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A novel fused-silica capillary dropping mercury electrode with long drop-time and its application on determination of critical micelle concentration

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ABSTRACT

A novel long drop time mercury electrode has been constructed from common fused-silica capillary (50 μm I.D., 360 μm E.D.). Proposed device provides reproducible mercury drops with typical lifetime 40–120 s. The electrode was used for a set of electrocapillary measurements aimed at determination of critical micelle concentration of anionic surfactants by a convection controlled drop-time technique. A critical micelle concentration of sodium dodecyl sulfate 5.6 ± 0.4 mmol L^{-1} and 4.3 ± 0.4 mmol L^{-1} were obtained in 1 mmol L^{-1} and 5 mmol L^{-1} phosphate buffer (pH 7.0), respectively. The values were comparable to those obtained from conductometric measurements under the same conditions (7.0 ± 0.1 mmol L^{-1} and 5.2 ± 0.1 mmol L^{-1}, respectively) and the difference was explained in accordance with theory of hemi-micelle formation.

1. Introduction

A number of organic compounds tend to adsorb on almost any surface including fresh surface of dropping mercury electrode. In this case the adsorption leads to enhancement of the surface concentration on electrode/solution interface in comparison to the bulk phase [1]. Adsorbed molecules or aggregates modify properties of the surface and structure of the electrical double layer and thus, consequently, the interfacial tension γ. In other words, electrocapillary measurement of the interfacial tension can be used for investigation of the adsorption and aggregation properties of target compound. The method is based on the measurement of mercury drop time under defined potentials (electrocapillary curve) in solutions with different concentrations of target compound. The drop time t is directly proportional to the mercury surface tension γ [2] according to the Eq. (1)

$$t = \frac{2\pi r_c}{mg}\gamma \tag{1}$$

where r_c is the radius of a capillary, m is the mass flow rate of mercury and g is the standard acceleration of gravity.

Adsorption isotherms and basic adsorption parameters can be calculated from the dependences of surface tension on logarithm of concentration of target compound [3–12]. In the same way, the critical micelle concentration (CMC) of ionic and nonionic surfactants [13–15] could be determined from electrocapillary measurements. For this purpose mercury drop time measured at a constant potential (or respective surface tension at a constant potential) is plotted against logarithm of the surfactant concentration. The CMC value is obtained from concentration coordinate of the intersection of both extrapolated parts of the curve – steep part, usually measured at low concentration (below CMC) and flat part, common at higher concentration. In a similar way, the value of CMC is usually determined from conductometric [16–25], spectrophotometric [16,17,19,21,26], turbidimetric [27,28], tensametric [16,17,29–34], light scattering [18,35] and other physicochemical measurements.

The forming of the adsorbed layer at the dropping mercury electrode (DME) is limited by the rate of diffusion of the surfactant from the bulk of the solution towards the electrode. The process is very slow particularly at low surfactant concentration ($\leq 10^{-4}$ mol L^{-1}) [36] and relatively long time is required for achievement of adsorption equilibrium. Classical DME and its various modifications with a drop-time in several seconds had been used for surface tension measurement earlier [37]. However, proper establishment of equilibrium is somewhat questionable under these conditions, thus respective data were considered as less reliable afterwards [5,36,38].

Hence, several ways to overcome these problems have been suggested. For instance Novotný designed an appropriate type of glass spindle-shaped capillary for mercury electrodes with drop-time in tens of seconds [39,40], which provides very stable and reproducible drops. In this way equilibrium data became accessible.

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This construction of the electrode enabled introducing of the so-called controlled convection drop-time technique (CCDT) [41] that is suitable for investigation of adsorption behavior of surfactant in diluted solution under equilibrium conditions. Joining the mercury reservoir to a vacuum source or to a compressed gas according to automatic program further facilitated controlling of the size and the time of a mercury drop and thus contributed to the better monitoring of adsorptive behavior of surfactants at the electrode-solution interface [42].

