

Application of the vibrating plate (VP) technique to measuring electric surface potential, ΔV , of solutions; the flow cell for simultaneous measurement of the ΔV and the surface pressure, Π

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ABSTRACT

This paper describes the measuring procedure which enables overcoming the base difficulty in application of the vibrating plate (VP) technique to measuring electric surface potential (ΔV) of free solution surfaces, namely losing the zero level set for the reference sample (water) while replacing it with the solution measured. (The ΔV measurement is performed by comparing two measurements in series, i.e., for the pure interface and that containing a surface film.) Main improvement in the measuring procedure is achieved by (i) applying a flow for exchanging the reference sample with the measured solution and (ii) elimination of an error driven by dependency of the measuring signal on the air gap width. The air gap width is fixed by contact of the bottom edge of a platinum Wilhelmy plate with the solution surface which the plate is simultaneously used for measurement of the surface pressure (Π). The results received with the new methodology for n-decanoic acid, n-decyl-trimethylammonium bromide ($C_{10}TABr$) and sodium n-dodecyl sulphate (SLS) are discussed.

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1. Introduction

1.1. The earlier investigations on the electric surface potential of solutions with the VP technique

Measurements of electric surface potential (ΔV) of the air/solution interface are, so far, mostly addressed insoluble monolayers investigated with the Langmuir technique. For such systems, compression isotherms of electric surface potential, ΔV – A , are usually registered with the vibrating plate (VP) technique, concurrently with the surface pressure compression isotherms, Π – A . Principle of the VP technique – primarily named as the Kelvin probe (KP) or the vibrating/dynamic capacitor method, has been described in numerous papers [1–8], majority of them regarding the measurement on solid surfaces with the Scanning Kelvin Probe technique [3–5] or with the Kelvin Probe Force Microscopy (KPFM) [6–8]. To date, a relatively small number of attempts have been made to use the VP technique for measuring electric surface potential of aqueous surfactant solutions [9–21], despite, a great number of the measurements have been performed on the water/organic solution interfaces [12,22–30]. The relatively small number of applications

of the VP technique to solution surfaces seems be the result of numerous interferences inherent in the VP technique, as discussed in details by several authors [14,15,31–33], and of the surface impurity problems.

It is noteworthy that the earliest applications of the vibrating plate (VP) method to surfactant solutions – described by Haydon [23], Haydon and Phillips [22] and summarised by Davies and Rideal [34], were aimed to measuring the adsorption potential shift at the oil/water interface, such as, the petroleum ether/water [22] or n-heptane/water [23]. Haydon and Phillips [22,23] did not describe details of the experimental set-up used by them, referring only to the earlier paper [35] and the latter implies that a gold vibrating electrode was immersed in the organic phase. An apparatus set-up for such measurements is described in [34]. Methodology the investigations [22,23] was that, the surface active species (n-dodecyl-trimethyl-ammonium bromide [22,23] or sodium n-dodecyl sulphate [23]) was introduced by injecting a small volume of the concentrated solution to the system which was next well stirred with a magnetic stirrer and then allowed for establishing the adsorption equilibrium, during 15–30 min, usually. In this way, the surfactant concentration was increased step by step [23] to measure the equilibrium surface potential vs. concentration isotherm. Minc and Koczorowski [26] and later Koczorowski and Zagórska [29] described in details the apparatus set-up for application of the VP technique to measuring the partition potential of differ-

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ent salts at the water/organic solution interface. These authors [24,29] probed the water/organic solution interface with a vibrating plate faced – through an air gap – to surface of the organic phase adjacent to the aqueous solution. Other investigations of the authors with the VP technique were performed for the air/organic [24,29,37,38] and the air/aqueous solution interfaces [36,39]. The crucial difficulty of the investigations on the aqueous/organic or organic/organic solution interfaces [37,38,40,41] was to avoid a contribution of the diffusion potential developing from side of the organic phase. Minc and co-workers [24] eliminated this disadvantage by devising the salt bridge filled with tri-iso-*n*-butyl-ammonium tetraphenylboride in methyl cyanide – the bridge used for the surface potential measurement of salt solutions in organic solvents. Later, Koczorowski and co-workers [37,38,40,41] employed – as the salt bridge – the nitrobenzene/water partition system containing tetraethylammonium picrate (TEAPi). The investigations with the VP technique were discussed by Koczorowski and co-workers [29,37,38,40,41] in terms of voltaic cells. According to our knowledge, the earliest announcements about application of the VP technique to measuring surfaces of surfactant solutions were published in sixtieths [9–12]. The authors of the early papers [9–11,22,23] provide the ΔV measured using the opposite sign convention to that adopted for insoluble monolayers – presented in the review articles [42–44]. Recent approaches to applying the VP technique to measuring electric potential at the air/aqueous solution interface are described in [16–20,39].

It should be mentioned here the other methods of measuring electric surface potential (ΔV) of solution surfaces, namely the flowing jet technique and the air-ionising electrode. Principle of the latter technique may be found in [31,34,41,58,59]. Recently, an ionizing ^{241}Am electrode was used for measuring the electric surface potential vs. concentration isotherms of different type surfactants, i.e., anionic (sodium *n*-dodecyl sulphate), cationic (hexadecyltrimethyl-ammonium and tetramethyl-ammonium bromides) and nonionic one (octaethylene glycol mono-*n*-tetradecyl ether) [60,61].

Since, the greatest deal of investigations published, so far, on electric surface potential of surfactant solutions was performed with the flowing jet technique [45–57], it is worth recollecting principle of the method – described in [48,50,55]. The flowing jet technique is based on compensation of the outer potential difference of two flowing jets faced across an air gap (i.e., jet of one solution flows from a capillary situated in center of a glass tube and jet of the other solution flows along the tube's wall). The two solutions, containing the relatively high concentration of an inert electrolyte, such as, $1 \times 10^{-1} \text{ mol/dm}^3$ KCl used in [45–56] as the optimum (although the lower salt concentration may also be applied in the technique), are in contact with identical reference electrodes of low resistance (calomel electrodes) which supply outputs for the compensation. On principle, the flowing jet method is charged with a very short life-time of the constantly renewed surface of the flowing jet (ca. 0.01 s [10]). Such a short time does not allow for establishing the adsorption equilibrium of surface active species of a large size molecule, in particular at low concentrations. The second inconvenience of the technique is necessity of introducing the relatively high concentration of an inert electrolyte to the solution measured to avoid formation of a streaming potential drop at the capillary tip for the solution outflow [49,51,53,55]. It is commonly known that addition of an electrolyte to a surfactant solution changes notably the adsorption equilibrium, in particular of ionic surfactants. Influence of an inert electrolyte on the electric surface potential of sodium *n*-dodecyl sulphate solutions is discussed in our earlier paper [16]).

It should be emphasized here, that, in spite of the inconveniences mentioned above, the flowing jet technique was regarded by Kamiński [45–47] as the perfectly defined and the most pre-

cise as compared to the alternative techniques (the vibrating plate and/or the air-ionising electrode). The investigations of Kamiński were continued by Pytasz [10,48] and Paluch and Dynarowicz [49–57]. It is worth mentioning here that the similar (in a sense of the hydrodynamics) technique, named the streaming method, was used by Koczorowski and co-workers [62] for measuring the potentials of zero charge of immiscible water/organic solution interfaces in presence of various electrolytes. At last, it is worth mentioning here that the flowing jet technique was also used [63,64] to examine a dependence of the electric surface potential on permittivity of solution. Solutions of different permittivity were prepared by adding different molar fractions of 1,4-dioxane to water.

