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Cubic equations of state for adsorption layer: alkylthiopolyoxyethylene glycols

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Abstract: The van der Waals, Redlich–Kwong, Peng–Robinson and an equation of state derived by Smith were applied to approximate the run of surface pressure (Π) – area (σ) curves of the adsorption layer of *n*-pentyl to *n*-octyl thioethers of tri- and tetraoxyethylene glycols. The equation parameters: excluded molar area (σ_{oi}) and an interaction energy term (a_i) were determined by simplex method for Π values in the range of 2–23.5 mN/m. The equations parameters were found to be related to the structure of the amphiphile. The σ_{oi} decreased with the length of hydrocarbon thioether chain and was nearly uniform for equations of state in question except for Smith equation. The value of a_i was dependent on the amphiphile structure. It was used to obtain the interaction energy (ε_i) between amphiphiles in the adsorption layer. The values of ε_i determined as an increment per methylene group was in the range of ca. 0.2–0.32 $R*T$, depending on the equation of state used.

Key words: Adsorption layer – equations of state – nonionic surfactants – alkylthiopolyoxyethylene glycols

Introduction

Nonionic amphiphiles adsorbed on the surface of water form an adsorption layer whose nature may be compared to a two-dimensional gas. This brings an opportunity to describe the properties of the layer by means of equations of state similar in form to those used for common gases. For example, the surface pressure, Π, determined as a difference between surface tension of the solvent (water) and amphiphile solution, can be correlated with the adsorption area (per mole) occupied by the amphiphile, σ, by the equation of state

$$\Pi = R*T/\sigma\,, \tag{1}$$

where R is a gas constant, and T is absolute temperature. The above equation describes $\Pi - \sigma$ relationship of the adsorption layer in ideal state. Many amphiphiles which show moderate surface activity form gaseous films at a broad range of Π values, up to ca. 25 mN/m, and $\Pi - \sigma$ relationships of such films deviate considerably from ideality and therefore they cannot be represented by Eq. (1).

The equations of state suitable for non-ideal adsorption layers have also been proposed [1–4]. They only take into account finite dimension and interactions of the adsorbed molecules. An example is the modified Volmer equation presented in the following form

$$\Pi*(\sigma - \sigma_o) = Z'*R*T\,, \tag{2}$$

where σ_o is an excluded area (m^2/mol), a constant typical for the amphiphile, and Z' is the pseudo-compressibility factor, a measure of interactions between molecules in the film. Equation (2) was applied by Schoefield [5] and Gabrielli [6]. Recently, this equation has been used to characterize a number of amphiphiles of different surface activity which were the ethers of tri- and tetraoxyethylene glycols [7, 8]. The terms σ_o and Z' were determined by linear regression and the logical relationship between them and the structure of the amphiphiles was observed.

This paper may be seen as a result of further development of the studies presented in references [7, 8] and proposes application of other equations of state for a two-dimensional gas of the adsorption layer. The equations are

a) van der Waals equation of state

$$\Pi = R * T/(\sigma - \sigma_{\mathrm{ov}}) - a_{\mathrm{v}}/\sigma^2 \, ; \tag{3}$$

b) Redlich–Kwong equation of state [9]

$$\Pi = R * T/(\sigma - \sigma_{\mathrm{cr}}) - a_{\mathrm{r}}/\sigma(\sigma + \sigma_{\mathrm{or}}) \, . \tag{4}$$

For purposes of this work the constant a_{r} is assumed together with the temperature term. Originally, the second part of the Redlich–Kwong equation differed from (4) by the presence of $T^{0.5}$ term in the denominator and this had a distinct effect on dimension of the constant. Writing the Eq. (4) as above makes the dimension of the constants, a, to be the same in all equations of state used.

c) Peng–Robinson equation of state [10]

$$\Pi = R * T/(\sigma - \sigma_{\mathrm{op}}) - a_{\mathrm{p}}/(\sigma(\sigma + \sigma_{\mathrm{op}}) + \sigma_{\mathrm{op}}(\sigma - \sigma_{\mathrm{op}})) \, ; \tag{5}$$

d) equation of state derived by Smith [2]

$$\Pi = R * T * \sigma/(\sigma - \sigma_{\mathrm{os}})^2 - a_{\mathrm{s}}/\sigma^2 \, . \tag{6}$$

The Eqs. (3–6) belong to the same family of the cubic equations of state and contain two adjustable constants σ_{oi} and a_{i} (subscript $\mathrm{i} = \mathrm{v, r, p}$ or s depending on the equation). The physical meaning of the parameter σ_{oi} is like in Eq. (2): an excluded area expressed in $\mathrm{m}^2/\mathrm{mol}$. The parameter a_{i} is an interaction energy term expressed in $\mathrm{N} * \mathrm{m}^3/\mathrm{mol}$.

