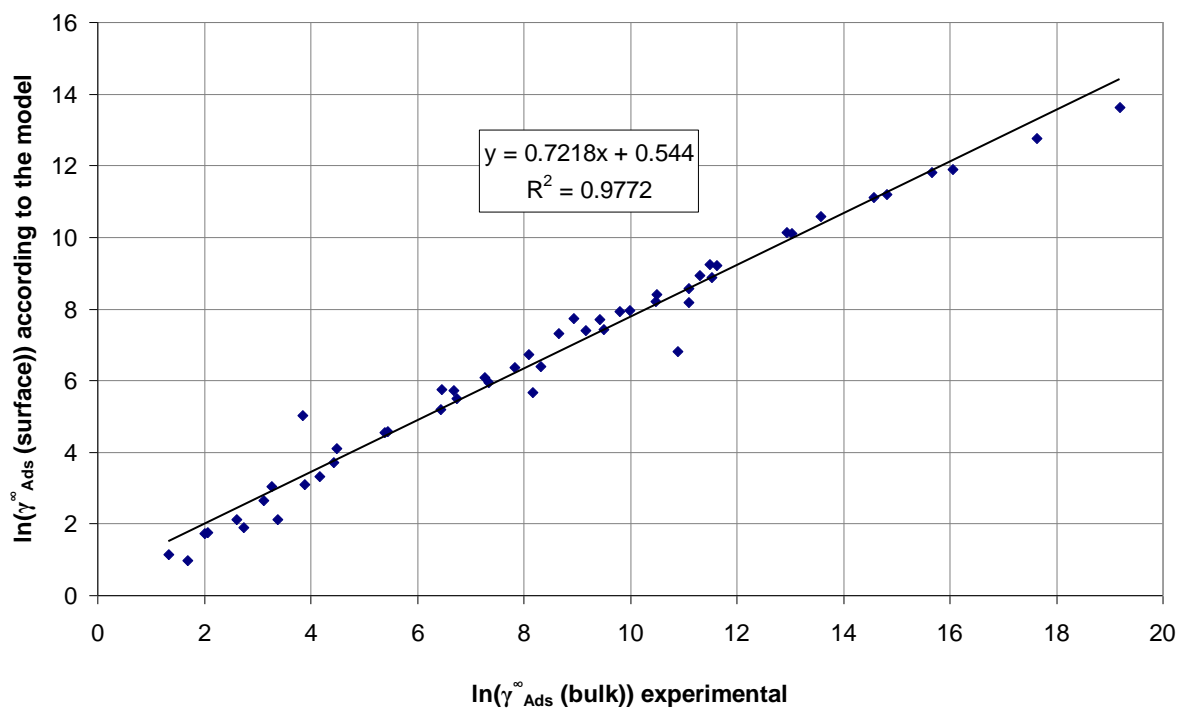(9)



Fig. 2. Activity coefficients for surface areas derived using Paquette volumes (equation (10))

# 4 Interpretation and refining of the linear correlation

Surface activity coefficient models used in metallurgy and materials science often assume that the activity coefficients have the same compositional dependency as those in the bulk but are scaled by some factor less than unity [5, 34, 41]. This is intuitively reasonable based on the reduced co-ordination number, and therefore reduced number of interactions, for the atoms and molecules on the surface layer. In classical treatises of surface thermodynamics [42] the reduced co-ordination number is typically assumed to have a value of 0.75, corresponding to the case of closely packed spheres, where six of the nearest neighbours of each sphere are in the same layer and three on both the layer above and below it. In more practically oriented studies of surface thermodynamics of mixtures [41, 43-44] the effective co-ordination number has been considered an empirical parameter (that can include the effect of surface relaxation and other phenomena) with values typically varying from about 0.75 to values slightly above unity.

