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Electrocapillary elements. II.
The choice of electrolyte composition for acceleration meters

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The choice of electrolyte composition for electrocapillary acceleration meters is discussed and the conclusions checked experimentally. An aqueous solution (1.1 M Na_2SO_4 + 0.1 M H_2SO_4) is proposed for filling the acceleration meters.

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1. Introduction

An important application of electrocapillary transducers is as sensing devices for measuring the acceleration amplitude of a vibrational movement [1–4]. In the range below the resonance frequency the frequency characteristics of electrocapillary acceleration meters have a plateau which is typical for other acceleration meters too, e.g. for capacitor or piezoelectric designs [5].

Examination of over twenty electrocapillary transducers filled with a liquid solution revealed that only few of them had the appropriate characteristics. In addition, their sensitivities were markedly different; some of them were several times more sensitive than others [6]. These complications were due to the omission of an essential factor determining the properties of electrocapillary elements and particularly the shape and reproducibility of their characteristics, namely the electrolyte composition.

This problem has not hitherto been discussed in the fundamental papers on electrocapillary elements [7–11]. Attention was paid only to the conductivity of the solution and the effect of the solution on the properties of the mercury electrodes formed at the mercury–electrolyte solution interface was neglected.

It is often necessary to use a liquid solution in electrocapillary transducers although such elements are less resistant against mechanical shocks than the gelled solution transducers [12]. Using liquid solutions makes it possible to obtain low resonance frequencies (below 100 Hz). Liquid solutions are necessary in some applications of electrocapillary transducers, e.g. in manometers which will be discussed in Part III of this series.

An analysis of the role of electrolyte and of the influence of its composition on the properties of electrocapillary acceleration meters is the subject of this study.

2. The basis for the choice of an optimum composition of electrolyte solution

According to the discussion presented in [12, 13], the electrocapillary transducers can be used as acceleration meters for frequencies lower than their resonance value ($f \ll f_0$) provided the impedance of the mercury–electrolyte solution electrode in the transducer consists mainly of a frequency-independent capacitance. In such a case the electrical equivalent circuit [10, 11] of an open transducer is reduced to a simple circuit [12, 13] which comprises a mercury–electrolyte solution capacitance, C_{el}, a capacitance C_m representing the elasticity of the transducer and a source of alternating voltage representing the mechanical force which stimulates the vibrations of the filling. Therefore, the electrolyte composition should assure a good reproducibility and stability of voltage representing the force and the C_{el} and C_m capacitance values.

It has been proved in earlier papers [3, 14] that the output effect of elements with no external polarization is due to the movement of electrical charge at the interfaces; this in turn results from the equilibrium

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$$2\,\mathrm{Hg} - 2e \rightleftharpoons \mathrm{Hg}_2^{2+}. \qquad (1)$$

Therefore, it is necessary for a correct response of an electrocapillary element that the mercury–solution electrodes are to a certain extent reversible.

The impedance of a mercury electrode immersed in a solution containing the mercurous ions comprises a Faradaic impedance parallel to the capacitance of the electric double layer [15–18]. The Faradaic impedance is determined mainly by the Warburg impedance, Z_W, representing the diffusion of the mercurous ions in the electrode layer and depending on the square root of frequency:

$$Z_W = A^{-1}\sigma\omega^{-1/2}(1-j). \qquad (2)$$

A denotes the electrode area and σ is the Warburg coefficient depending on the mercurous ion concentration [19]:

$$\sigma = RT/[n^2F^2c_{\mathrm{Hg}_2^{2+}}(2D_{\mathrm{Hg}_2^{2+}})^{1/2}]. \qquad (3)$$

$c_{\mathrm{Hg}_2^{2+}}$ and $D_{\mathrm{Hg}_2^{2+}}$ denote the concentration and the diffusion coefficient of the mercurous ions, respectively. Besides, the Faradaic impedance comprises a negligible contribution of the resistance representing the electrode reaction (Equation 1). Sometimes, a capacitance component due to the Faradaic reaction is also observed [13]. It has been interpreted as the adsorption capacitance [20] and is probably due to the presence of impurities which are hardly avoidable at an electrode with a non-regenerating surface.