Another possibility for extension of the drop time would be application of the sufficiently long flexible fused-silica capillary commonly used for instance in capillary electrophoresis (inner diameter about 0.05 mm) allowing easy preparation of the inexpensive capillary of almost any length in order to effectively control the mercury column height and, thus, the drop time. The latter approach is shown in this paper. The usability of this novel electrode is demonstrated on the electrocapillary measurement and determination of critical micelle concentration. Sodium dodecyl sulfate (SDS) serves as a model surfactant for the purpose, because its CMC has been measured by a range of different methods in various types and concentrations of supporting electrolytes and the values are easily accessible.

2. Experimental

2.1. Chemicals

Sodium dodecyl sulfate, phosphoric acid, sodium perchlorate, potassium chloride and sodium hydroxide were purchased from Fluka (Fluka, Buchs, Switzerland). All chemicals were of analytical grade. The single batch of SDS was used for all experiments without further purification [10]. Deionized water (18 MΩ) was used for preparation of all solutions. Phosphate buffer (pH 7.0) was prepared from 5.0 mmol L^{-1} phosphoric acid and 1.0 mol L^{-1} NaOH. Stock solution of sodium dodecyl sulfate (0.05 mol L^{-1}) was prepared by dissolution of the weighted amount in a phosphate buffer.

2.2. Working electrode

The working electrode was made from fused-silica capillary commonly used in capillary electrophoresis (50 μm I.D., 360 μm E.D.; Supelco, Bellefonte, PA, USA). The capillary was cut off to the length 40–60 cm with Shortix™ Fused Silica Tubing Cutter (Supelco, Bellefonte, PA, USA). Both ends of the capillary were carefully inspected with a binocular microscope in order to verify that the cutting plane is smooth and orthogonal to the capillary axis. External polyimide coating was removed at both ends of the capillary (approx. 1 cm in length) with a boiling concentrated sulphuric acid. One of the ends was fixed through the small silicone seal (cut from the silicone septum used in a gas chromatography; Agilent, Palo Alto, CA, USA) in a short glass tube (4 mm × 10 cm, see Fig. 1). The opposite end of the capillary was sealed into a mercury reservoir in the same way. The reservoir was made from a 20 mL plastic syringe without a needle. Drop time within the range 40–80 s and mercury mass flow rate 0.34–0.17 mg s^{-1} were measured in this setup. Variation of the mercury level in the 20 mL cylindrical reservoir during the working day was negligible.

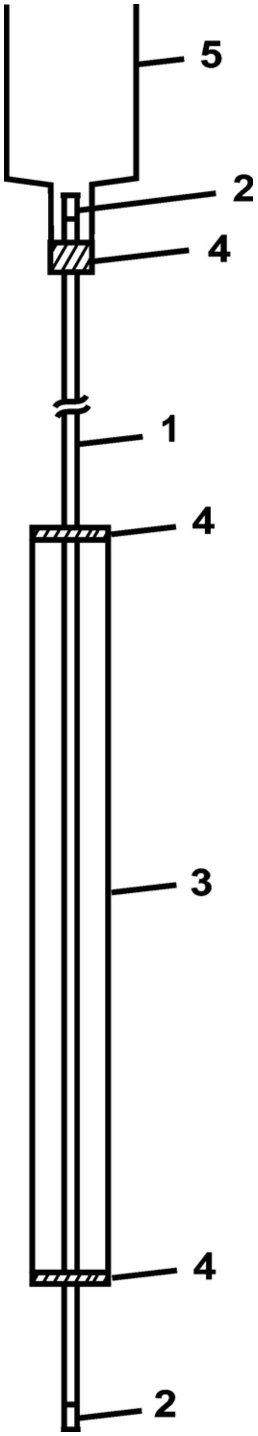

Fig. 1. Scheme of fused-silica capillary dropping mercury electrode: (1) fused-silica capillary, (2) removed polyimide, (3) glass tube, (4) silicone seal, 5 plastic syringe reservoir.

