

Electrocapillary elements. IV.

Constant pressure manometers with a frequency read out

Z. FIGASZEWSKI, Z. KOCZOROWSKI, J. MROWCZYNSKI

Institute of Basic Problems of Chemistry, Warsaw University, Warsaw, Poland

Received 12 December; and in revised form 29 June 1979

The idea of constant pressure measurement by means of an electrocapillary element is presented. Conditions required to obtain linear resonance frequency–pressure characteristics are determined experimentally and theoretically.

1. Introduction

Applications of electrocapillary elements have hitherto been limited to variable signal measurements. The development of the electrocapillary transducer as an acceleration amplitude sensing device is the most advanced [1, 2]. With a proper choice of the solution composition, good reproducibility of a flat frequency characteristic of acceleration meters (beginning from a frequency of 20 Hz) is obtained [3]. Recently, electrocapillary variable pressure sensing devices have been described [4].

The electrocapillary transducers cannot operate at zero frequency as they are voltage-generating elements and in such a case they cannot yield energy continuously [2, 5]. Applying electrocapillary elements to the measurement of constant values requires that advantage be taken of their parametric character and that they work in a system where a signal varying with time is generated.

This paper presents the idea of applying the electrocapillary elements to constant pressure measurements based on the dependence of their resonance frequencies on the gas column pressure within the element. Applying electrocapillary resonators [6–8] makes it possible to use an electric signal both at the input and at the output of the element.

2. Theory

According to the equivalent circuit, the resonance

frequency f_0 of an electrocapillary element working in the short-circuit mode and having a negligible solution resistance is determined by the mechanical parameters of the element [7, 8]. It results from the mechanical model of electrocapillary elements that the steady state resonance frequency is described by the relationship [2]:

$$f_0 = \frac{1}{2\pi} \left(\frac{k_p + k_\gamma}{m} \right)^{1/2} \quad (1)$$

where k_p and k_γ represent the pneumatic stiffness coefficient and the capillary stiffness coefficient, respectively, and m is the mass of vibrating filling consisting of a mercury and electrolyte solution. The pneumatic stiffness is the stiffness of air columns V_1 and V_2 which are present in a sealed capillary element at both sides of the filling. According to papers [2, 9], the stiffness of a pneumatic spring of this kind is determined by the relationship:

$$k_p = \chi p_i S_i^2 \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \quad (2)$$

where p_i is the pressure of the columns, S_i the intersection area and χ a coefficient equal to 1 for an isothermal process and 1.4 for an adiabatic one.

Equation 2 was obtained assuming the inner displacement of δ to be very small (i.e. $\delta S_i \ll V_i$) and neglecting the fact that the filling playing the role of the piston was liquid [2]. The flexibility of the mercury–electrolyte solution and mercury–air interfaces is taken into account by the capillary stiffness coefficient k which depends on the interfacial tension values and on the wetting angles

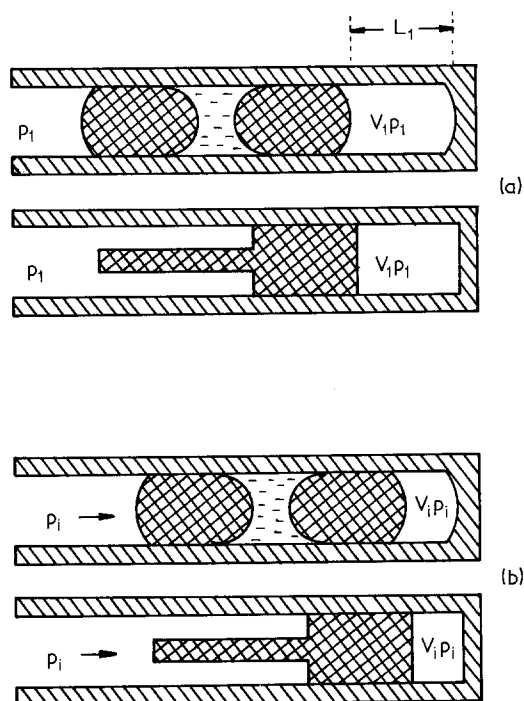


Fig. 1. Diagram illustrating the action of pneumatic spring modelling the pneumatic stiffness of an electrocapillary element in normal conditions (a) and subjected to an external pressure (b).

but is independent of the intersection area [2]. As was shown by theoretical analysis and by experiment, the compression and the decompression of air columns with a small V_1 value as those usually occurring in the electrocapillary elements should be isothermal [2].