The equivalent circuit of the electrode impedance of the electrocapillary elements [13] is presented in Fig. 1. One may conclude from it that the impedance of the Faradaic branch must be increased in order to assure the capacitative character of the electrode impedance. As it would be hard to decrease the capacitance C_a (Fig. 1) in a controlled manner because its origin is unclear, an increase in the capacitance of the Faradaic branch can be obtained by increasing the Warburg impedance. The increase in the Faradaic impedance cannot be too great, however, as a stable equilibrium (Equation 1) must be present at the electrode surface, as mentioned above, to assure a suitable charge density.

According to Equations 2 and 3, the increase in the Warburg impedance can be achieved by decreasing the mercurous ion concentration. If the values $C_0 = 30\ \mu\mathrm{F\ cm}^{-2}$ and $D_{\mathrm{Hg}_2^{2+}} = 9.5 \times 10^{-6}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$ are accepted [17] Equations 2 and 3 show that the mercurous ion concentration should be

$$c_{\mathrm{Hg}_2^{2+}} \ll 1.1 \times 10^{-7}\ \mathrm{mol\ dm}^{-3} \qquad (4)$$

in order to reduce the effect of the Warburg impedance on the open-circuit voltage to less than 5% at frequencies higher than 1 Hz. In this estimate, disadvantageous conditions expressed by the relationship

$$1/(\omega C_m) \gg Z_{\mathrm{el}} \qquad (5)$$

have been assumed to exist in the transducer; Z_{el} denotes the impedance of the mercury–solution electrode in the transducer. If Equation 5 is not fulfilled, the desired decrease in the Warburg impedance effect is attained at a higher mercury ion concentration. According to the electrical equivalent circuit, in the case where the mechanical impedance, Z_m [10–12], is negligible compared to the impedance Z_{el}, the open-circuit voltage would be independent of Z_{el}, and hence of Z_W. However, Equation 5 is fulfilled in most cases at low frequencies.

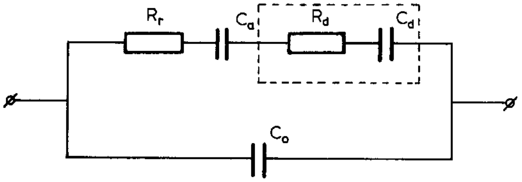

Fig. 1. The electrical equivalent circuit of the electrochemical impedance.

As it has been shown in [21], the open-circuit voltage is independent of the solution resistance in the transducer; the resistance contributed to the output resistance of the transducer but this problem will not be discussed in this work.

3. Experimental

The preparation of the electrocapillary transducers, the methods of study and the measuring apparatus were described earlier [3, 10, 11]. The composition of solutions and the principal construction parameters of the transducers will be presented in Section 4.

The potential-producing mercurous ions are formed in the transducers by the reaction of