2.3. Electrocapillary measurement

The measurements of the electrocapillary curves were performed with the computer-controlled Eco-Tribo Polarograph (ECO-TREND PLUS, Prague, Czech Republic) in three electrodes circuit with an auxiliary Pt electrode. A saturated calomel electrode was used as reference. The solutions of indifferent electrolytes in a polypropylene voltammetric cell were deaerated by bubbling nitrogen for 10 min. In each measurement the controlled convection was ensured by intensive stirring during the 2/3 of the time of the drop growth (from the beginning of each drop) [41]. The drop time was measured from the current maxima on i–t curves recorded at least for 6 drops under given conditions. Hanhart Classic stopwatch (Hanhart, Gütenbach, Germany) was used for simultaneous comparative measurements of the drop time. The electrocapillary curves were observed in the potential range 0.1 to −1.5 V (SCE) and the measurements were repeated at least three times. For determination of the dependence of drop time on the sodium dodecyl sulfate concentration at a constant potential the 0.05 mol L^{-1} stock solution of SDS in phosphate buffer was gradually titrated into the deaerated supporting electrolyte. After each addition, the solution was stirred and simultaneously bubbled with nitrogen for 1 min and than the *i*–*t* curve at a constant potential was recorded. A Haake C1 analog immersion circulator and B3 bath (Haake, Karlsruhe, Germany) were used to maintain constant temperature 298.2 ± 0.5 K.

2.4. Conductivity measurement

Conductometric measurements were carried out on a Jenway 4510 conductivity meter (Jenway, Dunmow, UK). The conductivity cell was calibrated with 0.01 mol L^{-1} aqueous KCl solution and cell constant of 1.02 corresponding to the value declared by producer was obtained. The stock solution of SDS (0.05 mol L^{-1}) was titrated into a stirred phosphate buffer solution in the polypropylene cell. The conductivity measurements were repeated three times. All measurements were performed at a temperature of 298.2 ± 0.5 K.

3. Results and discussion

3.1. Experimental setup

The proposed working electrode was made in our laboratory from cheap and easily available components: fused-silica capillary, glass tube, silicone septum and plastic syringe (Fig. 1). Common electrophoretic capillary (50 μm I.D., 360 μm E.D.) was cut to 40–60 cm with diamond edge of Shortix^{TM} Fused Silica Tubing Cutter and perpendicularity of both cutting planes was verified with a binocular microscope. Polyimide coating was removed from both ends and capillary was fixed into the short glass tube. The second end was sealed with the silicone septum into the 20 mL plastic syringe, serving as a mercury reservoir.In this arrangement the flexibility of the capillary brings great advantage consisting in possibility of more or less independent handling with mercury reservoir. This feature allows reducing the mercury column height and thus significant prolongation of the drop-time. The setup was adjusted so that the drop time within the range 40–80 s and respective mercury mass flow rate 0.34–0.17 mg s^{-1} was measured.

Electrocapillary measurements under CCDT conditions in 0.1 mol L^{-1} aqueous solution of sodium perchlorate were performed for testing the functionality of the fused-silica capillary dropping mercury electrode. The electrocapillary curve recorded in the potential range 0.1 V to −1.5 V is shown in Fig. 2. The electrocapillary maximum at −0.478 V (*vs.* SCE) corresponds to surface tension of 425.5 mN m^{-1} (calculated from the Eq. (1)), which is in agreement with data published previously [3,43]. The drop time reproducibility was better than 0.2%. The value is comparable to those obtained with spindle shaped DME under the same conditions.