The activity coefficient trends deduced above, especially the one using directly bulk molar volumes, do not seem to go through the origin, which would be desirable in order to reach an easily applicable and thermodynamically consistent surface activity coefficient model from a known bulk activity. It was decided to test how the scaling behaviour would change if it was assumed that the activity coefficients would include a simple Flory-Huggins like molar volume dependent combinatorial contribution that would not be scaled with the reduced co-ordination number, leading to equation (11)

$$\ln \gamma_{Ads}^{\infty,s} - \ln\left(V_{Ads}/V_{Solv}\right) - \left(1 - V_{Ads}/V_{Solv}\right) = \beta\left[\ln \gamma_{Ads}^{bulk,\infty} - \ln\left(V_{Ads}/V_{Solv}\right) - \left(1 - V_{Ads}/V_{Solv}\right)\right] \quad (11)$$

where $\beta$ is the reduced coordination number on the surface layer. Activity coefficient data has been plotted in the form of equation (11) for the two alternative surface area cases in Fig. 3 and Fig. 4. In the first case, the bulk molar volumes were used in the equation (11), while in the second case bulk volumes were applied for the bulk and Paquette volumes for the surface layer. In the second case equation (11) becomes

$$\ln \gamma_{Ads}^{\infty,s} - \ln\left(V_{Ads}^{Paq}/V_{S\ddot{o}v}^{Paq}\right) - \left(1 - V_{Ads}^{Paq}/V_{S\ddot{o}v}^{Paq}\right) = \beta\left[\ln \gamma_{Ads}^{bulk,\infty} - \ln\left(V_{Ads}/V_{Solv}\right) - \left(1 - V_{Ads}/V_{Solv}\right)\right] \quad (11b)$$