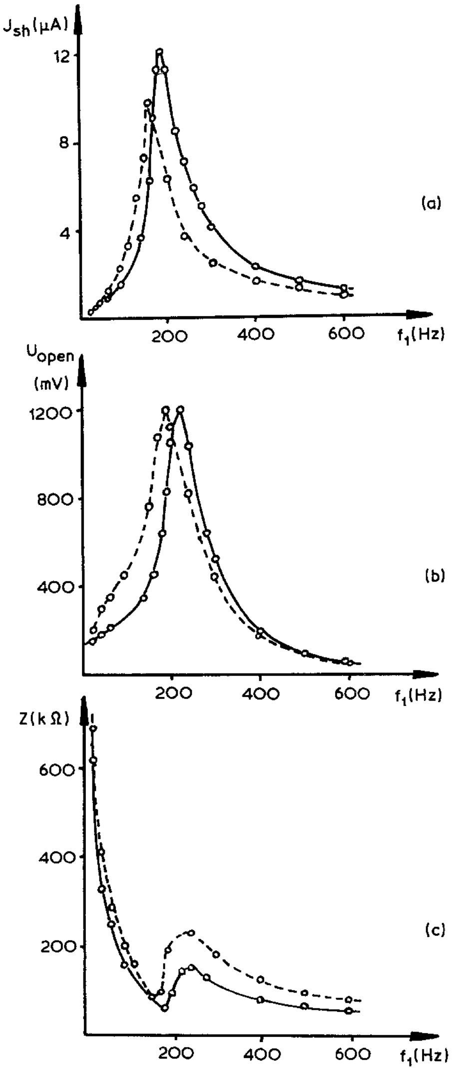

Fig. 2. The frequency characteristics of (a) the short-circuit current, (b) the open-circuit voltage, (c) the internal impedance, for transducers with two kinds of electrode: – – o – – 0.5 M $HClO_4$ + 0.5 M $NaClO_4$ (first kind); —o— 0.25 M H_2SO_4 + 0.25 M Na_2SO_4 (second kind).

mercury with dissolved oxygen. The attempts to introduce the desired concentration of mercury ions (10^{-8}–10^{-5} M) directly into the solution and to fill the transducers in an oxygen-free atmosphere failed because of technical difficulties, i.e. the results have proved irreproducible. The effect of formation of mercurous ions in the electrocapillary elements may prove to be of importance in their manufacture.

4. Results and discussion

Two series of transducers have been studied in order to compare the properties of transducers containing the two kinds of electrode. They have been made using the solutions:

$$0.5\ \mathrm{M}\ HClO_4 + 0.5\ \mathrm{M}\ NaClO_4$$

$$0.25\ \mathrm{M}\ H_2SO_4 + 0.25\ \mathrm{M}\ Na_2SO_4$$

Fig. 2 presents typical frequency characteristics of the short-circuit current, I_{sh}, the open-circuit voltage, U_{open}, and of the internal impedance, Z, for the two series of transducers. The minima occurring on the impedance curves are due to the mechanical impedance effect [10–12] where the condition of Equation 5 is not fulfilled. The transducers contained 20 interfaces each in capillaries of 0.30 mm diameter. The mass of filling amounted to 70–80 mg and the air-filled spaces at the capillary ends were about 1 mm long. The resonance frequencies ranged from 160–190 Hz.

In some transducers, the electrode impedance attained a capacitative character at low frequencies after a period of time; it was due to the appearance of the capacitance C_{a} (Fig. 1). In all cases C_{el} attained similar values for the electrodes of both the first and the second kind; they ranged from 6–13 nF and the α^{-1} values were about 160 μC m^{-1}. For the transducers where the electrode impedance did not attain a capacitance character (no plateau on the U_{open} curves, see Fig. 3) the Warburg impedance was observed to play an important role and its contribution was dominant at lower frequencies. The experimental Warburg impedance values corresponded to the mercurous ion concentration in the proximity of the electrode amounting to 10^{-5}–10^{-4} M; such values corresponded to the dissolved oxygen concentration [22]. The results obtained for the transducers filled with aqueous 1 M NaCl, 1 M NaOH, and 1 M and 3.7 M H_2SO_4 were similar.

It is possible to attain a mercurous ion concentration corresponding to that of dissolved oxygen in the case of perchlorates because of the high solubility of mercurous perchlorate in water whereas the presence of such a high concentration of mercurous ions in a chloride solution suggests that either complexes or undissociated salts were formed and were undergoing reduction at the mercury electrode [23]. A relatively high concen-