3.2. Electrocapillary behavior in the presence of SDS

In the second step, the proposed fused-silica capillary DME was used to study electrocapillary behavior in the SDS solution at various concentrations. The phosphate buffer was chosen as a supporting electrolyte because reference information about SDS micelle formation in this medium is broadly available [44] and it is one of the most widely used buffers suitable for many applications in molecular and cell biology. Fig. 3 shows a set of electrocapillary curves measured in a 5 mmol L^{-1} phosphate buffer with two different concentrations of SDS. The electrocapillary maxima of the curves obtained in the presence of SDS were depressed and deformed in comparison to the curve measured in the supporting electrolyte. In Fig. 3, trace 2 corresponds to SDS concentration less than the expected CMC value. There is an observable decrease and shift of the electrocapillary maximum towards the less negative potentials. Supposedly, in diluted solution SDS adsorbs as an individual ions contributing to the overall surface charge of the mercury electrode. Increasing of SDS concentration above the CMC value further decreases the electrocapillary maximum and shifts the maximum back to the more negative potential region (Fig. 3, trace 3), probably in consequence of more intensive association and formation of two-dimensional structures on the surface in analogy to three-dimensional micelle formation in the bulk (concept of so called hemi-micelles arises from the analogy for description of the surface structures) [45–47]. As can be seen from the differential curve (Fig. 3, trace 4), the most significant difference in electrocapillary behavior below and above the assumed CMC occurs in the potential region from −0.2 to 0.1 V. Therefore the constant potential of −0.2 V was chosen for measurement of *t*–*c* dependence in order to determinate the CMC value of SDS.

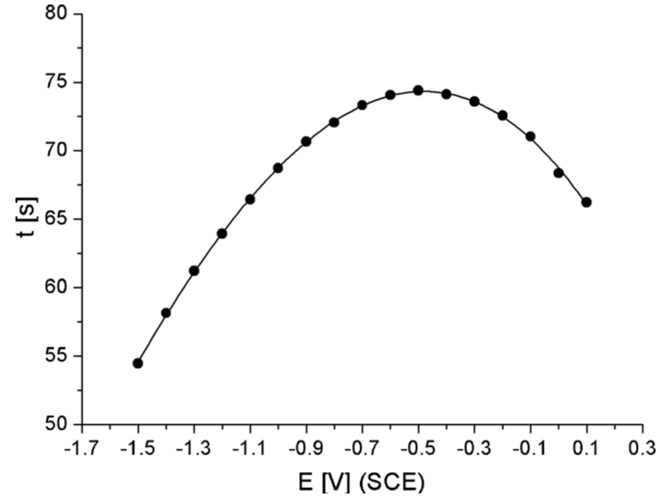

Fig. 2. Electrocapillary curve measured with the fused-silica capillary DME in 0.1 mol L^{-1} $NaClO_4$.

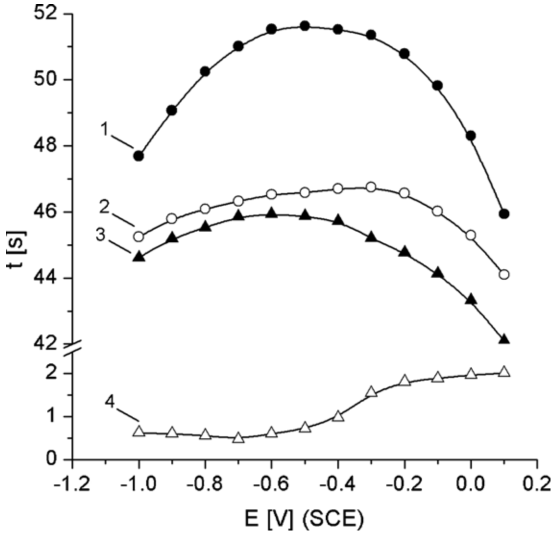

Fig. 3. Electrocapillary curves of sodium dodecyl sulfate in 5 mmol L^{-1} phosphate buffer (pH 7.0). (1) Phosphate buffer without SDS; (2) 0.98 mmol L^{-1} SDS; (3) 12.12 mmol L^{-1} SDS; (4) difference between 2 and 3.

