4 - 37 UTILISATION OF THE IMPEDANSOMETRIC METHOD FOR EVALUATING MEAT EMULSIONS STABILITY

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The stability and kinetics of ageing are a basic index for characterization and qualification of the emulsion colloid-dispersion systems /1,3/. Usually, when determining the index stability, the authors seek correlation with changes in the disperion systems colligative properties. These are osmotic pressure, steam pressure, molar enthalpy of a phase transition, light dispersion etc. These properties depend on the size and number of particles of the dispersion phase. Their change is connected with process ensuring the ageing as much as the final result of this process is enlarging and sedimentation of dispersion phase. The colligative status of dispersion system is being disturbed. In most cases this is a stage of storage or realization of the emulsion product. This substantially limits the possibility for utilisation of the data obtained concerning the system's stability in effective technological control realization. In literature no sufficiently reliable method for determining emulsive dispersion systems stability has been described, (EDS), in the course of their getting, /4,6 /.

A good possibility for getting information reflecting the processes in EDS which precedes visible structure changes is the low-frequency impedansometry /5.6/ . In the present work, by limiting ourselves only on the emulsified part of the filling mass in the production of boiled sausages, we discuss the question of low-frequency impedansometry applicability for exercising an effective control upon the stability and kinetics of ageing of emulsive dispersion systems oil/water (O/W).

The general current transmission in a unidispersion system is a sum of two addenda :

a/ volume current transmission $\varkappa$ realized by the loads contained in the water continium of the system;

b/ surface electroconductivity $\varkappa^{6}$, realized in the double electric layer (DEL) frames. It appears in the phase contact oil/water, Fig. 1. The thickness of DEL is in the limits from 10 Å to 100 Å /7/ , and depends on the character of the osculated phases. As Bockris /7,8/ showed, because of the loads small sizes and their high density, in the limits of DEL there is a big gradient in the value of the relative dielectric permeability (from 15 ÷ 20 to 80 for O/W EDS) and a high field intensity ($\sim 10^9$ V. am^{-1} in the limits of the layer of Stern). All this gives some specific properties to the medium included in the limits of DES. The current transmission in the volume of a salt system is made by means of migration or diffusion. Having in mind the indicated characteristics of the double-electric layer around the dispersion phase particles, in the limits of the phase contact oil/water of the emulsive dispersion systems, the loads are transmitted not rarely by means of a "baton" mechanism. It has a far greater transmission coefficient in comparison with the volumetric current transmission. In this case, the general resistance of the medium can be viewed upon as a sum of two addenda : R_V - ohmic resistance of the water continium, and R_6 - the resistance of the medium included in the limits of the double electric layer ($R_6 << R_V$).

The process of ageing of EDS is expressed in the merging of oil drops and demulsification of the system. This process is preceded by changes in DES structure, which arises on the place of the phase contact O/W. That is why, the value of $\varkappa^6$ and from there the general electroconductivity of the system also give a possibility to obtain information about the stability and ageing kinetics of the emulsive dispersion-systems.

In the course of helding the AC contact measurement, regardless of their character, some data are experimentally obtained, concerning the summing input impedance of the system Z_{Bx} .

j - imaginary unit

ω - angle frequency

For emulsive dispersion systems of the type O/W, in the low-frequency range (10 Hz) the inductive addendum of the impedance has not a real contribution 9,10 . At these conditions the equivalent electric circuit of a dielectrode cell can be presented as it is shown on Fig. 1a and a current characteristics of measuring the impedance - Fig. 2.

$$Z_{Bx} = j\omega L + R + j(\omega C)^{-1}$$

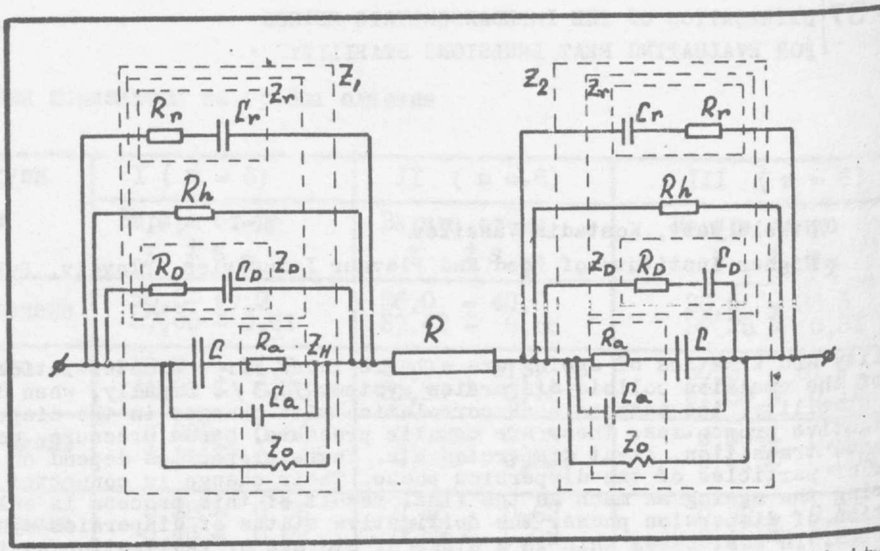

Fig. 1a. Equivalent electric circuit at low-frequency and conductivity measurement with a double-electrode cell, where, Z_1, Z_2 - summing electrode impedances; R - ohmic resistance of the solution; C - DES capacity at the electrodes; Z_r, R_r, C_r - impedance and its component elements reporting the electrode reactic; Z_D, R_D, C_D - diffusion impedans; Z_H, R_a, C_a - dipoloorientational impedans /11/; R_h a resistance of transmission.

