Preiss U., Jungnickel C., Thöming J., Krossing I., Łuczak J., Diedenhofen M., Klamt A., Predicting the Critical Micelle Concentrations of Aqueous Solutions of Ionic Liquids and Other Ionic Surfactants, Chemistry – A European Journal, Vol. 15, Iss. 35 (2009), pp. 8880-8885,

Predicting the Critical Micelle Concentration of Aqueous Solutions of Ionic Liquids and other Ionic Surfactants

U. Preiss[b], C. Jungnickel[c], J. Thöming[d], I. Krossing* [a], J. Łuczak[e], M. Diedenhofen[f], and A. Klamt[f,g]

Abstract: Some ionic liquids (ILs) are structurally analogous to surfactants, especially those which consist of a combination of organic and inorganic ions. The critical micelle concentration (CMC) constitutes a basic parameter of the surface chemistry and colloid science. A significant amount of research has already been done to determine the CMC of ILs. However, because of the many varied cation/anion combinations, it is a daunting task to measure the CMC of all possible ILs. Here we suggest a general rule to predict the CMC of ionic surfactants in water based on data received from COSMO-RS calculations. In accordance with the Stauff-Klevens-rule, the molecular volume (V_m) allows to sufficiently describe similar homologous series of cationic surfactants such as imidazolium- and ammonium-based ionic liquids with varying side-chain length. However, to also include anionic surfactants like Na[$C_\#SO_4$] into a more general correlation, V_m has to be exchanged by the cubed molecular radius (r_m^3) and the molecular surface has to be used as an additional descriptor. Furthermore, to describe double amphiphilic compounds like [C_4MIm][C_8SO_4], enthalpies of mixtures calculated by COSMO-RS are taken into account. The resulting equation allows us to predict the CMC of all of the 36 tested surfactants with an error similar to or smaller than the usual experimental errors (18 different cations, ten different anions: rmse = 0.191 logarithmic units; R² = 0.994). We show that the structure of our equation can be related to Gibbs' theory of crystallization. We discuss the factors governing micelle formation on the basis of our calculations and in the context of Gibbs' theory.

Keywords: ionic liquid, micelles, surfactant, molecular volume, COSMO-RS

[a] I. Krossing
Institute of Inorganic and Analytical Chemistry
University of Freiburg, Albertstraße 21
79104 Freiburg, Germany
Tel.: +49(0)761 2036121
e-mail: krossing@uni-freiburg.de

[b] U. Preiss
Institute of Inorganic and Analytical Chemistry
University of Freiburg, Albertstraße 21
79104 Freiburg, Germany

[c] C. Jungnickel
Chemical Faculty
Gdańsk University of Technology, ul. Narutowicza 11/12
80-952 Gdańsk, Poland

[d] J. Thöming
UFT - Centre for Environmental Research and Technology
University of Bremen, Leobener Straße
28359 Bremen, Germany

[e] J. Łuczak
Chemical Faculty
Gdańsk University of Technology, ul. Narutowicza 11/12
80-952 Gdańsk, Poland

[f] M. Diedenhofen, A. Klamt
COSMOlogic GmbH & Co. KG, Burscheider Straße 515
51381 Leverkusen, Germany

[g] A. Klamt
Insitute of Physical and Theoretical Chemistry
University of Regensburg, Universitätsstraße 31
93040 Regensburg, Germany

Introduction

Many ionic liquids (ILs) are structurally analogous to surfactants. That is, its anions or cations often consist of a charged hydrophilic head group and a hydrophobic tail domain. This characteristic amphiphilic composition of ILs indicates that surface behavior will influence the properties of the systems containing these compounds. The understanding of the molecular interface interactions of ILs in aqueous solutions is a prerequisite for sustainably predicting, controlling and designing IL properties for application in industrial scale processes. Prior to their distribution in the environment, a chemical fate analysis should be performed[1]. Therefore the knowledge of the aggregation behavior of ILs is a vital part of understanding how these compounds participate as components in an aqueous mixed solvent system. A number of researchers have investigated micelle formation in aqueous solutions of ILs[2-6]. To this date, aggregation behavior of imidazolium derivatives with variable chain length and mainly chloride and bromide anions were presented[2, 5, 7, 8]. Several methods to determine the critical micelle concentration (CMC) of ILs in aqueous solution were used including tensiometry, conductometry, small angle neutron scattering, turbidity, potentiometry etc.. The results suggest that micelle formation of 1-alkyl-3-methylimidazolium derivatives in water takes place, and that elongation of the alkyl chain in the imidazolium cation decreases the CMC similar to typical cationic surfactants. The CMC will also influence biological processes like biodegradation. The process of micellization can be directly correlated to the interaction of the amphiphiles with apolar surfaces such as micelles or cell membranes. Since the toxicity of amphiphiles is dominated by their physico-chemical properties, and therefore their ability to self-assemble, the CMC provides an important indicator to biodegradation[9].

