

APPLICATION OF TEMPERATURE COEFFICIENTS OF PERMITTIVITY FOR BINARY MIXTURES ANALYSIS

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A method is proposed for continuous analysis of liquid mixtures. The method is based on the fact that with increasing concentration of water (in general of a component of greater permittivity) the permittivity of the mixture increases, whereas with increasing temperature it diminishes with most substances. Compensation principle is used so that permittivity of the sample is kept at constant value. The changes of permittivity, caused by changes of concentration, are compensated by the changes of permittivity caused by temperature. Concentration measurements are converted to temperature measurements whereby temperature can be measured in any arbitrary way. The main advantage of the method is that the unfavourable effect of temperature fluctuations on the analyzer reading is compensated.

Measurement of permittivity is a method suitable for checking the purity of liquid chemical individualia as well as for analyzing binary and multicomponent systems. The best known example is the application of this method for the determination of water content in organic substances.

Static permittivity of binary mixtures of liquids is above all a function of temperature and composition of the mixture. With polar substances the changes of permittivity due to temperature fluctuations are comparable with the changes of permittivity caused by concentration changes, thus making in most cases an accurate determination of concentration impossible. Temperature dependence of permittivity can be eliminated *e.g.* by thermostating the sample or using a calibration graph. However, these methods are not suitable for automatic continuous industrial analysis.

The aim of the present work was to suggest a method for the determination of concentration of binary mixtures in which the effect of temperature on the concentration reading would be eliminated. Application of this method will form the subject of further papers.

THEORETICAL

Dependence of Permittivity on Temperature and Concentration

When proposing a measuring method in which the effect of temperature is compensated it is important to know the course of the temperature dependence of permittivity on both temperature and concentration. The relation of temperature dependence of permittivity of polar liquids to their structure was investigated *e.g.* by Dannhauser¹. Decroocq² and Horig³ studied the possibility to describe the permittivity of mixtures by means of molecular properties of the components. From the mentioned as well as from further papers it follows that the present state of knowledge of the structure of polar substances does not allow to calculate the dependence of permittivity of their mixtures on temperature and composition which must be determined experimentally. A number of empirical and semiempirical equations were proposed to describe phenomenologically the experimental data. A survey of equations, expressing the temperature dependence of permittivity, is given *e.g.* by Varshni⁴, the dependence on concentration is described by equations suggested by Pradhan⁵ and Reynolds⁶.

Temperature dependence of the permittivity of liquids is in most cases of a nearly linear character. Therefore it can be, in not too wide temperature intervals, characterized by an absolute temperature coefficient,

$$\alpha = d\varepsilon'/dt \approx (\varepsilon'_{t_1} - \varepsilon'_{t_2})/(t_1 - t_2). \quad (1)$$

Approximate values of absolute temperature coefficients of some groups of substances are given in Table I. With a few exceptions (dimethylethylcarbinol, triethylcarbinol, *etc.*) the temperature coefficient of permittivity has a negative sign.

The dependence of permittivity on mixture composition is mostly non-linear, attaining in some cases extrema. Decroocq² investigated the permittivity of 200

TABLE I
Temperature Coefficients of Permittivity

Substance	α , deg ⁻¹		Literature
Saturated hydrocarbons	-0.0012	to -0.0018	7-9
Halogen derivatives of hydrocarbons	-0.01	to -0.07	10, 11
Ketones	-0.03	to -0.1	12, 13
Alcohols	-0.1	to -0.18	14, 15
Water	-0.36		16

binary mixtures of common organic solvents of which 50 showed a linear dependence of permittivity on composition within the limits of 0.5%.

The linearity of this dependence is also influenced by the choice of concentration units. So, *e.g.*, the permittivity of a mixture of methanol with aliphatic alcohols is a linear function of volume fraction, whereas its dependence on molar fraction¹⁷ is markedly non-linear.

