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# APPARATUS FOR MEASURING THE POTENTIAL OF ZERO CHARGE AND FOR AUTOMATIC RECORDING THE CHARGE DENSITY AND DIFFERENTIAL CAPACITANCE CURVES OF MERCURY ELECTRODES BY THE VIBRATING INTERFACE METHOD

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The set comprises a glass vessel, an automatic voltage stabilizer, a system for analyzing and recording the output short-circuit current, an added signal system making it possible to record charge density curves (taking into account the sign), an optical system, and a system for stimulating the interface vibrations in the capillary. Typical experimental results for 0.1M aqueous NaCl and 0.1M-KPF<sub>6</sub> in acetone are given.

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The vibrating interface method is based on the phenomenon of generating an electrical signal by a mercury-electrolyte solution interface vibrating in a glass capillary. This method was proposed by Koczorowski and coworkers<sup>1</sup> and by Ueda and Urano<sup>2</sup> for determining the potential of zero charge. The authors' proposal was the consequence of the fact described in the work<sup>3</sup> that an output signal disappeared at the potential of zero charge. In the systems presented here-to<sup>1,2</sup> advantage was taken of the deformational movement of interface consisting in modifying the meniscus shape<sup>4</sup>. Similar measuring systems were also used by Minc and Brzostawska<sup>5</sup> and by Gerasimenko and coworkers<sup>6</sup>.

We extended the method applications on the measurements of charge density at the mercury — electrolyte solution interface<sup>4</sup>. The authors took advantage of the piston-like movement of the capillary filling consisting in „unfolding” the mercury meniscus without modifying its shape. The short-circuit current was used as the output signal; as it results from the theory of electrocapillary elements<sup>7,8</sup>, in conditions where the solution resistance can be neglected, its amplitude is expressed by the formula:

$$I_{sh} = 2\pi^2 \phi q f \delta, \quad (1)$$

where  $\phi$  denotes the capillary diameter,  $q$  the charge density at the interface,  $f$  the vibration frequency, and  $\delta$  the displacement amplitude of the mercury slug with respect to the capillary surface covered by a layer of liquid.

The advantages of the vibrating interface method demonstrated in the work<sup>4</sup> (a high accuracy of potential of zero charge measurement — better than 1 mV — and a good agreement of the results of charge density with the values obtained by other methods) encouraged us to develop it further. It is the aim of this work

to present an apparatus for automatic recording the charge density and the differential capacitance by this method.

The vibrating interface method based on the dependence<sup>1</sup> ( $I$ ) can also be used for determining the charge density in conditions of imperfect polarizability of the studied electrode. As it results from the theory of equivalent circuit of electrocapillary transducers<sup>7</sup>, a low resistance value compared with the electrochemical impedance of vibrating electrode is the condition of obtaining correct results.

## RESULTS

### Block Diagram

The block diagram of the measuring system for the vibrating interface method is presented in Fig. 1. The system comprises: 1) a measuring vessel; 2) a system for stimulating interface vibrations in the capillary; 3) an optical system for measuring the vibration amplitude of filling (not shown in Fig. 1); 4) a system for polarizing the interface with a constant voltage; 5) a system for measuring and analysis of the

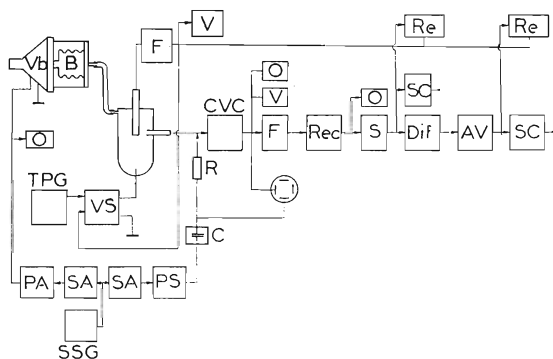


FIG. 1

Block diagram of the apparatus for studies by the vibrating interface method. Vb — vibrator; B — bellows; F — follower; F<sub>i</sub> — filter; V — voltmeter; Re — recorder; CVC — current-voltage converter; Rec — rectifier; S — smoothing; Dif — differentiation; TPG — triangular pulse generator; VS — voltage stabilizer; AV — absolute value; SC — sign change; PA — power amplifier; SA — signal amplifier; PS — phase shift; SSG — sinusoidal signal generator

output current of vibrating interface; it constitutes the main measuring line in the system; 6) an added signal system comprising a phase shift.