1.2. Difficulties in application of the vibrating plate technique to solution surfaces

The electric surface potential (ΔV) is determined as difference between the pure interface and that containing the surface film. For a soluble or an insoluble monolayer, the ΔV measurement is usually performed against on the air/water interface, though, the absolute potential of free water surface and/or a potential drop across the interface is still the topic of discussions [65]. For applying the VP technique to an aqueous solution surface one must first set the reference/zero level for the VP made vibrate above free water surface, next water should be replaced with the probed solution without causing a shift in the zero level. Unfortunately, manual operations in the VP' vicinity, in particular, that involving a notable change in the air gap width (by which exposing the VP to inductive interactions with the surrounding elements) generate a spurious charge on the VP by which a shift in the reference level may be driven during replacing the reference sample with the measured solution. On the other hand, turning off/on vibrations for time of the replacement operation produces a much greater shift of the measuring signal, ΔV , than the possible one on the VP made vibrate. Comparison with the reference level does not create a problem in the Langmuir technique, since, the operations made after setting the reference level for the pure subphase (i.e., spreading a gaseous film, equilibrating it and compression of the monolayer) do not involve changes in the air gap width. Comparatively, the ΔV measurements of solution surfaces (the rare application, so far) are much more difficult, since, replacing the reference sample with the solution measured requires more drastic operations below the VP made vibrate than that involved in the Langmuir technique. Conveniently, the water/solution exchange may be performed by sucking off water from the cell and pouring the solution in it, without translating any element underneath the VP. These operations however involve a notable change in the air gap width. More hazardous way of replacing the reference sample with the solution measured involves taking out the cell from under the VP made vibrate. As we found, both the ways often cause a notable shift in the zero level of the VP made vibrate, even by several tenths of mV. Technically, the water-solution exchange is the crucial stage of the ΔV measurement of solution surfaces and it determines accuracy and precision of the ΔV measurement. Unquestionably, a degree of disturbance of the ΔV measuring signal during the sample replacement depends on quality of the VP measuring head, actual state of its stability (requiring lack of static charges on elements inside the measuring head) and, to a degree, on arrangement of the measuring stand.

To overcome the base difficulty in application of the vibrating plate (VP) technique to measuring electric surface potential (ΔV) of solution surfaces we propose a cell (which is a development of that used earlier by Pytasz and Szeglowski [9b,10,11]) in which the exchange between the reference sample and the measured solution is performed in flow. This way is found by us the less disturbing the ΔV measuring signal, as possible. The improvement in the measuring procedure allows for prominent increase in reproducibility of

the ΔV measurement of solutions. Furthermore, in our measuring system, the air gap width is fixed by contact of the bottom edge of a platinum Wilhelmy plate with the solution surface, which the plate is positioned at constant height relative to the VP. The Wilhelmy plate at the minimum immersion is simultaneously used for measurement of the surface pressure (Π).

2. Experimental

2.1. Chemicals

N-decyl-trimethylammonium bromide (C_{10} TABr) – supplied by Sigma–Aldrich, was of the purity grade $\geq 98.0\%$ (AT) and it was used as received. N-decanoic acid – supplied by Fluka, was of the purity grade $\geq 99.5\%$ (GC) and used as received. Some measurements have been performed, for comparison, using n-decanoic acid of lower purity grade, purum, $\geq 98\%$ (GC) – supplied by Fluka and used as received. To suppress dissociation of n-decanoic acid of pK_a of ca. 4.9 [66], it was diluted in 5×10^{-3} mol/dm³ hydrochloric acid (HCl) prepared of the original 30% HCl solution (Ultrapur) supplied by Merck. To get entirely dissociated n-decanoic acid, it was diluted in 5×10^{-3} mol/dm³ sodium hydroxide prepared of 10 mol/dm³ NaOH of BioChemica Ultra purity grade, supplied by Fluka. Solutions of C_{10} TABr and n-decanoic acid were prepared with Milli-Q® water.

Sodium n-dodecyl-sulphate, named also sodium lauryl sulphate (SLS), was pro Analyse reagent purchased from Merck. The analogous reagent of Sigma was also used. Prior to the measurements, the stock solution (5×10^{-3} mol/dm³ SLS) was purified in the automatic purification apparatus described in details in [67]. Principle of the purification procedure is founded on preferential enriching surface-active impurities in the surfactant's adsorption layer. For it, a large area of the solution surface is formed in a closed container, then, after an equilibration period (most often between 10 min and 1 h) the surface is carefully compressed by tilting the glassware, such that, the solution gently flows into the narrow neck of this container. In this position, the compressed surface is sensitively aspirated (for half a second) by a thin capillary. This cyclic process consisting of (i) spreading the solution surface, (ii) equilibration of the adsorption layer, (iii) compression of it and (iv) suction off, is repeated until the grade of surface chemical purity (scp) is reached; most often 50–300 such cycles are required. The solution under the purification process is periodically tested according to the criterion of the surface-chemical purity (scp) described in [68]. Solutions of SLS were prepared with water triple distilled of a quartz distiller.

Electric surface potential and the surface pressure of n-decanoic acid and C_{10} TABr solutions were measured in the apparatus set-up described in details in the present paper (Section 2.2), at the temperature of 20.0 ± 0.5 °C. Measurements of electric surface potential (ΔV) of SLS solutions were performed in our older experimental set up equipped with the older version of the surface potential meter, SPD-1000, provided by the KSV firm (Helsinki). The ΔV of SLS solutions was measured independently of the surface pressure, at room temperature of 22 ± 3 °C. The surface pressure of SLS solutions was measured with the du Noüy' ring technique by applying an automatic Lauda tensiometer, TE-1 M. All the requirements for reliable measurements with a du Noüy' ring – discussed in [69], have been taken into account.

2.2. Apparatus

The computer processed apparatus was supplied together with the software by the Biolin Scientific Oy (former KSV Instruments Ltd.) from Finland. The setup was equipped with the surface poten-

tial meter stand alone – the Spot 2, and tensiometer for the surface pressure measurement – the Minibalance of the M1005 type. The surface pressure was measured with a platinum Wilhelmy plate (perimeter 39.24 mm). The Spot 2 was provided with the vibrating plate (VP) of a stainless steel. The vibrating plate (including the wire) was laser cut of thin (0.04 mm) stainless steel sheet. The small thickness of the VP was required because the integrated wire had to be thin and flexible to avoid microphonic effects [32]. The VP was supported (with help of a glue) on a plastic cone which of the top was mechanically connected (glued) to a small loudspeaker' baffle, so that, the cone moved with the VP. To minimize inductive coupling of the VP with elements of the circuit of a different potential, the Spot 2 was provided with an inner shielding mount around the VP. This shielding – made of the identical stainless steel with that of the VP, was connected to ground of the electrical network. The VP was virtually ground, i.e., it was connected to “+” input of the operational amplifier which was ground, so that, the Spot 2 was of the vibrating plate earthed configuration, vpe, discussed in [32]). The counter electrode (CE) of a stainless steel – supplied by the producer together with the instrument, was used for the measurements of surfactant solutions in water of pH ca. 5.5. (The CE was a plate 50 mm \times 50 mm ca. 3 mm thick with a massive leading). It was found that the metal CE could not be used for the surface potential measurement of more acidic solutions (such as, n-decanoic acid in 0.005 M HCl) because of an interfering surface reaction which probably occurred on the CE with participation of protons. Therefore, the acidic and alkaline solutions of n-decanoic acid were measured against on a silver/silver chloride (3 M KCl) counter electrode, supplied by the WTW.