In both Fig. 3 and Fig. 4 the shown regression line is the best least squares fit that goes through the origin. With both molar volume assumptions the inclusion of the Flory-Huggins adjustment to the activity coefficients resulted in a better fit with one adjustable parameter regression line than was originally obtained using two adjustable parameters. Overall, the model using Paquette volumes gives a marginally better fit, with the difference being most noticeable with the compounds having relatively small activity coefficient values. It should be noted that while the linear correlation fit is almost equally good for both surface layer molar volume assumptions, there is a significant difference in the resulting value for the reduced coordination number.
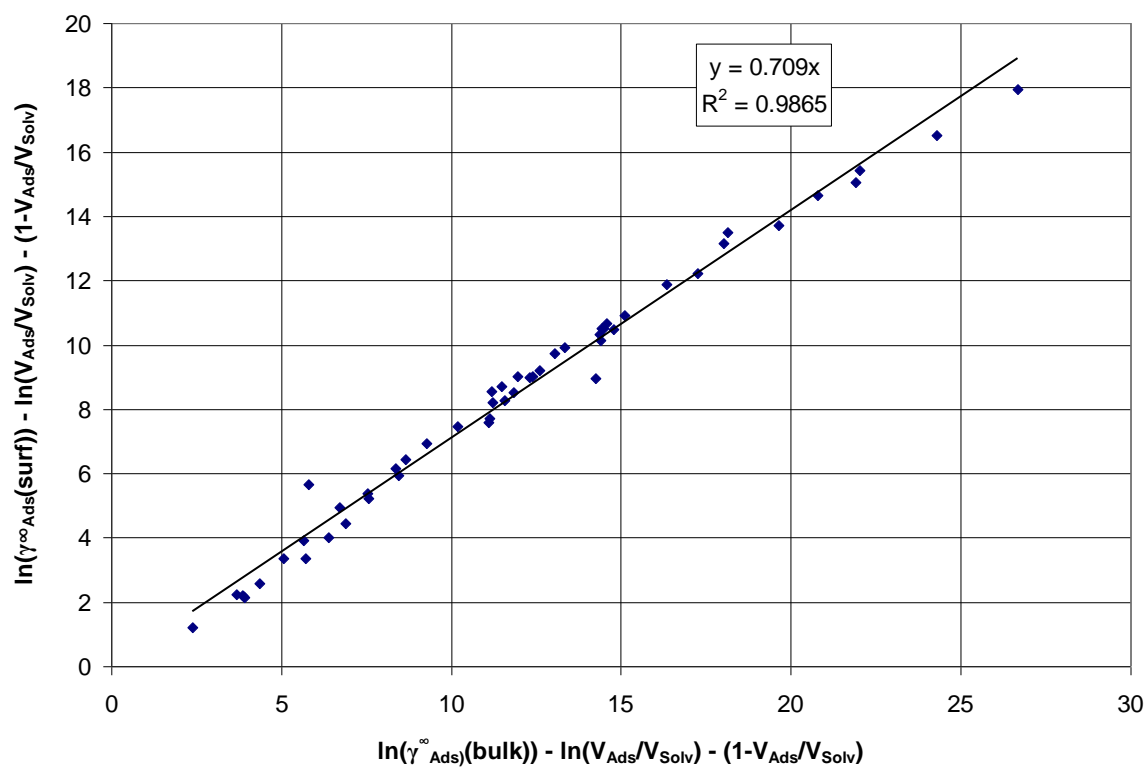
Fig. 3. Activity trends plotted using molar volume -based surface areas (equation 9)
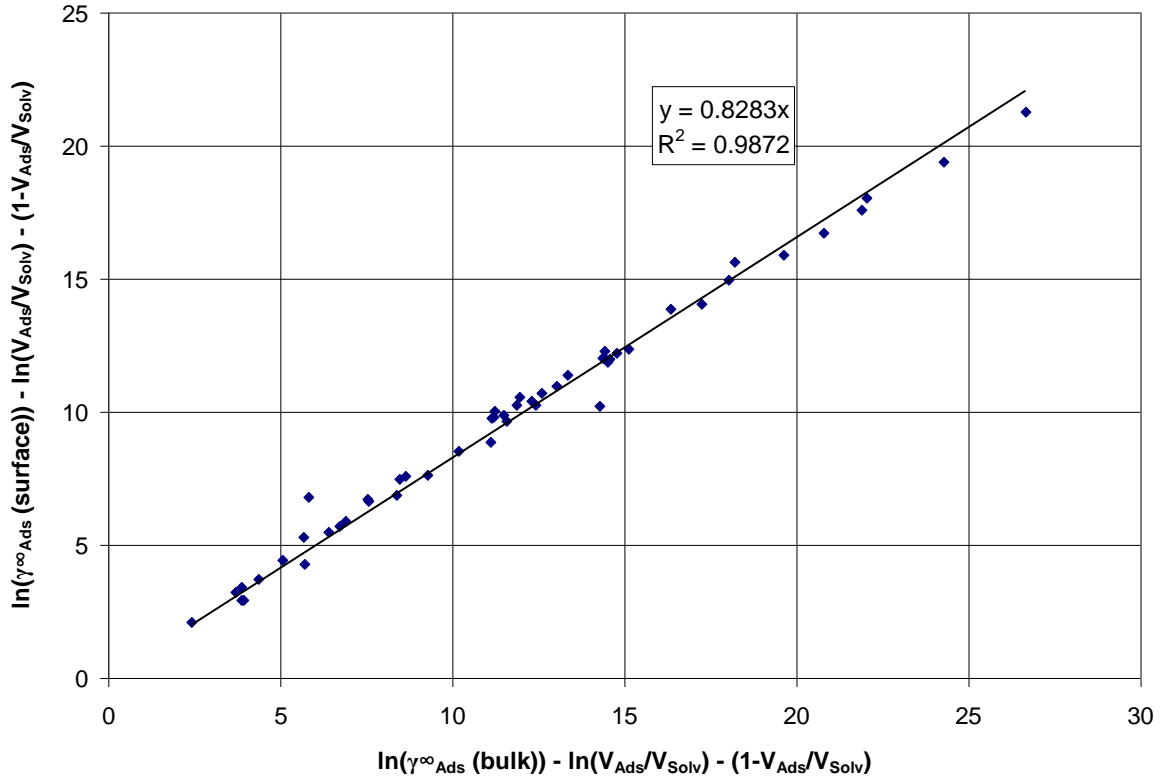
Fig. 4. Activity trends plotted using surface areas based on Paquette volumes (equations (10) and (11b))

## 5 Estimation of water surface adsorption coefficient based on other thermodynamic data

The final single adjustable parameter correlation between activity coefficients in the bulk and surface layers to be applied together with Paquette volumes with the surface layer is

$$\ln \gamma_{Ads}^{\infty,s} = 0.8283 \left( \ln \gamma_{Ads}^{\infty,b} - \ln\left( \frac{V_{Ads}}{V_{Solv}} \right) - \left( 1 - \frac{V_{Ads}}{V_{Solv}} \right) \right) + \ln\left( \frac{V_{Ads}^{Paq}}{V_{Solv}^{Paq}} \right) + \left( 1 - \frac{V_{Ads}^{Paq}}{V_{Solv}^{Paq}} \right) \tag{12}$$

