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Electrocapillary elements. I. Electrocapillary acceleration meters with electrolyte, especially in a gel form

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This work presents the principle of operation of electrocapillary gauges for measuring the acceleration of mechanical vibrations. It is shown that replacing a solution of electrolyte by its solution in a gel enhances the resonance frequency thereby extending the range of its applications. The effect of gelling the electrolyte solution on the electrochemical properties of the transducer is discussed. Electrocapillary transducers, particularly when used as acceleration meters, can be used in vibration diagnostics and in automatic systems.

1. Introduction

An increasing number of studies of various electrochemical phenomena have been reported in the last two decades as well as their application to the construction of sensing devices and instrumentation for measurement and automation. There are various types of electrochemical devices often called electrochemical elements or chemotrons [1, 2]; among them the electrocapillary elements deserve particular attention as they are able to interconvert electrical and mechanical signals. They are usually made of glass capillaries filled with alternating slugs of mercury and electrolyte solution [3–5]. They may be classified as the resonance-type mechanical–electrical (seismic) gauges. Their natural vibration frequencies range from less than 20 Hz to several hundred Hz depending on the mass of filling liquid (mercury + electrolyte), their internal stiffness and their damping.

Studies of electrocapillary elements have been sparse. The papers by Watanabe [6], Fain [7], Podolsky [8], Woszczerowicz [9], and Shorygin [10, 11] have presented the electrical equivalent circuits of these elements and their modes of operation based on the assumption that the mercury–electrolyte solution interfaces are perfectly polarizable electrodes. It has been proved [3] that the potential of electrocapillary elements in the absence of any external voltage is due to a reversible electrode equilibrium. The electrical equivalent circuits presented in [6–11] have not provided a satisfactory explanation for the experimentally found properties of electrocapillary elements; this is particularly so in the case of their frequency characteristics.

The studies carried out by us over several years have resulted in an extension to the theory of electrocapillary elements working in a piston-like regime consisting of displacements of the liquid filling (mercury + solution) relative to the capillary surface. Such a movement actually occurs in the electrocapillary elements with a low inner stiffness at frequencies below 100 Hz. With a higher stiffness or at higher frequencies the so-called deformational regime prevails and the charge flow through the element is caused by variations in the area of the mercury–electrolyte solution interface [6]. The change from a piston-like operation to a deformational operation is gradual and occurs over a wide range of frequencies (tens of Hz). The terms 'deformational regime' and 'piston-like regime' correspond to the terms 'U-II effect' and 'U-III effect' used by Watanabe [6] and by Podolsky *et al.* [8]. The theory was developed to devise the electrical and the mechanical equivalent circuits of electrocapillary elements and to interpret their components [3–5]; it describes their properties satisfactorily in the linear range. A good agreement of this theory with experiment makes it possible to construct the elements with the desired properties.

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There have been proposals to apply the electrocapillary elements to measurement techniques and in automation. Latour [12] has proposed the use of the electrocapillary effect in the microphone, Watanabe *et al.* [6] to use electrocapillary elements in the hydrophone, the disc player and the stethoscope, while Duckwald and Angell [13], Podolsky [14] and our studies have indicated the possibility of using these elements for measuring the displacement and the acceleration of mechanical vibrations. The electrocapillary elements are also useful gauges for medical diagnostics. Their usefulness in examining the pressure pulsations in the human body was described by Yoshimoto [15] and in ballistocardiography by Elliot *et al.* [16].

The studies on electrocapillary systems of the mercury–electrolyte solution interface type in a capillary can be of significance for fundamental problems of electrochemistry, e.g. for the study of impedance [6], of the potential of zero charge and of the charge density [17], and of electrode reactions [18].

In an electrocapillary transducer (Fig. 1), a mechanical stimulus generates an electrical signal at the output terminals of the element. The electrocapillary transducers are reversible: an electrical signal applied at the output terminals of the transducer causes movement of the capillary filling. In the case where an alternating voltage is applied, mechanical vibrations are generated in the capillary; hence the elements of this kind are called electrocapillary oscillators.

The main advantages of electrocapillary elements which justify their further study and improvement are the absence of an external energy source, a high sensitivity and selectivity, particularly at low frequencies (0.1–100 Hz), and a small size and weight (a few grams). Environmental properties such as humidity, acoustic noise, electrical and magnetic fields or radiation have practically no effect on the properties and stability of properly made electrocapillary transducers.

This work presents the principle of operation and mechanical properties of electrocapillary gauges for measuring the acceleration of mechanical vibrations. The idea of acceleration meters containing the electrolyte solution as an agar-agar gel and the results of their experimental examination are also presented. The experimental characteristics of the acceleration meters filled with a liquid electrolyte solution have been presented in earlier papers [3, 4, 19]; in the present work such gauges are referred to for comparison with the gelled solution elements.