Huibers[16] found correlations to predict the CMC of anionic surfactants in water, depending on QSPR studies. Since QSPR methods always rely on a multitude of different descriptors (e.g. chain length or number of functionalized groups) which are restricted to certain substance classes and need to be optimized using training sets from existing measurements, they are not universally applicable. Nagarajan[17] made an extensive first-principles approach to describe the thermodynamics of surfactant aggregation. However, he strongly differentiates between tail and head groups (a division which is not necessarily valid for more complicated compounds) and gives different models for different classes of surfactants. In this project, however, we were interested in making a simple and general approach suited for all types of ionic surfactants.

Results and Discussion

Ion size obviously includes information about the charge density; therefore, many physical properties of ionic liquids like density, viscosity, and conductivity[10-12] are governed by the molecular volume, V_m. In a 1:1 compound A^+X^-, it is defined as the sum of the ionic volumes $V_{ion}(A^+)$ and $V_{ion}(X^-)$:

$$V_m = V_{ion}(A^+) + V_{ion}(X^-) \tag{1}$$

Ionic volumes can be calculated from suitable X-ray crystal structures according to:

$$V_{ion}(A^+) + V_{ion}(X^-) = \frac{V_{cell}\,(A^+X^-)}{Z} \tag{2}$$

V_{cell} is the volume of the unit cell of the crystal and Z is the number of formula units in the cell. If the volume of one of the ions is accurately known (e.g. halide or alkaline metal ions)[13, 14], it may be used as a reference to determine the volume of the other ion in the structure. To be independent of the need for experimental crystal structures to establish the ion volumes, we recently showed that V_m and V_{ion} may also be calculated from tabulated atomic volumes or by simple semi-empirical or quantum-chemical DFT calculations[15]. The calculated volumes, V_c, correlate to the experimental V_{ion} according to

$$V_{ion}\ [\mathrm{nm}^3] = a \bullet V_c\ [\mathrm{nm}^3] + b \tag{3}$$

with different parameters a, b for cations and anions and for each of the methods. A Table in the Appendix includes all V_m values used in this work.

Table 1: The independently experimentally measured versus the extrapolated CMCs [mmol l^{-1}] from eqn. (7) of different ILs measured at 298 K.

compound	**surface tension**	**conductivity**	**other**	**extrap.**
$[N_{1,1,1,8}]Br$			225[18] 290[19]	188
$[N_{1,1,1,10}]Cl$	70[4]	94.7[20]		82
$[N_{1,1,1,10}]Br$		62.7[21]	62[18] 60.2[21]	55
$[N_{1,1,1,12}]Cl$	18[4]	22.2[20] 21.3[22]		22
$[N_{1,1,1,12}]Br$			14.3[18] 15[23]	15
$[N_{1,1,1,14}]Cl$	5.5[24] 4.5[4]	5.63[20] 5.5[25]		5.8
$[N_{1,1,1,14}]Br$		3.8[25]	3.5[23]	4.1
$[N_{1,1,1,16}]Cl$	1.3[4]	1.46[4]		1.5
$[N_{1,1,1,16}]Br$			0.9[23]	1.1
$[N_{1,1,1,18}]Cl$			0.35[26]	0.38
$[C_2MIm]Br$	2500[27]	1900[27]		2316
$[C_4MIm]Br$	800[27]	900[27]		1025
$[C_4MIm][BF_4]$	800[5] 1370*	820[5]		1153
$[C_4MIm][CF_3SO_3]$	782*			843
$[C_4MIm][C_8SO_4]$	40.5*	31[3]		23
$[C_6MIm]Cl$	900[4]			689
$[C_6MIm]Br$	600[27] 470[28]	400[27]	880[29] 800[29]	361
$[C_8MIm]Cl$	220[2] 100[5] 220[4]	234[2] 90[5]	200[4]	203
$[C_8MIm]Br$	150[27] 121[28]	150[27]	180[29] 190[29]	114
$[C_8MIm]I$	100[5]	150[5]		93
$[C_9MIm]Br$	40[27]	30[27] 74[6]		61
$[C_{10}MIm]Cl$	59.9[2] 55[4] 39.9[30]	53.8[2] 40.47[30]	45[4] 55[4]	56
$[C_{10}MIm]Br$	20 [28] 29.3 [31]	40[7] 41[6] 32.9 [31]	40 [32] 42 [29] 46 [29]	33
$[C_{12}MIm]Cl$	15[4] 13.17[30]	13.47[30]	7[4] 13[4]	15
$[C_{12}MIm]Br$	4.3[28]	9.8[6] 8.5[31] 9.5[33]	10[29] 12[29]	9.3
$[C_{12}MIm][BF_4]$	9.2[31]	7.6[31]		8.0
$[C_{14}MIm]Cl$	4[4] 3.4[2] 2.98[30]	3.15[2] 3.68[30]	3[4] 4[4]	4.0
$[C_{14}MIm]Br$		2.5 [6] 2.6 [33]		2.6
$[C_{16}MIm]Cl$	1.3[2] 0.88[34] 0.87[30]	1.14[2] 0.86[30]		1.0
$[C_{16}MIm]Br$		0.8[28] 0.61[6] 0.65[33]		0.71
$[C_{18}MIm]Cl$	0.4[2]	0.45[2]		0.27
$[C_8Py]Cl$		274[2]		292
$Na[C_8SO_4]$			134[35]	143
$Na[C_{10}SO_4]$			30[35]	30
$Na[C_{12}SO_4]$			7.6[36]	7.0
$Na[C_{14}SO_4]$			2.00[35]	1.6

*Measured for this work.