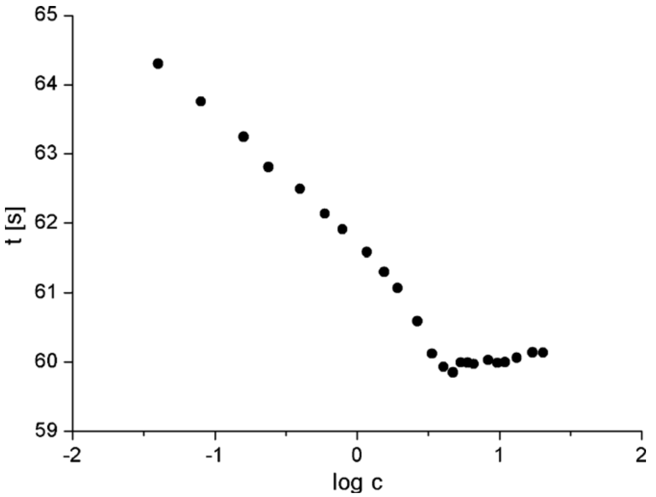

Fig. 4. Dependence of drop time on log *c* of SDS in 5.0 mmol L^{-1} phosphate buffer (pH 7.0).

3.3. *Determination of SDS critical micelle concentration*

The effect of SDS concentration on the mercury drop time under the controlled convection conditions was studied at the constant potential of −0.2 V (*vs.* SCE) in 5 mmol L^{-1} phosphate buffer (pH 7.0). The dependence of the drop time on the logarithm of SDS concentration consists of two parts with different slopes (Fig. 4). The first part corresponds to decreasing of the interfacial tension due to adsorption of individual molecules of surfactant onto the electrode surface. At sufficiently high concentration, molecules of the surfactant start to associate and form micelles. This phenomenon can be observed as a break point on the *t*–log *c* plot. The second part of the dependence corresponds to the adsorption of SDS micelles. Finally, the electrode surface is completely covered with the adsorbed layer of surfactant aggregates. Further increase of surfactant concentration only slightly influences the surface tension and drop time. The break points on the *t*–log *c* plot appears at the log *c* ranging within 0.67–0.61 which corresponds to CMC value 4.3 ± 0.4 mmol L^{-1}.

3.4. *Conductometric measurement*

The CMC obtained by the described electrocapillary drop-time method with fused-silica DME was compared to the results of conductivity measurements performed under the same experimental conditions.

Fig. 5 demonstrates the effect of SDS concentration on the specific conductance in 5 mmol L^{-1} phosphate buffer (pH 7.0). The plot consists of two straight lines with different slopes, which intersect at a point corresponding to CMC value. The obtained value of 5.2 ± 0.1 mmol L^{-1} is slightly higher than those found by the electrocapillary drop-time method. The difference of both values is statistically significant at 0.95 significance level and could be explained in accordance with the theory of so called hemi-micelles, which are formed on the electrode surface at somewhat lower concentrations of surfactant than micelles in the bulk of the solution [46,48]. The capability to measure values relevant for the aggregation on the surface or in the close vicinity of the surface could be considered as one of the great advantages of the electrocapillary drop-time method over the common techniques relevant for the bulk of the solution. To our knowledge, experimental methods involving the hemi-micelles formation usually offer better description of the real micellar systems whenever any kind of surface may participate in the aggregation (e.g. biological systems, (bio)sensors, electrochemical systems, nanosystems and so on).

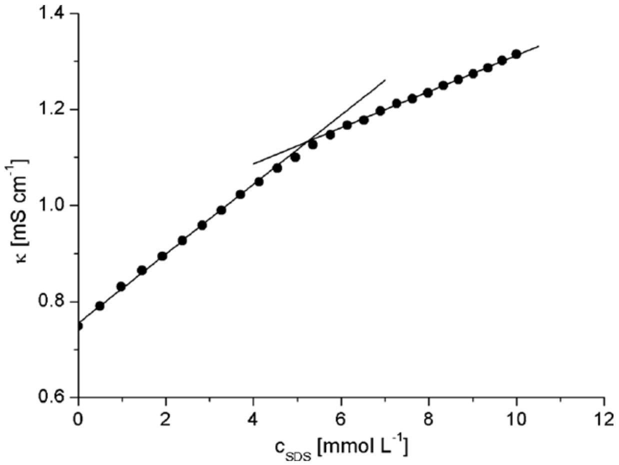

Fig. 5. Dependence of specific conductivity on concentration of SDS in 5.0 mmol L^{-1} phosphate buffer (pH 7.0).

