POLAROGRAPHIC BEHAVIOUR OF PETROLEUM COMPONENTS IN AQUEOUS SOLUTIONS: APPLICATION OF ELECTROCAPILLARY MEASUREMENTS AND CONVECTIVE ADSORPTION ACCUMULATION

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Electrocapillary investigations by the drop time method revealed a rather strong surface activity of aqueous petroleum solutions and some petroleum fractions in solutions of base electrolytes at the dropping mercury electrode, depending on the quality of the surfactant. The highest surface activity and sensitivity of analytical determination was found between −0·4 and −0·6 V (S.C.E.). The detection limit of the electrocapillary method was 10—20 μg/l for Diesel oil and up to 5 times higher for petroleum samples. The sensitivity of the measurements at lowest concentrations was increased by convective adsorption accumulation at the surface of the growing drop.

Electrocapillary methods belong to direct methods of study of the interface activity of solutions containing surface active substances. Such investigations can be carried out in polarography by measuring the dependence of the mercury-solution interface tension on the applied potential and on the composition of the solution. A classical method is, *e.g.*, the measurement of changes of the surface tension of mercury as function of the drop time[1,2]. The methods employing a dropping mercury electrode have an advantage over those based on measurement of changes of the capillary depression that diffusion to the mercury drop is less restricted and the influence of the capillary is minimized.

Electrocapillary or other interface effects of strongly adsorptive surfactants in highly diluted solutions can be enhanced by using the method of convective adsorption accumulation[3−6]. The surfactant is thus transported to the electrode by convective, rather than free, diffusion, so that the time necessary to attain equilibrium coverage is substantially shortened. Thus, the sensitivity of electrocapillary measurements is enhanced by up to two orders of magnitude[4].

The electrocapillary activity measured is the result of various electrochemical processes, hence it is generally not selective. Under simple defined conditions, *e.g.* in the presence of an inactive base electrolyte and a low concentration of a surface active substance, it is governed by thermodynamic relations. Then, the potential-dependent electrocapillary activity corresponds to the electrosorption characteristics of the system considered, and the selectivity of the method is improved.

The aim of our work is to elucidate the electrocapillary behaviour of aqueous extracts of petroleum or some petroleum products under the conditions of convective adsorption accumulation on a mercury electrode with regard to electroanalytical applications.

EXPERIMENTAL

Apparatus. A frequency counter of the type BM 520 was used in electrocapillary measurements by the drop time method. A polarograph of the type LP 7e (Laboratorní přístroje, Prague) served as a source of d.c. voltage, which was checked by a digital voltmeter NR 50. Measurements were carried out in a commercial two-electrode polarographic cell which belonged to the polarographic analyser PA 3 of the same manufacturer. The experimental setup was described earlier[3,4]. The polarization potential was referred to a saturated calomel electrode (S.C.E.).

Chemicals. Petroleum standard solution (0·73 mg/l) was supplied by the Central Geological Institute, Prague. Petroleum samples were from the Department of Fuels and Water, Institute of Chemical Technology, Prague. Chemicals were of reagent grade (Lachema, Brno), and the sodium salt of dodecylbenzenesulphonic acid (DBS) was product of Suchard, Munich. Solutions were prepared in redistilled water as described in the preceding communication (in substance, by diluting saturated oil solutions).

Method of measurement. During tensametric measurements, 0·01–2 ml of aqueous petroleum extract was added to 10 ml of the base electrolyte. The capillary was kept in vertical position and the change of the drop time Δt (proportional to the change of the surface tension, $\Delta\gamma$, of mercury) caused by adsorption of surfactants was referred to the $t-E$ curve of the pure base electrolyte. The capillary was spindle-shaped[3] with internal diameter of the upper cylindrical part 0·055 mm and internal diameter of the orifice 0·16 mm. Since the adsorption equilibrium at the surface at high dilution was not established even after 100 s drop time, convective adsorption accumulation was used to attain the equilibrium state (during interrupted stirring of the solution)[3]. The solution was stirred during growth of the drop and the stirrer was stopped about 10 s before breaking off of the drop. Thus, equilibrium $\gamma-t$ curves were obtained and the sensitivity of the measurement was increased.