In order to determine the extent of nonlinearities it is necessary to investigate the general form of the dependence of permittivity on both temperature and concentration. Permittivity of the mixture is measured usually in the vicinity of the operating point characterized by concentration c_0 (mass %) and temperature t_0 ($^{\circ}\text{C}$). In this region the dependence of permittivity on concentration and temperature can be expressed in terms of Taylor series

$$\begin{aligned} \varepsilon'(c, t) = \varepsilon'(c_0, t_0) + \left(\frac{\partial \varepsilon'}{\partial c}\right)_{c_0, t_0} \Delta c + \left(\frac{\partial \varepsilon'}{\partial t}\right)_{c_0, t_0} \Delta t + \frac{1}{2} \left(\frac{\partial^2 \varepsilon'}{\partial c^2}\right)_{c_0, t_0} \Delta c^2 + \\ + \frac{1}{2} \left(\frac{\partial^2 \varepsilon'}{\partial t^2}\right)_{c_0, t_0} \Delta t^2 + \left(\frac{\partial^2 \varepsilon'}{\partial t \partial c}\right) \Delta t \cdot \Delta c + \dots \end{aligned} \quad (2)$$

Values of the individual partial derivatives depend on the choice of operating point (c_0, t_0). To make the output signal of the analyzer to be a function of concentration only, we have to eliminate the effect of all terms containing temperature differences. If the concentration dependence of permittivity can be described with the necessary accuracy only by the first two terms of the series, *i.e.*

$$\varepsilon'(c, t) = \varepsilon'(c_0, t_0) + \left(\frac{\partial \varepsilon'}{\partial c}\right)_{c_0, t_0} \Delta c, \quad (3)$$

then the scale of the analyzer is linear. The value of the nonlinearities is given by the values of higher derivatives in Taylor series.

There is a lack of data in the literature concerning the dependence of permittivity both on temperature and concentration. Therefore the values of the partial derivatives in Taylor series (2) were determined only for mixtures of lower aliphatic alcohols and acetone with water. The operating point was chosen at 20 $^{\circ}\text{C}$, 0% H_2O , to determine the suitability of the suggested method for the measurement of low contents of water in alcohols and ketones. Experimental data were taken from the work of Akerlöf¹⁵. The values of the derivatives with respect to temperature were calculated according to the empirical equation

$$\log \varepsilon' = \log a - b_1(t - 20). \quad (4)$$

TABLE II
Values of Differential Quotients in the Taylor's Expansion Series

Substance	$\partial \epsilon' / \partial c$		$\partial^2 \epsilon' / \partial c^2$	
	(mass%) ⁻¹	rel. %	(mass%) ⁻²	rel. %
Methanol	0.422	100	0.035	0.8
Ethanol	0.377	100	0.0072	1.9
1-Propanol	0.210	100	0.0080	3.8
2-Propanol	0.208	100	0.0066	3.2
Acetone	0.480	100	0.0061	1.3

Values of the derivatives with respect to concentration were determined graphically. The results are summarized in Table II. Third-order derivatives are negligibly small (of the order of 10^{-6}) and therefore they were not included in the Table which also gives the relative values of individual derivatives (in rel. %).

Use of Table II: 1. The table can be used for determining the nonlinearity of analyzer scale. *E.g.* the problem of the determination of water content in ethanol in the range 0–2% is solved in the following way: The whole range of the analyzer is equivalent at constant temperature to a permittivity change $\Delta \epsilon'$

$$\Delta \epsilon' = \left(\frac{\partial \epsilon'}{\partial c} \right) \Delta c + \frac{1}{2} \left(\frac{\partial^2 \epsilon'}{\partial c^2} \right) \Delta c^2 = 0.377 \cdot 2 + \frac{1}{2} 0.0072 \cdot 2^2 = 0.768$$

Relative value of the nonlinear term is

$$\frac{0.0144}{0.768} \cdot 100 = 1.9\%$$

Consequently, the nonlinearity of scale can in this case become evident only in measurements with a relative error lesser than 2%. 2. The table can further be exploited for the determination of the temperature interval within which temperature can fluctuate without causing any increase in the relative error of measurements. Let us consider the same analytical problem. Again the permittivity change $\Delta \epsilon = 0.768$ corresponds to full deflection of the analyzer. Permittivity changes owing to temperature fluctuation ought not to exceed the value of relative error 2%, i.e. 0.015 permittivity units. When the measurement is carried out without temperature compensation, it is necessary to keep the temperature constant within an error $0.015/0.152 =$

TABLE II
(continued)

