Method for analysis of the composition of acid soaps by electrolytic conductivity measurements

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1. Introduction

The sodium and potassium carboxylates (dodecanoates, tetradecanoates, hexadecanoates, and octadecanoates, which are popular, respectively, as laurates, myristates, palmitates, and stearates) have a broad application in many consumer products like soaps bars; cleaning products; cosmetics; facial cleaners; shaving creams, and deodorants [1–3]. The dissolving of carboxylates in water is accompanied by increase of the solution’s pH due to the spontaneous hydrolysis (protonation) of the carboxylic anion [4]:

\[ Z^- + H_2O \leftrightarrow HZ + OH^- \]

Here we use the notations in Ref. [4], viz. \( Z^- \) is carboxylate anion, and \( HZ \) is non-dissociated carboxylic acid. The non-dissociated \( HZ \) with 12 and more carbon atoms is weakly soluble in water and forms crystalline precipitates at relatively low carboxylate concentrations (\( \leq 10^{-5} \) M). Moreover, the hydrogen-bonding interaction between the carboxylic-acid molecules and carboxylate anions leads to the formation of \( j:n \) acid-soap complexes that also form crystalline precipitates [5–9]:

\[ jHZ + nZ^- + nM^+ \leftrightarrow (HZ)_{j}(MZ)_n \]

Here, \( M^+ \) is a metal cation (usually \( Na^+ \) or \( K^+ \)), and \( (HZ)_{j}(MZ)_n \) is the acid soap. The acid soaps were investigated by Ekwall et al. [5–7,10–12], McBain et al. [8,9], and in subsequent studies [3,4,13–21]. Soaps of different stoichiometry, \( j:n = 1:1, 1:2, 2:1, 3:2, 4:1 \), etc., have been experimentally detected [3,12–14,19–21]. In fact, the turbidity of the soap solutions is due to the formation of fine (micrometer and submicrometer) \( j:n \) acid-soap crystallites.

As mentioned above, the solution’s pH increases with the rise of the total input concentration of carboxylate, \( c_j \). For the acid-soap precipitates, the ratio \( n:j \) increases with the rise of \( c_j \); its value can be determined from the slope of the experimental pH vs-\( c_j \) dependence, or from plots of precipitate characteristic functions [4,21]. Above a certain threshold concentration, separation of \( MZ \) from the solution begins in the form of either \( MZ \) crystallites [21] or micelles [22]. In the case of two coexisting solids, viz. acid-soap and \( MZ \) crystallites, the solution’s pH remains constant (independent of \( c_j \)) in agreement with the Gibbs phase rule [4,21]. In the case of coexisting \( j:n \) acid soap and micelles, the soap stoichiometry and micelle charge can be determined by analysis of experimental data from parallel \( in situ \) measurements of pH and conductivity [22].

Sometimes, the results obtained by \( in situ \) measurements with the carboxylate solutions can be uncertain. For example, the concentration range with a given acid-soap precipitate could be rather narrow, or the value of a given solubility product, which is needed to interpret the data, is unknown. For this reason, it is desirable to determine the acid-soap stoichiometry by using an independent method. We could separate crystallites from a given carboxylate solution and to subject them to chemical analysis. One analyti-
tical method, which has been applied to identify acid soaps, is the IR spectroscopy [3,15,23]. One difficulty with this method is the lack of reference spectra for the whole variety of possible jn acid soaps.

Here, we propose another direct method for analyzing the stoichiometry of (HZ)j(MZ)n acid soaps. The principle of this method is the following. Acid-soap crystallites of unknown stoichiometry are collected from a carboxylate solution at a given temperature. Further, these crystallites are dissolved in water at a higher temperature, at which HZ is insoluble, but MZ is dissociated to M+ and Z− ions. By measuring the conductivity of the latter solution, we can determine the stoichiometry of the dissolved acid soap.

The paper is organized as follows. In Section 2 we describe the proposed method. In Section 3 we quantify the dependence of the conductivity of MZ-solutions on the MZ concentration, for the case of potassium myristate (KMy) by using an approach based on the studies by Walden et al. [24,25]. Finally, in Section 4 we present experimental data and their interpretation; demonstrate how the proposed method works, and discuss the limits of its applicability.

2. Description of the proposed method

We assume that a sample of solid (crystalline) acid soap is available. This sample could be obtained by taking crystallites out of a carboxylate solution at a given temperature and carboxylate concentration (details in Section 4 below). Our aim is to determine the stoichiometry of the investigated sample of (HZ)j(MZ)n acid soap. For this goal, we propose the following working procedure.

First, we dissolve the acid-soap crystallites in water at appropriate working conditions. The latter are chosen in such a way that the only precipitate in the solution is that of HZ, whereas MZ is dissociated to M+ and Z− ions.

Second, the electrolytic conductivity, κ, of the solutions is measured. κ will be greater if the content of MZ in the (HZ)j(MZ)n acid soap is greater. In this way, by quantitative data analysis, we can determine the stoichiometry, j,n, of the acid soap (see below).

To illustrate the application of this method, in the present study we work with potassium myristate (KMy). To select the working conditions, we measured the dependence of pH of aqueous KMy solutions on the total input concentration of KMy, c1, at 40 °C; see Fig. 1. The data in Fig. 1 exhibit a break at c1 ≈ 7.5 mM. For c1 < 7.5 mM, the slope of the pH vs log(c1) plot is +1 (the straight line in Fig. 1), which indicates precipitation of HZ crystallites [4,21]; see Section 5.1 for details. At c1 > 7.5 mM, the solutions contain KMy micelles that coexist with acid-soap crystallites; this has been proven by combined pH, conductivity and oil-solubilization measurements in Ref. [22].