An electrocapillary element open at one end is represented by a single pneumatic spring (Fig. 1a) having a stiffness determined by the relationship [2, 9]:

$$k_p = \chi p_1 S_i^2 / V_1 \quad (3)$$

Taking into account that the external pressure p_1 (Fig. 1b) modifies the initial pressure, p_1 , and volume, V_1 , to the p_i and V_i values and that $p_i V_i = p_1 V_1$ Equation 3 can be written in the form

$$k_p = \frac{S^2}{p_1 V_1} p_i^2 = \frac{\pi \phi^2}{4 p_1 L_1} p_i^2 \quad (4)$$

where ϕ is the inner diameter of the capillary and L_1 is the length of the air column.

Assuming

$$k_p \gg k_\gamma \quad (5)$$

Table 1. Construction parameters of the electrocapillary resonators

Number	Electrolyte composition	Capillary diameter ϕ (mm)	Total mass of mercury and electrolyte m (mg)	Length of air column L_1 (mm)
1	3.7 M H ₂ SO ₄ (aq)	0.78	710	2.60
2	1.1 M Na ₂ SO ₄ + 0.1 M H ₂ SO ₄ (aq)	0.78	710	1.35
3	1 M NaCl(aq)	0.78	705	1.15
4	1 M NaClO ₄ (in CH ₃ OH)	0.78	720	1.25
5	3.7 M H ₂ SO ₄ (aq)	0.78	770	0.95
6	3.7 M H ₂ SO ₄ (aq)	0.78	765	3.65
7	3.7 M H ₂ SO ₄ (aq)	0.78	780	16.00
8	3.7 M H ₂ SO ₄ (aq)	0.78	785	14.20
9	3.7 M H ₂ SO ₄ (aq)	0.78	785	8.75
10	3.7 M H ₂ SO ₄ (aq)	0.78	765	6.35
11	3.7 M H ₂ SO ₄ (aq)	0.78	775	4.80
12	3.7 M H ₂ SO ₄ (aq)	0.78	790	3.20
13	3.7 M H ₂ SO ₄ (aq)	0.78	790	1.75
14	3.7 M H ₂ SO ₄ (aq)	0.78	780	4.15
15	3.7 M H ₂ SO ₄ (aq)	0.51	275	5.85
16	3.7 M H ₂ SO ₄ (aq)	0.51	275	8.59
17	3.7 M H ₂ SO ₄ (aq)	0.51	275	1.40
18	3.7 M H ₂ SO ₄ (aq)	0.51	275	3.20
19	3.7 M H ₂ SO ₄ (aq)	0.51	275	2.38

Equation 1 takes the form:

$$f_0 = [1/(2\pi)] \left(k_p/m \right)^{1/2} = B p_i \quad (6)$$

where

$$B = [\phi/(4\pi)] [\pi/(p_1 L_1 m)]^{1/2} \quad (7)$$

is a constant for a given element.

A result from Equations 4–7 is that a constant pressure acting indirectly or directly on the filling of an electrocapillary element modifies its inner stiffness and, consequently, its resonance frequency f_0 . Under these conditions and for $\chi = f_0$ should be proportional to the pressure.

3. Experimental

The preparation of the electrocapillary elements and of the materials have been described earlier [2, 7, 8]. The most important parameters of the resonators which are discussed in this paper are compiled in Table 1.

Measurements have been made by the filter method [4, 7, 8]. The apparatus used is presented diagrammatically in Fig. 2. The resonance frequency of the elements was determined as the frequency value corresponding to the maximum voltage measured by the voltmeter V_2 ; small load resistance values, R (usually 2–5 k Ω) have been used to assure a virtual short-circuit character of the output. Proportionality of the output voltage to the load resistance R has been accepted as the criterion of short circuit.

4. Results and discussion

Preliminary studies showed that the resonance fre-

quency was unstable for several minutes after a change in external pressure in the case of electrocapillary elements containing more than two interfaces in the oscillator and transducer parts. This effect was not observed in the case of elements with only two interfaces in each capillary segment; for such elements f_0 proved to be stable and reproducible. The instability of f_0 for the elements with more than two interfaces was probably due to the interface polarization caused by the displacement of the filling caused in turn by the pressure variation. The stationary state of the inner mercury slugs is re-established slowly unlike that of the outer slugs where the excess electric charge flows rapidly through the outer circuit. The dependence of the resonance frequency of the elements with two interfaces in each part and of various electrolyte compositions on the external pressure is shown in Fig. 3.