RESULTS AND DISCUSSION

The experimental electrocapillary curves, *i.e.* the dependences of the drop time t or interface tension γ on the applied potential E, were approximately parabolae. Their apexes were in the range from −0·3 to −0·6 V (S.C.E.) according to the type of the surfactant present. In calculating the surface tension (in absolute units) at the electrocapillary maximum[7], we assumed that $\gamma_m = 426{\cdot}2\ \text{mN m}^{-1}$ at 20°C, except for 5M-KF, where[8] $\gamma_m = 438{\cdot}9\ \text{mN m}^{-1}$.

The curves obtained in the presence of petroleum or petroleum products were lowered or deformed in the adsorption region in comparison with the curves of the base electrolytes. Without convective accumulation, more or less nonequilibrated curves were obtained. Changes of the equilibrium surface tension given by the thermodynamic equation[9–11]

$$\mathrm{d}\gamma = -q\,\mathrm{d}E - \sum_i \Gamma_i\,\mathrm{d}\mu_i - \sum_i \Gamma'_i\,\mathrm{d}\mu'_i \qquad (1)$$

or

$$\mathrm{d}\gamma = -q\,\mathrm{d}E - RT\Gamma\,\mathrm{d}\ln c \qquad (2)$$

were measurable at low concentrations only by the method of controlled convective accumulation[14]. We use the following notation: q charge density, E potential, μ_i chemical potential of surface active species i, Γ_i its relative surface excess (or its surface concentration), Γ total relative surface excess corresponding to total concentration c of surfactants, T absolute temperature, P pressure, and R gas constant; primes refer to those species that are not adsorbed.

Fig. 1 shows a set of electrocapillary curves recorded in 10 ml of 5M-KF with gradual additions of a saturated solution of the Saratov petroleum in water. The curves are approximately symmetrical with respect to the potential of zero charge, E_z (at $\gamma = \gamma_m$). The changes of the surface tension were most pronounced in the potential region from −0·4 to −0·5 V (S.C.E.). The region of maximum surface activity is apparent from Fig. 2, where the values of Δt are plotted against potential at constant concentration.

The dependences of the change of the drop time Δt_1 on the concentration of Saratov petroleum at −0·4 and −0·5 V (Fig. 3*a*, *b*) are approximately hyperbolae. In view of the high concentration of the base electrolyte, we also measured the changes of the drop time Δt_3 due to addition of pure water, and the blank curves were subtracted from the measured concentration dependences. The resulting hyperbolic

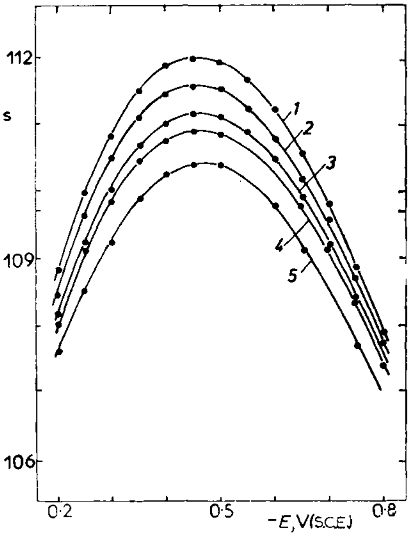

Fig. 1

Electrocapillary curves for 10 ml of 5M-KF + ΔV ml of a saturated solution of Saratov petroleum in water (about 20 g m^{-3}). ΔV (ml): *1* 0; *2* 0·18; *3* 0·3; *4* 0·4; *5* 0·5; natural drop time t = const. γ

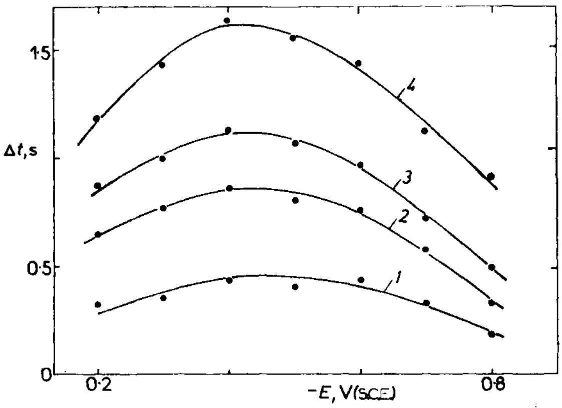

Fig. 2

Changes of the drop time Δt with potential E in 10 ml of 5M-KF + ΔV ml of a saturated solution of Saratov petroleum. ΔV (ml): *1* 0·18; *2* 0·3; *3* 0·4; *4* 0·5 dependences could be considered as calibration curves and corresponded to classical adsorption isotherms[10,11]. The following empirical equations were found in the concentration range 0·28–1·05 mg/l at −0·5 V (S.C.E.):