In view of the data in Fig. 1, we choose our working conditions (for KMy) to be T = 40 °C and c1 < 7.5 mM. Under these conditions, the only precipitate in the solution is that of HMy, whereas KMy is dissociated to K+ and My− ions.

By using equilibrium relationships for carboxylate solutions [4,21,22], one can prove that in the concentration zone, where only HZ precipitate is present (no micelles), the concentrations of carboxylate anions and metal cations, cZ and cM, are related as follows:

$$c_Z \approx c_M \left(1 - \frac{K_W}{K_{HZ}}\right)$$  \hspace{1cm} (1)

(no added acid). K_W is the solubility product of the carboxylic acid (HZ) and K_{HZ} is the dissociation constant of water. For the considered carboxylates we have K_W/K_{HZ} ≪ 1, which means that c_Z ≈ c_M. In other words, the amount of the HZ precipitate is much smaller than the amounts of the M+ and Z− ions in the solution; the concentrations of the latter two types of ions are approximately equal to each other, and to the ionic strength, I, of the carboxylate solution:

$$c_Z \approx c_M \approx c_I \approx I \left(\frac{1}{2} \sum_{i} z_i^2 c_i\right)$$ \hspace{1cm} (2)

(c_i and z_i denote concentrations and valences of the ionic species). Equation (2) is violated at concentrations higher than a given threshold concentration that corresponds to the beginning of separation of neutral soap (MZ) in the form of MZ crystallites as it is for NaMy, see Ref. [21], or in the form of MZ micelles as it is for KMy, see Fig. 1; details can be found in Ref. [22]. As already mentioned, to determine the stoichiometry of the acid-soap samples, we will work at sufficiently low concentrations and at a sufficiently high temperature, so that the carboxylate solutions contain only HZ precipitate, and Eq. (2) is applicable (see e.g. Fig. 1, the region at c1 < 7.5 mM).

Next, from a given sample of dried crystalline acid soap, we prepare a series of aqueous solutions and, at the working temperature, we measure their electrolytic conductivity, κ, as a function of the concentration, C, of the dissolved substance. The conductivity of the investigated 1:1 electrolyte solutions can be expressed in the form [26]:

$$\kappa = \kappa_0 + \lambda_0^{(0)} I + A I^{3/2},$$ \hspace{1cm} (3)

where

$$\lambda_0^{(0)} = \lambda_0^{(0)} + \lambda_0^{(0)}$$ \hspace{1cm} (4)

is the molar conductance of a MZ solution at infinite dilution; $\lambda_0^{(0)}$ and $\lambda_0^{(0)}$ are the respective molar ionic conductances at infinite dilution; Eq. (4) expresses the Kohlrausch law [27]; $\kappa_0$ and A are experimental constants; $\kappa_0$ accounts for possible trace amounts of other ionic species (like H+, OH−, HCO3−) in the used water. In the ideal case, $\kappa_0 \approx 0$ and Eq. (3) reduces to the known expression [26]: $\kappa = I \left(\frac{1}{2} \sum_{i} z_i^2 c_i\right) + A I^{3/2}$.

As already mentioned, the working temperature is chosen in such a way that the dissolution of (HZ)j(MZ)n acid soap yields M+ cations, Z− anions, and HZ crystallites. The concentration of the investigated solutions, C (g/L), can be expressed in the form

$$C \approx M_{MCM} + M_Zc_Z + M_{HZ}c_{HZ},$$ \hspace{1cm} (5)

where $M_{MCM}$, $M_Z$ and $M_{HZ}$ (g/mol) are the molecular masses of the respective components; $c_{HZ}$ is the concentration of HZ molecules.
in the form of HZ precipitate per unit volume of the solution; the concentration of molecularly dissolved carboxylic acid, \( c_{HZ} \), is very small and is neglected; here, the dimension of \( C_2 \), \( C_M \), and \( m_{HZ} \)

is mol/L. In view of the stoichiometry of the dissolved \((HZ)_j(MZ)_n\)

acid, we have:

\[
\frac{C_M}{m_{HZ}} = \frac{n}{j}, \quad \text{hence } m_{HZ} = \frac{j}{n} C_M. \tag{6}
\]

With the help of Eqs. (2) and (6), we can represent Eq. (5) in the form:

\[
I = \frac{C}{M_{HZ} + (j/n) M_{HZ}}. \tag{7}
\]

where \( M_{HZ} = M_M + M_Z \) is the molecular mass of the neutral soap.

The theoretical dependence \( \kappa(C) \) is determined by Eqs. (3) and (7). For a given C, and for a tentative value of \( j/n \), we calculate \( I \) from Eq. (7), and then the value of \( I \) is substituted in Eq. (3) to calculate \( \kappa \). The molecular masses \( M_{HZ} \) and \( M_{HZ} \)

are known. The parameters \( K_0 \), \( \lambda(0) \), and \( A \) are determined in a separate experiment (see Section 3). The ratio \( j/n \) can be determined as a single adjustable parameter from the fit of the data for \( \kappa(C) \); see Section 4.