The common feature of the Eqs. (3–6) is that they express surface pressure as the sum of two terms, a repulsion pressure Π_{R} and an attraction pressure Π_{A} as follows

$$\Pi = \Pi_{\mathrm{R}} + \Pi_{\mathrm{A}} \, . \tag{7}$$

The Eqs. (3–5) have the repulsion pressure expressed by the van der Waals hard sphere equation adjusted to two-dimensional gas concept, i.e.,

$$\Pi_{\mathrm{R}} = R * T/(\sigma - \sigma_{\mathrm{oi}}) \, . \tag{8}$$

The attraction pressure can be expressed as

$$\Pi_{\mathrm{A}} = - a_{\mathrm{i}}/f(\sigma) \, , \tag{9}$$

where $f(\sigma)$ is a function of the molar adsorption area. The parameter a_{i} can be regarded as a measure of the interaction force between amphiphiles in the adsorption layer.

The Eq. (6) derived by Smith [2] was based on Reiss scaled particle theory of fluids [11] and it was adopted for two dimensions by assuming interactions between amphiphiles in adsorption layer resembling interactions between hard disks. The interaction constant was defined as

$$a_{\mathrm{s}} = \pi * \varepsilon * n * d^2/4 \, , \tag{10}$$

where n is the number of disks (carbon atoms in aliphatic hydrocarbon chain), ε is the potential energy when two disks just touch (their centers separated by distance d). In other words,

$$\sigma_{\mathrm{os}} = \pi * d^2/4 \, . \tag{11}$$

The paper of Smith [2] dealt with the amphiphiles forming spread films rather than adsorption ones.

The purpose of this work was to find applicability of the above equations in description of $\Pi - \sigma$ relationship in the adsorption layer of tri- and tetraoxyethylene glycol thioethers having *n*-pentyl to *n*-octyl alkyl chains, and to correlate the adjustable parameters of the equations in question with the structure of the amphiphiles.

Materials and methods

The surfactants tested were thioethers of tri- and tetraoxyethylene glycols: *n*-pentyl to *n*-octyl (abbreviated C*x*SE*y*, *x* denotes the number of C atoms in an alkanethiol, *y* stands for number of oxyethylene units). Details on surface tension measurements of aqueous solutions and calculation of $\Pi - \sigma$ values from Gibbs adsorption equation by numerical methods were given in [7, 8]. About 25–30 $\Pi - \sigma$ points were generated for calculation of the constants of Eqs. (3–6) to cover the Π range from 2 to 23.5 mN/m.

Results and discussion

The basic task of this work was to determine the constants σ_{oi} and a_{i} of Eqs. (3–6) from $\Pi - \sigma$ data calculated from Gibbs adsorption equation. This task was realized by the simplex method of

Nelder and Mead [12,13] and details of the calculation procedure are given in the Appendix.

The values of the constants of Eqs. (3–6) are given in Table 1. Figure 1 shows how curves obtained by simplex method fit the sets of $\Pi - \sigma$ points for chosen equations of state. The run of the curves adjusted to the same amphiphile by various equations of state is very similar and a plot like those in Fig. 1 will not indicate which equation of state under question has been used to model the run of the curve. This may signify that each of the Eqs. (3–6) is equally good to describe $\Pi - \sigma$ run of the adsorbed amphiphiles. This is not true. In fact, the differences between equations of state are small but are visible if statistics is taken into account. In the method used the least sum of squares of deviations was a measure of curve adjustment and this signified that the best fit of experimental $\Pi - \sigma$ points gave the Eq. (6) followed by Peng–Robinson, Redlich–Kwong, and van der Waals equations of state. The standard deviation, being a measure of curve fitting, was usually higher for a more surface active compound but averaged for all the surfactants it was 0.618, 0.657, 0.662, and 0.684 mN/m for the mentioned equations, respectively.

