Journal of Colloid and Interface Science 412 (2013) 13–16

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Modeling the influence of salts on the critical micelle concentration of ionic surfactants

Ulrich P. Preiss [a], Philipp Eiden [b], Justyna Łuczak [c], Christian Jungnickel [c,*]

[a] Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany
[b] Freiburger Materialforschungszentrum (FMF), Universität Freiburg, Stefan-Meier-Str. 21, 79104 Freiburg, Germany
[c] Chemical Faculty, Gdańsk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 21 June 2013
Accepted 3 September 2013
Available online 17 September 2013

Keywords:
Ionic surfactants
Ionic liquids
Imidazolium salts
Hofmeister effect
Volume-based thermodynamic models

ABSTRACT

We show for the first time that a phenomenological, augmented volume-based thermodynamics (aVBT) model is capable to predict the critical micelle concentrations of ionic surfactants, including ionic liquids, with added salts. The model also adjusts for the type of salt added by including its molecular volume, which might form a connection to the Hofmeister effect. The other physico-chemically relevant quantities included in the model include surface area and solvation enthalpies.

1. Introduction

In previous studies, we investigated the surface activity of various structural combinations of alkyl-imidazolium compounds in water. We found that this superset of ionic liquids (ILs) behaves similarly to ionic surfactants, due to their amphiphilic structure, and its ability to reduce surface tension, form micellar aggregates, and solubilize hydrocarbons [1–4].

Measuring and comparing the various properties of these compounds is important yet challenging as the number of ionic surfactants is enormous. As a consequence, many methods have been developed to predict critical micelle concentration (CMC) for aqueous solutions of nonionic [5,6], anionic [7,8], and cationic surfactants [9]. A number of phenomenological correlations were found to describe the behavior of non- and anionic surfactants in water as a result of Quantitative Structure-Property Relationship (QSPR) studies [5,7]. However, these methods often feature somewhat ill-explained group or atomic contributions, or a dependency on – both from a theoretical and application point of view – restricted neural networks, leading to more or less moderate validity ranges. In contrast to these methods, in recent years, we found many correlations connecting key physico-chemical properties of (usually ionic) systems with easy-to-obtain molecular descriptors [10–20]. Because of the recognition of the a molecule's size as one of the main ordering parameters [21], the group of these methods was called "augmented volume-based thermodynamic" (aVBT) models [22]. Generally, the advantage of these methods over QSPR is that they are strongly connected to simple physical foundations, and generally consist of lean formulas. This greatly increases the validity range that can be expected, and also enhances both the ease of a computational implementation and the potential speed of high-throughput *in silico* batch assessments in order to find a substance with desired properties, even before its synthesis. Thus, aVBT methods can serve as valuable tools for science and industry alike to save on experiments that consume time and money, and produce waste.

In this framework, we previously found a formula for predicting the CMC and linked it to nucleation thermodynamics [17]. It was found to be valid for a wide range of cationic and anionic surfactants including ionic liquids. As a natural extension of this work, we determined the effect of the salt addition to the IL/water *binary* system [1–3,23]. In our experimental study [23], we found that with decreasing size and polarizability of the anion of the added salt, the CMC was also reduced, which we attributed to the Hofmeister effect. In this publication, additional experimental results and a model for calculating CMCs of *ternary* mixtures of ionic surfactant, water and salt will be introduced for the first time.

2. Methodologies

2.1. Experimental CMC determination

The ionic surfactants [C_8MIm]Cl and [C_{10}MIm]Cl were obtained from Merck KGaA (Darmstadt, Germany), while NaCl was obtained from POCh (Gliwice, Poland). The ionic surfactants were degassed

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* Corresponding author. Fax: +48 58 347 2065.
E-mail address: cahj@chem.pg.gda.pl (C. Jungnickel).

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http://dx.doi.org/10.1016/j.jcis.2013.09.003

and dried prior to use. Reverse osmosis purified water with an average conductivity of 0.15 μS cm^{-1} was used (HLP smart 2000, Hydrolab, Poland). To determine the CMCs, the conductivity of various solutions of the appropriate ionic surfactant/salt combinations were measured at 298 ± 0.1 K using a conductivity meter equipped with an autotitrator (Cerko Lab System CLS/M/07/06, Poland) and a microconductivity electrode (Eurosensor, EPST-2ZA, Poland). Stable temperature was maintained using a thermostatic water bath (PolyScience 9106, USA). Every titration was repeated three times to exclude experimental errors [23]. CMCs were determined from the second derivative of the conductivity curve using OriginLabPro 7.5 and are given in Table 1. For calibration of the mathematical models, other values were taken from literature; if more than one value was found for a given system, their geometric mean was taken.

3. Computational details

With the TURBOMOLE program package (version 5.10) [24], BP86/SV(P) [25–28] optimizations using Resolution of Identity (RI) [29] were performed in the highest possible point group. To make sure every ion represents a true minimum, vibrational frequencies were calculated with AOFORCE for these structures [30,31]. A full optimization with the TZVP basis set [32] and COSMO [33] (using optimized radii; dielectric constant set to ∞) without symmetry was then appended. The free solvation enthalpy in an ideal electric conductor $\Delta_{solv}G^{\infty}$ and solvent accessible surface area S are the direct output of this calculation; the molecular volume V_m was calculated according to the best-fit method according to Ref. [10]

The coefficients used in the final formula were found using an ordinary least-square fit (OLS) as implemented in GNU Octave version 3.2.4 according to the following formula [34]:

$$(\mathrm{II})\, y = \mathbf{A} \cdot \beta + \varepsilon$$

y is a vector containing the target data, in this case the measured CMC values. **A** is a matrix made of physicochemical descriptors coming from gas-phase DFT, COSMO (COnductor like Screening MOdel), or COSMO-RS (COSMO for real solvents) calculations. β is a vector containing the coefficients. ε is the associated error vector which should be minimal. To find the smallest possible, physically well-founded descriptor matrix **A** which delivers an error ε as small as possible is the challenge in this type of procedure.