Given the typical univalent charges of IL ions, V_m may also be viewed as an indicator for hydrophobicity and thus should also correlate with the solubility of ILs in water and their tendency to aggregate and form micelles. To establish a correlation, we calculated the ionic volumes, V_{ion}^+ and V_{ion}^-, both taken from a BP86/TZVP COSMO calculation, scaled with a linear fit. We chose this method as it is very reliable and there are only very few crystal structures available that contain the investigated cations to infer the molecular volumes from[15]. First, we investigated 30 compounds with micelle-forming cations, i.e. 1-methyl-3-alkyl-imidazolium, alkyl-trimethyl-ammonium and alkyl-pyridinium. In detail, we explored $[C_{\#}MIm]^+$ chlorides and bromides, with # = 6, 8, 10, 12, 14, 16; $[C_{\#}MIm]^+$ bromides, with # = 2, 4, 9; $[C_{\#}MIm][BF_4]$, with # = 4, 12; $[C_8MIm]I$, $[C_{18}MIm]Cl$; $[N_{1,1,1,\#}]^+$ chlorides and bromides, with # = 10, 12, 14, 16; $[N_{1,1,1,8}]Br$, $[N_{1,1,1,18}]Cl$; and $[C_8Py]Cl$. Indeed, we found the CMC to be exponentially dependent on V_m according to equation (4)

$$\ln\,(\mathrm{CMC}\ [\mathrm{mmol\ l^{-1}}]) = a \bullet V_\mathrm{m}\ [\mathrm{nm^3}] + b \qquad (4)$$

with a = –26.3 and b = 13.7 being empirical constants derived from best fit. The root mean squared error (rmse) for this fit is 0.339 logarithmic units. Since the correlation is exponential, we took the geometric mean of the known CMC values collected in Table 1 as a basis for our fit. When we further investigated sodium alkyl sulfates ($\mathrm{Na[C_\#SO_4]}$ with # = 8, 10, 12, 14) and double amphipilic compounds ($\mathrm{[C_4MIm][CF_3SO_3]}$ and $\mathrm{[C_4MIm][C_8SO_4]}$), we found them to pose exceptions to the rule. The sodium compounds, however, formed an independent series and correlated nicely with V_m as well (rmse = 0.109), but with different constants a and b (–31.9 and 13.5). Figure 1 is a graphical representation of these findings.

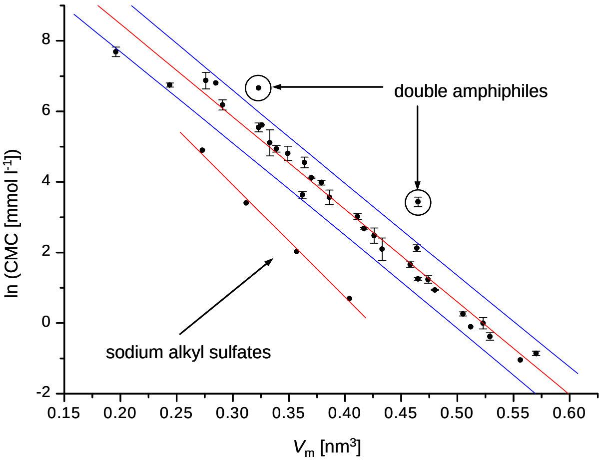


Figure 1: The correspondence of calculated V_m and measured CMC of 30 cationic surfactants (imidazolium-, ammonium- and pyridinium-based ionic liquids; shown along with the 95% prediction bands), four anionic surfactants (sodium alkyl sulfates) and two “mixed” surfactants ($\mathrm{[C_4MIm][CF_3SO_3]}$ and $\mathrm{[C_4MIm][C_8SO_4]}$). The latter two do not fit with any of the former series. Error bars are shown where they could be determined.

To eliminate all exceptions, we sought for a better description for the charge density and included the solvent accessible surface, denoted as $\hat{S}$, as put out by several programs; in this case, we employed COSMOtherm[39]. For a combination of $\hat{S}$ and V_m, i.e.

$$\ln(\mathrm{CMC}\ [\mathrm{mmol\ l^{-1}}]) = (a \bullet V_\mathrm{m}\ [\mathrm{nm^3}] + b \bullet \hat{S}\ [\mathrm{nm^2}] + c) \qquad (5)$$

we found rmse = 0.479, for the first time including all alkyl sulfates.