The correlation was applied together with the bulk activity coefficient, surface tension, vapour pressure, and molar volume data to equation (13)

$$K_{i/a} = \frac{RT}{A_{Solv}\gamma_{Ads}^{\infty,s} p_{Ads}^{vap}} \exp\left( \frac{A_{Ads}\left( \sigma_{Solv} - \sigma_{Ads} \right)}{RT} \right) - \frac{RT}{A_{Solv} p_{Ads}^{vap} \gamma_{Ads}^{\infty,b}} \tag{13}$$

As the comparison is made within the same data set which was used to derive the activity coefficient relation in the first place, this is not a truly predictive test. However, the activity coefficient correlation has only one adjustable parameter, and based on the Fig. 4, a rather small subset of the used data would have produced closely the same value for that parameter. Comparison of the correlated and experimental adsorption coefficient values are given in Fig. 5 and Table 2.
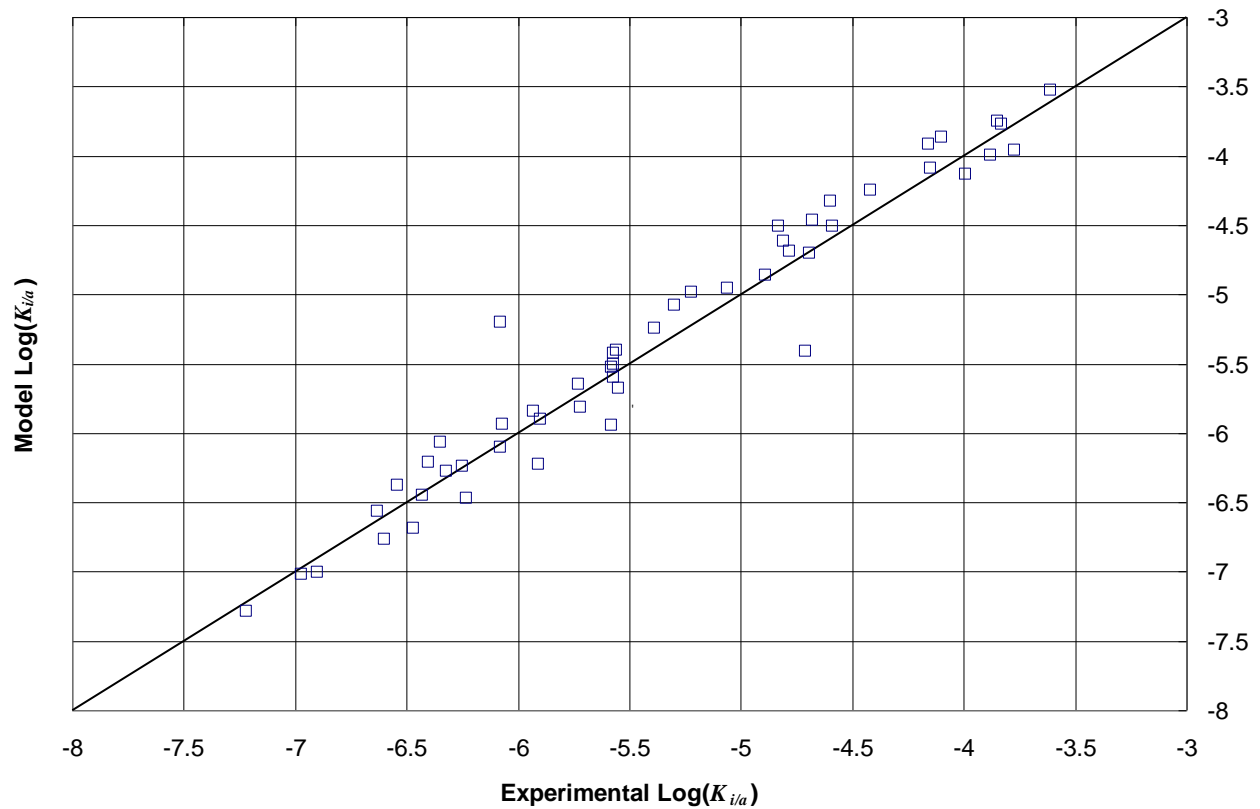
Fig. 5. Comparison of experimental adsorption coefficients and those calculated from equation (13) applying the correlated surface activity coefficient values.