The system for stimulating interface vibrations comprises a sinusoidal signal generator, a signal amplifier, a power amplifier, a vibrator, a metal bellows and a control oscilloscope. The amplitude of interface vibrations was measured with a microscope enlarging 25 times. A scale with 0.05 spacings was installed in its ocular. The capillary has been illuminated with a microscope lamp.

The system for polarizing the interface with a constant voltage consists of a voltage stabilizer operating in a feed-back with a voltage follower<sup>9</sup>. The vibrating electrode has the potential of casing because it is connected with the input of the current-voltage converter. The voltage stabilizer is controlled by a triangular pulse generator which makes it possible to vary the potential smoothly. The extremum voltage values and the polarization variation rate are controlled independently. In addition, a system of manual polarization control is installed in the voltage stabilizer; it is necessary for an accurate potential of zero charge determination. A digital millivoltmeter is connected with the follower output for the readout of potential of zero charge.

The main measuring line of the system is the circuit for measuring and analyzing the output short-circuit current of the vibrating interface. The vibrating electrode is connected with the input of the current-voltage converter; it assures that the short-circuit condition is fulfilled since the input resistance of the converter is very low, at most several ohm. A control oscilloscope and a selective nanovoltmeter serving for the potential of zero charge measurements are connected with the output of converter. The use of the nanovoltmeter makes it possible to carry out point-by-point measurements and the oscilloscope made it possible to monitor the input signal and to detect possible perturbations or noises. The voltage signal from the converter output is passed through a filter and is fed to a full-period rectifier. It is a linear rectifier comprising rectifying diodes working in the feed-back of an operational amplifier; its voltage characteristic is linear from a voltage equal practically zero. The rectified signal is smoothed and fed to the Y axis of the recorder. The polarization potential of the vibrating electrode is fed through a follower to the X axis of the recorder. The sign change circuit is connected at the output of the output of the smoothing system; it makes it possible to choose the direction of charge density curve recording.

The above presented fragment of the main measuring line makes it possible to record the absolute value of charge as a function of vibrating electrode potential. The output current vanishes as the potential of zero charge is approached and then increases again, but with the opposite phase. This phenomenon is shown in Fig. 2.

If one wants to obtain a charge density curve taking into account the change of sign, one should add a signal of the same frequency as that of alternating signal of vibrating electrode and with the same or opposite phase. In the system described here such a signal is added as a current at the input of the current-voltage converter.

At the potential of zero charge no signal is generated by the vibrating electrode and, therefore, a voltage signal corresponding to the added signal only appears at the output of the converter. In such a case a constant voltage originating from the added signal appears at the output of the smoothing circuit; it corresponds to the absence of a vibrating electrode signal, *i.e.* to the zero charge density. At a potential differing from the potential of zero charge the added signal superposes with the vibrating electrode signal having a given sign; on the opposite side of the potential of zero charge the sign of the vibrating electrode signal is opposite due to phase reversal upon crossing the potential of zero charge. It is necessary to attain a phase agreement of the added signal and of the vibrating electrode signal since the both signals sum up arithmetically in such conditions only.