As can be seen in Fig. 1 at certain areas the experimental points lie below the ideal state curves. This fact has been known and many compounds able to form spread films showed such a run. It can be clearly seen in the case of higher fatty acids [2]. A possible explanation of this fact could be a change of the surfactant position from horizontal to vertical. At slant position of the surfactant molecule (intermediate state) it is possible that the residual area prescribed to one molecule may be overlapped partially by another molecule. This may be supported by an observation that, in the case of surfactants having spacious hydrophilic group which determine residual area in adsorption layer no such phenomenon was observed.

The parameters of Eqs. (3–5) can be well correlated with the structure of the amphiphiles. The constants σ_{0i} tend to decrease with the hydrocarbon chain length and is higher for E4 series as compared with E3 one (tetraoxyethylene and trioxyethylene thioethers, respectively). It is logical that decreasing tendency of σ_{0i} must be accompanied by enhanced attraction interaction of the amphiphile molecules and the strength of the attraction is in relation to a_i constant. It is thus obvious that the value of a_i increases with the length of the hydrocarbon part of the surfactant. The hydrophilic part of the surfactant molecule

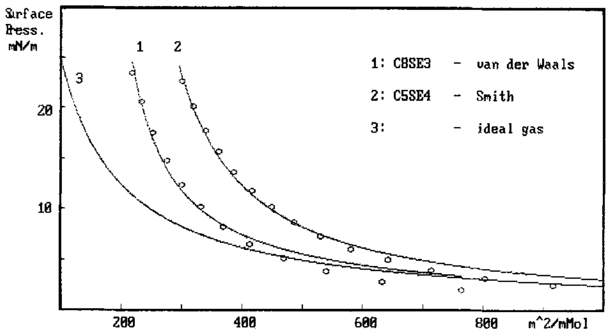

Fig. 1. Surface pressure vs molar area, approximation by equations of state

Table 1. The constants of the equations of state

Compound	σ_{0i} m^2/mol				a_i/1E + 8 N * m^3/mol			
	σ_{ov}	σ_{or}	σ_{op}	σ_{os}	a_v	a_r	a_p	a_s
C5SE3	165680	165140	165520	113281	1.378	2.030	2.444	3.871
C6SE3	156780	155390	155850	107220	2.105	2.970	3.551	4.468
C7SE3	146920	144820	145330	100390	2.602	3.588	4.274	4.800
C8SE3	138830	135900	136440	94850	3.215	4.353	5.171	5.229
C5SE4	187520	189830	189980	128100	− 1.023	− 1.076	− 1.202	1.777
C6SE4	179140	180220	180460	122410	0.029	0.288	0.397	2.709
C7SE4	171000	171050	171390	116840	0.871	1.371	1.671	3.428
C8SE4	162270	161140	161830	110940	1.644	2.373	2.850	4.086
C7OH*)	118790	114750	115360	81410	4.170	5.585	6.614	5.997

*) *n*-heptanol, data of ref. [16]

played an opposite role. It determined the residual area in adsorption layer and therefore affected σ_{oi}. A consequence of increased residual area was weaker attraction interaction between hydrocarbon chains clearly expressed by decrease of the a_{oi} values.

The molecule of the surfactant had 3 or 4 oxyethylene units, which means 9 to 12 structure units (methylene and ether oxygene) in the hydrophilic part, whereas the hydrophobic part had 5 to 8 carbon atoms. The residual area of C5SE4, C6SE4, C7SE4, and C8SE4 in adsorption layer at $\Pi = 24$ mN/m was 290, 277, 267, and 253 m^2/mmol, respectively, and the values for trioxyethylene derivatives were lower by ca. 35 m^2/mmol (1 A^2 per molecule corresponds to 6.023 m^2/mmol). For *n*-heptanol and *n*-octanol the analogous values were 188 and 161 m^2/mmol [7]. The cross-sectional area of the aliphatic chain is commonly assumed to be ca. 115 m^2/mmol (ca. 19 A^2) [3].

Basing on the above data it was assumed that the polyoxyethylene chain was a factor determining the residual area of the molecule and coiled under the interface. The shape of the molecule then resembled "a club with thin aliphatic chain with vertical position above the interface" [8]. Since the area of polyoxyethylene coil is greater than cross-sectional area of the hydrocarbon chain the latter will not be closely packed even at saturation of the adsorption layer. An alternative image of the molecule can be a candle in a paper boat floating on water.