Table 2. Comparison of experimental and estimated adsorption coefficients.

| | Log($K_{i/a}$) (experimental) | Log($K_{i/a}$) (estimated) | | Log($K_{i/a}$) (experimental) | Log($K_{i/a}$) (estimated) |
|---|---|---|---|---|---|
| n-pentane | -7.22 | -7.29 | 2-butanone | -4.6 | -4.33 |
| n-hexane | -6.9 | -7.00 | pentanal | -4.68 | -4.47 |
| n-heptane | -6.6 | -6.76 | cyclopentanone | -3.77 | -3.96 |
| n-octane | -6.23 | -6.46 | diethyl ether | -5.3 | -5.08 |
| n-nonane | -5.91 | -6.22 | diisopropyl ether | -4.83 | -4.51 |
| n-decane | -5.58 | -5.94 | di-n-propyl ether | -4.81 | -4.62 |
| 2,2,4-trimethylpentane | -6.47 | -6.68 | methylphenyl ether | -4.89 | -4.86 |
| 1-nonene | -5.72 | -5.81 | 1,4-dioxane | -3.88 | -4.00 |
| cyclohexane | -6.97 | -7.02 | methyl formate | -5.55 | -5.68 |
| cyclooctane | -6.25 | -6.24 | ethyl formate | -6.08 | -5.20 |
| benzene | -6.32 | -6.28 | methyl acetate | -5.06 | -4.96 |
| toluene | -5.93 | -5.84 | ethyl acetate | -4.59 | -4.51 |
| p-xylene | -5.57 | -5.43 | isobutyl acetate | -4.16 | -3.92 |
| ethylbenzene | -5.58 | -5.52 | dichloromethane | -6.63 | -6.57 |
| isoprpylbenzene | -5.39 | -5.24 | chloroform | -6.4 | -6.21 |
| styrene | -5.56 | -5.40 | 1-chlorobutane | -6.35 | -6.07 |
| biphenyl | -4.1 | -3.87 | 1-bromobutane | -6.07 | -5.94 |
| naphtalene | -4.69 | -4.70 | 1,1,2,2-tetarachloroethane | -5.22 | -4.99 |
| nitrobenzene | -3.99 | -4.14 | 1,1,1-trichloroethane | -6.54 | -6.38 |
| thiophene | -6.43 | -6.45 | 1,2-dichloroethane | -6.08 | -6.10 |
| ethanol | -4.15 | -4.09 | chlorobenzene | -5.9 | -5.90 |
| 1-propanol | -3.83 | -3.78 | iodobenzene | -4.71 | -5.41 |
| 2-propanol | -3.85 | -3.76 | bromobenzene | -5.73 | -5.64 |
| 2-methyl-1-propanol | -3.61 | -3.53 | 1,3-dichlorobenzene | -5.57 | -5.60 |
| acetone | -4.78 | -4.69 | 1,4-dichlorobenzene | -5.57 | -5.50 |
| 3-Methylbutan-2-one | -4.42 | -4.25 | | | |

The two outliers with more than 0.4 Log units difference between the correlated and actual log $K$ values are ethyl formate and iodobenzene, which were outliers also in all activity coefficient correlations.

The second term in equation (13) is for all the substances discussed here small enough to be ignored. This enables presenting the adsorption coefficient in the form

$$\log K_{i/a} = \log \frac{RT}{A_{Solv}\gamma_{Ads}^{\infty,s}p_{Ads}^{vap}} + \left( \frac{A_{Ads}(\sigma_{Solv} - \sigma_{Ads})\log(e)}{RT} \right) \qquad (14)$$

which readily enables estimation of the effect of changes in the various experimental parameters of the model on the predicted adsorption coefficient. A change of 0.1 Log units is caused by an approximately 20% relative change in vapour pressure or in the (surface) activity coefficient value, or an absolute change of 570 J/mol in the value of $A_{Ads}\sigma_{Ads}$.