The operational scheme of the measuring head circuitry (KSV Spot 2) – galvanically coupled with the measuring system, is presented in Fig. 1. The actuator (loudspeaker) modulates vibrations of the VP with the frequency of 159.4 Hz. As a result of the sinusoidal change of capacity of the capacitor formed between the VP and surface of the solution measured, an alternating current (ac) is generated on the VP and the primary signal is transformed in the VP circuit (Fig. 1) as follows: the ac current is converted to voltage with an operational preamplifier (denoted in Fig. 1) which has a very low input current (~ 2 fA). To get reasonable gain, a very large feedback resistor (100 M Ω) is used. Further, the signal is amplified with a factor of 50 by an additional amplifier, then, fed to an analog multiplier which works as a phase detector (cf. Fig. 1). For the phase correction, the reference signal is derived from the loudspeaker through a special circuitry (Fig. 1) which adjusts the phase difference between the measured and the reference signal to zero. The multiplier' output gives dc voltage (modulated by the double frequency signal) which is proportional to the current produced by the VP made vibrate. This dc signal is fed to an integrator. The output voltage of the integrator (V_{comp}) is connected to the counter electrode (CE), so that, it compensates (i) the voltage across the capacitor formed between the VP and the solution surface, V_c , and (ii) the voltages connected in series between the solution surface and the counter electrode. The voltages summarise as follows:

$$V_c = \Psi_{VP/air} + \Psi_{soln/air} + V_{CE/soln} + V_{comp}, \quad (1)$$

where the $\Psi_{VP/air}$ and $\Psi_{soln/air}$ are outer/Volta potentials of the VP and free solution surface, respectively, and $V_{CE/soln}$ is potential across the interface between the counter electrode and the solution. A potential drop across the solution layer may be neglected for aqueous solutions which show a significant conductivity. Scheme illustrating the voltage loop formed in the measuring system is shown in Fig. 2.

The V_{comp} value is changing until the voltage in the integrator input is zero. It is zero provided, the voltage across the vibrating capacitor formed by the VP and the solution surface is zero, i.e., in

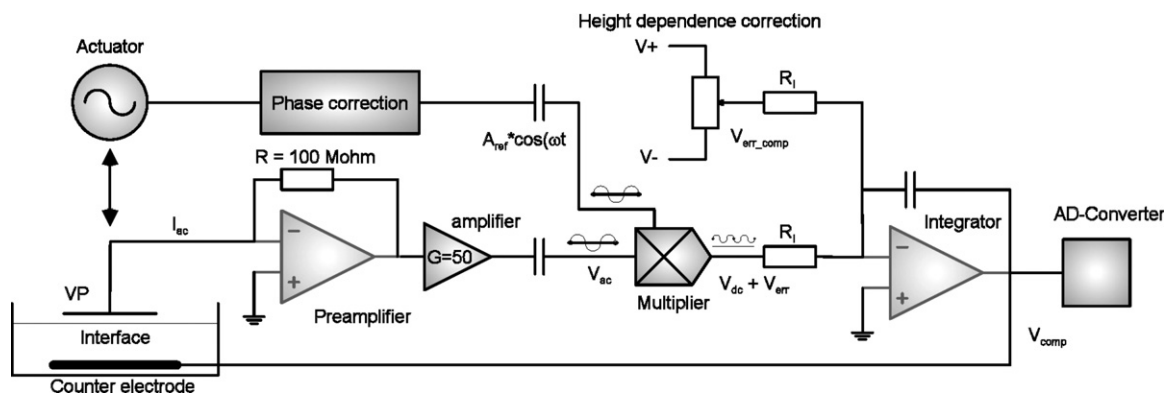


Fig. 1. Operational scheme of circuitry of the surface potential meter – the KSV Spot 2. The alternating voltage (V_{ac}) produced by the vibrating plate (VP) vibrations is multiplied by the reference signal derived from the loudspeaker, $A_{ref} \cos(\omega t)$, to get the direct voltage, V_{dc} ; (A_{ref} is amplitude of the reference signal assumed arbitrary to be 1); V_{err} is a spurious voltage superposing to the V_{dc} by inductive/capacitive coupling of the actuator currents and offset voltages in multiplier output or integrator itself; $V_{err,comp}$ – the voltage used for compensation of the V_{err} .

case if no spurious voltages occur. At the compensation equilibrium, i.e., at the null current measured in the circuit loop, the potential drop between the VP and the solution surface, V_c , decreases to zero, so that, the following is valid:

$$-V_{comp} = V_{VP/air} + \Psi_{soln/air} + V_{CE/soln}. \quad (2)$$

The value of $-V_{comp}$ is constantly monitored with computer *via* analog-digital (AD) converter and the value corresponding to the null current is displayed, $-V_{comp} = \Delta V_{(i=0)}$. Since, the ΔV measurement of surfactant solutions is performed relative to free water surface, the $\Delta\Delta V$ difference corresponds directly to difference in outer potentials of the two air/liquid interfaces compared, assuming that the voltage drops across the VP/air and the CE/solution interfaces are constant for the two measurements compared in series.

In Fig. 1, there is also denoted the possibility of regulating a dependency of the measuring signal on the static air gap width – named the height dependency, ΔV vs. $d_{a.g.}$. Such dependency, discussed in [32], may contribute a serious error to the $\Delta\Delta V$ measurement performed by comparing two liquid interfaces of different meniscus, when control of the air gap width is performed only by height positioning of the cell or of the measuring head. It is difficult to eliminate entirely the height dependency by proper construction of the measuring head for the Kelvin Probe (KP) technique, hence, the dependency usually occurs in instruments of the type. The greatest contribution to the height dependency seems to be produced by capacitive/inductive coupling of the VP with driving current of the actuator and by superposing offset voltages of the preamplifier and, in particular, of the multiplier. (An error caused by preamplifier in the KP technique was earlier discussed in [33].) When a spurious voltage, V_{err} , superposes to the dc voltage coming from the multiplier, an error is contributed to the measured sur-

face potential by the following interdependence of the V_{err} with the compensation potential:

$$V_{comp} = -\Sigma\psi_i - d_0^2 \times \frac{V_{err}}{K_1}, \quad (3)$$

where $\Sigma\psi_i$ is sum of the interfacial potentials involved, i.e., the VP/air, air/solution and CE/solution; d_0 denotes the static air gap width and K_1 is a constant (for the details see the Appendix A). Eq. (3) implies that in case if a spurious voltage would be superposed to the V_{dc} signal derived from the VP, the voltage measured is dependent on square of the static air gap width. The quadratic dependence was announced earlier by Baikie and co-workers [32] basing on analysis of stray capacitance effects. The Spot 2 is provided with the facility for compensating the offset voltage with help of a special screw. Using it, the height dependency was diminished to ca. 10 mV/mm. The residue height dependency should be described to residue offset voltages and leakage currents produced in the Spot 2 owing to increasing temperature of the not thermostated circuit.

2.3. The measuring cell and the stand

The electric surface potential, ΔV , and the surface pressure, Π , measurements have been performed in a flow-cell schematically shown in Fig. 3. The cell enables replacing the reference sample with the measured solution in flow, which the way allows for elimination of manual operations in vicinity of the VP made vibrate. In addition, a change in the air gap width during the sample replacement procedure was eliminated to a minimum to avoid inductive coupling of the VP with the surrounding elements (stray capacitance effects). We found this measurement procedure as the less disturbing the VP as compared to the other ones, mentioned above.

The height regulation table of a brass (Zn–Cu alloy) was constructed using a micrometer screw by means of which the cell was located precisely below the vibrating plate. The distance between

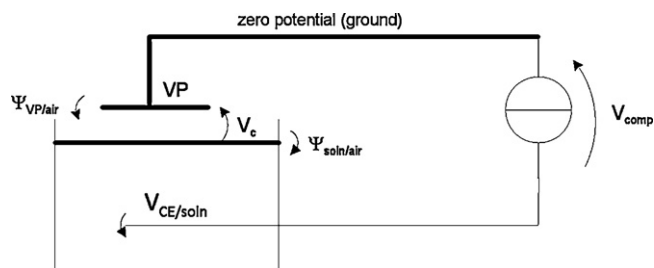


Fig. 2. Scheme illustrating the voltage loop formed in the VP measuring system at the compensation equilibrium.