The CMC value of 6.09 mmol L^{-1} has been reported in the literature [44] for SDS solution in 5 mmol L^{-1} phosphate buffer (pH 7.0) solution at 298.2 K. In the same way, the CMC was measured in 1 mmol L^{-1} phosphate buffer (pH 7.0) and values 5.6 ± 0.4 mmol L^{-1} and 7.0 ± 0.1 mmol L^{-1} were obtained from electrocapillary and conductometric measurements, respectively (relevant value 7.6 mmol L^{-1} results from the Ref. [44]).

4. Conclusions

Proposed long drop time mercury electrode from fused-silica capillary seems to be a reasonable alternative to the spindle-shaped electrode, e.g. for electrocapillary measurements. It provides stable and reproducible drop, which is a prerequisite for the proper application of the controlled convection drop-time technique and acquisition of the correct equilibrium data.

The fused-silica DME provides some unquestionable advantages: it is readily available, inexpensive and in particular, it can be easily "renovated" by carefully cutting off the capillary end in case of need. The newly proposed DME was successfully utilized for electrocapillary measurements and determination of critical micelle concentration of SDS under the CCDT conditions in 5 and 1 mmol L^{-1} phosphate buffer equal to 4.3 ± 0.4 mmol L^{-1} and 5.6 ± 0.4 mmol L^{-1}, respectively.

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References

[1] B.B. Damaskin, O.A. Petrii, V.V. Batrakov, Adsorption of Organic Compounds on Electrodes, Plenum Press, New York, 1971.
[2] A.J. Bard, L.R. Faulkner, Electrochemical Methods Fundamentals and Applications, second ed., John Wiley & Sons, New York, 2001.
[3] L. Novotný, I. Smoler, J. Kůta, Collect. Czech. Chem. Commun. 48 (1983) 964–975.
[4] L. Novotný, R. Kalvoda, Collect. Czech. Chem. Commun. 51 (1986) 1595–1603.
[5] L. Novotný, T. Navrátil, S. Sander, P. Bašová, Electroanalysis 14 (2002) 1105–1109.
[6] L. Novotný, T. Navrátil, S. Sander, P. Bašová, Electroanalysis 15 (2003) 1687–1692.
[7] J. Kůta, I. Smoler, Collect. Czech. Chem. Commun. 40 (1975) 225–235.
[8] J. Rudovský, L. Novotný, Vod. Hosp. B 4 (1984) 97.
[9] T. Wandlowski, M. Heyrovský, L. Novotný, Electrochim. Acta 37 (1992) 2663–2672.
[10] I.M. Umlong, K. Ismail, Colloid Surf. A 299 (2007) 8–14.