Instead of V_m, we then considered the cubic molecular radius, r_m^3, to represent the size of a compound. The molecular radius r_m is the sum of anionic (r_m^-) and cationic radius (r_m^+), which are both calculated from ionic volumes according to the following formula (shown for the cationic case):

$$r_\mathrm{m}^+ = \sqrt[3]{\frac{3V_\mathrm{m}^+}{4\pi}} \qquad (6)$$

The ratio of V_m to r_m^3 is almost 1 ($\pi/3$, to be exact) if cationic and anionic radii are identical ($r_\mathrm{m}^+ = r_\mathrm{m}^-$), and gets larger the more they differ, until it quadruples when one radius vanishes. Therefore, r_m^3 could be better suited for describing the compound-specific interactions for molecules where cation and anion strongly differ in size, which is especially the case for sodium alkyl sulfates. Indeed, if we exchanged V_m for r_m^3 in eqn. (5), we found the rmse to decrease to 0.325 logarithmic units. This means that the dependency of the CMC on the alkyl chain length is better captured with both r_m^3 and $\hat{S}$, and that the impact of the variation of the head group diminishes.

So we were left with $\mathrm{[C_4MIm][CF_3SO_3]}$ and $\mathrm{[C_4MIm][C_8SO_4]}$ as problem cases: they are double amphiphilic, meaning both cation and anion contain hydrophobic and hydrophilic groups. At this point, we started to use further ion-specific output from COSMO-RS to model residual interactions. COSMO-RS (“COSMO for Real Solvents”) is based on COSMO, the “COnductor-like Screening MOdel” approach which belongs to the continuum solvation models, i.e. the electrostatic behavior of a solvent is described by a dielectric continuum[49]. Instead of using the exact dielectric boundary condition, COSMO applies the simpler boundary condition of the vanishing potential on the surface of a conducting medium. The polarization of the continuum, induced by the charge density of the solute, is represented by the screening charge density σ appearing on the continuum solvent boundary surface and can be calculated by solving the boundary condition problem. The used cavity is of molecular shape consisting of sufficiently small segments leading to a discretization of the problem. The procedure can be implemented in self-consistent field (SCF) calculations (Hartree-Fock or Kohn-Sham). In order to cross over to a dielectric continuum the screening charge density σ can be scaled down to a finite dielectric constant ε. COSMO-RS now is a predictive method for the calculation of thermodynamic properties of fluids that uses a statistical thermodynamics approach based on the results of COSMO SCF calculations for molecules embedded in an electric conductor, i.e. using $\varepsilon = \infty$. The liquid can be imagined as a dense packing of molecules in the described reference state. For the statistical thermodynamic procedure, this system is broken down to an ensemble of pair-wise interacting surface segments. The interaction can be expressed in terms of surface descriptors, whereof σ is the most important one. The interaction energy modes, i.e. electrostatics (H_MF) and hydrogen bonding (H_HB), are described as functions of the screening charge densities of two interacting surface segments σ and σ’. The less specific van-der-Waals (H_vdW) interactions are taken into account in a slightly more approximate way by element-specific interaction terms. A more detailed description, which is beyond the scope of this article, can be found in ref. [50]. In this case, we included the enthalpies of mixtures calculated by COSMO-RS in the liquid state (enthalpies in a 1:1 mixture of cation and anion as well as both cation and anion in infinite dilution in water).

Overall and converged, we found the CMC to be depending on the following expression:

$$\ln\,(\mathrm{CMC}) = a \bullet r_\mathrm{m}^3 + b \bullet \hat{S} + \sum_\mathrm{i}\left(\frac{c_\mathrm{i} \cdot H_\mathrm{i}^\mathrm{diff}}{\hat{S}}\right) + d \bullet H_\mathrm{ring} + e \qquad (7)$$

with a-e being empirical constants derived from best fit. The coefficients are given in Table 2, all descriptors (r_m, $\hat{S}$, $H_\mathrm{i}^\mathrm{diff}$, H_ring) are included in Table 3 in the Appendix. With this approach, the remaining two exceptions have been eliminated and the overall error greatly reduced with this equation. Here, rmse = 0.191 logarithmic units; R^2 (the squared correlation coefficient) = 0.994.

The sum of the c_i H_i^{diff} denotes the difference of the interaction of the surfactant's ions with water and the interaction of both ions in the pure compound (which is idealized as being liquid: a valid assumption, since, at the CMC, aggregates possess no long range order). The different enthalpy contributions that COSMO-RS calculates are denoted with index i; they are hydrogen bonding (HB), van-der-Waals (vdW), and misfit (MF) interaction, the latter of which describes the interaction of surface areas with different polarities. All of these enthalpies are scaled by the reciprocal surface area. A correction for ring size, H_{ring}, also put out by COSMO-RS, is included with the coefficient d; this term is solvent-independent. All individual terms are given in the appendix in Table 3.