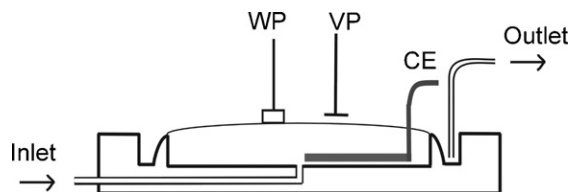


Fig. 3. The flow cell for measuring the electric surface potential, ΔV , simultaneously with the surface pressure, Π , of surfactant solutions. The denotations: WP – Wilhelmy plate, VP – vibrating plate, CE – counter electrode.

the vibrating plate and the solution surface (the air gap width, $d_{a.g.}$) was adjustable in the range of 0.5–10 mm. The spherical flow cell was of the diameter of 10 cm, the depth of 0.8 cm and the volume of 100 ml. The solution was put in flow by means of a peristaltic pump with the flow rate of ca. 50 ml/min. The solution was introduced from a thermostated container to the inlet channel (of the diameter of 4 mm) leading to the center of the cell' bottom. Excess of the solution which overflowed the cell' edge to the surrounding circular channel was sucked in a capillary connected to the pump. Tubes conducting the solution to/throughout the peristaltic pump were of polytetrafluoroethylene (PTFE) of the inner diameter of 4 mm. To not wet the VP by a flowing solution, the air gap width was increased to ca. 4 mm for time of the flow. After pumping out a volume of the solution (300–400 ml), the flow was stopped and the air gap width was adjusted to the standard value of 2 ± 0.2 mm. It was performed by lifting up the table with the cell (with help of a screw regulated manually) up to reaching contact of bottom edge of the platinum Wilhelmy plate with the solution surface. The Wilhelmy plate was hanging on hook of the minibalance' positioned so that the Wilhelmy plate' bottom edge was at the height 2 mm below the VP. Attainment of the minimum contact of the Wilhelmy plate with the solution surface was eye discernible (as a jump of meniscus onto the bottom edge of the Wilhelmy plate) during lifting up the cell slowly. The Wilhelmy plate at the minimum immersion was used for the concurrent measurement of the surface pressure (Π) with the electric surface potential (ΔV).

The cell was made of a conductive material named tarflen (the counterpart of Teflon produced by Zakłady Azotowe, Tarnów, Poland). The tarflen contained the 3.5% admixture of carbon nanoparticles (supplied by the Degussa firm) which assured a significant conductivity of this material attested to antistatics. A conductivity of the cell was desired to avoid induction of negative charges on the cell edges which may cause a detrimental effect on the ΔV measurements with the VP technique.

The measuring stand with the cell was shielded with a Faraday cage (FC) made of two layers of copper grid of ca. 1 mm and ca. 10 mm mesh, respectively. The FC was earthed to the ground of the electrical network together with the stand. As the Spot 2 was of the vpe configuration, the cell was isolated from the stand with a plate of polycarbonate glass of ca. 6 mm thick and a layer of filter papers of ca. 5 mm thick. Inside the FC, a thermo stating system was mounted of a spiral-shaped copper tube of the inner diameter of 4 mm, connected to the circulation thermostat (RC6CS Lauda). On the external side of the FC, a heat isolation box was arranged. It was made of two layers – one of a polycarbonate glass plate (6 mm thick), the second – of a polystyrene foam plate (4 cm thick). The temperature was controlled with a contact thermometer (Pt 385/100 Ω , the KFAP firm, Poland) placed ca. 3 mm above the solution surface measured. The temperature was maintained in the range of 20.0 ± 0.5 °C.

2.4. The measuring procedure

Prior to each measurement, the Wilhelmy plate was purified on the standard way, i.e., by washing (at least 1 h) in pure ethanol or, in case of a stronger contamination – in 1:1 chloroform–ethanol mixture and ethanol. Next the plate was glowed in flame of a Bunsen burner to red heat (during ca. 2 min) and immediately after it was immersed in water (for seconds) and made dry in the flame (now, not allowing for red heat). Then, it was hung on hook of the tensiometer and immersed in pure water on the depth of ca. 2 mm (by lifting up the cell filled with water) to let moisten the surface pores. Next, fresh sample of water was introduced in flow for setting the reference level. To secure the VP against wetting during pumping water/solution throughout the cell, the latter was slightly lowered for time of the operation, so that, the Wilhelmy plate' bottom edge

was ca. 2 mm above the liquid surface and the VP – above ca. 4 mm. After stopping the flow, the cell was lifted up again to reach contact of bottom edge of the Wilhelmy plate with water surface. At this position, indications of the surface potential meter and of the balance were set zero. For checking stability of the reference level with respect to the sample exchanging operation, an amount of water (ca. 200 ml) was again pumped throughout the cell (at the safe distance of the VP from the liquid surface), then, after adjusting the standard air gap width to 2 mm, indications of the measuring heads were checked. If a departure of the ΔV was observed from the zero level previously set – greater than ± 3 mV, the value was zeroed and the procedure of checking the zero' stability repeated. Small changes of Π in the range of ± 0.5 mN/m were observed as a result of exchanging water in the cell – ascribed to moistening surface pores of the Wilhelmy plate. The balance's indication just before introducing the surfactant solution was taken as the $\Pi = 0$. It should be emphasized here, that, stability of the measuring signal against the sample exchanging operation determines accuracy of the measurement. When the ΔV was stable with respect to the pumping operation, the solution to be measured was introduced into the cell (by pumping out ca. 300 ml of the solution) and – after stopping the flow – the cell was lifted up again to reach the minimum immersion of the Wilhelmy plate in the solution. This moment was regarded as the start point of the measurement. Before the next measurement, the cell was washed with a stream of water in flow (ca. 1 l) and the procedure described above repeated. Since, instruments for the KP technique are very prone to shifting the measuring signal by manual operations in vicinity of the VP made vibrate, we did not measure more than one solution after setting zero for water. The second reason was that, the Π measurement at the minimum immersion of Wilhelmy plate requires careful purifying the plate after each contact with a solution. It should be stressed here that the ΔV measurements were performed for stagnant solutions. Flow of solution causes an insignificant change in the ΔV measured, mostly it was lowering the ΔV by 2–10 mV, as compared to the stagnant solution at the same air gap width. The Π and ΔV were measured during 30 min, however, we discuss herein the initial Π and ΔV values, i.e., established after ca. 1 min. (For the ΔV measurements performed in our older apparatus set-up, the ΔV measured after 30 min is regarded as the most representative value.)

It is worth mentioning here the Π - t and ΔV - t changes encountered by us. The Π slightly increased with time at the rate of ca. 1 mN/m per 1 h, at maximum. These changes – dependent on the substance and the concentration, are described by us principally to diffusion of surface-active impurities to the interface. A relatively less contribution to the Π drift with time might occur owing to a change of meniscus at the Wilhelmy plate' bottom edge owing to evaporation of water. The ΔV - t change revealed by a descending or an ascending course, depending on the substance and the concentration. The ΔV - t change was mostly contained in the range of ± 20 mV. Several effects might superpose to the ΔV - t change. First, it could be contributed by a shift of the zero level of the surface potential meter – generally prone to stray capacitance effects, as mentioned above (Section 2.2). Secondly, conformation/orientation change of the adsorbate – reflecting to a great degree in the ΔV , may attain the equilibrium much slowly as compared to the adsorption equilibrium. Third, diffusion of the parent surface-active impurities to the interface may also contribute to ΔV - t change. The latter effect seems however be much less important for ΔV than for Π . This hypothesis is supported by the ΔV - c isotherms measured by us for solutions of several surfactants before and after purification in the automatic apparatus described in [67]. As we found (unpublished results), shape of the ΔV - c isotherm was not principally changed by a low content of surface-active impurities. Comparing the ΔV - c and the Π - c isotherms for the original solutions and that – after the purification – judged as

surface-chemically pure (undissociated n-decanoic acid, n-octyl- and n-decyl- β -D-glucopyranosides and tert-isopropyl-phosphine oxide) we found much greater influence of surface-active impurities on Π than on the ΔV . The result is reasoned by the fact that Π reflects principally mutual interactions at the interface, so that, the impurity effect is dependent on product of the surface concentrations of the main surfactant and the impurity. On the other hand, the ΔV reflects sum of dipole moments vectors of all species present at the interface, so that, a minute surface concentration of an impurity contributes proportionally to the ΔV .