As indicated by the data of Table 1, the values of σ_{oi} depend on the kind of the amphiphile. This tendency is evident and can be supported by the equations of state used. There are, however, differences between values obtained by various equations. The van der Waals, Redlich–Kwong, and Peng–Robinson equation of state gave nearly equal σ_{oi} values for the same amphiphile. This means that a part of the surface pressure, Π_R (repulsive) is uniform for these equations of state. Contrary to that, the Eq. (6) derived by Smith [2] gave lower σ_s values and higher Π_R. Equation (6) has good theoretical background, but values of excluded area seem to disagree with commonly assumed standards. It was between 130 m^2/mmol (21.3 A^2) for C5SE4 and 94.8 m^2/mmol (15.7 A^2) for C8SE3. The latter value was lower than cross-sectional area of the aliphatic hydrophilic chain and for *n*-heptanol the result was even more distinct, yielding $\sigma_{os} = 13.5\ A^2$. Nevertheless, the Eq. (6) was the best regression equation for the experimental data.

As regards the part of surface pressure called attraction pressure the Eq. (6) and van der Waals equation give the same mathematical expression, but the values of Π_A calculated by these equations are different because of difference in a_i value. A feature which determines the Π_A in the remaining two equations is the function $f(\sigma)$. Its form is responsible for quality of $\Pi - \sigma$ curve approximation to experimental points and indirectly it affects the value of the interaction parameter a_i. An example of the relationship between Π_A, Π_R and molecular area is shown in Fig. 2.

The parameters a_i have dimension of $N * m^3/mol$. They were determined as regression coefficients (together with σ_{oi}) within definite range of surface pressure and, as such, they have features of the regression coefficients with all advantages and disadvantages. Unfortunately, critical temperature and critical pressure of the adsorption layer have not yet been defined and therefore it was impossible to calculate the equation parameters in a direct way like in the case of real gases.

Nevertheless, the constant a_i being an energy term can be related to the interaction energy between adsorbed molecules. If one assumes the hydrophobic part of the amphiphile to be a stack of disks formed by methylene groups, the interaction energy can be correlated with disk diameter

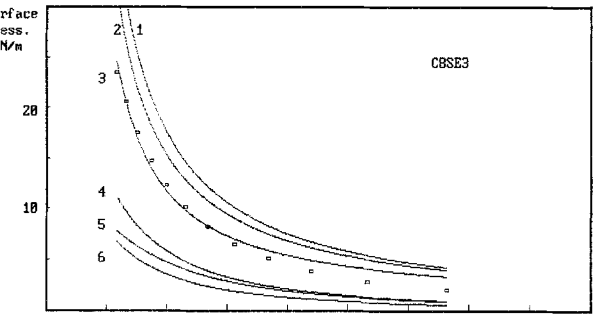

Fig. 2. Contribution of attraction (Π_A) and repulsion (Π_R) pressure to surface pressure as a function of molar area of C8SE3. 1: Π_R (Smith), 2: Π_R (van der Waals), 3: $\Pi - \sigma$ isotherm (Smith), 4: Π_A (Smith), 5: Π_A (Peng–Robinson), 6: Π_A (van der Waals)

in a similar way to the Smith concept presented by Eqs. (10) and (11), yielding potential energy of interaction ε_i. The only difference will be that the distance at which the disks interact in our case is determined by excluded area σ_{oi} and is given by

$$\varepsilon_i = a_i/\sigma_{oi} . \qquad (12)$$

The problem is that using four equations of state results in four values of a_i (and, consequently, ε_i) for each amphiphile. On the other hand, all of them can be interrelated with the structure of the amphiphile and the relationship presented in the form

$$\varepsilon_i = A + B * x + C * y . \qquad (13)$$

Table 2 contains the coefficients of multiple regression A, B and C (x, y as previously mentioned, ε_i in $R * T$ units). The constant B signifies interaction energy per methylene group. It was lowest when calculated from van der Waals equation of state and was 0.203 $R * T$, and was highest when derived from Peng–Robinson equation of state (0.314 $R * T$). The first value is in good agreement with that obtained by Eq. (2) combined with van der Waals equation of state and reported in [7].

The negative value of C supports observations that the spacy hydrophilic group of the polyoxyethylene type acts as a disjoining factor for the adsorption layer.

