
POLAROGRAPHIC BEHAVIOUR OF PETROLEUM COMPONENTS IN AQUEOUS SOLUTIONS: A STUDY USING DPP AND CONVECTIVE ADSORPTION ACCUMULATION

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Tensametric behaviour of solutions of petroleum and its fractions in aqueous base electrolytes was studied by the differential pulse polarographic method (DPP) using a stationary mercury drop electrode with adsorptive accumulation. The results indicate that water pollution with petroleum can be determined by DPP, the sensitivity of the determination depending on the quality of the pollutant and on the composition of the base electrolyte. Well utilizable calibration curves were obtained with Diesel oil at concentrations from 30–50 $\mu\text{l/l}$ to 0.5 mg/l and with Saratov petroleum from 0.1–0.2 mg/l to 3.3 mg/l. Use of adsorptive accumulation led to a marked increase of the sensitivity of the analysis.

The published polarographic determinations of petroleum components in water are based on their surface properties. Gosman and Heyrovský¹ studied their influence on the polarographic maximum of copper. They distinguished various petroleum fractions, or petroleum of various origin, according to the sample dilution at which the maximum is suppressed to one half of its original height. A similar phenomenon was used later² in following the content of petroleum and its fractions in sea water. The attention was focussed on water-soluble substances obtained by shaking petroleum, heating oils, kerosene, and various fractions of aromatic and saturated hydrocarbons with water. To this end, the authors made use of the suppression of the polarographic maximum of mercury or of the change of charging current caused by adsorption of these substances on the dropping mercury electrode during switching over of the polarizing voltage by the Kalousek switch. The mentioned substances could be thus determined in concentrations ranging from 0.01 to 100 mg/l. The ability to suppress the polarographic maximum was found to be higher in the case of higher petroleum fractions. The concentration measurement was based on comparison of the effects found with the adsorption effect of Triton X-100, which served as standard, to the concentration of which the contents of the petroleum components were referred. Polarography with alternating current component^{3,4} (so-called a.c. polarography) was also used in following the tensametric peaks in waters accompanying petroleum in the oil fields. The authors⁵ were thus able to distinguish various geological formations in which oil is found. Adsorption of C_6 and higher fractions on the dropping mercury electrode was studied by the method of oscillographic polarography with alternating current⁶.

All the methods mentioned are based on nonselective measurements of changes of the interface activity of aqueous solutions, which may lead to difficulties in cases where a sample is to be analysed which contains more than one surface active substance. Nevertheless, the determination of the total content of surface active substances in water (*i.e.* its total interface activity) is extremely

important in view of their toxic influence on both lower and higher organisms living in fresh and sea waters. This is because the petroleum components dissolve in the cell membranes and may destroy them⁷.

The object of the present work is to study the behaviour of aqueous extracts of petroleum and its components by differential pulse polarography (DPP) using, if necessary, adsorptive accumulation of the petroleum components on the mercury electrode.

EXPERIMENTAL

Apparatus. A polarographic analyser of the type PA 3 (Laboratorní přístroje, Prague) was used in the DPP mode. The electrode was a static mercury drop electrode (S.M.D.E.) of the same producer, polarized by "fast scan" at 20 mV/s, pulse amplitude 50 mV, and time constant of the memory circuits 10 ms. The other electrode was a saturated calomel reference (S.C.E.), serving at the same time as counter-electrode.

Chemicals. Petroleum standards containing 0.73, 0.088, and 0.00585 mg/l were obtained from the Central Geological Institute, Prague*. Other petroleum samples were furnished by the Department of Fuels and Water, Prague Institute of Chemical Technology, Prague*, similarly as the sample containing a mixture of naphthenic acids (acidity number 157 mg KOH per gram). Sodium salt of dodecylbenzenesulphonic acid (DBS) was product of Schuchard, Munich; other chemicals were products of Lachema, Brno, and were of reagent grade. Solutions were prepared from redistilled water.