The dependence presented in Fig. 3 confirms the theoretical prediction that the resonance frequency f_0 should be a linear function of pressure. The scattering of experimental points, particularly at high frequencies, can be attributed to the solution resistance. According to the electrical equivalent circuit [7, 8], the charge accumulated at the interfaces during the shift of filling is hampered in its flow through the outer circuit by the solution resistance. Fig. 3 also shows, that least scatter was obtained for the resonators filled with the 3.7 M H_2SO_4 solution. This solution assures a low electrolyte resistance and a good wetting of the capillary surface; the electrical short circuit conditions are hence fulfilled over a broader

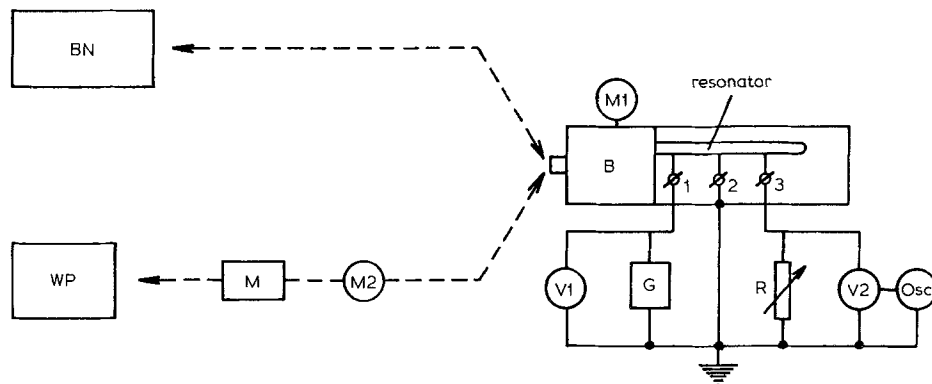


Fig. 2. Apparatus for measuring the pressure effect on the resonance frequency of electrocapillary resonators. B, pressure housing; BN, compressed nitrogen bottle; WP, water pump; V_1 and V_2 , alternating voltage meters; G, generator of a sinusoidal signal; Osc, oscilloscope; M_1 and M_2 , pressure and underpressure manometers; M, manostat; R, decade resistor.

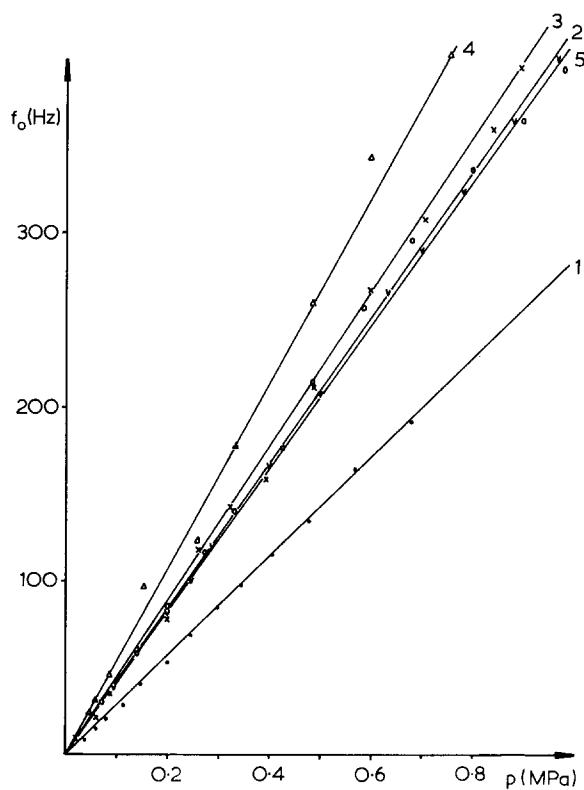


Fig. 3. Pressure characteristics of electrocapillary manometers containing solutions of various compositions. Numbers on the curves correspond to the numbers in Table 1. The construction parameters are also given in the table.