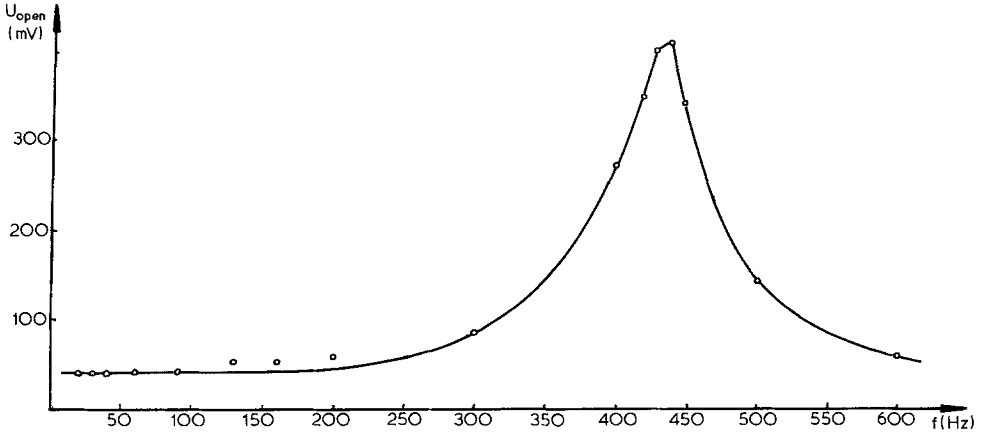

Fig. 3. The frequency characteristic of the open-circuit voltage for a transducer containing the 1.1 M Na_2SO_4 + 0.1 M H_2SO_4 solution.

tration of mercury ions in the non-complexing media of sulphate solutions can be explained by low SO_4^{2-} ion concentration.

Sulphuric acid behaves in an aqueous solution like a strong acid at its first dissociation step and like a weak acid at the second one. The dissociation constant of the second step [24] is:

$$K_2 = \frac{[H^+]\,[SO_4^{2-}]}{[HSO_4^-]} = 1.2 \times 10^{-2}. \qquad (6)$$

Therefore, it may be assumed that

$$[H^+] \approx [HSO_4^-] \qquad (7)$$

at the concentrations discussed here (1 and 3.7 M). Hence the SO_4^{2-} ion concentration is independent of the concentration of the acid and amounts to 1.2×10^{-2} g-ion dm^{-3}. It may be concluded from this value and from the solubility product of mercurous sulphate (6.2×10^{-7} [24]) that the maximum mercurous ion concentration in a sulphuric acid solution is about 5×10^{-5} M. This is in agreement with the value obtained from the Warburg coefficient estimated from the frequency characteristic of the impedance of the studied electrocapillary transducers.

The equality

$$[H^+] \approx [SO_4^{2-}] \qquad (8)$$

applies to solutions containing equivalent amounts of H_2SO_4 and Na_2SO_4. This equality combined with the K_2 value given above and with the solubility product of mercurous sulphate yields the maximum mercurous ion concentration in this solution, i.e. 8×10^{-6} M; it is also similar to the value found from the Warburg coefficient.

The mercurous ion concentration in a sodium hydroxide solution is determined by the stability product [25]

$$I_s = [Hg_2^{2+}]\,[OH^-]^2 = 1.8 \times 10^{-24}. \qquad (9)$$

Besides, the solution contains complex $HgOH^+$ and $Hg(OH)_2$ ions having stability constants [25]:

$$\beta_1 = \frac{[HgOH^+]}{[Hg^{2+}]\,[OH^-]} = 2 \times 10^{10} \qquad (10)$$

$$\beta_2 = \frac{[Hg(OH)_2]}{[Hg^{2+}]\,[OH^-]^2} = 5 \times 10^{21}. \qquad (11)$$

For a solution in contact with metallic mercury the ratio of mercurous and mercuric ion concentrations is a concentration independent constant [26]:

$$K = \frac{[Hg_2^{2+}]}{[Hg^{2+}]} = 235. \qquad (12)$$

The above data give the maximum concentration of complexed mercury ions as 4×10^{-5} M for transducers filled with a 1 M NaOH solution.

Formation of very stable complexes between mercuric and hydroxide ions causes their concentration in alkaline, neutral and weakly acid solutions to be as high as mercurous ion concentration. The total concentration of mercury complexes with the hydroxide ion is

$$[HgOH^+] + [Hg(OH)_2]$$
$$= \frac{[Hg^{2+}]\,[OH^-]}{K}(\beta_1 + \beta_2\,[OH^-]). \qquad (13)$$

It may be assumed that the effect of complexes on the electrode impedance is practically eliminated in the case of electrocapillary transducers if their concentration is ten times smaller than that of the mercurous ion:

$$\frac{[\mathrm{HgOH^+}] + [\mathrm{Hg(OH)_2}]}{[\mathrm{Hg_2^{2+}}]} \leqslant 0.1 \qquad (14)$$

From Equation 13 and from the above presented K, β_1 and β_2 values it follows that Equation 14 is fulfilled when $[\mathrm{OH^-}] \leqslant 6.7 \times 10^{-11}$ M, i.e. when $\mathrm{pH} \leqslant 3.8$.