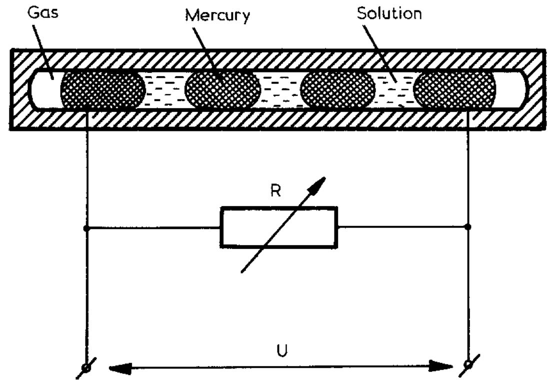

Fig. 1. An electrocapillary transducer.

2. Electrocapillary acceleration meters

According to the general equivalent circuit [4], an electrocapillary transducer can be used for acceleration measurements in the frequency range below the resonance value, i.e. for $f \ll f_0$, provided the impedance of the mercury–electrolyte solution electrodes is mainly capacitative. This requirement can be fulfilled by adjusting the electrolyte composition [2]. In such a case, the general equivalent circuit of the electrocapillary transducer assumes the simple form presented in Fig. 2. The output voltage, U, measured across a load resistance considerably greater than the inner impedance of the transducer is expressed by the relationship:

$$U = EC_{\mathrm{m}}/(C_{\mathrm{m}} + C_{\mathrm{el}}) \tag{1}$$

where E is the electromotive force, C_{m} the mechanical capacitance and C_{el} the electrochemical capacitance of the mercury–electrolyte solution interface. The physical interpretation of these magnitudes is given in [4].

From the equations

$$F = m\ddot{x} \tag{2}$$

$$\alpha = E/F \tag{3}$$

$$C_{\mathrm{m}} = \alpha^{-2}k^{-1} \tag{4}$$

together with Equation 1, it can be seen that in the case where $C_{\mathrm{el}} \gg C_{\mathrm{m}}$ (a condition which is

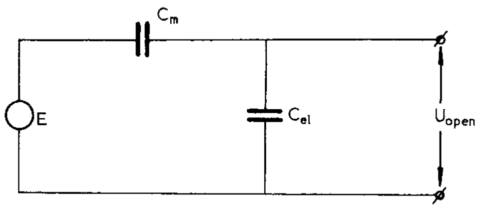

Fig. 2. The electrical equivalent circuit of an electrocapillary acceleration meter.

fulfilled by most electrocapillary transducers)

$$U = m\ddot{x}/(k\alpha C_{el}) \tag{5}$$

where $\ddot{x}$ is the amplitude of the stimulating vibration, k is the coefficient of stiffness, m the mass of the filling, and α the coefficient characterizing the mechanical–electrical transduction of the element.

It can be seen from Equation 5 that the frequency characteristics of the output voltage, U, at a constant acceleration amplitude is independent of the frequency f. It is the so-called acceleration meter range (Fig. 4).

Practically, an electrocapillary transducer works as an acceleration meter for frequencies up to $2/3f_0$. Therefore, it is advisable to attain a high f_0 value in order to apply the transducer as an acceleration meter; this can be done by suitably modifying the mechanical properties of the element.

3. Mechanical properties

In the mechanical model of the electrocapillary transducer (Fig. 3) the natural vibration frequency f_0 depends on the mass of the vibrating filling, m,

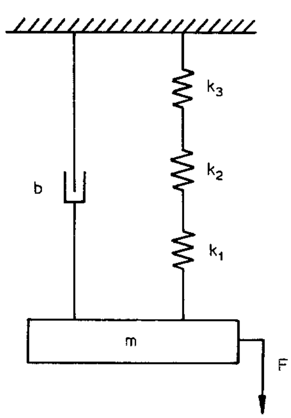

Fig. 3. Mechanical model of the electrocapillary transducer.

the stiffness, k, and on the damping, b, as expressed by [5]

$$f_0 = [1/(2\pi)]\{(k/m) - [b/(2m)]\}^{1/2}. \tag{6}$$

A controlled increase in the f_0 value required to extend the range of the acceleration meter can be most conveniently attained in our laboratory by increasing the inner stiffness, k. Therefore, an analysis of its components is presented below.