The terms in eqn. (7) are highly independent. The strongest correlation by far is between $H_{\mathrm{MF}}^{\mathrm{diff}}/\hat{S}$ and $H_{\mathrm{HB}}^{\mathrm{diff}}/\hat{S}$, with $R^2 = 0.830$, however the physical realities behind these terms are not interconnected. The second-strongest is between $H_{\mathrm{MF}}^{\mathrm{diff}}/\hat{S}$ and $\hat{S}$, with $R^2 = 0.628$. As all other internal correlations are between 0 and 0.5, we believe that none of the terms could be omitted.

Table 2: The coefficients for eqn. (7) and their values of best fit.

coefficient	a	b	c_i			d	e
unit	nm^{-3}	nm^{-2}	$\mathrm{nm}^2\ \mathrm{mol\ kJ}^{-1}$			$\mathrm{mol\ kJ}^{-1}$	
i			vdW	MF	HB		
value	17.48	–4.44	0.29	–0.17	0.07	–0.09	15.36

Table 1 and Figure 2 show the quality of the predictions. Since the correlation is exponential, errors are quite large for higher CMC values; however, the error bars are in the same order of magnitude as the errors of the experimental CMC determination (see Figure 2).

At this point, we noted a striking similarity to the thermodynamics of crystal formation. In a solution, the Gibbs energy of crystal formation ($\Delta_c G$) is composed of the Gibbs energies of phase transition ($\Delta_n G$) and phase boundary formation ($\Delta_\gamma G$), augmented by an – often disregarded – elasticity term ($\Delta_e G$) which models the influence of adjacent particles within a rigid phase. This relation has already entered into many textbooks and can in principle be traced back to the work of Gibbs in the 19th century[37,38]:

$$\Delta_k G = \Delta_n G + \Delta_\gamma G + \Delta_e G \tag{8}$$

$\Delta_n G$ is proportional to ar^3, where r is the radius of the crystal nucleus, $a < 0$ (chemical bonds are formed in the three dimensions of a crystal, which is energetically advantageous); $\Delta_\gamma G$ is proportional to br^2, with $b > 0$ (a new surface has to be formed at the phase boundary, which is energetically disfavoured). So we get:

$$\Delta_k G = ar^3 + br^2 + \Delta_e G \tag{9}$$

For the Gibbs energy of micelle formation, we can set:

$$\Delta_m G = -RT \ln K \tag{10}$$

where $K = \ln(a(\text{micellized surfactant})/a(\text{solvated surfactant}))$ and a = activity. Assuming T is constant and the concentration of the solvated surfactant is in high excess, making it quasi-constant, we obtain:

$$-\Delta_m G \propto \ln(a(\text{micellized surfactant})) \tag{11}$$

At the critical point, we can substitute ln(CMC) in eqn. (7) for $-\Delta_m G$ and it becomes clear that $\Delta_k G$ and $\Delta_m G$ have the same constituents if r^3 in eqn. (9) gets substituted for r_m^3, r^2 for $\hat{S}$, and the different interaction enthalpies take the part of the elastic contributions $\Delta_e G$. Also, as should be expected from eqn. (11), the signs of a and b in eqn. (7) and (9) are opposite. Therefore, crystal and micelle formation seem to follow similar rules – a finding that deserves its own further investigation.

Figure 2 is a graphical representation of eqn. (7). The coefficients c_i may include repulsive and attractive forces, and may include contributions that stem from overcompensation of the other coefficients, especially a and b. Also, the interaction enthalpies have no physically verifiable size and therefore, their size may not mirror the real nature of the interaction. Combined, however, they are well suited to describe the missing parts of the correlation.

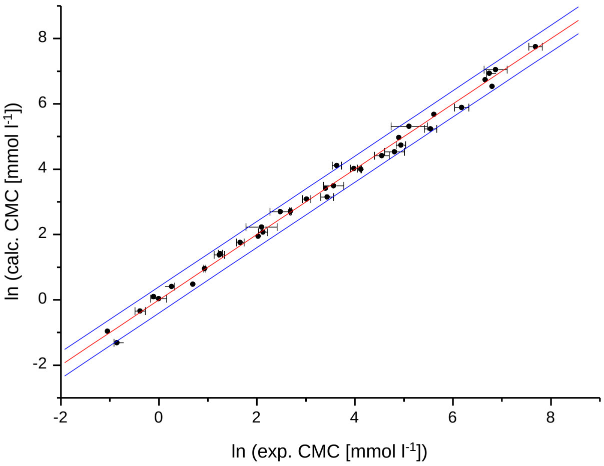


Figure 2: The correspondence of the experimental and calculated CMC of all 36 surfactants tested, shown along with error bars and the 95% prediction bands. Calculations were performed using eqn. (7).

For data collected between 23 and 25 °C, as well as data with no given temperature, standard conditions have been assumed. We did not take the work of Modaressi et al.[40] into account since their measurements, especially for $[\mathrm{C_{10}MIm}]\mathrm{Cl}$ and $[\mathrm{C_{12}MIm}]\mathrm{Br}$, deviate strongly from those of all other authors. Their methodology was unclear, and the determination of the breakpoint the authors describe is questionable.