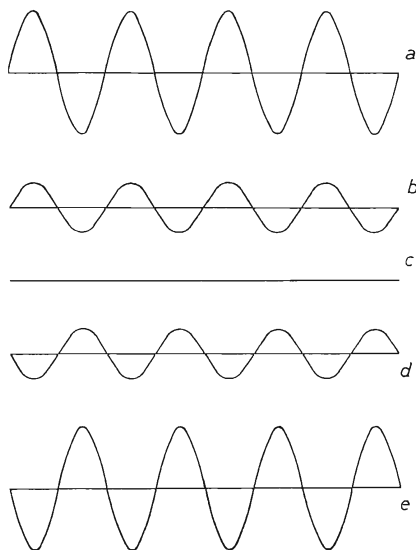


FIG. 2

Sign change of the short-circuit current on passing through the potential of zero charge  $a E - E_2 = 100$  mV,  $b 50$  mV,  $c 0$ ,  $d -50$  mV,  $e -100$  mV

The source of added signal in the measuring system is the generator of sinusoidal signal which controls the system for stimulating the interface vibration. It assures that the frequencies of the added signal and of the interface vibration are exactly the same. The generator signal is fed to a signal amplifier having a controlled amplification value and then to a phase shift. It is necessary to control the added signal phase since the elements of the system for stimulating vibrations (*e.g.* the vibrator, the pneumatic elements) provoke a phase shift of the signal. The output signal of the phase shift is fed to an impedance comprising a resistance connected with the input of the converter and a capacitor, both connected in series. In this way the added signal is fed into the converter input as a current. It is advisable to have a possibility to switch in a capacitor to the added signal circuit because the range of phase shift is from  $0^\circ$  to almost  $180^\circ$  and from  $180^\circ$  to almost  $360^\circ$ ; the remaining ranges are not covered by it. Therefore, switching in a capacitor renders it possible to carry out the phase corrections in the range of full angle. A desired value of added signal fed into the converter can be set by means of the amplification control of the amplifier and by varying the resistance  $R$  (Fig. 1).

Agreement of the signal phases is observed by means of the oscilloscope: the added signal and the sum of the two signals are fed to the  $X$  and  $Y$  amplifiers of the oscilloscope, respectively. Generally, an ellipse is observed on the oscilloscope screen; a straight line is observed when the phases are identic or opposite.

The phase agreement evaluation based on the maximum and minimum values of the summed signal proved to be insufficiently sensitive. The added signal fed to the oscilloscope amplifier is taken from the resistor  $R$  (Fig. 1) and the summed signal from the converter output. The vibrating electrode signal cannot be used directly for estimating the phase agreement because of its current character.

In order to assure phase agreement of the vibrating electrode signal and of the added signal the phase of interface vibration should be made independent of the mercury-electrolyte solution interfacial tension. It has been attained by a suitable construction of measuring vessel. The problem will be discussed later.

Differentiating the charge density curve obtained as above with respect to potential yields the differential capacitance curve,  $C_{d1}$ . Differentiation operation can be done with respect to time if the potential variation rate  $dE/dt$  is constant. It results from the following transformations

$$\frac{dq}{dt} = \frac{dq}{dt} \frac{dE}{dE} = \frac{dE}{dt} \frac{dq}{dE} = \frac{dE}{dt} C_{d1} . \quad (2)$$

Stability of  $dE/dt$  in the system is assured by including a voltage stabilizer and a triangular signal generator.

The signal from the smoothing circuit is fed to the differentiating system input. The signal derivative is fed to the input of a linear full-period rectifier yielding on its

output the absolute value of the signal fed to its input. The rectifier is used in the system because a reversal of the  $dE/dt$  sign is accompanied by sign reversal of the  $dq/dt$  derivative as it results from the relationship (2). Therefore, a signal corresponding to the differential capacitance with opposite sign would appear when the negative slope of triangular signal is generated. The linear full-period rectifier removes this inconvenience. The rectified signal is fed to the recorder Y amplifier. The polarization potential of vibrating electrode is fed through a follower on the recorder X axis. A sign change system is connected with the rectifier enabling one to choose the direction of differential capacitance curve recording.

The use of two XY recorders or of a two-channel  $XY_1Y_2$  recorder and of the above described apparatus makes it possible to record the charge density curve and the differential capacitance curve at the same time as functions of polarization.