Preparation of water samples containing petroleum components. 5 g petroleum or petroleum product was shaken vigorously for 1 h with 100 ml of distilled water. The water extract was used in the experimental work after two days, when no opalescence was observable. The relative proportion of the petroleum components in the water extract did not correspond to the composition of the petroleum used. (The solubility of petroleum in water is about 20 mg/l⁸.) Some petroleum solutions were prepared from artificial sea water (0.6M NaCl, 0.001M KBr, and 0.003M NaHCO₃). Saturated petroleum solutions can also be obtained by contacting petroleum with water for a longer time than two days.

Method of measurement. For recording tensametric curves, 0.1 to 1.0 ml of the sample was pipetted into the polarographic cell with a supporting electrolyte and the solution was deaerated. The hanging mercury drop electrode was then formed and a DPP curve was recorded from positive to negative potentials, or the electrode was polarized to a potential at which adsorptive accumulation proceeded⁹⁻¹¹ and the DPP tensametric curve was recorded afterwards. The adsorptive accumulation was carried out either in quiet or in stirred solution⁹⁻¹².

RESULTS AND DISCUSSION

Tensametric Measurements

All sorts of petroleum and petroleum products (raw petroleum, motor oil, kerosene, lubricants) and distillation fractions with boiling point above 373 K gave blunt

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tensametric desorption peaks in the potential region from -1.2 to -1.3 V (S.C.E.) in 0.1 – 1.0 molar supporting electrolytes. The peaks were time-independent, reproducible, and were somewhat shifted to more negative potentials with increasing concentration of the surfactants. A typical example is the tensametric behaviour of Saratov petroleum in 1M NaOH (Fig. 1). In the medium of 5 – 7M KF (Fig. 2), the peaks were shifted to -1.4 to -1.5 V (S.C.E.). The peaks were higher in the more concentrated supporting electrolyte, but the measurement of their height was more difficult since the blank curve (without petroleum) was strongly nonlinear. Besides the peaks mentioned, sharp, needle-like peaks were obtained at potentials -0.6 , -0.75 , and -1.0 V (Fig. 3), especially with lower distillation fractions of petroleum. Their form and heights were time-dependent and they disappeared when the lower petroleum fractions were removed from the solution, *e.g.* by bubbling with an inert gas or by allowing the solution to stand open to the air for several hours. A similar needle-like peak was observed in 1M NaOH in the presence of benzene (at -0.8 V), toluene (-0.75 V), xylene (-0.95 V), or mesitylene (-1.0 V).

Blunt desorption peaks, as in the case of water extracts of petroleum, were also obtained with biphenyl (at -1.0 V), cyclohexane (-1.0 V), and decaline (-1.2 V)

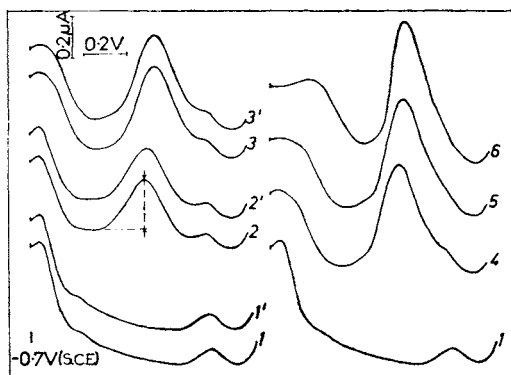


FIG. 1

DPP curves for solutions of Saratov petroleum in 1M NaOH at concentration c (mg/l): 1, 1' 0; 2, 2' 1.8; 3, 3' 3.3; 4 4.6; 5 5.7; 6 7.5. Fast scan 20 mV/s , potential pulse 50 mV . Convective adsorption accumulation (c.a.a.) at 0.7 V (S.C.E.) for 120 s , S.M.D.E. in the H.M.D.E. (hanging Hg drop electrode) mode