3. Concentration dependence of the conductivity of carboxylate solutions

3.1. Theoretical background

As known, with the increase of the total carboxylate concentration, \( c_z \), different kinds of solid precipitates (HZ and j:n acid soaps) and micelles appear in the aqueous carboxylate solutions [3,12–14,19–21]. The electrolytic conductivity of these solutions, \( \kappa \), may exhibit one or more kinks when plotted as a function of \( c_z \) [21,22,28–30]. This is due to the fact that the appearance of micelles and/or acid soap precipitates of different stoichiometry affects the types and concentrations of the ionic species in the solution. In principle, the detailed analysis of the composition of the carboxylate solutions, like that in Refs. [4,21,22], could reveal the types of the precipitates/micelles and allow a quantitative interpretation of the data for \( \kappa \) vs \( c_z \).

According to the theory by Onsager and Fuoss [31], the molar conductance of a binary solution can be expressed in the form [26,31]:

\[
\lambda = \lambda(0) - (A_1 + A_2)(2I)^{1/2}. \tag{8}
\]

where

\[
A_j = \frac{1.970 \times 10^6 |z_1 z_2| q_j^2}{(\varepsilon \eta T)^{3/2}} + \frac{28.98 |z_j|}{\eta^2 (\varepsilon \eta T)^{1/2}} \quad (j = 1, 2). \tag{9}
\]

\( \varepsilon \) and \( \eta \) are the dielectric constant and viscosity (in poises) of the solvent; \( T \) is the absolute temperature; \( z_1 \) and \( z_2 \) are the valences of the cations and anions; \( \lambda_{1(0)} \) and \( \lambda_{2(0)} \) are their molar conductances at infinite dilution:

\[
q = \frac{|z_1 z_2| (\lambda_{1(0)} + \lambda_{2(0)})}{(|z_1| + |z_2|)(|z_1| \lambda_{1(0)} + |z_2| \lambda_{2(0)})}. \tag{10}
\]

For 1:1 electrolyte, we have \( q = 0.5 \). In addition, the ionic molar conductance can be expressed in the form [26]:

\[
\lambda_{j(0)} = \frac{z e^2 N_A}{6 \pi \eta r_j}. \tag{11}
\]

where \( e \) is the electronic charge, \( N_A \) is the Avogadro number, and \( r_j \) is the radius of the ion.

The first term in the right-hand side of Eq. (9) accounts for the relaxation effect; this term depends on the ionic radius, \( r_j \), through \( \lambda_{j(0)} \). The last term in Eq. (9) accounts for the electrophoretic effect; this term is independent of the ionic radius, \( r_j \), and is the same for different ions of the same valence.

On the basis of a set of experimental data, Walden et al. [24,25] arrived at the following semiempirical equation:

\[
\lambda = \lambda(0) - A I^{1/2}, \quad A \approx 65.7 \frac{M_m}{\varepsilon \eta}, \tag{12}
\]

which was found to be applicable to a large number of electrolytes in different solvents [26]. Equation (12) implies that only \( \lambda(0) \) is sensitive to the type of the ion (through \( r_j \)—see Eq. (11)), whereas the parameter \( A \) in the correction term is the same for different 1:1 electrolytes [24–26].

To check the applicability of the Walden’s approach, in Fig. 2 we have plotted literature data for \( \lambda \) from Refs. [26] and [32] for four electrolytes, NaCl, KCl, NaI, and KI, at 25 °C. On the one hand (Fig. 2a), there is a difference between some of the experimental curves, which are mostly due to the different \( \lambda_j(0) \) for the Na\(^+\) and K\(^+\) ions (\( \lambda_{Na}(0) = 50.1 \text{ cm}^2 \text{ S/mol; 25°C} \)). On the other hand, the correction term, \( \Delta \lambda = \lambda(0) - \lambda \), is almost the same for these four different electrolytes (Fig. 2b). This result is agreement with the Walden’s approach; see Eq. (12). In view of Eq. (9), this implies that the electrophoretic effect is predominant. [If the
relaxation effect were important, this would lead to influence of $r_j$ on $\Delta \lambda$ through $\lambda_j^{(0)}$, see Eqs. (9) and (11), which is not the case.]

Following the Walden’s approach, below we check whether the correction term, $\Delta \lambda \equiv \lambda_j^{(0)} - \lambda$, is the same for KCl and KMy. If this is confirmed, we may use $\Delta \lambda$, obtained from the available accurate set of data for the conductivity of KCl, to interpret the conductivity data for solutions of KMy and its acid soaps.

### 3.2. Temperature dependence of $\lambda_j^{(0)}$

To analyze our data, we need the values of $\lambda_j^{(0)}$ for $\text{K}^+$ and $\text{Cl}^-$ ions at 40 °C. For this goal, we used literature data for $\lambda_j^{(0)}(T)$ from Ref. [33], which were interpolated to determine the value at 40 °C, see Fig. 3. The same interpolation curves might be used to obtain the value of $\lambda_j^{(0)}$ at other temperatures. We utilized the fact that the main temperature dependence of $\lambda_j^{(0)}$ originates from the strong dependence of the viscosity of water, $\eta$, on temperature. For this reason, in Fig. 3 we plot $\lambda_j^{(0)}$ vs $\eta^{-1}$, which turns out to be a straight line:

$$\lambda_j^{(0)} = \alpha_x + \frac{b_x}{\eta}$$  \hspace{1cm} (13)

### Table 1

Molar ionic conductances, $\lambda_j^{(0)}$ (cm$^2$/S/mol), of several ions in aqueous solutions at infinite dilution, and at three different temperatures.