There are several sources of experimental uncertainties which can explain the large variation in some of the measured data. The typical CMC measurements present not a single value, but rather a range during which the phenomenon of micelle formation takes place. This generates some difficulty in comparing results measured with different methods. Also, traces of organic compounds (grease, 1-methylimidazol) can lead to a decline in surface tension, thus increasing the CMC; traces of inorganic salts (halides) can influence the ion product of water, therefore decreasing the CMC. Both imperfections can be introduced by the typical production processes of ionic liquids.

Conclusion

We found a semi-empirical rule for the prediction of the aqueous critical micelle concentration of cationic, anionic and double amphiphilic surfactants. For the 30 cationic surfactants tested - comprising of alkyl-substituted ammonium and imidazolium compounds and one pyridinium compound -, a simple linear dependence on the molecular volume, V_m, was found to sufficiently describe the CMC. This is in good agreement with the Stauff-Klevens rule that correlates the CMC with the chain length. To also include anionic and double amphiphilic surfactants, a linear extension of the equation with additional descriptors (molecular surface area, mixing enthalpies) was necessary. To determine these descriptors, we employed COSMO-RS and could successfully predict the CMC of 36 compounds where it does not matter whether the micelles are formed by cations or anions or both. The resulting formula resembles the known one for crystal formation. In contrast to QSPR methods, no individual training sets are needed for our method, much broadening the applicable range.

Computational Details

From reasonable starting structures, BP86/SV(P)[41-44] optimizations have been carried out with the TURBOMOLE program package (version 5.10)[45] using the Resolution of Identity (RI) approximation. Then, vibrational frequencies were calculated with AOFORCE for each molecule to make sure they represent a true minimum[46, 47]. These structures were then used for further optimization with the TZVP basis set[48], after which a full optimization with COSMO[49] (dielectric constant set to infinity) was appended. All gas-phase structures have been calculated in the highest possible point group; COSMO calculations were always done without symmetry (C_1). The output files were then read in by COSMOtherm (the employed implementation of COSMO-RS, using the BP_TZVP_C21_0105 parameterization)[50] All enthalpies necessary for the correlation in eqn. (7) were calculated at 298K.

Acknowledgements

This work was supported by the Albert-Ludwigs-Universität Freiburg, the DFG priority program SPP 1191, and the Polish Ministry of Education and Research under grant N205 041 32/2340. We would like to acknowledge the use of computing resources provided by the Black Forest Grid Initiative.

Appendix

Table 3: The molecular volumes and radii as well as the solvent-accessible surface and the different enthalpies calculated with COSMO-RS. Only the H_i^diff terms are included, a full table including all individual values in water and the IL itself is deposited with the supporting information.

IL	V_m	r_m	$\hat{S}$	$H_\mathrm{MF}^\mathrm{diff}$	$H_\mathrm{vdw}^\mathrm{diff}$	$H_\mathrm{HB}^\mathrm{diff}$	H_ring
unit	**nm^3**	**nm**	**nm^2**	**kJ mol^{-1}**			
[N$_{1,1,1,8}$]Br	0.323	0.628	3.207	47.59	-13.97	-72.10	0.00
[N$_{1,1,1,10}$]Cl	0.364	0.640	3.547	52.25	-17.89	-81.88	0.00
[N$_{1,1,1,10}$]Br	0.370	0.650	3.605	47.96	-13.69	-80.94	0.00
[N$_{1,1,1,12}$]Cl	0.411	0.659	3.947	52.67	-17.48	-90.72	0.00
[N$_{1,1,1,12}$]Br	0.417	0.670	4.005	48.72	-13.30	-89.82	0.00
[N$_{1,1,1,14}$]Cl	0.458	0.678	4.344	53.14	-17.34	-99.51	0.00
[N$_{1,1,1,14}$]Br	0.465	0.688	4.403	49.50	-13.14	-98.60	0.00
[N$_{1,1,1,16}$]Cl	0.505	0.694	4.741	53.66	-17.38	-108.28	0.00
[N$_{1,1,1,16}$]Br	0.512	0.705	4.799	50.29	-13.11	-107.38	0.00
[N$_{1,1,1,18}$]Cl	0.556	0.711	5.147	54.55	-16.84	-117.25	0.00
[C$_2$MIm]Br	0.196	0.553	2.208	47.10	-24.99	-52.55	-4.09
[C$_4$MIm]Br	0.244	0.585	2.608	45.21	-24.27	-61.09	-4.09
[C$_4$MIm][BF$_4$]	0.276	0.627	2.928	26.90	-8.30	-51.75	-4.09
[C$_4$MIm][CF$_3$SO$_3$]	0.323	0.672	3.300	27.99	-13.78	-61.85	-4.09
[C$_4$MIm][C$_8$SO$_4$]	0.465	0.761	4.600	40.29	-17.28	-96.74	-4.09
[C$_6$MIm]Cl	0.285	0.601	2.946	48.69	-30.85	-68.63	-4.09
[C$_6$MIm]Br	0.291	0.612	3.004	44.43	-24.12	-69.79	-4.09
[C$_8$MIm]Cl	0.333	0.625	3.345	48.60	-30.31	-77.33	-4.09
[C$_8$MIm]Br	0.339	0.636	3.403	44.67	-23.59	-78.44	-4.09
[C$_8$MIm]I	0.349	0.651	3.493	38.07	-18.08	-91.02	-4.09
[C$_9$MIm]Br	0.362	0.646	3.603	44.78	-23.68	-82.91	0.00
[C$_{10}$MIm]Cl	0.379	0.646	3.743	49.00	-29.68	-86.07	-4.09
[C$_{10}$MIm]Br	0.386	0.657	3.801	45.27	-23.01	-87.30	-4.09
[C$_{12}$MIm]Cl	0.426	0.665	4.142	49.37	-29.56	-94.83	-4.09
[C$_{12}$MIm]Br	0.433	0.676	4.200	45.86	-22.84	-96.04	-4.09
[C$_{12}$MIm][BF$_4$]	0.464	0.717	4.519	34.79	-7.33	-86.12	-4.09
[C$_{14}$MIm]Cl	0.474	0.683	4.538	49.78	-29.56	-103.56	0.00
[C$_{14}$MIm]Br	0.480	0.694	4.596	46.47	-22.77	-104.74	0.00
[C$_{16}$MIm]Cl	0.523	0.700	4.937	50.33	-29.46	-112.35	0.00
[C$_{16}$MIm]Br	0.529	0.711	4.995	47.22	-22.65	-113.46	0.00
[C$_{18}$MIm]Cl	0.570	0.716	5.333	50.94	-29.28	-121.09	0.00
[C$_8$Py]Cl	0.326	0.622	3.273	49.46	-23.65	-76.09	-4.90
Na[C$_8$SO$_4$]	0.273	0.507	2.965	50.75	0.00	-61.30	0.00
Na[C$_{10}$SO$_4$]	0.312	0.525	3.366	51.35	0.00	-70.13	0.00
Na[C$_{12}$SO$_4$]	0.357	0.545	3.761	51.76	0.00	-78.80	0.00
Na[C$_{14}$SO$_4$]	0.404	0.564	4.158	52.12	0.00	-87.58	0.00

