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USE OF THE RESONANCE PRINCIPLE IN THE PERMITTIVITY DETECTORS FOR LIQUID CHROMATOGRAPHY

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SUMMARY

Theoretical analysis of the resonance principle has been carried out from the point of view of its use for detection in liquid chromatography. Equations have been derived for the response of the detector to either the real or imaginary component of complex permittivity of the binary mixture: carrier liquid–analyzed component. It is shown that the response on either of the components is a linear function of concentration. The use is advantageous for a liquid with a very low tgδ and dielectric constant for the carrier.

INTRODUCTION

The detectors hitherto employed in liquid chromatography were recently evaluated by HUBER[1]. Whereas the other parts of the channel in a liquid chromatograph have attained remarkable parameters, the detector appears to be the weakest link of the chain at the present time. The development of the analytical utilization of liquid chromatography will depend to a considerable extent on the improvement of these detectors.

For the time being, there is no detector in liquid chromatography that could represent, with respect to the versatility of utilization, the detectors used in gas chromatography, and it seems that this situation will exist also in the near future. Therefore, new detection principles are searched for. One of them is the change of the permittivity brought about by the presence of the component under analysis in the carrier liquid and, consequently, the change in the parameters of the measuring condenser. The methods for measuring both components of the complex permittivity have been given considerable attention[2] owing to the direct relationship between the above parameters and the dipole moments as well as the relaxation constants of molecules in the alternating electric field. Some possibilities of utilizing the principle of the change of the real component of the complex permittivity, ε', in transforming the capacitance change into a frequency change and in measuring the capacity change with the aid of a.c. bridges of the Wheatstone type, are quoted in the literature[3]. The

great influence of the changes of capacitance and losses on the amplitude of the voltage or current in a resonant electrical circuit with low losses around the resonance offers further possibilities for the development of a detector with a very high sensitivity towards changes in the permittivity.

The aim of this paper is to carry out a theoretical analysis of the resonance principle with respect to the utilization of the latter for the detection in liquid chromatography and to the determination of the possibilities the resonance detector is capable to afford.

PRINCIPLE OF THE DETECTOR

If a voltage of constant amplitude U_g is applied to a series resonance circuit composed of fixed inductance L, variable capacity C, and resistor R, then, at a constant frequency, it holds[4] for the dependence of the voltage at the condenser terminals, U_c, on the tuning capacity C:

$$\frac{U_c}{U_r} = \frac{1}{\sqrt{1 + Q^2(\Delta C/C_r)^2}} \tag{1}$$

where U_c is the effective value of the voltage across the condenser at the capacity C, U_r stands for the same quantity, but at a resonance capacity C_r, Q is the quality
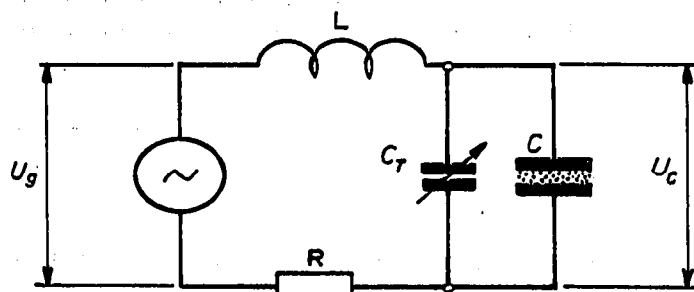

Fig. 1. Schematic of the detecting circuit in the use of the resonance principle.

factor of the resonance circuit, and $\Delta C/C_r$ is the relative capacity increment; $\Delta C/C_r = (C - C_r)/C_r = (C/C_r) - 1$. A graphical illustration of eqn. 1 for the capacity values $C \geqq C_r$ is given in Fig. 2.