As was demonstrated by us [3, 19], the inner stiffness of an electrocapillary transducer is the sum of springs connected in series and representing:

(a) the stiffness of the filling, k_1;

(b) the stiffness of the filling–capillary sealing interface, k_2;

(c) the stiffness of the seals, k_3 (Fig. 3).

The stiffness of the filling is determined, depending on the element construction:

(i) by the stiffness of deformed menisci which constitute the mercury–electrolyte solution interface for the transducers with no air columns (the length of air columns $L_p = 0$);

(ii) by the total stiffness of the springs connected in parallel representing the pneumatic stiffness of the gas columns, k_p, and the capillary stifness, k_γ, for the transducers containing gas columns ($L_p > 0$) and liquid electrolyte, or by the stiffness of the gas columns and the stiffness of the electrolyte (k_p + k_s) if the electrolyte is a gel, e.g. agar-agar.

The stiffness of the capillary filling–capillary sealing interface, k_2, for transducers with no air columns consists of the stiffness of the mercury–sealing interface.

According to the principle of stiffness summation, the resultant stiffness of the component stiffness connected in series is described by

$$1/k = \sum_i (1/k_i). \tag{7}$$

This expression indicates that the stiffness of the element is determined by the smallest stiffness, i.e. by the stiffness of the softest spring.

The stiffness of the system in the case of a transducer with no air column ($L_p = 0$) is described by the full expression (Equation 7). In this case the stiffness of the seals, k_3, is only poorly reproducible, the stiffness k_2 is governed by some undetermined factors and the movement of a deformed mercury–solution interface is still not described. Therefore, it may not be possible at present to carry out a detailed stiffness analysis for transducers with no air columns. Undetermined conditions of k_2 and k_3 reproducibility cause a considerable scattering of resonance frequencies for the transducers with $L_p = 0$. Thus our studies have been hitherto confined mainly to transducers with air columns.

Transducers with gas columns fulfil the conditions:

$$k_1 \ll k_2 \tag{8}$$

$$k_1 \ll k_3. \tag{9}$$

Hence their internal elasticity can be identified with the elasticity of the filling, k_1.

As it has been shown in [3, 20], the elasticity k_1 of transducers containing a liquid electrolyte can be increased by varying L_p and a resonance frequency of up to 250 Hz can be obtained in a controlled way. We have succeeded in further increasing the inner stiffness of the electrocapillary transducers in a controlled way by replacing a liquid electrolyte solution by an electrolyte in an agar-agar gel form.

It can be concluded from the above considerations that the stiffness of a transducer containing gas columns and a gelled electrolyte is described by the relationship

$$k = k_1 = k_p + k_{gel}. \tag{10}$$

If the total length of the gas columns $L_p \geq 1$ mm (for a typical inner capillary diameter of about 0.35 mm) then

$$k_p \ll k_{gel} \tag{11}$$

and

$$k \approx k_{gel}. \tag{12}$$

The conditions required to fulfil Equations 11 and 12 have been checked experimentally by us.

4. Experimental

4.1. *Preparation of the electrocapillary transducers*

The transducers were prepared by filling glass capillaries with mercury and electrolyte solution by means of a syringe in such a way as to obtain mercury slugs separated by solution. A 1 M NaCl solution was used as the electrolyte. The gel solutions of electrolyte contained 2 wt% agar-agar. In this case the capillaries were filled at 70–80° C; upon cooling to room temperature the electrolyte solution gelled and the capillary ends were then sealed tight with an epoxy resin. Platinum wires in the terminal mercury slugs served as electrical contacts. The salt was crystallized twice from triply distilled water; the analytical grade mercury was distilled twice *in vacuo*.

Transducers were made of capillaries having a 0.35 mm inner diameter. The mass of filling was constant within this series (160 mg). Total lengths of the gas columns varied from less than 0.1 mm to 15 mm. Some specimens were left open, in this case $L_p = \infty$.

4.2. *Measurement method*

The output voltage was measured across a 10 MΩ resistance, the frequency characteristics were recorded at a constant acceleration amplitude of stimulating mechanical vibrations equal to 10 m s^{-2} and the amplitude characteristics were measured at a frequency of 70 Hz. The inner impedance was measured by the method described in [4].

5. Results and discussion

The resonance frequency of the transducers containing the electrolyte in an agar-agar gel form with L_p greater than 1 mm have been found to be 450 ± 10 Hz and to be independent of L_p. This corroborates the above analysis (Equation 11). Similar results were obtained when other gels, e.g. polyvinyl alcohol, were used. It offers the possibility of constructing the elements of a desired resonance frequency which should practically depend only on the gel stiffness which can be controlled by varying the concentration or the type of gelling agent. The significance of gelling the electrolyte solution for the resonance frequency f_0 of an electrocapillary element is well illustrated by the frequency characteristics of the output voltage of two transducers with the same filling structures (i.e. with the same diameters and mercury, electrolyte and air column lengths). Both elements contained a 1 M NaCl solution as the electrolyte; in one specimen the solution was liquid (curve a of Fig. 4, $f_0 = 200$ Hz) while in the other it was an agar-agar gel form (curve b, $f_0 = 540$ Hz).