<table>
<thead>
<tr>
<th>Conductance</th>
<th>10 °C</th>
<th>25 °C</th>
<th>40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{K}}^{(0)}$</td>
<td>34.88</td>
<td>50.10</td>
<td>67.56</td>
</tr>
<tr>
<td>$\lambda_{\text{Na}}^{(0)}$</td>
<td>52.96</td>
<td>73.50</td>
<td>95.69</td>
</tr>
<tr>
<td>$\lambda_{\text{Cl}}^{(0)}$</td>
<td>54.32</td>
<td>76.35</td>
<td>100.6</td>
</tr>
<tr>
<td>$\lambda_{\text{K}^+}^{(0)}$</td>
<td>275.4</td>
<td>349.8</td>
<td>419.1</td>
</tr>
<tr>
<td>$\lambda_{\text{OH}^-}^{(0)}$</td>
<td>141.4</td>
<td>198.3</td>
<td>260.6</td>
</tr>
<tr>
<td>$\lambda_{\text{HCO}_3^-}^{(0)}$</td>
<td>30.34</td>
<td>44.50</td>
<td>60.66</td>
</tr>
<tr>
<td>$\lambda_{\text{Z}^+}^{(0)}$</td>
<td>47.24</td>
<td>69.30</td>
<td>94.47</td>
</tr>
</tbody>
</table>

Fig. 4. Plot of experimental data for the conductivity, $\kappa$, of KCl solutions vs the KCl concentration, $c$. The line is the best fit by Eq. (14).

(X = K, Cl, ...). The coefficients $d_X$ and $b_X$, determined from the interpolating linear regression, are given in Fig. 3. Similar approach is applicable also to other ions. For example, for Na$^+$ ions, Eq. (13) is applicable with $d_K = 2.19$ and $b_K = 42.70$ (the same units as in Fig. 3). As an illustration of the temperature effect, results that are useful for the analysis of conductivity of carboxylate solutions are shown in Table 1 for several ions at three different temperatures: 10, 25 and 40 °C.

### 3.3. Comparison of the conductivities of KMy and KCl at 40 °C

In this case, the conductivity of the investigated solutions can be described by the expression:

$$\kappa = \kappa_0 + \lambda_j^{(0)} c - Ac^{3/2} \quad (T = 40 \text{ °C}),$$  \hspace{1cm} (14)

where $c = I$ is the concentration of the 1:1 electrolyte solution; $\kappa_0$ is the same as in Eq. (3).

Fig. 4 shows our experimental data for the conductivity $\kappa$ of KCl at 40 °C. For this system, the coefficient $\lambda_j^{(0)}$ in Eq. (14) is known: from Table 1 we find $\lambda_j^{(0)} = \lambda_{\text{K}}^{(0)} + \lambda_{\text{Cl}}^{(0)} = 196.29$ cm$^2$/S/mol. Using the latter value, we fitted the data in Fig. 4 by means of Eq. (14), and determined $\kappa_0$ and $A$ as adjustable parameters. Thus, we obtained: $\kappa_0 = 0.064 \pm 0.02$ mS$^{-1}$, $A = 204.4 \pm 1.5$ mS$^{-1}$ M$^{-3/2}$.

In addition, we obtained data for the conductivity of KMy solutions at 40 °C and at concentrations $c < 7.5$ mM (below the CMC). Under these conditions, the solutions contain $\text{K}^+$ and $\text{Z}^+$ ions, and HZ precipitate. To process the conductivity data for KMy, we will apply Eq. (14). Following the Walden’s approach we will use the
same value of $A$ as for KCl. In such a case, Eq. (14) can be represented in the form:

$$
\kappa + 204.4c^{3/2} = \kappa_0 + \lambda^{(0)}c.
$$

(15)

The data for the conductivity $\kappa(c)$ of KMy solutions at 40°C are plotted in Fig. 5 in accordance with Eq. (15). The fit by linear regression has intercept $\kappa_0 = 0.007 \pm 0.003$ mS/cm; slope $\lambda^{(0)} = 123.6 \pm 0.8$ cm$^2$/S/mol, and regression coefficient $= 0.99994$. The latter coefficient indicates that the data in Fig. 5 excellently comply with a straight line, which means that the Walden’s approach is applicable, i.e. the same value of $A$ can be used for KCl and KMy.

Furthermore, with the above value of $\lambda^{(0)}$, and with $\lambda^{(0)}_K$ from Table 1, we determine the molar conductance of the My$^-$ ion:

$$
\lambda^{(0)}_{My} = \lambda^{(0)}_K - \lambda^{(0)} = 27.9 \text{ cm}^2\text{S/mol at 40°C}.
$$

(16)

Additional results presented in Section 3.4 will confirm that the latter value of $\lambda^{(0)}_{My}$ is reasonable.

In summary, in the present section, we determined the values of the coefficients in Eq. (3) for KMy at 40°C, as follows:

$$
\kappa = 0.007 + 123.6I - 204.4I^{3/2} \quad (T = 40°C)
$$

(17)

$I = c$ for 1:1 electrolyte). Equation (17) will be applied in Section 4 for determination of the stoichiometry of acid soaps.

3.4. Comparison of the conductivities of KMy and KCl at 25°C

To confirm the correctness of the above approach, and of the obtained value of $\lambda^{(0)}$, we will process in a similar way data for the conductivity of KCl and KMy solutions at 25°C. Unlike the case at 40°C, an expression in the form $\lambda = \lambda^{(0)} - Ac^{1/2}$ is insufficient to describe the concentration dependence of the molar conductance of KCl at 25°C, in the concentration range $c \leq 150$ mM. For this purpose, an augmented expression for $\lambda$ can be used [26]:

$$
\lambda = \lambda^{(0)} - Ac^{1/2} + Bc \quad (T = 25°C).
$$

(18)

For KCl at 25°C, we have $\lambda^{(0)} = 149.85$ cm$^2$/S/mol. We determined the coefficients $A$ and $B$ by fit of literature data [26,32] for $\lambda$ of KCl, see Fig. 6. The best fit in the latter figure yields: $A = 95.20 \pm 0.72$ mS/cm$^{-1}$M$^{-3/2}$, $B = 92.72 \pm 2.7$ mS/cm$^{-1}$M$^{-2}$; the regression coefficient is 0.99993. Note that the last term, $Bc$, is negligible for $c \leq 15$ mM.