Let us suppose the use of a carrier liquid with a "dielectric constant", ε'_c, smaller than ε'_x of the analyzed component and having a loss tangent δ_c very close to that of the detected component tgδ_x. In this case, it is necessary to detune by the trimming condenser C_T the resonant circuit in such way that the zero point P_1 is located on the upper outset of the linear part of the resonance curve when the carrier liquid flows through the measuring condenser C. Then, if the analyzed component with $\varepsilon'_x > \varepsilon'_c$ occurs in the carrier liquid, the resultant real part of the permittivity, ε'_m, is larger than that of the carrier liquid, so that the capacity of the measuring condenser increases proportionally to the concentration of the component and the voltage U_c on the condenser terminals falls. The voltage across the condenser is measured by a diode electronic voltmeter, in which the background voltage, $U_{c(0)}$ may be easily backed off, so that the slide-back recorder connected to the terminals of
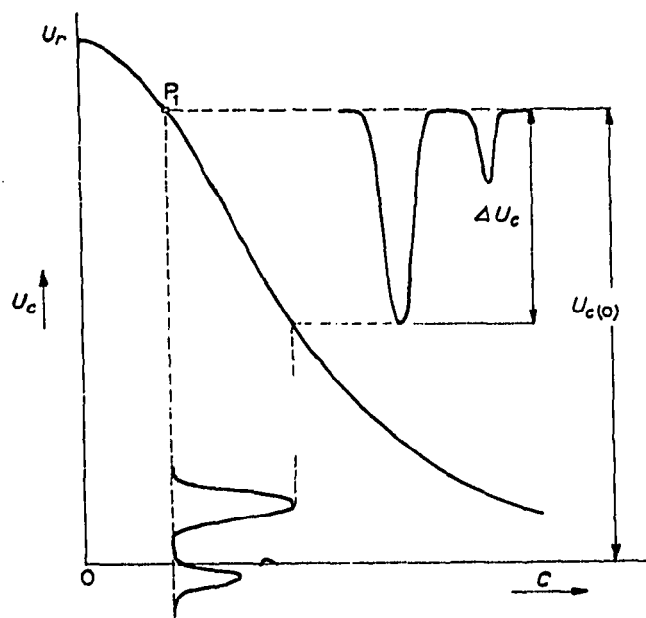
Fig. 2. Zero-point setting of the resonance detector.

the measuring instrument of the diode voltmeter will provide a conventional chromatographic record (Fig. 2).

DYNAMIC RANGE

According to eqn. 1, the slope of a resonance curve is given by:

$$y' = - Q^2 x / \sqrt{(1 + Q^2 x^2)^3} \tag{2}$$

The greatest slope is attained in the point of inflexion, $P_{\text{inf}}(x_0, y_0)$, given by the condition:

$$y'' = 0 \tag{3}$$

from which it follows for the coordinates of the latter:

$$x_0 = 1/Q\sqrt{2}, \quad y_0 = 0.8165 \tag{4, 5}$$

It is apparent from eqn. 5 that the inflexion point occurs at a constant relative height, regardless of the magnitude of the quality factor Q. It follows from eqn. 2 for the slope at the point of inflexion:

$$y_0' = -Q^2 x_0 / \sqrt{(1 + Q^2 x_0^2)^3} = -0.3848 \, Q \tag{6}$$

The dynamic range of linearity is defined as the concentration region in which the differential sensitivity is equal to the integral sensitivity[5] or where the difference between both types of sensitivity does not exceed certain limits; LOVELOCK[6] recommends a tolerance of 3%. The tangent line in the point of inflexion is given by the equation:

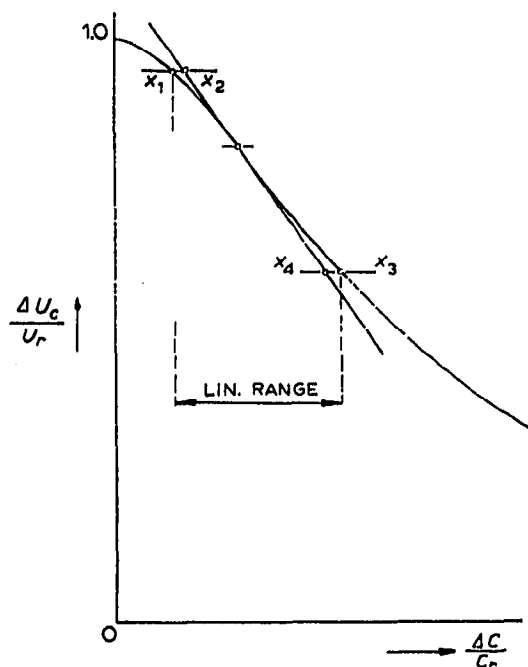$$y - 0.8165 = -0.3848 \, [x - (1/Q\sqrt{2})] \tag{7}$$

Fig. 3. Dynamic range of the resonance detector.