# 6 Conclusions

In this paper a thermodynamic model for adsorption on the aqueous-air interface was developed leading to an expression for the adsorption coefficient as a function of surface area, surface tension, vapour pressure, and infinite dilution activity coefficient on the surface in the monolayer surface approximation. The experimental data set used indicates that the infinite dilution surface activity coefficients can be estimated based on the corresponding bulk values assuming that the energetic interactions at the surface are scaled by the amount given by a reduced surface coordination number, same for all organic solvents, while an entropic Flory-Huggins like contribution would be assumed not to scale with the coordination number. The presented model describes successfully the adsorption behaviour of a wide range of organic compounds while using only one adjustable universal parameter (the reduced coordination number). The thermodynamic model allows more extensive usage of bulk liquid thermodynamic values for the estimation of adsorption coefficients than has been possible so far. It also offers further confirmation to the idea that the monolayer approach is a fruitful method for investigating properties of liquid-gas interfaces.

# 7 Acknowledgments

**Nomenclature**

| | |
|---|---|
| $A$ | total surface area (m$^2$) |
| $A_X$ | molar surface area of species X (m$^2$/mol) |
| $Ads^{\alpha}$ | molecule of the adsorbing species in phase or layer $\alpha$ |
| $a_X^{\alpha}$ | activity of species $X$ in phase or layer $\alpha$ |
| $C_a$ | concentration of the adsorbing species in air (mol/m3) |
| $\Delta G_{Adsosrption}^{0}$ | standard Gibbs energy change for the adsorption reaction (J) |
| $K_{eq}$ | thermodynamic equilibrium coefficient of an adsorption reaction |
| $K_{i/a}$ | adsorption coefficient (m) |
| $N_a$ | Avogadro constant (mol$^{-1}$) |

| | |
|---|---|
| $n_X^\alpha$ | amount of species X in phase or layer $\alpha$ (mol) |
| $p^0$ | standard state pressure (1 bar) |
| $p_{Ads}^{vap}$ | equilibrium vapour pressure of the adsorbing species (bar) |
| $R$ | gas constant (J mol$^{-1}$ K$^{-1}$) |
| $Solv^\alpha$ | solvent molecule in phase or layer $\alpha$ |
| $T$ | temperature (K) |
| $V^g$ | gas volume (m$^3$) |
| $V_X$ | molar volume of species X (m$^3$/mol) |
| $V_X{}^{crit}$ | critical molar volume of species X (m$^3$/mol) |
| $V_X{}^{Paq}$ | Paquette molar volume of species X (m$^3$/mol) |
| $x_X^\alpha$ | mole fraction of species X in phase or layer $\alpha$ |
| $\beta$ | reduced coordination number |
| $\Gamma_i$ | adsorbed amount at the air-water interface (mol/m$^2$) |
| $\gamma_{Ads}^{\infty,\alpha}$ | infinite dilution activity coefficient of the adsorbing species in phase or layer $\alpha$ |
| $\mu_X^{0,\alpha}$ | standard state chemical potential for species $X$ in phase or layer $\alpha$ (J/mol) |
| $\sigma_X$ | surface tension of the pure liquid substance $X$ (N/m) |

superscripts

| | |
|---|---|
| b | bulk liquid phase |
| g | gas phase |
| s | surface layer |

## References

[1] C. P. Kelly, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 1008 (2004) 12882

[2] C. M. Roth, K. U. Goss R. P. Schwarzenbach, J. Colloid Interface Sci. 252 (2002) 21

[3] S. Raja, F. S. Yaccone, R. Ravikrishna, K. T. Valsaraj, J. Chem. Eng. Data 47 (2002) 1213

[4] T. Tanaka, S. Hara, Z. Metallkd. 90 (1999) 348

[5] J. Lee, K. Morita ISIJ Int. 42 (2002) 588

[6] B.D. Smith, R. Srivastava, Thermodynamic Data for Pure Compounds, Elsevier, Amsterdam, 1986

[7] L. Mosteiro, E. Mascato, D. González-Salgado, B. E. de Cominges, M. M. Piñeiro, J. Therm. Anal. Calorim. 70 (2002) 255

[8] A. A. H. Pádua, J. M. N. A. Fareleira, J. C. G. Calado, W. A. Wakeham, J. Chem. Eng. Data 41 (1996) 1488

[9] G. H. Montillon, K. L. Rohrbach, W. L. Badger, Ind. Eng. Chem. 23 (1931), 763