References

[1] Vision 2020 (Oak Ridge National Laboratory, USA) **2003**, 1-30.

[2] C. Jungnickel, J. Łuczak, J. Ranke, J. F. Fernández, A. Müller, J. Thöming, *Colloids Surf., A* **2008**, 316, 278-284.

[3] Z. Miskolczy, K. Sebok-Nagy, L. Biczok, S. Gokturk, *Chem. Phys. Lett.* **2004**, 400, 296-300.

[4] M. Blesic, M. H. Marques, N. V. Plechkova, K. R. Seddon, L. P. N. Rebelo, A. Lopes, *Green Chem***.** **2007**, 9, 481–490.

[5] J. Bowers, C. P. Butts, P. J. Martin, M. C. Vergara-Gutierrez, *Langmuir* **2004**, 20, 2191-2198.

[6] R. Vanyur, L. Biczok, Z. Miskolczy, *Colloids Surf., A* **2007**, 299, 256-261.

[7] J. Sirix-Plenet, L. Gaillon , P. Letellier, *Talanta* **2004**, 63, 979-986.

[8] Q. Q. Baltazar, J. Chandawalla, K. Sawyer, J. L. Anderson, *Colloids Surf, A* **2007**, 302, 150-156.

[9] O. V. Vieira, D. O. Hartmann, C. M. P. Cardoso, D. Oberdoerfer, M. Baptista, M. A. S. Santos, L. Almeida, J. Ramalho-Santos, W. L. C. Vaz, *PLoS ONE* **2008**, 3, e2913.

[10] J. M. Slattery, C. Daguenet, P. J. Dyson, T. J. S. Schubert, I. Krossing, *Angew. Chem. Int. Ed.,* **2007**, 46, 5384-5388.

[11] C. Ye, J. M. Shreeve, *J. Phys. Chem. A* **2007**, 111, 1456-1461.

[12] I. Krossing, J. M. Slattery, *Z. Phys. Chem.* **2006**, 220, 1343-1359.

[13] L. Glasser, H. D. B. Jenkins, *Chem. Soc. Rev.* **2005**, 34, 866-868.

[14] H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. *Glasser, Inorg. Chem.* **1999**, 38, 3609-3620.

[15] U. P. R. M. Preiss, J. M. Slattery, I. Krossing, *Ind. Eng. Chem. Res*. **2009**, *48*, 2290-2296.

[16] P. D. T. Huibers, V. S. Lobanov, A. R. Katritzky, D. O. Shah, M. Karelsonr, *Langmuir* **1996**, 12, 1462-1470.

[17] R. Nagarajan, E. Ruckenstein, *Langmuir* **1991**, *7*, 2934-2969.

[18] G. D'errico, O. Ortona, L. Paduano, V. Vitagliano, *J. Colloid Interface Sci.* **2001**, 239, 264-271.