It holds for the point with the coordinate x_1 (Fig. 3), on the resonance curve above the point of inflexion, in which the deviation from the straight line drawn through the point of inflexion equals 3%:

$$x_1 = 0.97 \, x_2 \tag{8}$$

When substituting y and x in eqn. 7 by the respective quantities from eqns. 1 and 8, one obtains for x_1 the equation:

$$0.1574 \, Q^4 x_1^4 - 0.8637 \, Q^3 x_1^3 + 1.3423 \, Q^2 x_1^2 - 0.8637 \, Q x_1 + 0.185 = 0 \tag{9}$$

On introducing a new variable by $z_1 = Q x_1$, one obtains for the root of the above equation, using the *regula falsi* method:

$$x_1 = 0.413/Q \tag{10}$$

The end point x_3, below the point of inflexion, is given by:

$$x_3 = 1.03 \, x_4 \tag{11}$$

A procedure analogous to that used in case of the point x_1 leads to the following equation for the point x_3:

$$0.1396 \, Q^4 x_3^4 - 0.8134 \, Q^3 x_3^3 + 1.3245 \, Q^2 x_3^2 - 0.8134 \, Q x_3 + 0.1849 = 0 \tag{12}$$

and the coordinate of the point x_3 is given by:

$$x_3 = 1.201/Q \tag{13}$$

Hence, the linearity region characterized by the 3% deviation corresponds to the following limiting capacities:

$$x_3 - x_1 = (\Delta C_3 - \Delta C_1)/C_r = 0.788/Q \tag{14}$$

The capacity of the measuring condenser is necessarily composed of two components: a variable capacity C_x, the magnitude of which varies with the ε' of the liquid, and a constant capacity C_k, formed by the fixed dielectric determining the mutual position of the electrodes and providing the closure of the condenser cavity. Hence, it holds for the total capacity:

$$C = C_k + C_x = C_k + \varepsilon_0 \varepsilon' \, A/d = C_k + \varepsilon' C_0 \tag{15}$$

where ε_0 is the permittivity of the void space ($10^{-9}/9 \times 4\pi$ Farad/m), ε' is the relative real component of the complex permittivity, A is the cross-section of the dielectric, and d is the thickness of the dielectric.

If a carrier liquid with the real part ε'_c flows through the measuring condenser, it is necessary that the zero point be located at the place corresponding to the coordinate x_1. In order to set precisely this point, it is necessary to use the auxiliary trimming condenser C_T, as has already been quoted (Fig. 1). It apparently holds for the relative detuning of the capacity to the points x_1 and x_3:

$$\frac{\Delta C_1}{C_r} = \frac{\varepsilon'_c C_0 + C_T + C_k}{\varepsilon'_c C_0 + C_k} \tag{16}$$

$$\frac{\Delta C_3}{C_r} = \frac{\varepsilon'_m C_0 + C_T + C_k}{\varepsilon'_c C_0 + C_k} \tag{17}$$

where ε'_c, ε'_m are the real parts of the relative complex permittivity of the carrier, and of the mixture, respectively. On comparing the above equations with eqn. 14, there results the following general relation for the dynamic linearity range:

$$\frac{(\varepsilon'_m - \varepsilon'_c)C_0}{C_k + \varepsilon'_c C_0} = \frac{\varepsilon'_m - \varepsilon'_c}{(C_k/C_0) + \varepsilon'_c} = 0.788/Q \tag{18}$$

Thus, the relative real component of the permittivity of the carrier liquid with an admixture of the analyzed component may attain, within the dynamic linearity range, a maximum value given by:

$$\varepsilon'_m = 0.788 \, Q^{-1}\left(\frac{C_k}{C_0} + \varepsilon'_c\right) + \varepsilon'_c \tag{19}$$

Now, let us investigate the limits in which the concentration of the substance under analysis, m_x, may vary without the deviation from the linear course exceeding the above 3%.