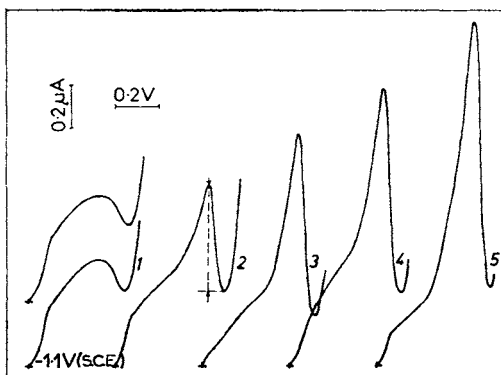


FIG. 2

DPP curves for Saratov petroleum in 7M KF at concentration c (mg/l): 1 0; 2 0.95; 3 1.82; 4 2.61; 5 3.33. H.M.D.E., fast scan 20 mV/s , potential pulse 50 mV ; c.a.a. for 200 s at -1.1 V

which were, however, very little soluble in water. Similar desorption peaks at -1.2 V were obtained with polar, at least little soluble compounds, *e.g.* higher fatty acids (oleic, stearic, and palmitic acid) and naphthenic acids. DBS gave similar peaks at -1.1 V under the same conditions. More surface active petroleum fractions, *e.g.* Diesel oil (Fig. 4) gave high and narrow symmetrical peaks at concentrations 0.3 mg/l and lower.

Most of the DPP curves were recorded after adsorptive accumulation at constant potential. At higher surfactant concentrations, *e.g.* after addition of more than 3 ml of aqueous extract of Saratov petroleum into 10 ml of 1M NaOH (Fig. 1), the curves with and without preceding accumulation were identical.

Desorption tensametric peaks were usually more negative than -1.1 V. Sharp, needle-like peaks at more positive potentials were probably due to desorption of lower petroleum fractions or to sudden changes of the interface behaviour of the surfactants, such as reorientation of their molecules, mutual attraction or repulsion *etc.* (provided that no electrode reaction took place).

Fig. 5 shows the position of a sharp desorption DPP peak at potential E_p in comparison with the dependence of the drop time, t , on the applied potential^{12,13}, E , in the presence and in the absence of a lower petroleum fraction (boiling point in the range $105-130^\circ\text{C}$). It can be seen that the appearance of the peak at $E_p = -0.76$ V is accompanied by disappearance of the surface activity, *i.e.* desorption

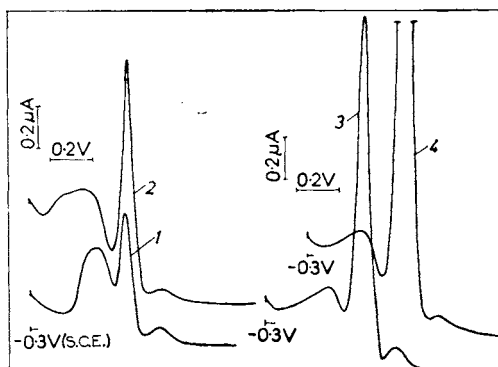


FIG. 3

Sharp DPP peaks of petroleum fractions boiling at $378-403$ K (curves 1, 2) and $403-423$ K (curves 3, 4) in 1M NaOH. 1, 3 0.25 mg/l; 2, 4 0.48 mg/l. H.M.D.E., fast scan 20 mV/s, pulse 50 mV. 1, 2 immediately after formation of the H.M.D.E.; 3, 4 *c.a.a.* at -0.3 V for 120 s

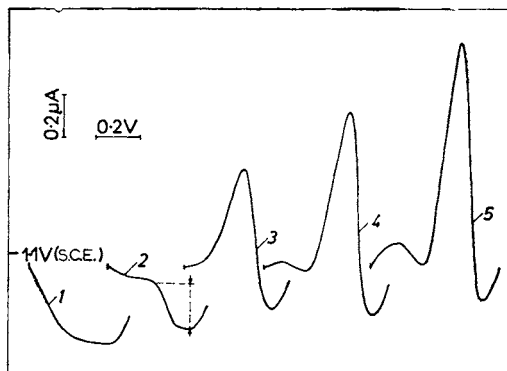


FIG. 4

Tensametric DPP peaks of Diesel oil in 5M KF; c (mg/l): 1 0; 2 0.07 ; 3 0.20 ; 4 0.33 ; 5 0.46 . H.M.D.E., fast scan 20 mV/s, pulse 50 mV, *c.a.a.* on open circuit for 120 s

of the petroleum components. The measured changes of the current can in all cases be expressed as

$$\Delta i \sim \frac{\partial q}{\partial t} \sim \Delta C, \quad (1)$$

where Δi is the peak height, q charge density on the electrode surface, and ΔC change of the differential capacity of the electrode.