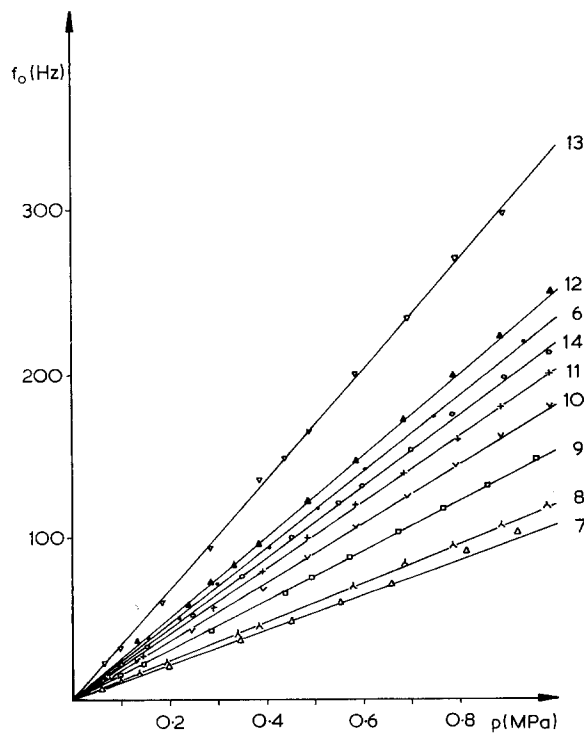


Fig. 4. Pressure characteristics of electrocapillary manometers (with a frequency read-out) for various air/column lengths L_1 . Numbers on the curves correspond to the numbers in Table 1.

frequency range and the possible effect of k_γ is minimized. On this basis, the resonators filled with the 3.7 M H_2SO_4 solution were used in further studies.

Figs. 4 and 5 illustrate the effect of the length L_1 of the gas column on the dependence $f_0 = f_0 p$ for the resonators made of two capillaries of different diameters.

As could be expected from Equations 6 and 7 the slopes of the straight lines $f = f_0 p$ decrease with increasing L_1 which implies a decreasing k_p value. The slopes define the frequency response to the pressure, i.e. the pressure coefficient B of the resonator as defined by Equation 7. The B value is proportional to $L_1^{1/2}$. Fig. 6 presents the experimental data of Figs. 4 and 5 shown in these co-ordinates. Lines 1 and 2 have been traced through the experimental points for the larger and smaller diameter, respectively, while $1'$ and $2'$ are the theoretical values calculated from Equation 7.

It can be observed in Fig. 6 that deviations from linearity are smaller and agreement with the theoretical slopes is better for the larger diameter. This seems to be due to a smaller perturbing effect of the capillary elasticity, k_γ . As k_γ is independent of diameter [2] and k_p is proportional to ϕ^2 , according to Equation 4 an increase in ϕ makes the

contribution of k_γ smaller relative to k_p . (Equation 1).

4. Conclusions

It has been confirmed experimentally that electrocapillary resonators can be applied to constant pressure measurements. Obtaining a linear $f = f_0 p$ dependence required that $k_p \gg k_\gamma$ and that the gas column compression is isothermal. These conditions are fulfilled if the inner capillary diameter is above 0.7 mm and the electrolyte is a H_2SO_4 solution to assure a good wetting of the inner capillary surface; the f_0 measurement occurs in the electric short circuit conditions if a 3.7 M H_2SO_4 solution corresponding to the maximum specific conductance is used.

The range of measurable constant pressure values can be set within broad limits by means of suitably stiff membranes or bellows. The membrane or the bellows separate the space in which the pressure is measured from the capillary thereby reducing the pressure difference and protecting the capillary filling.

The electrocapillary resonator operates with a measuring system. Beside the filter system (Fig. 2) one can devise a generator system [6–8] where the

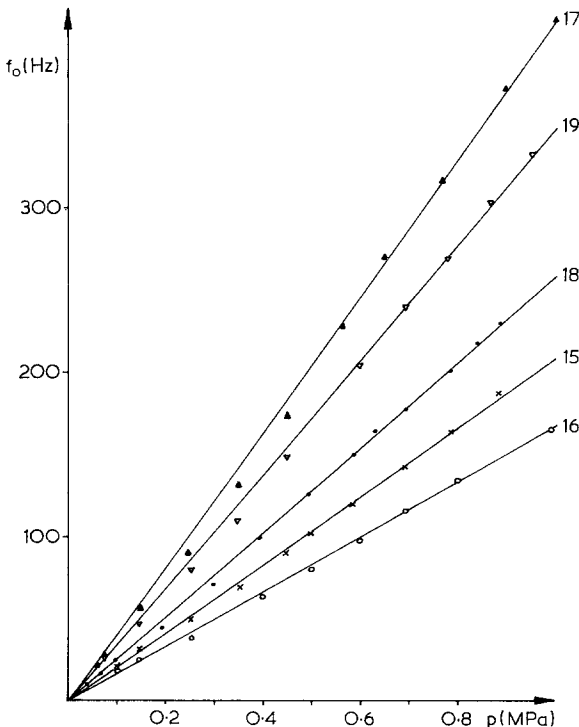


Fig. 5. Pressure characteristics of electrocapillary manometers for various air column lengths L_1 . Numbers on the curves correspond to the numbers in Table 1.