The additive physical quantity is the polarization[7]. However, it may be assumed for the range of low concentrations that the linear additivity relation applies also to the real permittivity component so that the relation between the concentration of the analytical substance, m_x, with the permittivity ε'_x, the concentration of the carrier liquid, m_c, having the permittivity ε'_c, and the resultant permittivity ε'_m may be described by the linear equation:

$$\varepsilon'_m = m_c \varepsilon'_c + m_x \varepsilon'_x \tag{20}$$

where the concentrations m_x and m_c are expressed in volume fractions.

Thus, we obtain for a binary system:

$$\varepsilon'_m = (1 - m_x)\, \varepsilon'_c + m_x \varepsilon'_x \tag{21}$$

and the real component of the resultant permittivity is given by:

$$\varepsilon'_m = m_x(\varepsilon'_x - \varepsilon'_c) + \varepsilon'_c = 0.788\, Q^{-1}\!\left(\frac{C_k}{C_0} + \varepsilon'_c\right) + \varepsilon'_c \tag{22}$$

The maximum concentration of the analyzed component is defined by:

$$m_{x(\text{max.})} = 0.788\, \frac{\dfrac{C_k}{C_0} + \varepsilon'_c}{Q(\varepsilon'_x - \varepsilon'_c)} \tag{23}$$

SENSITIVITY TO THE CHANGE OF ε'

In chromatography, the sensitivity of the concentration detectors has been defined as the response in mV to 1 mg of the analyzed substance contained in 1 m of the column effluent. Since the concentration is expressed by volume fractions i our case, we shall define the sensitivity as the response in mV to 1 μl of the substance in 1 ml of the effluent. The sensitivity values expressed according to this definition will differ inappreciably from those based on the original "response to weight pc volume" definition.

Since the d.c. voltage $U_{c(0)}$ at the point x_1 is supposed to be backed off (Fig. 2 the absolute value of the d.c. response is equal to the difference between the ampl tudes of the high frequency voltage U_c across the condenser at the points x_3 and x_1

$$U_{c(1)} - U_{c(3)} = U_r\!\left(\frac{1}{\sqrt{1 + Q^2 x_1^2}} - \frac{1}{\sqrt{1 + Q^2 x_3^2}}\right) \tag{24}$$

which yields on substituting for Qx_1 and Qx_3 from eqns. 10 and 13:

$$U_{c(1)} - U_{c(3)} = 0.284\, U_r \tag{25}$$

With regard to the definition suggested, it may then be written for the sens tivity to the change of the real component of permittivity:

$$S_{\varepsilon'} = \frac{0.284\, U_r}{m_{x(\text{max.})}} = 0.36\, U_r Q\, \frac{\varepsilon'_x - \varepsilon'_c}{\dfrac{C_k}{C_0} + \varepsilon'_c} \tag{26}$$

Since it holds[4]:

$$Q = U_r / U_g \tag{27}$$

where U_g is the driving generator voltage, one may write the following practicall advantageous formula for the sensitivity $S_{\varepsilon'}$:

$$S_{\varepsilon'} = 0.36\, U_g Q^2\, \frac{\varepsilon'_x - \varepsilon'_c}{\dfrac{C_k}{C_0} + \varepsilon'_c} \tag{28}$$

Example:

$$C_0 = 40 \text{ pF}, C_k = 10 \text{ pF}, \varepsilon'_x = 4, \varepsilon'_c = 2, Q = 200, U_g = 0.1 \text{ V}.$$

$$S_{\varepsilon'} = 0.36 \times 0.1 \times 200^2 \times \frac{(4-2)}{0.25+2} = 1280 \frac{\text{mV}}{\mu\text{l/ml}}$$

The concentration dynamic range extends from zero to:

$$m_{x(\text{max.})} = 0.788 \frac{\dfrac{10}{40} + 2}{200 \, (4-2)} = 4.433 \times 10^{-3}$$

i.e., within $0 - 4.433 \, \mu\text{l/ml}$.