2.5. The height dependency parameter, HDP, in the vibrating plate technique

Reasons for a dependence of the ΔV on the air gap width ($d_{a.g.}$) in the KP technique was discussed in [32]. The dependence, ΔV vs. $d_{a.g.}$, was occasionally checked in our measuring system by increasing the $d_{a.g.}$ by 1 mm, step by step, in the range of 1–10 mm. As we found, the steeper was the ΔV vs. $d_{a.g.}$ dependence, the greater was instability of the surface potential (SP) measuring head (noise problems) and worse reproducibility of the measurements. Similar correlation was described by Rohwerder and Turcu [6] for the Scanning Kelvin Probe Force Microscopy, SKPFM. These authors noticed that increase in the height dependency of the signal produced by a vibrating tip was accompanied by a less reproducibility of the obtained results. Having the above in mind, the ΔV vs. $d_{a.g.}$ dependency was used by us for characterizing stability of the VP measuring head, by comparing the ΔV change observed after increasing the air gap width from 2 to 3 mm. This change in mV/mm was called by us as the “height dependency parameter” (HDP). It should be mentioned here that the HDP was changeable from day to day. Since, no changes in the measuring stand were made during the measurement series and the measuring system was shielded with a Faraday cage, changeability of the ΔV vs. $d_{a.g.}$ dependency had to come from the measuring head itself, probably, owing to induction of stray capacitances in the circuitry (microphonic effects). Starting the measurements with the new Spot 2 we encountered the relatively steep ΔV vs. $d_{a.g.}$ dependency characterized by the HDP above 100 mV/mm. The HDP was diminishing during operating the SP measuring head for a period of weeks/months (while the Spot 2 have been working several hours per day) up to reaching the value of $ca. 20 \pm 10$ mV/mm. At the state, the SP measuring head shown relatively good stability, enabling reproducible ΔV measurements, ± 5 mV. It is worth mentioning here that by prolonging period of operating the Spot 2 for several hours, an increase of the HDP was caused which should be described to increasing temperature inside the SP head.

3. Results and discussion

Results of the measurements performed in the above described apparatus set up are shown in Figs. 4–7.

Fig. 4 shows the electric surface potential (ΔV) vs. concentration (c) isotherms of n-decanoic acid in 5×10^{-3} mol/dm³ HCl or 5×10^{-3} mol/dm³ NaOH. The concurrently measured surface pressure (Π) vs. concentration (c) isotherms are presented in Fig. 5. The addition of acid (HCl) or base (NaOH) was to suppress dissociation of n-decanoic acid or to make the species entirely dissociated, respectively. The acid/base concentration was the low as possible for assuring the extreme dissociation state. For non dissociated n-decanoic acid (in 5×10^{-3} mol/dm³ HCl), the ΔV and Π increase with the concentration, so that, the ΔV - c and Π - c isotherms start approximately at the same concentration of $ca. 2 \times 10^{-5}$ mol/dm³. Shape of the isotherms is not influenced – in range of the measurement accuracy, by the purity grade

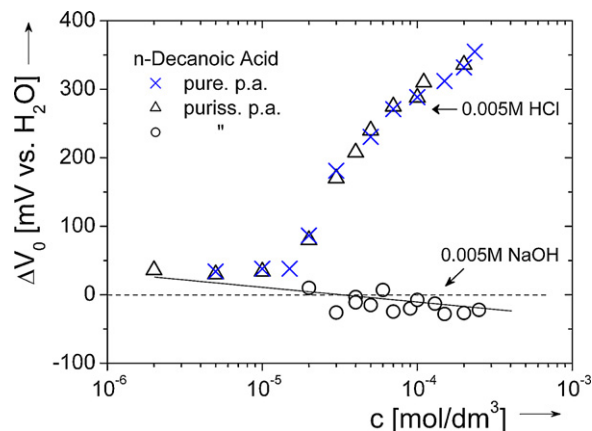


Fig. 4. The electric surface potential (ΔV) vs. concentration (c) isotherm of n-decanoic acid in the presence of 5×10^{-3} mol/dm³ HCl or 5×10^{-3} mol/dm³ NaOH. The different purity grade of the substance is displayed in the figure.

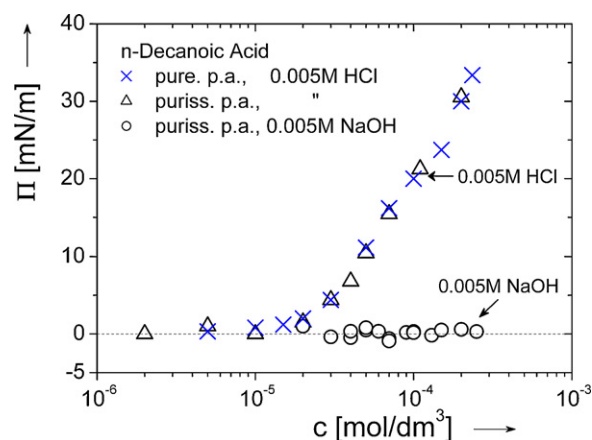


Fig. 5. The surface pressure (Π) vs. concentration (c) isotherm of n-decanoic acid in the presence of 5×10^{-3} mol/dm³ HCl or 5×10^{-3} mol/dm³ NaOH. The measurements made concurrently with that presented in Fig. 4.

of n-decanoic acid (99.5% or 98%). Essentially different results are obtained for n-decanoic acid in 5×10^{-3} mol/dm³ NaOH. For the dissociated species, the surface pressure close to zero and slight, negative surface potential values (approaching to -28 mV) were obtained within the measured concentration range below 3×10^{-4} mol/dm³. For the sake of simplicity, the ΔV - c and the

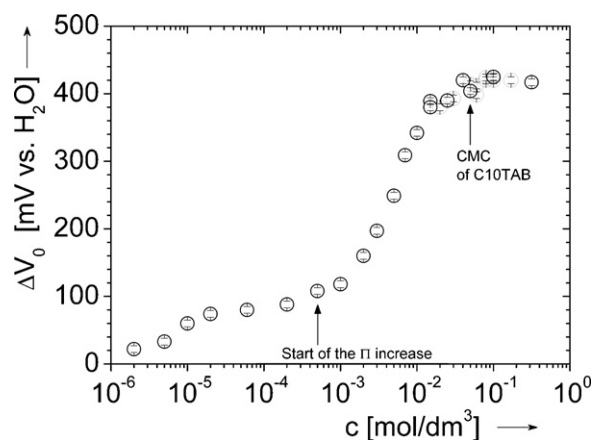


Fig. 6. The electric surface potential (ΔV) vs. concentration (c) isotherm of n-decyltrimethylammonium bromide, C₁₀TABr, in pure water. The error bar of ± 5 mV is displayed.