$$\Delta t_2 = \Delta t_1 - \Delta t_3 = 2{\cdot}57\Delta V/(6{\cdot}1 - 9{\cdot}1\Delta V)\,, \quad (3)$$

$$\Delta t_3 = 0{\cdot}083\Delta V - 0{\cdot}09\,, \quad (4)$$

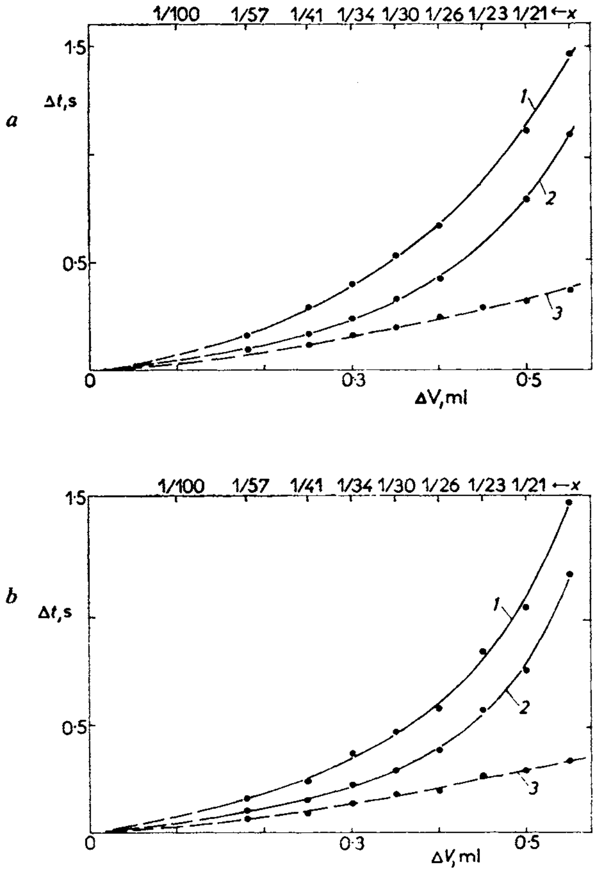

FIG. 3

a Concentration dependence of the change of the drop time at −0·400 V *vs* S.C.E. *1* Δt_1 measured after addition of ΔV ml of saturated petroleum extract; *3* Δt_3 measured after addition of ΔV ml of pure water; *2* $\Delta t_1 - \Delta t_3$ against ΔV; *x* dilution of the saturated petroleum solution.

b Concentration dependence of the change of the drop time at −0·500 V *vs* S.C.E. *1* Δt_1 measured (Fig. 3*a*); *3* Δt_3 measured (Fig. 3*a*); *2* $\Delta t_1 - \Delta t_3$ *vs* *E*; *x* dilution of the saturated petroleum solution where the changes of the drop time before and after the correction for the background are denoted as Δt_1 and Δt_2 and ΔV is the volume of saturated solution of Saratov petroleum added into 10 ml of 5M-KF.

When the aqueous extract of Saratov petroleum was added into 0·5M-NaCl (Fig. 4) or to the artificial sea water, the series of electrocapillary curves was somewhat asymmetrical. In contrast to surface inactive KF (Fig. 1), the surface activity of Cl^- ions came into play at potentials more positive than the electrocapillary maximum and the changes of Δt with concentration became smaller. The potential of maximum adsorption was shifted to more negative values between −0·55 and −0·6 V (S.C.E.). The influence of potential on the concentration dependence of the interface tension is shown in logarithmic coordinates in Fig. 5. In the region from −0·5 to −0·7 V, the hyperbolic curves can be shifted to almost coincide; this is sometimes called in the literature[10-13] as congruence with respect to an electrical variable, in our case to the potential. Outside the given region, the $\gamma - \log c$ curves are more or less incongruent, and at potentials more positive than −0·3 V or more negative than −0·9 V the changes of γ with $\log c$ cease to be sufficiently pronounced. The changes of the congruence of the isotherms (hence of the sensitivity of the