EFFECT OF ε'' ON THE DETECTOR RESPONSE

We have supposed in our considerations until now that the loss tangent, tgδ, of the carrier liquid is approximately the same as that of the components under detection, so that the resultant loss tangent, tgδ_m, remains practically unchanged when changing the concentration. The detector then reacts linearly by a voltage change on the concentration m_x of the component detected, within the linearity concentration range.

It is apparent from eqn. 1 that the detector response is a function of the capacity change, $\Delta C/C_r$, and of the quality factor Q. If the quality factor Q is considered to be a variable quantity and assuming that $\Delta C/C_r$ is constant, the relations derived will hold true analogously for the response to the presence of a substance the "dielectric constant" of which is approximately equal to the ε'_c of the carrier liquid, but whose losses are higher than that of the carrier liquid. The resonance detector may be highly sensitive even to very small loss changes, where the other methods, *e.g.* bridge ones, show already low sensitivity.

It follows from the first Maxwell equation for the electric current density J in the condenser:

$$\vec{J} = g\vec{E} + \varepsilon^*_a \frac{\partial \vec{E}}{\partial t} \tag{29}$$

where g is the conductivity of the dielectric, E is the electric field intensity, and ε^*_a is the absolute complex permittivity, given by:

$$\varepsilon^*_a = \varepsilon'_a - j \, \varepsilon''_a \tag{30}$$

After substituting for ε^*_a in eqn. 29 and multiplying the whole equation by the dielectric cross-section A, and assuming a homogeneous electric field and isotropic dielectric (liquid), one gets for the current in the condenser with the dielectric thickness d:

$$\vec{I} = g \frac{A}{d} \vec{U}_c + \omega \varepsilon''_a \frac{A}{d} \vec{U}_c + j\omega \, \varepsilon_0 \varepsilon' \frac{A}{d} \vec{U}_c = G_g \vec{U}_c + G_{\varepsilon''} \vec{U}_c + j\omega \, C \vec{U}_c \tag{31}$$

It follows from the above equation that the behavior of a real condenser with liquid showing dielectric losses and a non-zero conductivity may be modelled by an
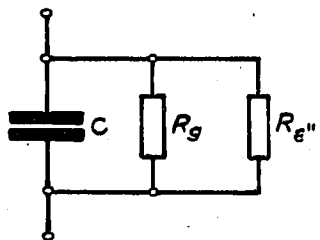
Fig. 4. Equivalent circuit for the condenser with a liquid with losses.

equivalent electric circuit in which resistances equal to the inverse values of the respective conductances are connected in parallel to an ideal condenser without loss (Fig. 4):

$$R_g = \frac{1}{G_g} = \frac{d}{gA} \tag{32}$$

$$R_{\varepsilon''} = \frac{1}{G_{\varepsilon''}} = \frac{d}{\omega \varepsilon''_a A} = \frac{d}{\omega \varepsilon_0 \varepsilon'' A} \tag{33}$$

It holds for the reciprocal value of the quality factor[4]:

$$\frac{1}{Q} = \frac{1}{Q_L} + \frac{1}{Q_c} = \frac{1}{Q_L} + \frac{G}{\omega_r C_r} \tag{34}$$

where

Q_L is the quality factor of the inductive coil,
Q_c is the quality factor of the measuring condenser,
ω_r is the angular resonance frequency,
C_r is the resonance capacity value, and
G is the total parallel conductance of the condenser.