The elements of the system are mostly made using the technique of integrated operational amplifiers<sup>10-13</sup>; only the power amplifier which drives the vibrator, the feeder of that amplifier and the feeder for operational amplifiers are based on transistors; a 10 W electrodynamical loudspeaker was used as vibrator.  $\mu A$  709 or  $\mu A$  741 integrated operational amplifiers were mostly used; amplifiers of very low input current are needed for some elements as the voltage follower and the differentiating system. Suitable amplifiers are *e.g.* of the  $\mu A$  740 type or  $\mu A$  108 type. It is advisable to use a very high amplification rate amplifiers (*e.g.*  $\mu A$  740 or  $\mu A$  108) in the current-voltage converter in order to assure a low input resistance even if a high resistance is connected in the feed-back.

### Measuring Vessel

The measuring vessel used in the system is an improved modification of the vessel described in<sup>4</sup>. The funnel-shaped connection of the capillary with the reservoir used there has been removed. In this way the interface can be placed just at the capillary end in order to lower the solution resistance.

The measuring vessel is presented in Fig. 3. The reservoir 13 is equipped with the ground glass joints 3, 6 and 7 serving for passing nitrogen or argon 10, for placing the reference electrode 20 and for applying a variable overpressure, respectively. The ground joint 2 facilitates washing and assembling the vessel. The stopcock 1 serves for closing the vessel tightly after the solution is deaerated by bubbling nitrogen or argon. It is necessary to close the vessel tightly in order to create a necessary overpressure during the measurement. The reference electrode tube is closed with cotton wool, paper or a glass sinter 11. Penetration of the reference electrode solution to the studied solution is prevented by an additional tube 8 ending with a glass sinter 12. The additional ground glass joint 4 facilitates assembling and washing the vessel. When the vessel is full, volume between the tubes 8 and 9 is filled with the studied solution. A platinum contact is fixed at the vessel bottom.

The reservoir is equipped with a side tube having a ground joint at its end, where the vibrating electrode construction is located. The mercury-electrolyte solution interface vibrates within the capillary 15. As the vibration amplitude is measured optically, the capillary end is placed in the tube fragment unaffected by fastening.

The phase of interface movement has been made independent of the interfacial tension by making the pneumatic stiffness dominate owing to a controlled small air volume left in the mercury

vessel 17. In some cases, particularly when large amplitudes of vibrating interface movement are needed, more gas is left in the mercury vessel 17 and the constant phase is then maintained by applying a high damping. It is done by shaping the capillary on the mercury vessel side into one or several narrowings (not shown in the Fig. 3). The movement of capillary filling can also be damped by inserting a platinum wire or a thin glass rod into it. However, this method of assuring a constant phase has an inconvenience: the mercury column disrupts readily if solution penetrates to the damping element (a narrowing, a rod or a wire) and it is very difficult to remove the solution occupying the entire capillary intersection.

The position of interface within the capillary is controlled by means of a threaded iron piston sticking in the capillary 18. The piston 19 serves also for removal of the vibrating electrode surface by squeezing out a drop of mercury.

The hanging electrode construction described by Kemula and Kublik<sup>14,15</sup> and later improved by Kublik<sup>16</sup> was used unmodified for obtaining a vibrating electrode in a stable and precisely determined position. The use of hanging electrode as a vibrating electrode presents a number of advantages: its construction is simple and its dismantling, washing and assembling again is simple and takes little time. It is particularly important when it is used as a vibrating electrode as it must be washed each time before replacing the solution because the solution penetrates into the capillary. In addition, the Kemula and Kublik construction assures purity of mercury during the measurement.

The electrode is filled with mercury either by pouring it into the vessel before assembling the electrode or by applying vacuum after assembling to remove air as described by Kemula<sup>17</sup>. A small amount of gas (5–20 Torr) was left during the vacuum filling to render the mercury column movement in the capillary possible.