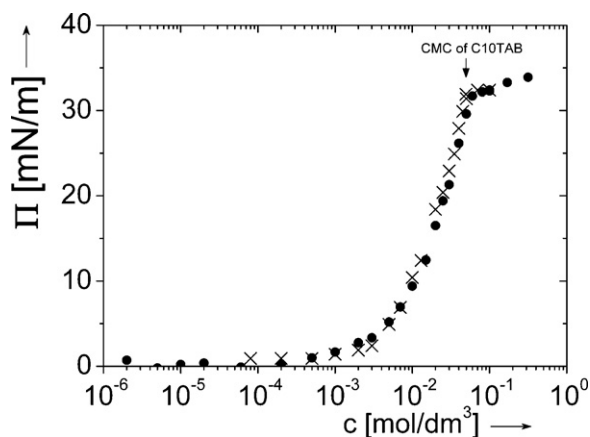


Fig. 7. The surface pressure (Π) vs. concentration (c) isotherm of n-decyl-trimethylammonium bromide, $C_{10}TABr$, in pure water; circles – the results received with a Wilhelmy plate at the minimum immersion, cross marks – the results received by drop shape analysis method.

Π – c isotherms of n-decanoic acid (Figs. 4 and 5) are given relative to free water surface. However, it should be mentioned here, that, for the pure electrolytes a low positive ΔV value was measured, i.e., of ca. 20 mV in case of 5×10^{-3} mol/dm³ HCl and ca. 15 mV in case of 5×10^{-3} mol/dm³ NaOH. The results presented in Figs. 4 and 5 corroborate the rule that the surface activity region of a nonionic surfactant starts at a lower concentration (by ca. two orders of magnitude) as compared to an ionic surfactant of identical hydrocarbon chain. (This relation is illustrated in [71] by comparing the surface tension vs. concentration isotherms of n-decanol and n-decyl-sulphate or n-dodecanol and n-dodecyl-sulphate.)

Fig. 6 shows electric surface potential (ΔV) vs. concentration (c) isotherm of n-decyl-trimethylammonium bromide ($C_{10}TABr$) in pure water. The concurrently measured surface pressure (Π) vs. concentration (c) isotherm is presented in Fig. 7. The surface pressure isotherm received by us with the Wilhelmy plate at the minimum immersion is compared with the literature [70] results obtained for the same compound ($C_{10}TABr$) using the drop shape analysis method. (The experimental set up for the latter technique is described in details in [71].) One can notice a very good consistency of the surface pressure isotherms obtained for $C_{10}TABr$ with the two different techniques. It is interesting, that, the onset of the Π vs. c isotherm of the cationic surfactant, $C_{10}TABr$, falls at ca. 5×10^{-4} mol/dm³, while the ΔV starts to increase with the concentration at 5×10^{-6} mol/dm³ $C_{10}TABr$, which is lower by two orders of magnitude as compared to the Π – c onset. The critical micelle concentration (cmc) of $C_{10}TABr$ amounts to 5×10^{-2} mol/dm³, as found from the surface pressure isotherm. Course of the ΔV – $\log c$ isotherm measured by us (Fig. 6) looks like being composed of two sigmoid branches, one falling below the surface activity region (characterized by zero Π) and the second covering the range characterized by increase of Π with the concentration, up to the cmc. Each of the branches spans over the concentration range of two orders of magnitude.

For comparison with the cationic surfactant, $C_{10}TABr$, the corresponding results obtained by us for anionic surfactant – sodium n-dodecyl-sulphate (SLS) in pure water are presented in Fig. 8. (As mentioned in Section 2.1, these measurements were performed in our older apparatus set-up, opposite to other results discussed herein.)

It is well known from the literature that n-alkyl sulphates usually contain a trace of n-alkanol as residue of the synthesis' parent compound. It may also be formed by decomposition of the alkyl-sulphate (ester). It was shown [67], that the parent impurity influences notably surface pressure of the ionic surfac-

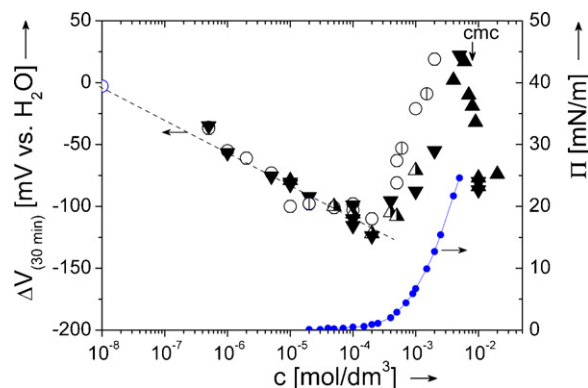


Fig. 8. The electric surface potential (ΔV) and the surface pressure (Π) vs. concentration (c) isotherms of sodium n-dodecyl-sulphate (SLS) in water. The ΔV was measured for solutions of different purity grade: circles – the surface-chemically pure (scp) solutions of two stocks independently purified in the automatic apparatus, triangles – the original solutions of different origin (filled triangles – two substances of Merck, half-filled triangles – of Sigma). The Π vs. c isotherm was independently measured for the scp solutions with the du Noüy' ring technique.

tant, SLS, which is in accord with the fact that surface activity of a nonionic species reveals at much lower concentration as compared to an ionic one of the same carbon chain. Since, no announcements were made, so far, about influence of surface active impurities on electric surface potential of n-alkyl sulphates, we compared in Fig. 8 the ΔV vs. c isotherms for two original SLS solutions and that which-after purification in the automatic apparatus [67]-were judged as surface-chemically pure. The Π – c isotherm shown in Fig. 8 was measured for the pure (scp) SLS solution. One can notice that, the onset of the surface activity region of SLS solutions – determined by measurable values of the surface pressure, falls at the concentration of ca. 2×10^{-4} mol/dm³ SLS, while the ΔV adopts measurable values within the lower concentration range, 5×10^{-7} – 1×10^{-4} mol/dm³ SLS – spanning over three decades below the Π – c onset. In this range, the ΔV decreases with the concentration, arriving at ca. –120 mV at the Π – c onset. At this point, the ΔV vs. c isotherm of SLS is transferring from the descending to the ascending dependence (i.e., comes through the minimum). The ascending branch covers the surface activity region determined by the Π – c increase up to the critical micelle concentration, cmc. The cmc of SLS in water, at 25 °C, falls at ca. 8×10^{-3} mol/dm³ SLS [61], which is denoted by arrow in Fig. 8. One can notice that the purity grade of SLS solutions does not essentially influence the descending branch of the ΔV vs. c isotherm, in range of the measurement reproducibility. On the other hand, it essentially influences the ascending branch of the ΔV vs. c isotherm, so that, the impurity's effect on the ΔV seems to increase with the surfactant concentration. Above the cmc, the ΔV falls down with the concentration to ca. –80 mV. (The region above the cmc was investigated by us only for the original SLS solution.)