$\partial\epsilon'/\partial t$		$\partial^2\epsilon'/\partial t^2$		$\partial^2\epsilon'/(\partial c \partial t)$	
deg ⁻¹	rel. %	deg ⁻²	rel. %	deg ⁻¹ (mass%) ⁻¹	rel. %
-0.174	41	0.00094	0.2	0.0031	0.7
-0.152	40	0.00092	0.2	0.0028	0.7
-0.140	67	0.00094	0.4	0.00081	0.4
-0.133	64	0.00095	0.5	0.00043	0.2
-0.091	19	0.00042	0.09	0.0032	0.7

= 0.1°C. When using linear temperature compensation we can evaluate the admissible temperature fluctuation from the relation

$$0.015 = \frac{1}{2}(\partial^2\epsilon'/\partial t^2) \Delta t^2$$

and hence

$$\Delta t = \sqrt{\frac{0.015 \cdot 2}{0.00092}} \approx 5.8^\circ\text{C}.$$

Technique of Measurement

The proposed method is based on the fact that with increasing concentration of water (or in general of a component with higher permittivity) the permittivity of sample increases, whereas with most organic liquids it decreases with the increase of temperature. The compensation is applied in the way that the permittivity of sample is maintained constant, its changes owing to concentration changes being compensated by the changes caused by temperature. So *e.g.* if the permittivity of sample increases as a result of the change in water concentration, the sample is heated to reconstitute the initial value of the permittivity. In this way temperature becomes a measure of the concentration of water in organic liquid.

The relation between temperature and concentration can be derived from Taylor series (2). Permittivity of the sample is kept at constant value during measurement which means that the deviations from the required value $\Delta\epsilon'$ are zero

$$\Delta\epsilon' = \epsilon'(c, t) - \epsilon'(c_0, t_0) = 0. \quad (5)$$

After substitution from series (2) into Eq. (5) we obtain, neglecting third-order terms

$$\begin{aligned} & \left(\frac{\partial \varepsilon'}{\partial c} \right)_{c_0, t_0} \Delta c + \left(\frac{\partial \varepsilon'}{\partial t} \right)_{c_0, t_0} \Delta t + \frac{1}{2} \left(\frac{\partial^2 \varepsilon'}{\partial c^2} \right)_{c_0, t_0} \Delta c^2 + \\ & + \frac{1}{2} \left(\frac{\partial^2 \varepsilon'}{\partial t^2} \right)_{c_0, t_0} \Delta t^2 + \left(\frac{\partial^2 \varepsilon'}{\partial c \partial t} \right)_{c_0, t_0} \Delta c \Delta t = 0. \end{aligned} \quad (6)$$

Eq. (6) gives a physically unambiguous relation between temperature Δt and concentration Δc . Temperature can be expressed explicitly in the following form

$$\Delta t = \frac{\frac{\partial \varepsilon'}{\partial t} - \frac{\partial^2 \varepsilon'}{\partial t \partial c} \Delta c \pm \sqrt{\left[\left(\frac{\partial \varepsilon'}{\partial t} + \frac{\partial^2 \varepsilon'}{\partial t \partial c} \Delta c \right)^2 - \frac{\partial^2 \varepsilon'}{\partial t^2} \left(2 \frac{\partial \varepsilon'}{\partial c} \Delta c + \frac{\partial^2 \varepsilon'}{\partial c^2} \Delta c^2 \right) \right]}{\frac{\partial^2 \varepsilon'}{\partial t^2}}. \quad (7)$$

Taking into account that the value of second-order terms amounts only a few per cent as compared with the first-order terms (see Table II), it is possible to employ Eq. (8) instead of Eq. (7) to a fairly accurate estimation of the necessary temperature increase. Eq. (8) is obtained from Eq. (6) by omitting the second-order terms

$$\Delta t = \frac{(\partial \varepsilon' / \partial c)_{c_0, t_0}}{(\partial \varepsilon' / \partial t)_{c_0, t_0}} \Delta c. \quad (8)$$

Block diagram of the proposed method is shown in Fig. 1. The sample to be ana-

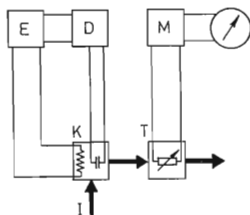


FIG. 1

Block Diagram of the Analyzer

K Measuring cell, D deviation indicator, E controller, T thermometer, M measuring bridge, I inlet of the analyzed sample.

lyzed is led through cuvette K the first part of which is formed by a miniature heat exchanger. Permittivity changes of the sample are reflected as capacity changes of the measuring condenser connected into the resonance circuit fed from a high-frequency supply. This circuit is modulated by 50 Hz frequency voltage. The course of phase and amplitude of the demodulated voltage indicates the deviation of the desired value of the real component of permittivity. Signal from the indicator is processed in the controller. According to the sign of the control deviation the heating input in the heat exchanger is controlled so that to make the deviation from the desired value of permittivity equal zero. Temperature of the leaving sample which is proportional to the concentration is measured by a thermometer and registered by a recorder.