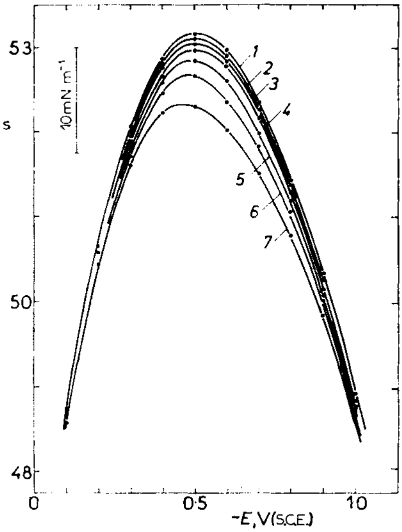

FIG. 4

Electrocapillary curves for 10 ml of 0·5M-NaCl + ΔV ml of saturated aqueous extract of Saratov petroleum. ΔV (ml): *1* 0; *2* 0·05; *3* 0·10; *4* 0·18; *5* 0·50; *6* 0·70; *7* 1·00

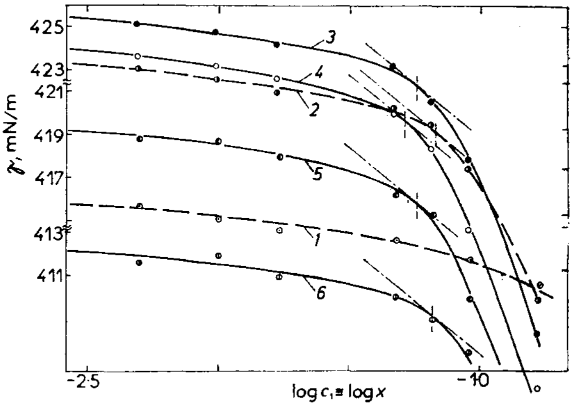

FIG. 5

Dependence of interface tension γ on dilution of saturated Saratov petroleum solution, $x = \Delta V/(V + \Delta V)$, in 0·5M-NaCl at constant potential $-E$ (mV): *1* 300; *2* 400; *3* 500; *4* 600; *5* 700; *6* 800 measurement) with respect to the potential are related mainly to the potential changes of the adsorption coefficients. The general form of the adsorption isotherm is

$$f_1(\Theta) = \beta a \,, \tag{5}$$

where the coverage $\Theta = \Gamma/\Gamma_{\max}$ is defined as usual, β denotes adsorption coefficient or its mean value, and a activity, which can approximately be set equal to the concentration c. From Eq. (*5*) we obtain by simple rearrangement

$$\log \beta = -\log c_1 + \log f(\Gamma) + \log k' = -\log c_1 + k \,, \tag{6}$$

where $\Gamma \sim (\partial\gamma/\partial \log c)_E = \text{const.}$ The concentration $c_1 = c/k'$ can be expressed in arbitrary units.

Eq. (*6*) indicates one of possible ways how to determine the potential dependence of the coefficient β (influencing the sensitivity of the measurement) from the dependence of $\log c_1$ on E at $\Gamma = \text{const.}$, or at $(\partial\gamma/\partial \log c)_E = \text{const.}$ In the case of Saratov petroleum in 0·5M-NaCl, we set $(\partial\gamma/\partial \log c)_E = 10\ \text{mN m}^{-1}$, *i.e.* approximately $\Gamma = 1{\cdot}75 \,.\, 10^{-6}\ \text{mol m}^{-2}$ (see tangents in Fig. 5). The curve showing the dependence of $-\log c_L$ or $\log \beta$ on potential E (Fig. 6) has in the region of maximum adsorption an approximately parabolic shape as expected, its maximum corresponding ot $E = E_{\max} \approx -0{\cdot}6$ V.

The decrease of the adsorption coefficient with potential is manifested not only by decrease of the sensitivity of the measurement but also by a more pronounced sigmoidal shape of the curve for the standard in the lowest concentration region (Fig. 7). This effect can be attributed to the fact that the decrease of β and c and hence of the interaction free enthalpy of the surfactants with mercury, $\Delta G_{\text{Hg-org}} \sim \log \beta$, leads to a stronger influence of the energetic contributions due to salting out, ΔG_S, surface interactions with other solution components, $\Delta G_{\text{Hg-H}_2\text{O}}$, or $\sum \Delta G_{\text{Hg-A}_i}$, mutual interactions of the adsorbed components $\Delta G'$, *etc.*[7-11]. The adsorption process has then the character of a substitution according to the scheme