Data about the position and shape of the peaks corresponding to various petroleum fractions are summarized in Table I. The potentials of the desorption peaks became more negative with increasing concentration. The values of the shift of the peak potentials, ΔE_p , with respect to the potentials of maximum adsorption are given in Table II. In the case of Saratov petroleum in 1M NaOH and in 7M KF, the following equations are valid, respectively¹⁴:

$$(\Delta E_p)^2 = 0.0851 \ln x + 0.599, \quad (2)$$

$$(\Delta E_p)^2 = 0.0173 \ln x + 1.225, \quad (3)$$

where x denotes volume fraction of petroleum in aqueous solution.

The height of the desorption peak depends on the concentration of the sample, composition of the supporting electrolyte, and on the parameters of the apparatus,

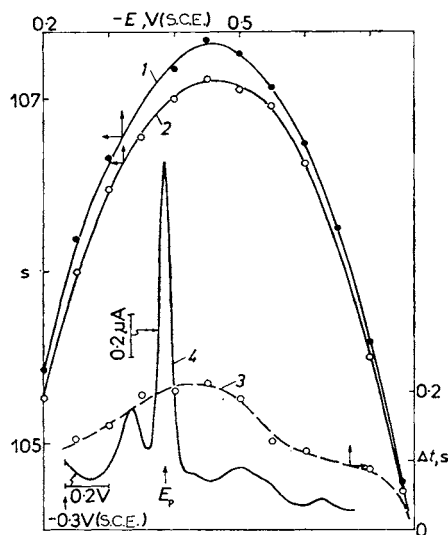


FIG. 5

Dependence of the drop time t (curves 1, 2) and its change Δt (3) on potential E in 0.1M NaOH in the absence (1) and in the presence (2, 3) of petroleum fraction boiling at 378–403 K; 4 corresponding DPP curve. 2, 3 $c = 0.74$ mg/l, c.a.a. for 95 s; 4 $c = 0.25$ mg/l, H.M.D.E., fast scan 20 mV/s, pulse 50 mV, c.a.a. at -0.3 V for 120 s

and it attains a limiting value with increasing concentration (Fig. 6). The concentration dependence is more or less linear, *e.g.*, in the region from 5 to 50% saturation with Karatyubinskaya (U.S.S.R.) and Alkyö (Hungary) petroleum, or in the range from 1 to 10% saturation with Hodonín (Czechoslovakia) and Saratov (U.S.S.R.) petroleum, or from 0.25 to 10% saturation with Diesel oil. In a broader concentration range, the peak height satisfies the semiempirical equation

$$\Delta i = \frac{k_1(c - c_0)}{1 + k_2(c - c_0)}, \quad (4)$$

where the concentration c can be expressed in mg/l or other units and the value of c_0

TABLE I

Characteristics of DPP tensametric peaks for petroleum fractions in supporting electrolyte solutions

B.p. range K	E_p, V				Equivalent conc. of DBS, mg/l
	sharp peaks -0.65	-0.75	-1.0	blunt p. -1.2	
up to 343	+	0	0	0	—
343—363	+	+	0	0	—
363—378	+	+	+	0	—
378—403	+	+	+	+	0.8
403—423	+	+	+	+	4.0
423—573	+	+	+	+	40

TABLE II

Dependence of peak potential E_p on $\ln x$ in 1M NaOH and 7M KF, where x denotes volume fraction of Saratov petroleum in the supporting electrolyte solution