The conductivity component in eqn. 32 may be included into losses, which yields, after substituting from eqn. 33 into eqn. 34, the equation that interprets the effect of the imaginary component of the complex permittivity on the resultant quality factor of the measuring resonant circuit:

$$\frac{1}{Q} = \frac{1}{Q_L} + \frac{\varepsilon_0 \varepsilon'' A}{C_r d} \tag{35}$$

In the case of the flow of pure carrier liquid with ε'_c the circuit is supposed to be in resonance. Hence, there holds for the resonance capacity:

$$C_r = \varepsilon_0 \varepsilon'_c \frac{A}{d} = \varepsilon'_c C_0 \tag{36}$$

so that it holds for the resultant quality factor at the flow of pure carrier liquid:

$$\frac{1}{Q} = \frac{1}{Q_L} + \frac{\varepsilon''_c}{\varepsilon'_c} = \frac{1}{Q_L} + \mathrm{tg}\delta_c \tag{37}$$

If a detected component is present having the parameters ε'_x, ε''_x, it will analogously hold for the resultant quality factor:

$$\frac{1}{Q_m} = \frac{1}{Q_L} + \mathrm{tg}\delta_m = \frac{1}{Q_L} + \frac{\varepsilon''_m}{\varepsilon'_m} \tag{38}$$

Provided a linear relationship holds between the concentration expressed in volume fractions, m, and the imaginary component of the complex permittivity, ε'', for low concentrations, analogously to eqn. 20, one gets for the resultant real part of the imaginary component of the permittivity of a binary mixture:

$$\varepsilon''_m = m_c \varepsilon''_c + m_x \varepsilon''_x = (1 - m_x)\,\varepsilon''_c + m_x \varepsilon''_x \tag{39}$$

and, after substituting into eqn. 38,

$$\frac{1}{Q_m} = \frac{1}{Q_L} + \frac{\varepsilon''_c + m_x(\varepsilon''_x - \varepsilon''_c)}{\varepsilon'_m} = \frac{1}{Q_L} + m_x \frac{\varepsilon''_x}{\varepsilon'_m} + \mathrm{tg}\delta_c - m_x\,\mathrm{tg}\delta_c \tag{40}$$

which yields for the quality factor of the mixture with the component under detection:

$$Q_m = \frac{Q}{m_x Q \left(\dfrac{\varepsilon''_x}{\varepsilon'_m} - \mathrm{tg}\delta_c \right) + 1} \tag{41}$$

As it is supposed that $\varepsilon'_x \doteq \varepsilon'_c$, the capacity remains constant during detection, which corresponds to the zero point at the flow of pure carrier:

$$\frac{\Delta C_1}{C_r} = 0.413\,Q^{-1} \tag{42}$$

but the quality factor falls from the initial value Q to Q_m due to the presence of the substance detected and it holds:

$$Q_m \frac{\Delta C_1}{C_r} = 0.413 \frac{Q_m}{Q} \tag{43}$$

The detector response to the effect of ε''_x will be:

$$\Delta U_c = U_{c(1)} - U_{c(2)} = \frac{U_g Q}{\sqrt{1 + 0.413^2}} - \frac{U_g Q_m}{\sqrt{1 + 0.413^2 Q^2_m/Q^2}} \tag{44}$$

From eqn. 41 it follows:

$$\frac{Q_m}{Q} = \frac{1}{m_x Q \left(\dfrac{\varepsilon''_x}{\varepsilon'_c} - \mathrm{tg}\delta_c \right) + 1} \doteq \frac{1}{m_x Q\,(\mathrm{tg}\delta_x - \mathrm{tg}\delta_c) + 1} \tag{45}$$

and substituting into eqn. 44 one gets for the response to ε''_x:

$$\Delta U_c = U_g Q \left(0.924 - \frac{1}{\sqrt{[m_x Q\,(\mathrm{tg}\delta_x - \mathrm{tg}\delta_c) + 1]^2 + 0.413^2}} \right) \tag{46}$$

Fig. 5 shows the plots of the courses of the function $\Delta U_c = f_{\varepsilon''}(m_x)$ for the case of $Q = 200$, $U_g = 0.1$ V, and $\mathrm{tg}\delta_c = 10^{-3}$. Plots A and B have been calculated for the $\mathrm{tg}\delta_x$ of 2×10^{-3} and 11×10^{-3}, respectively.