Descriptors and nomenclature are given in the Supporting information.

4. Results and discussion

It has been well established that the addition of inorganic salts to aqueous solutions of ionic surfactants lowers the concentration at which surfactants begin to form micelles (microphase separation point). Increasing the salt concentration favors micellization and micelle stability. This phenomenon is a result of a decrease in the coulombic repulsion of the head groups, due to the shielding of the charge on the surfactant [35]. Changing the type of salt alters this effect slightly. This is due to the different abilities of specific salts to distort chemical interactions in their vicinity. These changes in water structure promote or inhibit micelle formation, thereby decreasing or increasing the CMC, respectively [36].

Table 1
Measured CMCs for different aqueous systems of surfactant and NaCl.

Surfactant	Salt conc. (mM)	CMC (mM)
$[C_8MIm]Cl$	–/–	220
$[C_8MIm]Cl$	100	110
$[C_8MIm]Cl$	500	30
$[C_8MIm]Cl$	1000	12
$[C_{10}MIm]Cl$	–/–	57.2
$[C_{10}MIm]Cl$	50	40.5
$[C_{10}MIm]Cl$	150	25.5

In this study, we collected CMC data of 151 aqueous systems (144 taken from literature and 7 measured on our own). They comprised 18 cationic and anionic surfactants (imidazolium, pyridinium, quaternary ammonium, alkyl sulfates and sulfonates, and carboxylates) in combination with eight inorganic salts (sodium and potassium halides and nitrates) (Supporting information Table S4). The latter occurred in concentrations between 0 and 1 M.

Based on this data, combinations of up to five descriptors (not counting the intercept) were tested with respect to their quality of modeling the CMC. The descriptors included 11 unique property descriptors pertaining to the IL with or without interaction with water, and 21 additional descriptors deemed to describe the effect of the salt (multiplied with concentration of the salt). The following relationship was found to be the best out of 0.24 million combinations:

$$\ln\,(\mathrm{CMC}) = a_0 + a_1 \cdot \widehat{S} + a_2 \cdot \Delta_{\mathrm{solv}}G^{\infty} + a_3 \cdot c \cdot V_{\mathrm{m}} \qquad (1)$$

Here, c is the salt concentration. The other descriptors are all properties of the surfactant in question: $\widehat{S}$ is the solvent-accessible surface area, $\Delta_{solv}G^{\infty}$ is the free solvation enthalpy in an ideal electric conductor, and V_m is the molecular volume. The coefficients $a_0, \ldots, a_3$ were adjusted by best fit. No particular outliers were observed.

For the data series collected in Table S4, we obtained a squared correlation coefficient r^2 of 0.859 and a standard error of the estimate σ_{xy} of 0.68 log mM as calculated by the following equation:

$$\sigma_{xy} = \sqrt{\frac{\sum_i (x_i - y_i)^2}{N}} \qquad (2)$$

Here, N is the number of data points, y_i are the measured and x_i the calculated values.

These good results notwithstanding, it became apparent that the effect of the change of salt was not represented. For example, the system $[C_6MIm]Cl$ – water with 0.5 M NaX, where X = Cl, Br, I, shows an experimental CMC range of 0.07–0.15 M, while the calculated value for all three remain constant at 0.13 M. Therefore, the search for a fitting formula was extended. This time, a total of 69 supplementary, combined descriptors, mainly formed by addition, multiplication or division of the already examined ones, were included, resulting in nearly 60 million unique formulas. The end result was:

$$\ln\,(\mathrm{CMC}) = b_0 + b_1 \cdot \widehat{S} + b_2 \cdot \Delta_{\mathrm{solv}}G^{\infty} + b_3 \cdot c \cdot V_{\mathrm{m,s}} \cdot V_{\mathrm{m}} \qquad (3)$$

$V_{m,s}$ is the molecular volume of the salt. With the CMC given in mM, we obtained $b_0 = 24.2$, $b_1 = -3.21\ \mathrm{nm}^{-2}$, $b_2 = 15.2\ \mathrm{mol\ MJ}^{-1}$, and $b_3 = -0.171\ \mathrm{M}^{-1}\ \mathrm{nm}^{-6}$. We observed $r^2 = 0.879$ and $\sigma_{xy} = 0.63$ log mM. Results are displayed in Fig. 1.

The inclusion of the additional $V_{m,s}$ descriptor could satisfyingly account for the effect of the salt variation. In the above example, the calculated CMCs now range from 0.085 to 0.16 M, with a correct representation of the trend measured from X = Cl over Br to I. This shows that the regression quality alone is not sufficient to judge a statistical model, but a detailed analysis of the data based on chemical knowledge must be performed.

The inclusion of up to two additional descriptors (summands) could not lift r^2 beyond 0.911. If one summand was removed, however, we could not raise r^2 beyond 0.733. Thus, Eq. (3) was found to contain the lowest number of summands which would give a good correlation quality and, at the same time, a physically sound foundation.