DISCUSSION

The described method can be in principle applied to all mixtures of liquids whose temperature coefficient of permittivity is different from zero and has the same sign over the whole measured range. It cannot be applied only in a few exceptional cases, as *e.g.* in the determination of water, which has a negative temperature coefficient, in an organic substance with a positive temperature coefficient. In this case the temperature coefficient of the mixture changes its sign. So, *e.g.* the temperature coefficient of permittivity of the mixture water-acetic acid changes its sign at the concentration of water 0.52% (see¹⁸).

The sensitivity and accuracy of the suggested analyzer is given by the relative values of temperature and concentration coefficients of permittivity in the given case as well as by the accuracy of temperature measurement. For instance, let us suppose that temperature is measured with an error $\pm 0.05^\circ\text{C}$. If we want to measure the concentration, *i.e.* also the temperature with a relative error $\pm 2\%$, the minimum temperature interval must be $\Delta t_{\min} = 2.5^\circ\text{C}$. The minimum measuring range Δc_{\min} (in mass%) can be evaluated, if we express Δc explicitly from Eq. (6) and if we substitute $\Delta t = \Delta t_{\min}$. This interval can be, however, calculated with sufficient accuracy using Eq. (9), in which the effect of higher derivatives is neglected

$$\Delta c_{\min} = \frac{\partial \epsilon' / \partial t}{\partial \epsilon' / \partial c} \Delta t_{\min} \quad (9)$$

Table III gives the minimum measuring ranges of the analyzer allowing to determine the content of water with a relative error $\pm 2\%$. The values were calculated according to relation (7) using the data from Table II. They are valid for the vicinity of the operating point 20°C , 0 mass% water, under the assumption that temperature is measured with a relative error $\pm 0.05^\circ\text{C}$. A still higher accuracy than that mentioned in the case of alcohols can be attained with substances having a lower ratio of tempera-

TABLE III
Minimum Measurement Ranges of the Analyzer and Error in Water Determination

Substance	Min. range %	Error, %
Methanol	1.8	± 0.04
Ethanol	1.9	± 0.04
1-Propanol	3.0	± 0.06
2-Propanol	3.0	± 0.06
Acetone	0.9	± 0.02

ture and concentration coefficients, as it is *e.g.* with ketones and organic halogen derivatives.

An important condition for correct functioning of the control circuit is that the dynamic properties of the controlled system allow a sufficient control performance. A transfer lag between the point of heating and the measuring condenser should be eliminated. It depends above all on the design of the measuring cell.

Further prerequisite is a sufficient accuracy of the deflection indication. Changes of permittivity, corresponding to the accuracy of temperature measurement, must be detectable. This demand can easily be satisfied, since the sensitivity of the devices for permittivity measurement attains $5 \cdot 10^{-5}$ to $5 \cdot 10^{-7}$ permittivity units, whereas with alcohols, as above mentioned, the accuracy of $5 \cdot 10^{-3}$ is sufficient.

The main advantage of the presented method of concentration determination in binary mixtures is that the unfavourable effect of temperature fluctuations of the measured sample is compensated. Moreover, the method employs the compensation procedure, thus having all advantages of zero methods, as *e.g.* the independence of the reading on amplification, as well as on voltage supply and other disturbing effects.

The classical technique of determining concentration by measuring the permittivity of a thermostated sample with the use of compensation needs two control loops – one for temperature regulation and the other one, providing the compensation of permittivity by means of an electronic compensator. The analyzer which operates on the basis of the proposed method, combines both these functions so that only one control circuit is necessary. All advantages of this arrangement (economy, lower failure rate) are obvious.

Verification of the new method by measuring the content of water in cyclohexanone in the concentration and temperature ranges 0–0.6% and $26 \pm 3^\circ\text{C}$ respectively, will be the subject of the next publication.

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