According to these results, the solution used for filling the electrocapillary acceleration meters should not contain any ions which are able to form complexes with the mercury ions and the mercury ion concentration should be about 10^{-7} M. In addition, the solution should be acidified to $\mathrm{pH} \leqslant 3.8$. It is difficult to prepare a solution fulfilling all these requirements exactly. Our conclusions have been checked by examining transducers containing a 1.1 M Na_2SO_4 + 0.1 M H_2SO_4 solution with pH = 2.6. The transducers used for this check were prepared in capillaries of diameter 0.41–0.44 mm and containing up to ten interfaces; the mass of the filling was 80–90 mg.

The concentration of free SO_4^{2-} ions in this solution was about 1 M. A greater sodium sulphate concentration would be more advantageous at room temperature as the free sulphate ion concentration would then be greater and the mercury ion concentration would be lower. However, the salt solubility is so temperature dependent that the crystallization would occur at a slightly lower temperature causing inconvenience in practical applications.

The open-circuit voltage, the short-circuit current and the impedance of transducers filled with this solution reached constant values after several days and did not change further during the several months the study lasted. The open-circuit voltage of transducers containing 1 mm long air-filled spaces at their ends was about 20 mV s^2 m^{-1} in the acceleration meter range; it amounted to 3–5 mV s^2 m^{-1} only for the transducers with no air space. Fig. 3 presents the frequency characteristics of the open-circuit voltage for a transducer with no air spaces at a 10 mV s^2 m^{-1} acceleration amplitude. The acceleration meter range of this transducer is about 200 Hz.

A study by the bridge method confirmed that the impedance of transducers filled with a 1.1 M Na_2SO_4 + 0.1 M H_2SO_4 solution was indeed mainly capacitive; the capacitance component was 8–9 fold greater than the real resistance. The bridge measured capacitance was practically frequency independent in the low frequency range (the lowest frequency studied was 10 Hz). The capacitance jump below the resonance frequency

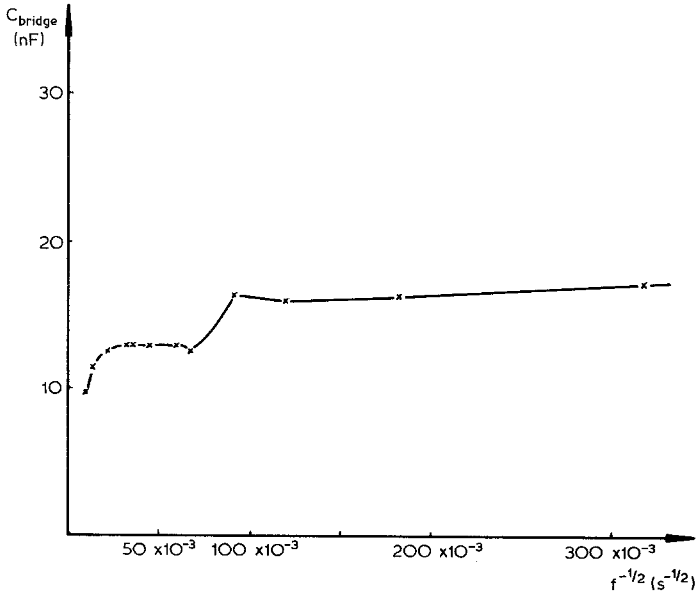

Fig. 4. The frequency characteristic of the bridge capacitance for a transducer with a 1.1 M Na_2SO_4 + 0.1 M H_2SO_4 solution.

as shown in Fig. 4 is due to the mechanical capacitance. According to the electrical equivalent circuit, this capacitance enhances the inner capacitance of the transducers at frequencies below the resonance frequency.

We have also attempted to decrease the mercury ion concentration in a controlled way by forming stable complexes or insoluble salts. KCN + KOH and Na_2S + NaOH solutions have been used for this purpose but the results proved unsatisfactory.

Thus, it may be stated at the present stage of the studies that the 1.1 M Na_2SO_4 + 0.1 M H_2SO_4 solution or a solution with a similar composition is the optimum liquid solution to be used for filling the electrocapillary acceleration meters.

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