Amplitude characteristics of the output voltage for transducers containing the electrolyte in a gel

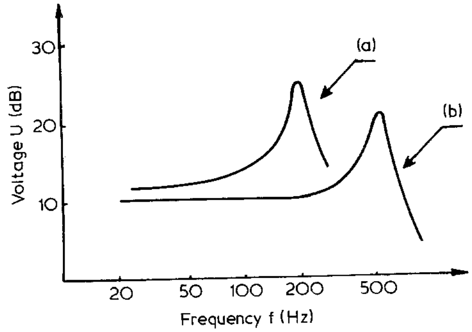

Fig. 4. Frequency characteristics of the electrocapillary transducer. The output voltage in the acceleration meter range: (a) 4.2 mV, (b) 3.6 mV; acceleration of stimulating mechanical vibrations 10 m s^{-2}.

form are shown in Fig. 5. The output voltage, U, increased with decreasing inner stiffness of the element (k); k was inversely proportional to the gas column lengths, i.e. to L_p [3].

Fig. 6 shows the frequency characteristics of the inner impedance for the same transducers. The shape and characteristics of the dependences presented in Figs. 5 and 6 are similar to those for electrocapillary transducers containing liquid electrolytes [4, 19, 20].

The plateau range in which the transducer can be applied to the amplitude measurements is greater for the transducers with the electrolyte in

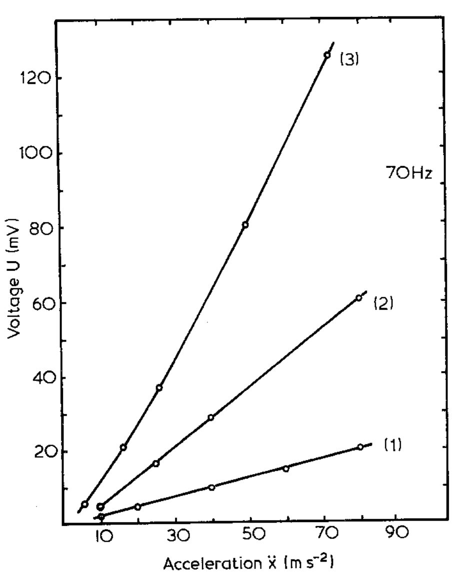

Fig. 5. Amplitude characteristics of the output voltage of gel-containing electrocapillary acceleration meters with different L_p values: (1) $L_p < 0.1$ mm; (2) $L_p = 0.8$ mm, (3) $L_p = 1.5$ mm.

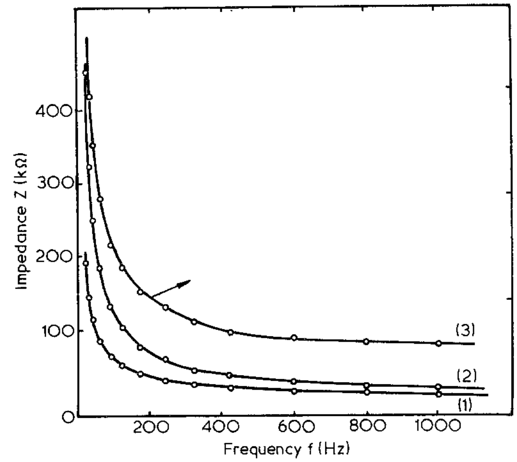

Fig. 6. Frequency characteristics of the internal impedance of gel-containing electrocapillary acceleration meters with various structures of the filling.

gel form than for a typical construction with a liquid electrolyte (Fig. 4). This is due to an increase in the diffusion impedance of mercury ions caused by the greater viscosity of the gel, as can be deduced from an analysis of the electrical equivalent circuit of an electrocapillary transducer. Equation 5 is thus fulfilled over a greater frequency range; it also assures a good stability of the voltage sensitivity over long time periods.

As with most electrochemical elements the electrocapillary transducers are temperature sensitive; their working range is between 5 and 40° C. Therefore, at the present stage of development they require thermostating if used outside the laboratory.

Studies of the element resistance against shocks acting both axially and transversely on the capillary have shown that the gel separating the mercury slugs practically eliminates the possibility of damaging the structure. This assures a good stability for the exploitation of the element.

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