Furthermore, we obtained conductivity data for KMy at 25°C for concentrations below the CMC. To fit these data, we used the expression

$$
\kappa = \kappa_0 + \lambda^{(0)}c - Ac^{3/2} + Bc^2 \quad (T = 25°C),
$$

(19)

which is an upgraded version of Eq. (14), in view of Eq. (18). Following the Walden’s approach, we assumed that the correction term, $-Ac^{3/2} + Bc^2$, is the same for KCl and KMy, and processed the data for KMy by means of the expression:

$$
\kappa + 95.20c^{3/2} - 92.72c^2 = \kappa_0 + \lambda^{(0)}c \quad (T = 25°C).
$$

(20)

The data for the conductivity $\kappa(c)$ of KMy solutions at 25°C are plotted in Fig. 7 in accordance with Eq. (20). The fit by linear regression has intercept $\kappa_0 = 0.002 \pm 0.004$ mS/cm; slope $\lambda^{(0)} = 93.94 \pm 0.8$ cm$^2$/S/mol, and regression coefficient $= 0.9997$. The latter coefficient indicates that the data in Fig. 7 excellently comply with a straight line, which means that the Walden’s approach is applicable again.

Furthermore, with the above value of $\lambda^{(0)}$, and with $\lambda^{(0)}_K$ from Table 1, we determine the molar conductance of the My$^-$ ion:

$$
\lambda^{(0)}_{My} = \lambda^{(0)} - \lambda^{(0)}_K = 20.44 \text{ cm}^2\text{S/mol at 25°C}.
$$

(21)
On the other hand, using Eq. (16) we calculate
\[ \lambda_{\text{My}}^{(0)}(25^\circ C) \approx \frac{\eta(40^\circ C)}{\eta(25^\circ C)} \lambda_{\text{My}}^{(0)}(40^\circ C) = 20.5 \text{ cm}^2/\text{mol}, \tag{22} \]
where the intercept \( a_0 \) in Eq. (13) has been neglected, and the respective values of the viscosity of water have been substituted: \( \eta(25^\circ C) = 0.8903 \) and \( \eta(40^\circ C) = 0.6531 \) (mPa s). The values of \( \lambda_{\text{My}}^{(0)} \) in Eqs. (21) and (22) agree very well, which confirms the applicability of the used approach.

In summary, in the present section, we determined the coefficients in the concentration dependence of conductivity for KMy at 25\(^\circ\)C:
\[ \kappa = 0.002 + 93.94 I - 95.20 j^{3/2} + 92.72 l^2 \quad (T = 25^\circ C), \tag{23} \]
which is used for interpretation of our data for the conductivity of KMy solutions in Ref. [22].

4. Determination of the acid-soap stoichiometry

4.1. Experimental procedure

Solutions of potassium myristate (KMy) were prepared by using two different procedures.

Procedure 1: KMy solutions were obtained by dissolving stoichiometric amounts of myristic acid (HMy, Fluka, 98% pure) and potassium hydroxide (KOH, Teokom, pure for analysis) at 60 \(^\circ\)C, and stirring for 30 min. Then, the solutions were cooled down to 25 \(^\circ\)C.

Procedure 2: The same as Procedure 1, but commercial KMy (producer Viva Corporation) was dissolved.

In some experiments (Procedure 1), the amount of KOH was 87.5\% of that needed for full neutralization of HMy. The obtained solutions contain 87.5\% KMy and 12.5\% HMy. Thus, we checked the effect of added HMy on the precipitates in the investigated solutions. In other experiments, KCl (product of Sigma) was added to the solutions.

In many of the investigated solutions, we observe the formation of crystallites of size greater than 1 \( \mu \text{m} \), which can be seen by optical microscopy. To separate these crystallites from the solution, the latter was poured in a filtration module, with a porous glass filter \( \Phi \) at the bottom. In our experiments, we used a glass membrane of maximum pore size 33 \( \mu \text{m} \). The aqueous phase is sucked out from the filtration module by a water pump for about 5–10 min depending on the volume of the filtrated solution. The crystallites are deposited at the upper surface of the glass filter. After that, they are placed in a Petri dish and dried in a vacuum drier at room temperature.

The working solutions for conductivity analysis were prepared by dissolving corresponding amounts of the collected crystallites at 60 \(^\circ\)C to obtain a solution of a given concentration, \( C \) g/L. Finally, the solutions were cooled down to the working temperature of 40 \(^\circ\)C, and their electrolytic conductivity, \( \kappa \), was measured. In our first set of \( \kappa \)-measurements, we maintained 40 \( \pm \) 2 \(^\circ\)C, which led to some scattering of the data. Further, we improved the temperature control and succeeded to maintain 40 \( \pm \) 0.1 \(^\circ\)C, which resulted in smoother experimental curves.