The functions $\Delta U_c = f_{\varepsilon'}(m_x)$ and $\Delta U_c = f_{\varepsilon''}(m_x)$ are linear within low concentration limits. Owing to the law of superposition, the resultant response is also linear, being the sum of the response to ε'_x and ε''_x.
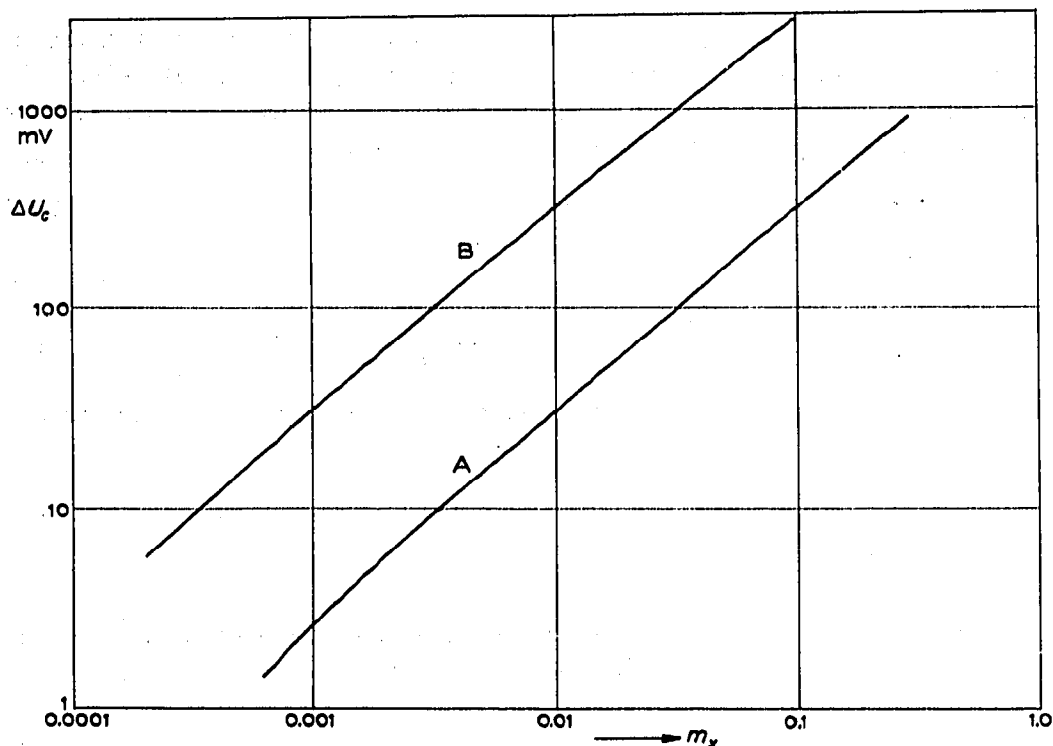
Fig. 5. Dependence of the response brought about by ε''_x on concentration for different $\mathrm{tg}\delta_x$.

CONCLUSION

A theoretical analysis of the basic characteristics of the LC permittivity detector was performed in which the principle of resonance has been used. In the detection of liquid components having $\varepsilon'_x > \varepsilon'_c$ and approximately the same loss tangent, $\mathrm{tg}\delta_x \doteq \mathrm{tg}\delta_c$, the predominating component of the response is the voltage drop across the condenser due to the capacity change. In the opposite case, where $\varepsilon'_x \doteq \varepsilon'_c$, but $\mathrm{tg}\delta_x > \mathrm{tg}\delta_c$, there predominates in the response the voltage drop across the condenser caused by the decrease of the quality factor Q of the resonant circuit. As both responses are approximately linear in the limits of low concentrations, the resultant response is the sum of both partial responses.

It is always advantageous to choose a non-conductive substance having lowest possible dielectric losses as the carrier liquid in employing the resonance principle.

In respect to the present-day state of the engineering in the resonance methods, when it is possible to attain $Q = 1000$ with both coaxial resonators as well as in circuits with lumped parameters[8], the resonance principle of detection presents remarkable possibilities.

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