[11] I. Frese, S. Ruppert, M. Sugar, H. Schmidt-Lewerkuhne, K.P. Wittern, V.B. Fainerman, R. Eggers, R. Miller, J. Colloid Interface Sci. 267 (2003) 475–482.
[12] T.D. Gurkov, D.T. Dimitrova, K.G. Marinova, Ch. Bilke-Crause, C. Gerber, I.B. Ivanov, Colloid Surf. A 261 (2005) 29–38.
[13] W.U. Malik, P. Chand, J. Am. Oil Chem. Soc. 46 (1969) 285–288.
[14] J. Garcia-Anton, J.L. Guinon, Colloid Surf. 61 (1991) 137–145.
[15] W.U. Malik, P. Chand, S.M. Saleem, Talanta 15 (1968) 133–136.
[16] S. Mukherjee, D. Mitra, S.C. Bhattacharya, A.K. Panda, S.P. Moulik, Colloid J. 71 (2009) 662–671.
[17] C. Das, T. Chakraborty, S. Ghosh, B. Das, Colloid Polym. Sci. 286 (2008) 1143–1155.
[18] E. Tesařová, Z. Tuzar, K. Nesměrák, Z. Bosáková, B. Gaš, Talanta 54 (2001) 643–653.
[19] E. Fuguet, C. Ràfols, M. Rosés, E. Bosch, Anal. Chim. Acta 548 (2005) 95–100.
[20] J.I. Briz, M.M. Velázquez, J. Colloid Interface Sci. 247 (2002) 437–446.
[21] M. Müllerová, M. Šváb, M.M. dos Snatos, Chem. Listy 101 (2007) 509–514.
[22] M. Miura, M. Kodama, Bull. Chem. Soc. Jpn. 45 (1972) 428–431.
[23] P.A. Koya Kabir-ud-Din, Z.A. Khan, J. Colloid Interface Sci. 342 (2010) 340–347.
[24] M.S. Bakshi, S. Sachar, N. Mahajan, I. Kaur, G. Kaur, N. Singh, P. Sehgal, H. Doe, Colloid Polym. Sci. 280 (2002) 990–1000.
[25] P. Burgo, E. Aicart, E. Junquera, Colloid Surf. A 292 (2007) 165–172.
[26] E. Fuguet, C. Ràfols, E. Bosch, M. Rosés, Langmuir 19 (2003) 55–62.
[27] M. Hisatomi, M. Abe, N. Yoshino, S. Lee, S. Nagadome, G. Sugihara, Langmuir 16 (2000) 1515–1521.
[28] M.A. Abed, A. Saxena, H.B. Bohidar, Colloid Surf. A 233 (2004) 181–187.
[29] Ch. Das, B. Das, J. Mol. Liq. 137 (2008) 152–158.
[30] D. Das, K. Ismail, J. Colloid Interface Sci. 327 (2008) 198–203.
[31] Ch. Frese, S. Ruppert, M. Sugár, H. Schmidt-Lewerkühne, K.P. Wittern, V.B. Fainerman, R. Eggers, R. Miller, J. Colloid Interface Sci. 267 (2003) 475–482.
[32] Y. Li, J. Hao, G. Li, J. Dispers. Sci. Technol. 27 (2006) 781–787.
[33] A. Patist, S.S. Bhagwat, K.W. Penfield, P. Aikens, D.O. Shah, J. Surf. Deterg. 3 (2000) 53–58.
[34] G. Paddon-Jones, S. Regismond, K. Kwetkat, R. Zana, J. Colloid Interface Sci. 243 (2001) 496–502.
[35] M. Kodama, Y. Kubota, M. Miura, Bull. Chem. Soc. Jpn. 45 (1972) 2953–2955.
[36] B. Behr, M. Drogowska, J. Electroanal. Chem. 82 (1977) 317–326.
[37] J. Heyrovský, J. Kůta, Základy Polarografie, NČSAV, Praha, 1962, pp. 31.
[38] R.G. Barradas, F.M. Kimmerle, J. Electroanal. Chem. 11 (1966) 128–136.
[39] L. Novotný, M. Heyrovský, Trends Anal. Chem. 6 (1987) 176–181.
[40] M. Heyrovský, L. Novotný, I. Smoler, in: J.T. Stock, M.V. Orna (Eds.), Electrochemistry, Past and Present, American Chemical Society, Washington, DC, 1989, pp. 370–379.
[41] L. Novotný, I. Smoler, J. Electroanal. Chem. 146 (1983) 183–188.
[42] L. Novotný, Electroanalysis 8 (1996) 135–138.
[43] L. Novotný, I. Smoler, Collect. Czech. Chem. Commun. 50 (1985) 2525–2534.
[44] E. Fuguet, C. Rafols, M. Roses, E. Bosch, Anal. Chim. Acta 548 (2005) 95–100.
[45] P. Somasundaran, T.W. Healy, D.W. Fuerstenau, J. Phys. Chem. 68 (1964) 3562–3566.
[46] W.U. Malik, O.P. Jhamb, J. Am. Oil Chem. Soc. 49 (1972) 170–173.
[47] S. Manne, J.P. Cleveland, H.E. Gaub, G.D. Stucky, P.K. Hansma, Langmuir 10 (1994) 4409–4413.
[48] D.W. Fuerstenau, J. Phys. Chem. 60 (1956) 981–985.