4.2. Experimental results and their interpretation

Fig. 8a shows \( \kappa \)-vs-\( C \) experimental data for dissolved acid-soap crystallites that have been initially formed in a solution of 8.5 mM KMy at 25 \(^\circ\)C, prepared by Procedure 1. This concentration is just above the CMC, which is 7.5 mM KMy for this system [22]. During the conductivity analysis, the temperature was maintained 40 \( \pm \) 0.1 \(^\circ\)C for the points denoted by circles, and 40 \( \pm \) 2 \(^\circ\)C for the points denoted by triangles. The theoretical line is drawn by means of Eqs. (7) and (17) for \( j/n = 1 \). The fact that this theoretical line complies very well with the experimental data indicates that the investigated crystallites are of 1:1 acid soap.

Fig. 8b shows \( \kappa \)-vs-\( C \) experimental data for dissolved acid-soap crystallites that have been initially formed in a solution of 20 mM KMy at 25 \(^\circ\)C, prepared by Procedure 2. This concentration corresponds to about 3 times the CMC. During the conductivity analysis, the temperature was maintained 40 \( \pm \) 0.1 \(^\circ\)C for the points denoted by circles, and 40 \( \pm \) 2 \(^\circ\)C for the points denoted by triangles. The theoretical line is drawn by means of Eqs. (7) and (17) for \( j/n = 1 \). Again, the theoretical line agrees very well with the experimental data indicating that the investigated crystallites are of 1:1 acid soap.

Fig. 9a shows \( \kappa \)-vs-\( C \) experimental data for dissolved acid-soap crystallites that have been initially formed in a 100 mM KMy solution at 25 \(^\circ\)C (without added KCl), prepared by Procedure 1. This concentration is 10 times the CMC, which corresponds to a total surfactant concentration of 10 mM for this system [22]. During the conductivity analysis, the temperature was maintained 40 \( \pm \) 0.1 \(^\circ\)C. The theoretical line, which is drawn by means of Eqs. (7) and (17) for \( j/n = 1 \), complies very well with the experimental data indicating that the investigated crystallites are of 1:1 acid soap, again.
Fig. 9. $\kappa$-vs-$C$ plot of experimental data for dissolved acid-soap crystallites that have been initially formed in a 100 mM solution of 87.5% KMy and 12.5% HMy at 25 $^\circ$C, prepared by Procedure 1: (a) Without added KCl at $T = 40 \pm 0.1$ $^\circ$C; the fit is drawn for $j/n = 1$. (b) With added 100 mM KCl at $T = 40 \pm 2$ $^\circ$C; the fit is drawn for $j/n = 3/2$. In both cases, Eqs. (7) and (17) have been used to fit the data.

Fig. 10. Comparison of $\kappa$-vs-$C$ plots of experimental data and theoretical curves obtained for different samples of soap crystallites. The upper curve (A) represents a part of the results for KMy shown in Fig. 5. The other curves are obtained by dissolving (at 40 $^\circ$C) crystallites that have been collected at 25 $^\circ$C from the following aqueous solutions: B—8.5 mM KMy (Fig. 8a); C—20 mM KMy (Fig. 8b); D—100 mM solution of 87.5% KMy and 12.5% HMy (Fig. 8a); E—100 mM solution of 87.5% KMy and 12.5% HMy + 100 mM KCl (Fig. 9b); F—4 mM KMy; G—150 mM KMy.

supposedly the working temperature during the conductivity measurements (40 $^\circ$C in the present study) is maintained with a sufficient accuracy.

4.3. Discussion

A new step in the present article is that the conductivity is used as a quantitative method for analysis of carboxylate solutions. In the previous papers on this theme [21,28–30], only the kinks in the conductivity curves were used as indicators for the appearance of micelles or changes in the stoichiometry of the acid-soap precipitates. This is related to the known fact that the popular theoretical expression by Onsager and Fuoss, Eqs. (8)–(9), is not quantitative, i.e. it does not agree well with the experiment. Here, we combined an empirical (but quantitative) expression for conductivity, Eq. (3) or Eq. (19), with the Walden’s finding [24,25] that the correction term, and in particular the coefficients $A$ and $B$ (unlike $\lambda^{(0)}$) are not sensitive to the ionic size. We first determined $A$ and $B$ for KCl (Figs. 4 and 6), and the results were further applied to KMy solutions to determine $\lambda^{(0)}$ My at the respective temperature (Figs. 5 and 7). In this way, we find all coefficients in Eq. (3) or Eq. (19), which in combination with Eq. (7) gives the theoretical dependence $\kappa(C)$. The latter contains a single adjustable parameter, the acid-soap stoichiometry, $j/n$, which is finally determined from the fit of the experimental data for $\kappa$; see Figs. 8–10.

From the viewpoint of future applications, it should be noted that the values of the coefficients $A$ and $B$ can be found in some handbooks [34] for many electrolytes at some temperatures. Alternatively, we could experimentally determine $A$ and $B$ at the working temperature, as this is done in the present study.

One limitation of the proposed method is that it is not applicable when the ratio $j/n$ is very small. Indeed, the term $(j/n)M_{2Z}$ in Eq. (7) must not be negligible in comparison with $M_{2Z}$. Otherwise, the solution’s ionic strength and conductivity will be insensitive to the stoichiometry of the dissolved acid soap.