$-E_p, V$	$\Delta E_p, V$	$\ln x$	$-E_p, V$	$\Delta E_p, V$	$\ln x$
1.230	0.630	-2.398	1.530	1.080	-3.434
1.270	0.670	-1.792	1.534	1.084	-2.773
1.287	0.687	-1.466	1.538	1.088	-2.398
1.303	0.703	-1.253	1.543	1.090	-2.140
1.315	0.714	-1.097			

depends on the method of measurement of the peak height. Equation (4) can be linearized in the form

$$\frac{c - c_0}{\Delta i} = \frac{1}{k_1} + \frac{k_2}{k_1}(c - c_0). \quad (5)$$

This is in good agreement with the experimental data (Fig. 7). The values of the constants were determined as follows.

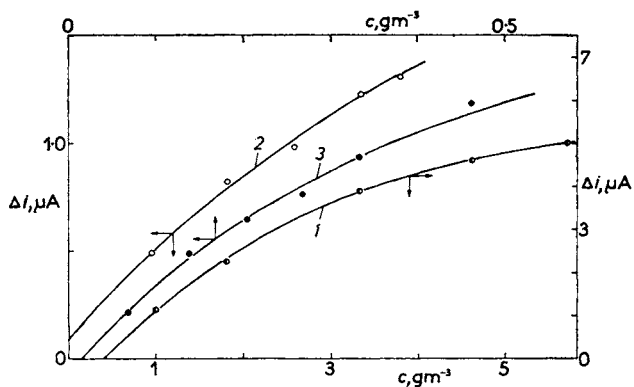


FIG. 6

Concentration dependence of the peak height for Saratov petroleum in 1 M NaOH (1) and 7 M KF (2) and for Diesel oil in 5 M KF (3). Peak heights measured according to Figs 1, 2, and 4

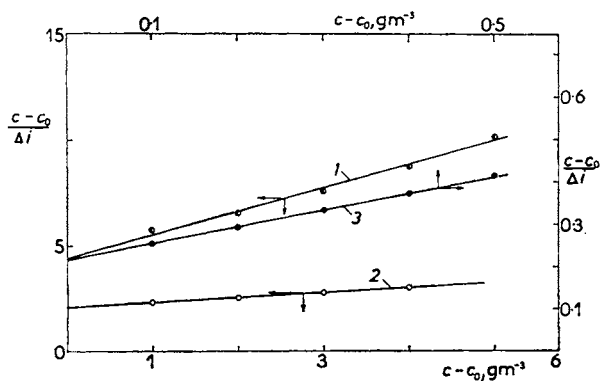


FIG. 7

Linearized concentration dependence of the peak height for Saratov petroleum in 1 M NaOH (1) and 7 M KF (2) and for Diesel oil in 5 M KF (3). See Eq. (5) for c_0

Composition of solution	k_1 $\text{g}^{-1} \text{m}^3 \mu\text{A}$	k_2 $\text{g}^{-1} \text{m}^3$	c_0 g m^{-3}
Saratov petrol. in 1M-NaOH	0.227	0.252	0.4
Saratov petrol. in 7M-KF	0.488	0.116	0.015
Diesel oil in 5M-KF	4.608	1.558	-0.2

In this way, it was not possible to determine the total concentration or the sort of the surfactant present in solution. However, a comparison of the tensametric peak with that of DBS of known concentration permits to evaluate the interface activity. The equivalent concentration of DBS (Table I) thus obtained is higher by a factor of 1.25 than the analogous value referred to a standard solution of Triton X-100, used by Yugoslav authors². The peak of DBS was analogous in form to that of the petroleum components and its concentration dependence was linear in the range from $1 \cdot 10^{-6}$ to $8 \cdot 10^{-6}$ mol/l.

It can be concluded that differential pulse polarography can be used in the determination of the contamination of water with petroleum with a sensitivity depending on the quality of the impurity and on the composition of the supporting electrolyte. Well utilizable calibration curves can be obtained, e.g., with Diesel oil in the range 30–50 mg/l and with Saratov petroleum in the range 0.1–0.2 mg/l. The sensitivity of the determination is increased by the use of the method of adsorptive accumulation.

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