It is worth mentioning here, that, the ΔV vs. c and Π vs. c isotherms of SLS solutions were earlier discussed by Warszyński and co-workers [16] in relation to theoretical models formulated in the literature for adsorption of ionic surfactants at the air/solution interface. These authors proved that the previously formulated models have not described satisfactory the Π – c and ΔV isotherms of SLS. They proposed a new model [16], developed in [70,72], which is named as "surface quasi-two-dimensional electrolyte" (STDE). It assumes that the surfactant ions and the counter ions undergo non-equivalent adsorption within the Stern layer at the interface. Recently, the authors [70] proved that, the STDE model describes satisfactory a series of Π vs. c isotherms of n-decyl- and n-hexyl-trimethylammonium salts containing different counter ion: Cl^- , Br^- , F^- , J^- , NO_3^- , ClO_4^- or CH_3COO^- , in presence/or not of var-

ious concentrations of the potassium salts. They [73] also used the model for describing surface tension vs. concentration isotherms of mixtures of *n*-octanoic acid and sodium *n*-octanoate. According to the STDE model, the ΔV vs. c isotherm is contributed by potential drops of ionic and dipole origin. The ionic contribution dominates the ΔV within a very low concentration region in which hydrocarbon chains hydrated (at least partially) are mostly oriented parallel to the interface. At the higher concentrations, at which the chains are expelled for the air phase and tend to orient themselves perpendicular to the interface, the ΔV drop is dominated by a dipolar contribution. According to the theory formulated by Vogel and Möbius [42,43], the dipolar contribution originates mainly from orientation of dipoles of terminal methyl groups of the surfactant' hydrocarbon chains. The prevailing contribution to the ΔV by terminal dipoles is reasoned by a significant drop of the permittivity across the adsorption layer at the air/solution interface. As a charge (ionic or dipole) contributes to the ΔV reciprocally to the local permittivity value, a small charge in the chain' terminal region (of the local permittivity of ca. 2) may bring in a greater contribution to the ΔV than a greater charge within the head group region, wherein the local permittivity arrives at several tenths (below 80). Furthermore, the contribution by the head group dipoles is partially compensated by the hydration water and the latter is probably of no importance within the chains' terminals region.

Basing on the ΔV vs. c and the Π vs. c isotherms of C_{10} TABr and SLS solutions (Figs. 6–8), one may presume that the general property of ionic surfactants is that, the onset of the ΔV vs. c isotherm falls at a lower concentration (by ca. two orders of magnitude) as compared to the Π vs. c onset. This conclusion is reasoned by the fact that increase of the surface pressure is driven by van der Waals forces which are the short-range interactions, in contradistinction to the long-range electrostatic forces which drive the electric surface potential, ΔV . The van der Waals forces include the all interactions between electrically neutral molecules, i.e., dipole–dipole (including hydrogen bond) and London dispersion forces (between instantaneous dipole and induced dipole). The electric surface potential (ΔV) is principally driven by mutual electrostatic interactions of ions and dipoles (ion–ion and ion–permanent dipole) and the interactions with the interface. The ΔV is also influenced by the short-range interactions by a dependence of the ΔV on the surface excess, Γ . [All the interactions are anisotropic which means that they depend on relative orientations of the molecules at the interface/. There is a range of the lowest concentrations – identified with a gaseous state of monolayer, wherein, average molecular distances do not allow for van der Waals interactions, however, electrostatic interactions operate. We put forward that it is the range below the Π – c onset in which the ΔV adopts measurable values. In this region, surfactant ions entirely hydrated are preferentially accumulated at the interface to oppose the electric potential drop developed across the pure interface, so that, centers of the molecular ions are located closer to the interface than centers of the counter ions. Such array of ions results in formation of the electric double layer reflecting in the ΔV . (In fact, the ΔV denotes the potential drop across the adsorption layer measured relative to the pure interface.)

Comparison between the ΔV vs. c isotherms of C_{10} TABr and SLS suggests that the maximum ΔV effect contributed by purely electrostatic (long-range) interactions at the air/solution interface amounts to ca. 100 mV and the effect is positive in sign for cationic surfactant and negative in sign for anionic one. The ΔV – c isotherm of entirely dissociated *n*-decanoic acid (Fig. 4) also corroborates formation of a negative ΔV drop by molecular anions. However, in case of *n*-decanoic acid, the maximum ΔV effect – of ca. –40 mV relative to pure water (regarding the slight positive potential of the pure electrolyte, NaOH), is less as compared to SLS or C_{10} TABr. It should be described to presence of HCl which simultaneously acts

as electrolyte, which of the concentration is much higher (by an order of magnitude) as compared to the surface active species. The screening effect of electrolyte on the ΔV of SLS was discussed in our earlier paper [16]. A detailed analysis of the electric surface potential isotherms of the ionic surfactants goes beyond frame of this paper which concentrates on application of the vibrating plate technique to surfactant solutions. The more detailed analysis of the ΔV – c isotherms will be given in our next papers.

At last, it is interesting to discuss our results in comparison with that recently published by Nahahara and co-workers [60,61] for hexadecyl-trimethylammonium bromide (CTAB) and sodium *n*-dodecyl sulphate (SLS) using an ionizing ^{241}Am electrode. Despite, the authors [60,61] present the ΔV vs. c isotherms in the linear concentration scale (instead of the commonly adopted logarithmic scale) the common features of the isotherms may be distinguished as follows. For SLS: (1) the descending branch of the ΔV – c isotherm shows within the concentration range below $1 \times 10^{-4} \text{ mol/dm}^3$ SLS and it is followed by a region of the ΔV – c minimum in the range of $1 \times 10^{-4} \text{ mol/dm}^3$ – $3 \times 10^{-4} \text{ mol/dm}^3$ SLS (we put forward that a width of the minimum region depends on purity grade of SLS solution); (2) the ΔV – c minimum of SLS reaches ca. –100 mV; (the value found by us, –120 mV, is slightly less as compared to –80 mV found in [61]); (3) in the region above the cmc, the ΔV falls down with the concentration to value of ca. –80 mV, comparable to the ΔV – c minimum revealing close to the Π – c onset. This result suggests that in the concentrations range above the cmc, the surfactant (SLS) ions orient to the interface with the head group.

The ΔV vs. c isotherm presented in [60] for hexadecyl-trimethylammonium bromide (CTAB) do not let evaluate the concentration range below the Π – c onset, $1 \times 10^{-5} \text{ mol/dm}^3$ CTAB. The common feature of the ΔV vs. c isotherms measured in [60] for CTAB and by us for C_{10} TABr is the ΔV plateau of 420 mV in the above cmc region (Fig. 6). In the region, a very slight increase of Π with the concentration was measured consistently by us (Fig. 6) and in [60]. On the contrary, Nahahara and co-workers [60] observed for CTAB a jump up in the ΔV , by ca. 30 mV, just above the cmc, which was not observed by us for C_{10} TABr. On the other hand, we observed the greatest scatter of the ΔV just at the cmc, which may be described to shifting the micellisation equilibrium owing to an uncontrolled change in the experimental conditions. The ΔV jump up observed by Nahahara and co-workers [60] was explained by them in frame of their theory that, close to the cmc, a bimolecular layer is formed at the air/solution interface which disappears above the cmc, as a result of transferring molecules from the bilayer to stable micelles in the bulk. So far, however, no an evidence was given with a structural method for formation of a surfactant bilayer below the cmc, hence, this explanation is disputable.

4. Conclusions

Measurement of electric surface potential of solution surface with the vibrating plate (VP) technique (the rare application, so far) is much more difficult than the measurement combined with the Langmuir technique. It is because, replacing the reference sample with the solution measured requires some manual operations below the VP made vibrate, so that, it is near impossible not to cause a shift of the reference level by exchanging samples. On the other hand, turning off/on vibrations for replacing water with the solution measured results in a much greater shift of the measuring signal, ΔV , than the mentioned above. Consequently, the water–solution exchange is the crucial stage of the ΔV measurement of free solution surfaces and it in fact determines accuracy and precision of the ΔV measurement. A degree of disturbance of the ΔV measuring signal during the sample replacement depends on quality of the VP measuring head, actual state of its

stability and – to a degree – on arrangement of the measuring stand.