The second limitation of this method, and of all methods that are based on the use of samples of dried acid- or neutral-soap crystals, is that in some cases the amount of crystallites in the solution is very small, or their size is very small (smaller than 1 μm), so that it is very difficult to prepare samples of dried crystals. In the latter case, one could use the in situ method [4,21,22], which is based on pH measurements directly in the mother solutions, without the necessity to separate and dry crystallites; see Section 5.
5. Confirmation of the results by independent pH measurements

5.1. Theoretical background

In the case when a precipitate of carboxylic acid (HZ) crystallites is present in the solution, the respective chemical equilibrium relation reads [4,21]:

\[ c_H^i c_Z^j = K_{HZ}. \]  

(24)

where \( c_H^i \) and \( c_Z^j \) are the concentrations of the respective ions in the solution; \( K_{HZ} = \text{const.} \) is the solubility product of HZ; \( \gamma_{Z^j}^f \) is the activity coefficient tabulated in [33]. The combination of Eq. (24) with the electroneutrality condition and other chemical-equilibrium relationships leads to the expression [4,21]:

\[ \gamma_{Z^j}^f c_H^i c_Z^j = K_{HZ} = \text{const.} \]  

(25)

The total input concentration of carboxylate (in our case KMy) is known, and \( c_H^i \) is determined by pH measurements \([pH = -\log(c_H^i c_Z^j)]\). Equation (25) can be compared with the experimental data in two different ways.

First, as suggested by Lucassen [4] for \( c_H^i \ll c_I \) and \( \gamma_{Z^j}^f \approx 1 \), Eq. (25) can be represented in the form:

\[ \text{pH} \approx \log c_H - \log K_{HZ}, \]  

(26)

i.e. the slope of the pH vs \( \log c_H \) plot is +1 if a HZ precipitate is present [4]; see Fig. 11a.

Second, taking log of Eq. (25) we define the characteristic function for precipitate of carboxylic acid [21]:

\[ f_{HZ} \equiv \log(c_H^i + c_I c_Z^j) = \log K_{HZ} = \text{const.} \]  

(27)

The concentration region, in which HZ precipitate is present, is identified in the following way. The function \( f_{HZ} \), defined by Eq. (27), is plotted vs \( c_I \) using the experimental \( c_H^i \) and \( c_Z^j \) dependence (determined by pH measurements). In the concentration region where a precipitate of HZ is present, the curve \( f_{HZ}(c_I) \) exhibits a plateau, whose height is equal to \( \log K_{HZ} \); see Fig. 11b.

Further, in the case when a precipitate of \( j:n \) acid soap, \((HZ)_j (MZ)_n\), is present in the solution, the respective chemical equilibrium relation reads [21]:

\[ c_H^j c_M^m c_Z^j c_A^n = K_m \]  

(28)

where \( K_m = \text{const.} \) is the solubility product for the \( j:n \) acid-soap crystallites. Under typical experimental conditions, we have \( c_H^j \approx c_I \) and \( c_M \approx c_A \) [21], where \( c_A \) is the concentration of the added inorganic electrolyte (in our case KCl), and then Eq. (28) acquires the form:

\[ c_H^j (c_I + c_A)^n c_Z^j c_A^{2n} = K_m = \text{const.} \]  

(29)

Equation (29) can be compared with the experimental data in the following two ways.

First, for \( \gamma_{Z^j}^f \approx 1 \) and \( c_A = 0 \), Eq. (29) can be represented in the form [21]:

\[ \text{pH} \approx (1 + 2n/j) \log c_H - (1/j) \log K_m, \]  

(30)

i.e. the slope of the pH vs \( \log c_H \) plot is equal to \((1 + 2n/j)\) if a \( j:n \) acid-soap precipitate is present; see e.g. Fig. 11a, where \((1 + 2n/j) = 3\) for 1:1 acid-soap precipitate.

Second, taking log of Eq. (29) we define the characteristic function for precipitate of \( j:n \) acid soap [21]:

\[ f_m \approx \log[(c_I + c_A)^n c_Z^j c_A^{2n}] - j \log K_m. \]  

(31)

\( j = 1, 2, 3, \ldots \) The concentration region, in which \( j:n \) acid-soap precipitate is present, is identified in the following way. The function \( f_m \), defined by Eq. (31), is plotted vs \( c_I \) using the experimental \( c_H^i(c_I) \) dependence (determined by pH measurements). In the concentration range where a precipitate of \( j:n \) acid soap is present, the curve \( f_m(c_I) \) exhibits a plateau, whose height is equal to \( \log K_m \). We have to check for which values of \( j \) and \( n \) the characteristic function \( f_m \) exhibits a horizontal plateau. In Fig. 11b, this is the case of \( j = n = 1 \), i.e. the precipitate is of 1:1 acid soap.

5.2. Solutions of KMy at 25 °C

Fig. 11a shows experimental data for pH vs \( c_I \) measured for KMy solutions at 25 °C. In the concentration range 0.008 < \( c_I < 1.6 \) (mM) the data comply with a straight line of slope +1, which indicates that the precipitate in these solutions is of HZ; see Eq. (26). This is confirmed by the plateau of the function \( f_{HZ}(c_I) \) in Fig. 11b.

Further, in the concentration range 1.6 < \( c_I < 10 \) (mM) the data in Fig. 11a comply with a straight line of slope +3, which indicates that the precipitate in these solutions is of 1:1 acid soap; see Eq. (30). This is also confirmed by the plateau of the function \( f_m(c_I) \) in Fig. 11b. Because the concentrations 4 and 8.5 mM, at which crystallites have been taken from a KMy solution at 25 °C, belongs to the interval 1.6 < \( c_I < 10 \) (mM), these crystallites are of 1:1 acid soap, which is in agreement with the result of the independent conductivity method proposed in the present article; see Fig. 8a, Fig. 10—curve F, and the related text.

The results in Fig. 11a indicate also that in the region 1.6 < \( c_I < 10 \) (mM) the precipitate cannot be a mixture of acid soaps. This is guaranteed by the Gibbs phase rule. Indeed, if a second kind of acid-soap crystals (of different stoichiometry) were present, the pH would be constant as it follows from the Gibbs phase rule [4], which is not fulfilled in this concentration region.