[19] W. Mosquera, *J. Colloid Interface Sci.* **1998**, 206, 66-76.

[20] T. M. Perger, M. Bester-Rogac, *J. Colloid Interface Sci.* **2007**, 313, 288-295.

[21] I. Chakraborty, S. P. Moulik, *J. Phys. Chem. B* **2007**, 111, 3658-3664.

[22] S. K. Metha, K.K. Bhasin, R. Chauhan, S. Dham, *Colloids Surf., A* **2005**, 255, 153-157.

[23] P. Hansson, B. Joensson, C. Stroem and O. Soederman, *J. Phys. Chem. B* 2000, 104, 3496-3506.

[24] Y. Hayami, H. Ichikawa, A. Someya, M. Aratono, K. Motomura, *Colloid Polym. Sci.* **1998**, 276, 595-600.

[25] S. Durand-Vidal, M. Jardat, V. Dahirel, O. Bernard, K. Perrigaud, P. Turq, *J. Phys. Chem. B* **2006**, 110, 15542-15547.

[26] R. Ueoka, Y. Murakami, *J. Chem. Soc., Perkin Trans. 2* **1983**, 219 - 224.

[27] I. Goodchild, L. Collier, S. L. Millar, I. Prokeš, J. C. D. Lord, C. P. B. Butts, J. Bowers, J. R. P. Webster, R. K. Heenan, *J. Colloid Interface Sci.* **2007**, 307, 445-468.

[28] Q. Q. Baltazar, J. Chandawalla, K. Sawyer, J. L. Anderson, *Colloids Surf., A* **2007**, 302, 150-156.

[29] J. Wang, ., H. Wang, S. Zhang, H. Zhang, Y. Zhao, *J. Phys. Chem. B* **2007**, 111, 6181-6188.

[30] O. A. El Seoud, P. A. R. Pires, T. Abdel-Moghny, E. L. Bastos, *J. Colloid Interface Sci.* **2007**, 313, 296-304.

[31] B. Dong, N. Li, L. Zheng, L. Yu, T. Inoue, *Langmuir* **2007**, 23, 4178-4182.

[32] J. Sirex-Plenet, L. Gaillon, P. Letellier, *Talanta* **2004**, 63, 979-986.

[33] T. Inoue, H. Ebina, B. Dong, L. Zheng, *J. Colloid Interface Sci.* **2007**, 314, 236-241.

[34] S. Thomaier, K. Werner, *J. Mol. Liq.* **2007**, 130, 104-107.

[35] F. Quina, *J. Phys. Chem.* **1995**, 99, 17028-17031.

[36] T. Sasaki, M. Hattori, J. Sasaki, K. Nukina, *Bull. Chem. Soc. Jpn.* **1975**, 48, 1397-1403.

[37] J. Bohm, *Kristallzüchtung*, Verlag Harri Deutsch: Frankfurt/Main **1988**.

[38] J. W. Gibbs, *Am. J. Sci.* **1878**, 16, 441-458.

[39] F. Eckert, A. Klamt, COSMOtherm *Version C2.1, Release 01.06;* COSMOlogic GmbH & Co. KG, Leverkusen, Germany, 2006.

[40] A. Modaressi, H. Sifaoui, M. Mielcarz, U. Domanska, M. Rogalski, *Colloids Surf., A* **2007**, 302, 181-185.

[41] A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571-2577.

[42] A. D. Becke, *Phys. Rev. A* 1988, 38, 3098-3100.

[43] S. Vosko, L. Wilk , M. Nusair, *Can. J. Phys.* **1980**, 58, 1200-1211.

[44] J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822-8824.

[45] TURBOMOLE V5.10 2008, a development of University of Karlsruhe, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[46] P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett*. **2002**, 362, 511-518.

[47] P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, 117, 9535-9538.

[48] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, 100, 5829-5835.

[49] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 5, 799-805.

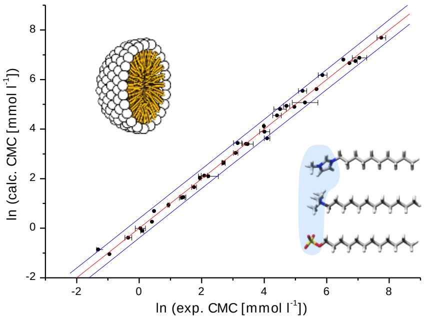
[50] F. Eckert, A. Klamt, *AlChE Journal* **2002**, 48, 369-385.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Ionic Liquids

U. Preiss, C. Jungnickel, J. Thöming, I. Krossing, J. Łuczak, M. Diedenhofen, and A. Klamt*

Predicting the Critical Micelle Concentration of Aqueous Solutions of Ionic Liquids and other Ionic Surfactants



A new method for predicting the CMC of ionic liquids and other ionic surfactants that is free from any need for experimental input is presented, extending common volume-based thermodynamics equations to include different interaction enthalpies calculated with COSMO RS.