To overcome the base difficulty in application of the vibrating plate (VP) technique to measuring electric surface potential (ΔV) of solution surfaces, we propose a cell in which the exchange between the reference sample and the measured solution is performed in flow. This improvement enables prominent increase in reproducibility of the ΔV measurement of solutions. Furthermore, we propose the simultaneous measurement of the surface pressure (Π) with a Wilhelmy plate (WP) positioned at a constant height relative to the VP, so that, the minimum immersion of the WP fixes the air gap width, $d_{a.g.}$. Changes in the latter, such as that caused by different meniscus of the reference and the measured solution (if only position of the cell would be controlled) may result in a notable error of the ΔV measurement, owing to a dependency of the ΔV measuring signal on the air gap width. In practice, the height dependency is inherent in instruments for the VP technique and it may change with time of operating the measuring head. Changes in the height dependency from several to more than one hundred mV/mm were found for the newest generation instrument (Spot 2) of Biolin Scientific Oy (former KSV Instruments Ltd.). Therefore, lowering the height dependency to a minimum by proper regulation of the instrument and arrangement of the measuring stand and checking up the air gap width are essential for the ΔV measurement of solutions.

The surface pressure (Π) measurement with the platinum Wilhelmy plate (WP) at the minimum immersion gives correct Π values, provided the WP is suitably purified after each measurement. We proved a good consistency of the Π – c isotherms measured at the minimum immersion of the WP with that obtained by the drop shape analysis method.

Course of the ΔV – $\log c$ isotherms of the ionic surfactants (C_{10} TABr and sodium n-dodecylsulphate, SLS) shows similar properties. The ΔV – $\log c$ isotherms look like being composed of two branches, one falling below the surface activity region (of zero Π) and the second one – covering the surface activity region characterized by the Π increase with the concentration up to the cmc. Each of the branches spans over the concentration range of ca. two orders of magnitude. Comparison between the ΔV vs. c isotherms of C_{10} TABr and SLS suggests that the ΔV change of ca. 100 mV (positive in sign for cationic surfactant and negative in sign for anionic one) is the maximum effect contributed by purely electrostatic, long-range interactions of molecular ions entirely hydrated at the air/solution interface – the state attributed to the Henry region. Lowering of the ΔV by surfactant anions at their concentrations below the surface activity region (i.e., at no measurable surface pressure) revealed also in the ΔV vs. c isotherm measured by us for entirely dissociated n-decanoic acid (in 5×10^{-3} mol/dm³ NaOH), however, this effect was screened by presence the electrolyte (NaOH).

Acknowledgements

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Appendix A. Analysis of errors in the VP technique

First, let's regard the ideal vibrating plate (VP) measuring system in which no spurious currents/voltages occur. Voltage across the vibrating capacitor – formed between the VP and the solution surface, V_c , is given as follows:

$$V_c = \Sigma \Psi_i + V_{\text{comp}}, \quad (\text{A1})$$

where $\Sigma \Psi_i$ represents sum of the all interfacial potential drops (VP/air, air/solution and CE/solution) and V_{comp} is the compensating voltage. Assuming that the VP vibrations fit cosine function, the separation distance between plates of the vibrating capacitor, $d(t)$, is described as follows:

$$d(t) = d_0 + d_1 \cos(\omega t) \quad (\text{A2})$$

where d_0 is the static air gap width, d_1 is amplitude of the vibrations and ω is the vibrations' angular frequency measured in radians per second, so that, $\omega = 2\pi f$ where f is the ordinary frequency measured in hertz. The alternating current produced due to the VP vibrations is as follows [3a,6–8,73–75]:

$$I_{\text{ac}} = V_c \varepsilon \varepsilon_0 A d_1 \omega \frac{\cos(\omega t)}{(d_0 + d_1 \sin(\omega t))^2} \quad (\text{A3})$$

where A is surface area of the VP, V_c – voltage across the vibrating capacitor and $\varepsilon \varepsilon_0$ – the dielectric permittivity of the medium filling it. For $d_1 \ll d_0$ we obtain:

$$I_{\text{ac}} = \frac{V_c \varepsilon \varepsilon_0 A d_1 \omega \cos(\omega t)}{d_0^2} \quad (\text{A4})$$

and consequently:

$$V_{\text{ac}} = \frac{V_c \varepsilon \varepsilon_0 A d_1 R_1 G \omega \cos(\omega t)}{d_0^2} \quad (\text{A5})$$

where R_1 is the feedback resistance of the first amplifier (100 M Ω) and G is the gain of the second amplifier: 50 (cf. Fig. 1). By multiplying the V_{ac} by $A_{\text{ref}} \times \cos(\omega t)$, where A_{ref} is amplitude of the reference signal assumed arbitrary to be 1, we get the V_{dc} out:

$$V_{\text{dc}} = \frac{V_c \varepsilon \varepsilon_0 A d_1 R_1 G \omega A_{\text{ref}} \cos^2(\omega t)}{d_0^2} \quad (\text{A6})$$

Since,

$$\cos^2(\omega t) = \frac{1 - \sin(2\omega t)}{2}, \quad (\text{A7})$$

and average value of the above expression is 1/2, Eq. (A6) simplifies to the following:

$$V_{\text{dc}} = \frac{V_c \varepsilon \varepsilon_0 A d_1 R_1 G \omega A_{\text{ref}}}{2 d_0^2} \quad (\text{A8})$$

After substituting $K_1 = \varepsilon \varepsilon_0 \times A \times d_1 \times R_1 \times G \times \omega \times A_{\text{ref}}/2$ to Eq. (A8) we obtain the voltage fed to the integrator input, as follows:

$$V_{\text{dc}} = V_c \times \frac{K_1}{d_0^2}. \quad (\text{A9})$$

At the compensation equilibrium, the current fed to integrator must be zero, so that, we get $V_{\text{dc}} = 0$ and consequently we obtain:

$$(\Sigma \Psi_i + V_{\text{comp}}) \times \frac{K_1}{d_0^2} = 0 \quad (\text{A10})$$

which does mean that $V_{\text{comp}} = -\Sigma \Psi_i$ and no height dependency occurs.

Now let's introduce an error component. There are at least three different sources of errors in the VP technique:

- (1) Stray capacitances;
- (2) Inductive/capacitive coupling of driver (loudspeaker) currents;
- (3) Offset voltages in multiplier output or integrator itself.

We assume that the common feature of all spurious currents/voltages coming to the circuit from the above mentioned sources is that they are not dependent on the static air gap width. All what they do is contributing a constant additional voltage (V_{err}) to the integrator input. Accordingly, Eq. (A9) may be modified as follows:

$$V_{\text{dc}} = V_c \times \frac{K_1}{d_0^2} + V_{\text{err}} = (\Sigma \Psi_i + V_{\text{comp}}) \times \frac{K_1}{d_0^2} + V_{\text{err}} \quad (\text{A11})$$

At the compensation equilibrium $V_{\text{dc}} = 0$ (since, current fed to integrator must be zero). Consequently we get:

$$(\Sigma \Psi_i + V_{\text{comp}}) \times \frac{K_1}{d_0^2} + V_{\text{err}} = 0 \quad (\text{A12})$$

and

$$V_{\text{comp}} = -\Sigma \Psi_i - d_0^2 \times \frac{V_{\text{err}}}{K_1}. \quad (\text{A13})$$

The above equation implies that a spurious voltage, V_{err} , multiplied by square of the static air gap width, d_0^2 , superposes to the voltage loop. We can get rid of this height dependency by adding opposite voltage to the integrator input, $V_{\text{err,comp}}$. Then, Eq. (A12) is expressed as follows:

$$(\Sigma \Psi_i + V_{\text{comp}}) \times \frac{K_1}{d_0^2} + V_{\text{err}} + V_{\text{err,comp}} = 0. \quad (\text{A14})$$

If $V_{\text{err,comp}} = -V_{\text{err}}$, we get:

$$(\Sigma \Psi_i + V_{\text{comp}}) \times \frac{K_1}{d_0^2} = 0 \quad (\text{A15})$$

and consequently: $V_{\text{comp}} = -\Sigma \Psi_i$ which does mean that no height dependency occurs.

The above analysis is valid for spurious voltages which are constant as a function of time and temperature.

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