In Fig. 11a, pH is constant for \( c_I > 10 \) mM. In addition, Fig. 11c shows that the conductivity of these solutions exhibits a kink at \( c_I = 10 \) mM. At \( c_I > 10 \) mM the conductivity increases, but with a smaller slope (as compared to the slope at \( c_I < 10 \) mM). Such a behavior of conductivity indicates the formation of micelles in these solutions for \( c_I > 10 \) mM. This is confirmed by independent oil-solubilization and film-stratification experiments in Ref. [22]. At 25 °C and \( c_I > 10 \) mM, the KMy solutions contain also microcrystalline precipitates, which are seen by direct microscopic observations. We collected such crystallites (from solutions of 20 and 150 mM KMy, see Fig. 8b and Fig. 10—curve C) as explained in Section 4.1, and subjected them to conductivity analysis at 40 °C. The results (like those in Fig. 10—curves C and G) show that the precipitate above the CMC is of 1:1 acid soap, at least in the investigated range, 10 < \( c_I < 150 \) mM, i.e. the micelles appear on the background of the 1:1 acid soap crystallites, which are also present in the solutions in the neighboring concentration region below the CMC, 1.6 < \( c_I < 10 \) mM; see above. In other words, the appearance of micelles does not change the stoichiometry of the acid-soap crystallites. In Ref. [22], this conclusion is confirmed by independent theoretical analysis from the value pH = 10.67 (Fig. 11a) and from the slope of the k vs \( c_I \) dependence (Fig. 11c) at \( c_I > 10 \) mM. It is worthwhile noting that the lack of a second kink of the k vs \( c_I \) dependence in the region 10 < \( c_I < 150 \) mM (Fig. 11c) indicates that there is no appearance of liquid-crystalline phases or other changes in the type of precipitate in this concentration region.

5.3. Solutions of 87.5% KMy and 12.5% HMy + 100 mM KCl at 25 °C

We chose to analyze this type of solutions, because the conductivity analysis (Fig. 9b) shows that they contain acid soap of different stoichiometry, viz. 3:2 acid soap.

Fig. 12a shows experimental data for pH vs \( c_I \) measured at 25 °C for solutions that contain 87.5% KMy and 12.5% HMy + 100 mM KCl. For \( c_I < 0.4 \) (mM) the data comply with a straight
Fig. 11. Data for solutions of KMy at 25°C. (a) Experimental data for pH vs $c_t$; the vertical dashed lines show the boundaries between zones with different precipitates. (b) Plots of the characteristic functions $f_{HZ}(c_t)$ and $f_{11}(c_t)$ calculated from Eqs. (27) and (31) using the experimental pH($c_t$) dependence. (c) Experimental data for $\kappa(c_t)$ for $c_t \leq 150$ mM.
Fig. 12. Data for solutions of 87.5% KMy and 12.5% HMy + 100 mM KCl at 25°C. (a) pH vs \( c_t \); the vertical dashed lines are boundaries between zones with different precipitates. (b) The characteristic functions \( f_{HZ}(c_t) \) and \( f_{32}(c_t) \) calculated from Eqs. (27) and (31) using the experimental pH\( (c_t) \) dependence. (c) Experimental data for \( \kappa(c_t) \) for \( c_t \leq 110 \text{ mM} \). \( c_t \) is the total input concentration of myristate due to both KMy and HMy; \( x = 0.125 \) is the molar fraction of HMy.
line of slope +1, which indicates that the precipitate in these solutions is of HZ; see Eq. (26). This is confirmed by the plateau of the slope at $c_1 > 5$ mM. In addition, Fig. 12c shows that the conductivity of these solutions exhibits a kink at $c_1 = 5$ mM. At $c_1 > 5$ mM the conductivity increases, but with a smaller slope (as compared to the slope at $c_1 < 5$ mM). As in Fig. 11c, such behavior of conductivity indicates the formation of micelles in the respective solutions (at $c_1 > 5$ mM). This is confirmed by independent oil-solubilization and film-stratification experiments in Ref. [22].

<table>
<thead>
<tr>
<th>Mother solution (25 °C)</th>
<th>$j/n$ Section 4</th>
<th>$j/n$ Section 5 and Ref. [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mM KMy</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>8.5 mM KMy</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>20 mM KMy</td>
<td>1:1</td>
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</tr>
<tr>
<td>150 mM KMy</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>100 mM (87.5% KMy + 12.5% HMy) + 100 mM KCl</td>
<td>3:2</td>
<td>3:2</td>
</tr>
</tbody>
</table>

6. Summary and conclusions

A method for determining the stoichiometry of acid soap crystallites is developed, which is based on electrolytic conductivity measurements. It is applied to aqueous solutions of potassium myristate (KMy), for which the working temperature is chosen to be 40 °C. At this temperature, the only precipitate is that of HZ for concentrations below the CMC (Fig. 1). In the theoretical model data interpretation, we took into account the dependence of the molar conductance on the electrolyte concentration by using the Walden’s approach, which is semiempirical, but quantitative (Section 3). The fits of the data were drawn by means of Eqs. (7) and (17). The method was applied to determine the composition of six different samples of acid-soap crystallites (Figs. 8–10). The method is sensitive enough to distinguish between acid soaps of different composition (Fig. 10). The stoichiometry of all samples obtained in the present study coincides with that independently determined by pH measurements in the mother solutions (from which the crystallites have been collected); see Section 5, Table 2, and Ref. [22].

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References