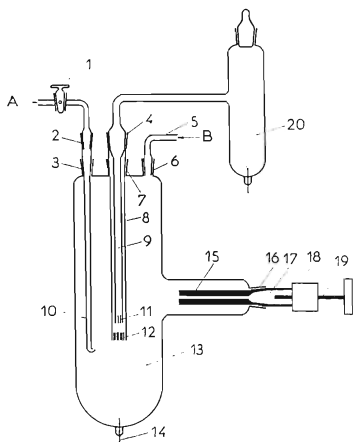


FIG. 3

Measuring vessel; description in text. A — Argon in; B — to bellows

The described measuring vessel does not present difficulties observed in the constructions described in<sup>1,4</sup>. The interface position is stable, there is no "floating" of its mean position. It makes it possible to shift the interface closely to the capillary end; it can even vibrate in such a way that it protrudes from the capillary in its extremum position.

#### *Remarks Concerning the Measurement*

After filling the vessel the solution is deaerated by passing nitrogen or argon saturated with the vapour of studied solvent. After passing through the solution nitrogen or argon was removed through the hose serving for applying variable overpressure during the measurement. A stopcock (not shown in the Figure) connecting the bellows with the atmosphere is installed to this aim near the bellows. Vibrator is switched in during last minutes of purging to remove air from the bellows, too. The stopcock is closed after the purging.

The amplitude of interface vibration is measured as the distance between the limiting positions; it is set in the 0.05–0.4 mm range. It is difficult to measure such displacements with the optical system used, but determining the amplitudes of vibration given by the distances separating two marks, e.g. 0.1 mm, presents no difficulty.

The vibrating interface is situated as close as possible to the capillary end. An optimum outer meniscus position (closer to the capillary end) is at 0.05–0.1 mm from the capillary end. If the resistivity of solution is high the outer meniscus position can be outside the capillary. If one suspects that the solution resistance is so high that it makes the short-circuit of impedance impossible, one should check if the output current is independent of the interface – capillary end distance down to the situation where the meniscus protrudes outside; particularly in diluted and non-aqueous solutions).

Optimum frequencies range from several to about 30 Hz. Frequency should be chosen in such a way that the extremum meniscus positions be clearly visible; it depends to a degree on the observer. It should be remarked that low frequencies are advantageous for high resistivity solutions as the electrode impedance increases in such cases, but the measurements can be made faster at higher frequencies since a lower time constant of the smoothing system is then needed to smooth the rectified sinusoidal signal and, consequently, the polarization potential can be varied at a higher rate.

Range settings of the individual components of the measuring system should guarantee that the saturation state of operational amplifiers is not attained. In the case of amplifiers used here their output voltage cannot exceed 10–12 V.

Time constants of the smoothing system and of the differentiating system should be chosen so as to avoid too strong vibrations of the recorder pen and so that the records at positive and negative polarization potentials superpose. These two contra-



dictory requirements can be met if sufficiently small  $dE/dt$  values are used depending on frequency. A good smoothing is particularly important when the differential capacitance curve is recorded for otherwise the signal vibrations are differentiated and a strongly vibrating signal results at the output of the differentiating system. Therefore, small  $dE/dt$  values are necessary for recording a differential capacitance curve.

The phase agreement of the vibrating electrode and of the added signal should be controlled during the entire measurement because small changes in the vibrating electrode phase can sometimes be observed, particularly at strong cathodic potentials. They can be corrected if the potential variation is slow and the phase shift is small, because the phase shifts is immediately observable on the oscilloscope whereas the change in the recorded signal is delayed depending on the time constant of the smoothing system and, in the case where the differential capacitance curve is recorded, on the time constant of the differentiating system.

The formulas to be used in practice for setting the recorder ranges result from the fundamental relationship (1) taking into account amplifications of the individual components of the system. The formula (1) can be expressed as follows for the output current peak value,  $I_{sh}^{max}$ , of the vibrating electrode

$$I_{sh}^{max} = \pi^2 \phi f \delta_0 q, \quad (3)$$

where  $\delta_0$  denotes the distance between the extremum meniscus positions.