[10] L. R. Grzyll, C. Ramos, D. D. Back, J. Chem. Eng. Data 41 (1996) 446

[11] P. S. Nikam, M. C. Jadhav, M. Hasan, J. Chem. Eng. Data 40 (1995) 931

[12] S. Aznarez, L. Mussari, M. Postigo, Monatsh. Chem. 125 (1994) 241

[13] R.H. Perry, D. Green, Perry's Chemical Engineering Handbook, 6th Edition, McGraw-Hill, New York, 1984

[14] I. Gascón, M. Domínguez, P. Cea, M. C. López, F. M. Royoa, J. Chem. Thermodynamics 33 (2001) 1361

[15] G. W. C. Kaye, T. H. Laby, Tables of Physical and Chemical Constants, 16th Edition, Longman 1995, accessed online: http://www.kayelaby.npl.co.uk/

[16] Q. Jia, Q. Wang, P. Ma, J. Chem. Eng. Data 53 (2008) 2606

[17] T. E. Daubert, J. Chem. Eng. Data 41 (1996) 365

[18] ProPred Version 3.6, Computer-Aided Process Engineering Center, Department of Chemical Engineering, Technical University of Denmark, 2003

[19] C. Tsonopoulos, D. Ambrose, J. Chem. Eng. Data 46 (2001) 480

[20] A. P. Kudchadker, D. Ambrose, C. Tsonopoulos, J. Chem. Eng. Data 46 (2001) 457

[21] J. J. Jasper, J. Phys. Chem. Ref. Data 1 (1972) 841

[22] J.A. Dean, Lange's Handbook of Chemistry, 15th Edition, McGraw-Hill, New York, 1999

[23] G. Wypych, Knovel Solvents - A Properties Database, ChemTec Publishing, Toronto, 2000

[24] K. Ruzicka, V. Majer, J. Phys. Chem. Ref. Data 23 (1994) 1

[25] T. Bobulík, V. Fried, E. Hála, The Vapour Pressures of Pure Substances, Elsevier, Amsterdam, 1984

[26] A. D. Site, J. Phys: Chem. Ref. Data 26 (1997) 157

[27] C. G. de Kruif, T. Kuipers, J. C. van Miltenburg, R. C. F. Schaake, G. Stevens, J. Chem. Thermodynamics 13 (1981) 1081

[28] E. J. Lynch, C. R. Wilke, J. Chem. Eng. Data 5 (1960) 300

[29] H. Toghiani, R. Toghiani, D. S. Viswanath, J. Chem. Eng. Data 39 (1994) 63

[30] D. Ambrose, C. H. S. Sprake, R. Townsend, J. Chem. Thermodynamics 6 (1974) 693

[31] M. Antosik, Z. Fra, and S. K. Malanowski, J. Chem. Eng. Data 47 (2002) 757-760

[32] J. M. Resa, C. González, B. Moradillo, J. Lanz, J. Chem. Thermodynamics 30 (1998) 1207

[33] R. D. Chirico, S. E. Knipmeyer, A. Nguyen, W. V. Steele, J. Chem. Thermodynamics 21 (1989) 1307

[34] R. Pajarre, P. Koukkari, T. Tanaka, J. Lee, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 30 (2006) 196

[35] D. H. Everett, Pure Appl. Chem. 58 (1986) 967

[36] E. D. Turkdogan, Physical Chemistry if High Temperature Technology, Academic Press, New York, 1980

[37] D. E. Goldsack, B. R. White, Can. J. Chem. 61 (1983) 1725

[38] K. Kojima, S. Zhang, T. Hiaki, Fluid Phase Equilib. 131 (1997) 145

[39] N. B. Vargaftik, B. N. Volkov, L. D. Voljak, J. Phys. Chem. Ref. Data 12 (1983) 817

[40] J. Marrero, R. Gani, Fluid Phase Equilib., 183-184 (2001) 183.

[41] T. Tanaka, K. Hack, T. Iida, S. Hara, Z. Metallkd 87 (1996) 380

[42] E. A. Guggenheim, Trans. Fraday Soc. 41 (1945) 150

[43] J. Park, J. Lee, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. 32 (2008) 135

[44] T. Ueda, T. Tanaka, S. Hara, , Z. Metallkd 90 (1999) 342