The equations of state give different sets of energy increments and all are well correlated with the amphiphile structure so that it would be very difficult to indicate the best set. The van der Waals and Eq. (6) have good theoretical justification to be used, but they give values of interaction energy rather far from each other (0.203 $R * T$ and 0.297 $R * T$ per methylene group, respectively. From the point of view of regression, Eq. (6) is the best, and that of van der Waals is the worst to suite the experimental data of the compounds under question. The Redlich–Kwong and Peng–Robinson equations of state may be treated like they have been in the case of real gases as those which improve the curve fitting. The attraction pressure Π_A is not strongly dependent on a_i. Since $f(\sigma)$ is a quadratic equation a slightly better adjustment of $\Pi - \sigma$ run will cause rather distinct change of a_i constant. Improvement of curve fitting by Redlich–Kwong and Peng–Robinson equation of state results in variation of energy increments shown in Table 2. It is noteworthy that Lennard–Jones energy parameters for the interaction of disks calculated for methane and higher hydrocarbons were reported to be in the range of $0.507 - 0.327\, R * T$ per methylene (methane) group with tendency to decrease with the size of the hydrocarbon molecule [13, 14]. The same Lennard–Jones parameters calculated for *n*-heptanol and *n*-octanol from second virial coefficients [7] was ca. 0.2 $R * T$ per methylene group. In light of this, the data of Table 2 seem to be reasonable and support the concept of non-ideal two-dimensional gas of the adsorption layer of the amphiphiles in question.

Table 2. The regression coefficients of Eq. (13)

Equation of state	A	B	C	R^2
van der Waals	0.910	0.203	− 0.532	0.9987
Redlich–Kwong	1.259	0.267	− 0.702	0.9990
Equation (6)	2.220	0.297	− 0.779	0.9984
Peng–Robinson	1.491	0.314	− 0.823	0.9990

Appendix

The best fit of the curve given by an equation of state to the set of i points of $\Pi - \sigma$ is achieved when the sum of squares of deviations reaches minimum.

$$\sum_{n=1}^{i} (\Pi^* - \Pi(i))^2 = \Phi = \min . \qquad (14)$$

Π^* signifies the value of surface pressure calculated from the equation of state at $\sigma(i)$, $\Pi(i)$ experimental value. The function Φ is determined by two variables of the equation of state, i.e., σ_{oi} and a_i. This means that to solve the minimization problem it is necessary to find a pair of values σ_{oi} and a_i which satisfies Eq. (14). To solve the problem the simplex procedure of Nelder and Mead [12, 13] was adopted. The simplex on the response surface Φ was a triangle as Φ was a function of two variables.

The calculation was carried out using an IBM computer equipped with a math coprocessor. The procedure required introducing the initial σ_{oi} and

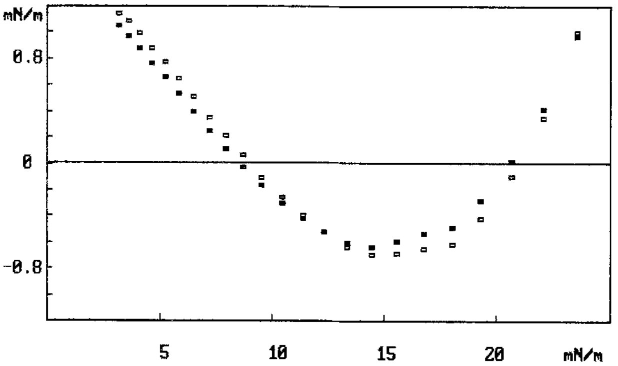

Fig. 3. $\Pi^* - \Pi(i)$ vs surface pressure at the condition of Φ = min for C5SE4. □ – van der Waals equation, ■ – Smith equation

a_i values and conditions to end the calculations. The calculation was stopped if the norm of the correction in the centroid and the distance between the best point and the centroid were both less than the threshold value required by the calculation program.

The algorithms had great versatility to adopt simplex to the local landscape of the function surface. It elongated and took a large step if it could do so; it changed direction on encountering a valley at an angle and it contracted in the neighbourhood of the minimum. Usually, 50–60 iterative steps were made to satisfy the conditions to finish calculations.

Figure 3 shows a typical distribution of $\Pi^* - \Pi(i)$ values vs. Π at a condition of Φ = minimum expressed by Eq. (14).

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