$$\text{O}_{\text{des}} + n_1(\text{H}_2\text{O})_{\text{ads}} + \sum_i n_i(\text{A}_i)_{\text{ads}} \rightleftarrows \text{O}_{\text{ads}} + n_1(\text{H}_2\text{O})_{\text{des}} + \sum_i n_i(\text{A}_i)_{\text{des}} \,, \tag{7}$$

where O, n_i, and A_i denote the adsorbed organic substance, number of moles, and other solution components, and the subscripts des and ads refer to the desorbed and adsorbed states. The resulting energetic changes are the algebraic sum of the individual contributions

$$\Delta G_a = \Delta G_S + \Delta G_{\text{Hg-org}} - \Delta G_{\text{Hg-H}_2\text{O}} - \sum_i \Delta G_{\text{Hg-A}_i} \pm \Delta G' \tag{8}$$

similarly to the standard changes

$$\Delta\bar{G}_a^0 = \Delta\bar{G}_S^0 + \Delta\bar{G}_{\mathrm{Hg-org}}^0 - \Delta\bar{G}_{\mathrm{Hg-H_2O}}^0 - \sum_i \Delta\bar{G}_{\mathrm{Hg-A_i}}^0 \pm \Delta\bar{G}^{0\prime} . \qquad (9)$$

The dependence of Θ or Γ on c can approximately be described by an adsorption isotherm of the Frumkin type[10]

$$c \frac{\exp\left(-\Delta\bar{G}_a^0/RT\right)}{55 \cdot 5} = \frac{\Theta}{1 - \Theta} \exp\left(-2a\Theta\right) \qquad (10)$$

or

$$c\beta = \frac{\Theta}{1 - \Theta} \exp\left(-2a\Theta\right), \qquad (11)$$

and not by the simpler Langmuir isotherm, where $a = 0$ (compare[14]).

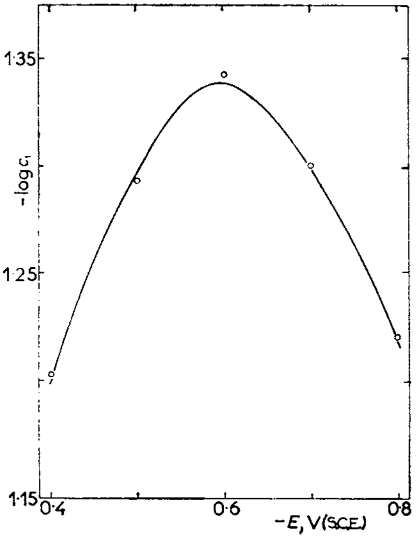

FIG. 6

Potential dependence of $\log c_1 = -\log \beta - \text{const.}$ (Eq. (6)) reflecting the potential dependence of the surface activity and the sensitivity of electrocapillary measurements

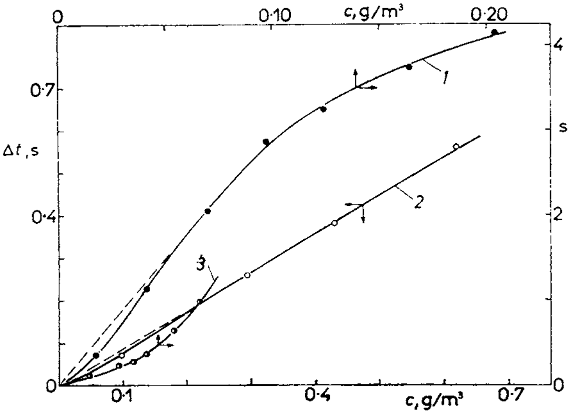

FIG. 7

Measured concentration dependences of the change of the drop time Δt. 1 Diesel oil in 0·1M-NaCl, $E = -400$ mV; 2 Saratov petroleum in 0·5M-NaCl, $E = -400$ mV; 3 petroleum standard in 0·5M NaCl, $E = -600$ mV (S.C.E.)

The character of the t–E dependences for petroleum and petroleum products of other sorts was similar to that of the Saratov petroleum. The curves corresponding to extracts of Alkyö (Hungary), Karatyubinskaya (U.S.S.R.), and Hodonín (Czechoslovakia) petroleums are shown in Fig. 8. The changes $\Delta\gamma$ were different although the petroleum concentrations were approximately the same, evidence for different surface activity (and detection limit) of the different extracts. This can also be seen from the course of the calibration curves (Fig. 7). A curve corresponding to a $5 \cdot 10^{-5}$ mol l^{-1} solution of DBS is shown in Fig. 8 for comparison.