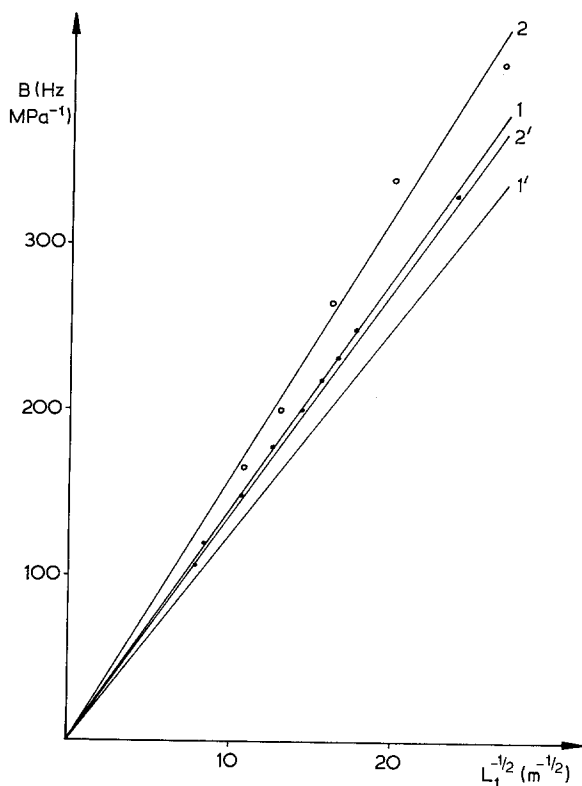


Fig. 6. Dependence of the pressure coefficient of the resonance frequency of electrocapillary resonators on the gas column length. Curves 1 and 2 refer to the experimental results obtained with resonators of diameter 0.78 and 0.51 mm, respectively. Curves 1' and 2' refer to the theoretical results.

resonator works in a feed-back mode with an amplifier without phase shift, K_u , as shown diagrammatically in Fig. 7. The resonator is represented in Fig. 7 by its equivalent circuit components L_m , R_m and C_m [7, 8]; F is a digital frequency measuring device, possibly scaled in pressure units. The pressure measurement in the generator system occurs automatically, a feature that may prove useful in automatic control systems.

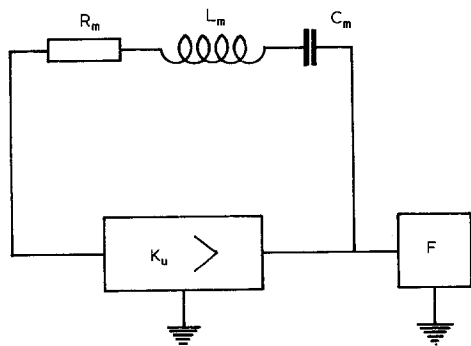


Fig. 7. The generator system for the automatic read-out of the resonance frequency of electrocapillary resonators.

Acknowledgements

Part of this work was supported financially by the University of Łódź through scientific programme MR I-11.

References

- [1] J. Kotowski, Z. Koczorowski and Z. Figaszewski, *J. Appl. Electrochem.* **10** (1980) 179.
- [2] Z. Koczorowski, 'Własności przetworników elektrokapilarnych', PWN Warsaw (1970).
- [3] Z. Figaszewski, E. Kucharska-Giziewicz, K. Lisowska, J. Kotowski and Z. Koczorowski, *J. Appl. Electrochem.* **10** (1980) 185.
- [4] Z. Koczorowski, E. Kucharska-Giziewicz and Z. Figaszewski, *ibid* **10** (1980) 191.
- [5] W. Bradley and E. E. Eller, 'Shock and Vibration Handbook', Vol. 1, (edited by C. M. Harris and C. E. Crede) McGraw-Hill, New York (1961) ch. 12.
- [6] Z. Koczorowski and L. Stawiszyński, Polish Patent No. 69 379 (1970).
- [7] Z. Figaszewski and Z. Koczorowski, *Roczniki Chem.* **46** (1972) 481.
- [8] *Idem, ibid* **48** (1974) 1577.
- [9] R. D. Cavanaugh, 'Shock and Vibration Handbook' Vol. 2 (edited by C. M. Harris and C. E. Crede) McGraw-Hill, New York (1961) ch. 33.