Taking into consideration the amplification of current-voltage converter determined by the resistance  $R_c$  in its feed-back and the amplification of the smoothing system for rectified sinusoidal signal which is equal to  $2/\pi$  one obtains the formula for the output voltage of the smoothing system

$$U = 2\pi\phi f \delta_0 R_c q. \quad (4)$$

Differentiation of this relationship with respect to time and taking into consideration the amplification of the differentiating system and the formula (2) result in a formula for voltage at the absolute value system located after the differentiating system

$$|U_{diff}| = 2\pi\phi f \delta_0 R_c C_1 R_2 \frac{dE}{dt} C_{d1}, \quad (5)$$

where  $C_1$  and  $R_2$  are the input capacitance and the feed-back resistance of the differentiating system.

If the magnitude occurring in the formulas (4) and (5) are for example:  $\phi = 0.4$  mm,  $f = 15$  Hz,  $\delta_0 = 0.1$  mm,  $R_c = 1$  M $\Omega$ ,  $C_1 R_2 = 10^3$  s,  $dE/dt = 2$  mV/s, then the

formulas assume the forms:

$$U \text{ [mV]} = 37.7q \text{ [\mu C/cm}^2\text{]} \quad (6)$$

$$U_{dif} \text{ [mV]} = 75 \cdot 4C_{d1} \text{ [\mu F/cm}^2\text{]}. \quad (7)$$

Accurate potential of zero charge measurements can be obtained by manual smooth variation of polarization potential after disconnecting the triangular pulse generator and the added signal source. The vibrating electrode potential is set in such a way that the noise only be seen on the oscilloscope screen. Sensitivity can be increased by switching in a selective amplifier between the converter and the oscilloscope.

### Checkout of the System

Agreement of the experimental results obtained with the system with the literature data was checked by measuring the potential of zero charge values and recording the charge density and differential capacitance curves of mercury electrodes in various solvents<sup>18</sup>. The examined solvents differed by such properties as dielectric constant

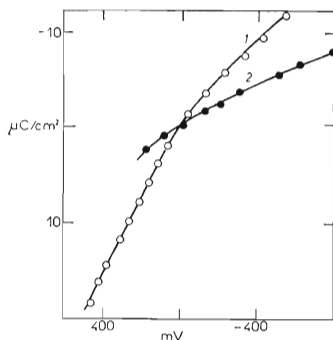


FIG. 4  
Potential dependence of charge density.  
1 0.1 mol/l aqueous NaCl; 2 0.1 mol/l  $KPF_6$   
in acetone

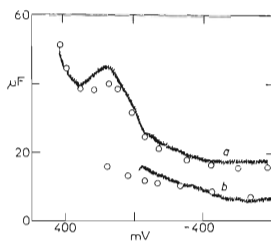


FIG. 5  
Differential capacitance curves. a 0.1 mol/l  
aqueous NaCl; b 0.1 mol/l  $KPF_6$  in acetone

or viscosity: water, formamide, dimethylformamide, propylene carbonate, acetone, glycerol, and water-dioxane mixtures. Detailed results are being elaborated and will be published later.

Typical plots of charge density and differential capacitance *vs* potential for a 0.1M-aqueous NaCl and for 0.1M-KPF<sub>6</sub> in acetone are presented in Figs 4 and 5. The potential values are given with respect to the potential of zero charge. The curves in Figs 4 and 5 have been recorded with the system and the literature values are represented by points. The literature data have been taken from the work<sup>19</sup> for the aqueous solution and from<sup>20</sup> for the acetone solution. The  $-464 \pm 0.5$  mV potential of zero charge with respect to an S.C.E. agrees well with the literature value of  $-465$  mV (ref.<sup>19</sup>). The potential of zero charge value of  $-210$  mV with respect to an S.C.E. has been obtained for 0.1M-KPF<sub>6</sub> solution in acetone; it has not been corrected for the diffusion and liquid potentials. The literature value for the same solution is  $-190$  mV (ref.<sup>21</sup>).

A comparison of experimental results obtained with the system with the literature data leads to the conclusion that the potential of zero charge values and charge density values given by the apparatus are correct. The differential capacitance values are less correct; the differences are particularly large at positive potentials.

Good wettability of glass by the studied solution is a condition for obtaining good results with the vibrating interface method. The values obtained using silicone-covered capillaries have been too low because the mercury column "glided" along the capillary surface.

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