Fig. 9 illustrates the potential-dependent interface activity of a 0·73 mg l^{-1} petroleum standard in 0·1M-KCl. As with the Saratov petroleum, the suppressed electrocapillary curve is asymmetrical, the maximum activity corresponding to −0·5 V. In addition to the equilibrium curve obtained during convective accumulation, also the nonequilibrium curve is shown, obtained with freely dropping electrode. In the region from −1·1 to −1·2 V, where both electrocapillary curves approach the curve of the base electrolyte, blunt tensametric desorption peaks were obtained by the DPP method. The detection limit of the electrocapillary method was about 0·05 mg .

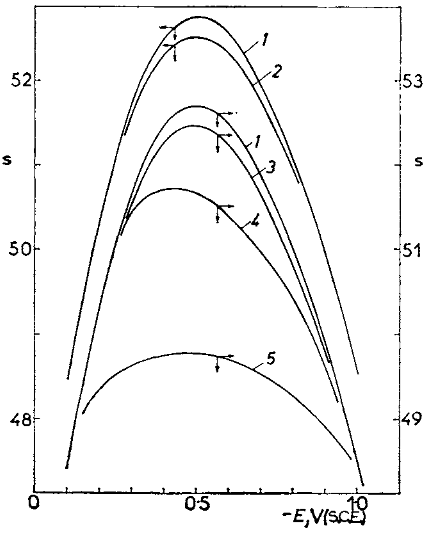

FIG. 8

Electrocapillary curves for 10 ml of 0·5M-NaCl before (curve 1) and after addition of 1 ml of a saturated petroleum solution; 2 Alkyö (Hungary); 3 Karatyubinskaya (U.S.S.R.); 4 Hodonín (Czechoslovakia); 5 comparative solution of $4 \cdot 5 \cdot 10^{-5}$ mol l^{-1} DBS

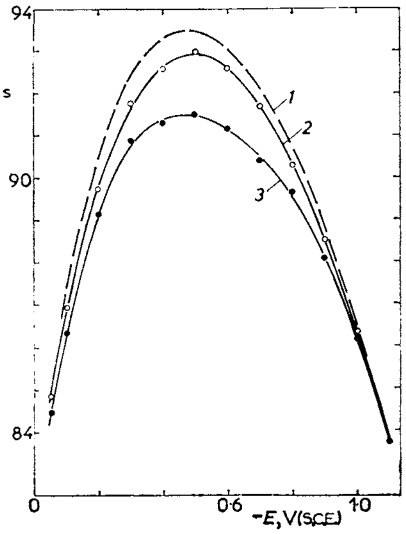

FIG. 9

Electrocapillary activity of a petroleum standard (0·22 g m^{-3}) in 0·1M-KCl. 1 base electrolyte; 2 after addition of petroleum, without convective adsorption accumulation; 3 t – E curve as 2 but with convective adsorption accumulation

$.l^{-1}$. A similar behaviour as with petroleum was observed with mixtures of naphthenic acids, which are present in various sorts of petroleum in concentrations 0·1 – 2%. The electrocapillary curves obtained in 0·5M-NaCl were in the region of the electrocapillary maximum nearly symmetrical with $E_{max} = -0{\cdot}55$ V.

It can be concluded that aqueous extracts of petroleum and its fractions were found to be rather strongly surface active at the mercury-solution interface, the surface activity depending on the quality of the substance. The electrocapillary behaviour corresponds to substances that are either neutral or cationic in character, the adsorption maximum being between –0·4 and –0·6 V (S.C.E.), where also the sensitivity of the analytical determination is highest (*e.g.* from the concentration dependence of the drop time). Close to the maximum, the adsorption behaviour corresponds approximately to the capacitor model of adsorption. Moderate deviations of the Δt–c dependence from linearity at lowest concentrations can be attributed to concurrent adsorption of trace impurities. The parameters of these curves depend on the quality of the surfactant. The detection limit is 10 – 20 μg/l with Diesel oil and up to five times higher with petroleum. The sensitivity of the measurement increases several times by using the convective adsorption accumulation on the growing mercury drop surface.

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