If we designate with Z_F all the contributions in the electrode impedances Z_1 and Z_2 except the double electric layer capacity at the electrodes C_1 and C_2 for the measurable input impedans Z_{BX} can be written in the following way :

$$Z_{Bx} = R + \underbrace{\frac{2 R_F C_F^2}{(\omega R_F C_F C)^2 + (C + C_F)^2}}_{Z'_{Bx}} - 2j \underbrace{\frac{(\omega R_F C_F)^2 C + C + C_F}{(\omega R_F C_F C)^2 + (C + C_F)^2}}_{Z''_{Bx}}$$

where : Z' Z'' - a substantial and imaginary addendum of Z_{BX}

$$Z_{Bx} = Z'_{\omega} + R + Z''_{Bx} = Z'_{Bx} + Z''_{Bx} \qquad /3/$$

Let us consider the substantial part Z'_{BX}. It is complied of two members : ohmic resistance of the investigated system R and the frequency dependent member Z'_{ω}. At impedance measurements with an alternating current bridge with a separated compensation on R and C, the measurable value for Z' is a complex function of R and Z'_{ω} /12/. The value Z_{ω} reports the polarizing effects in the intraelectrode space. If the contribution in Z' is significant, this leads to a frequency dependance of the substantial addendum of the impedance /13/.

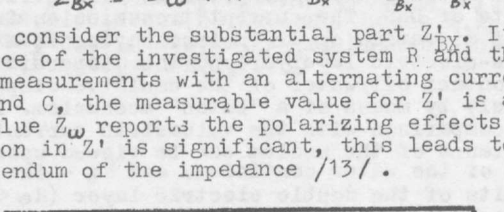

Fig. 2 Current circuits at the alternating current low-frequency impedansometry.

This creates great difficulties in the interpretation of the impedance frequency dependance in alternating current conductometry. The value of R contains the pure ohmic resistance of the medium R_m and the resistance determining the surface electroconductivity $R\sigma$. Consequently, in order to improve the low-frequency conductometry sensitiveness as regards the changes in the limits of the double electric layer as a result of the emulsive dispersion systems ageing, it is necessary :

1/ To realize a low-frequency contact conductometry at which the relative part of R in the substantial part of the measurable impedance should grow, and Z_ω to have the smallest contribution;

2/ To determine the analytical aspect of the dependance $R = f(\varkappa')$, in order to be possible to calculate $\varkappa^{\infty}$ from data for Z'.

In the work /14/it has been shown that when operating with a polarized functional and geometric, and not symmetric electrode system and an AC bridge, with a separated compensation on R and C, the measured values for Z', up to 10 kHz are frequency independent. i.e. $Z_\omega \to 0$. The substantial and imaginary part of Z_{BX} are built from the resistance of the system R and from the double electric layer capacity at the electrode with a smaller electrode surface, called indicative. In such case the equivalent electric circuit of the system is presented by means of a resistance and capacity switched in series, Fig. 3.

$$Z_{BX} = R + \frac{1}{j\omega C} \qquad /4/$$

In support of the conclusion drawn we should allow the affirmation of an opposite character. Let the equivalent electric circuit contain R_x and C_x elements dotting the capacity of the indicator electrode, Fig. 4.

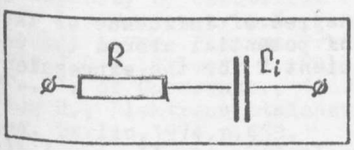

Fig. 3. Equivalent electric circuit /14/.

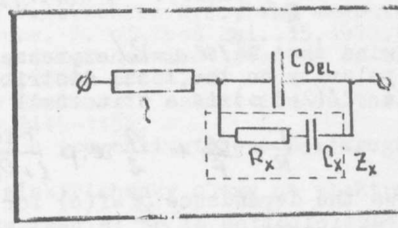

Fig. 4. Equivalent electric circuit complicated with and C_x.

The impedance of such a circuit will be :

$$Z_{BX} = R + \frac{Z}{1 + j\omega C Z_x} \qquad /5/$$

where

$$Z_x = \frac{j w C_x R_x + 1}{j\omega C_x} \qquad /6/$$

$$Z_{Bx} = R + \frac{1 + j\omega C_x R_x}{j\omega(C_x + C) - \omega^2 C_x R_x C} = R + Z_{xx} \qquad /7/$$

Let us show Z_{BX} in a complex way, by separating the real and the eimaginary part in Z_{XX}.

$$Z_{Bx} = R + \frac{R_x C_x^2}{(C_x + C_{DEL})^2 + (\omega R_x C_x C_{DEL})^2} - j\,\frac{(\omega C_x R_x)^2 \cdot C_{DEL} + C_x + C_{DEL}}{\omega(C_x + C_{DEL})^2 + \omega(\omega R_x C_x C_{DEL})^2} \qquad /8/$$

If we assume that C_x is a commensurate in its value with C_{DEL} at low frequencies, $\nu \leq 10$ kHz, because $\omega^2 R^2 C^2 \ll 1$ for Z_{BX} it can be written.

$$Z_{Bx} = R + \frac{1}{4} R_x - \frac{1}{2}\frac{1}{\omega C} = Z' - jZ'' \qquad /9/.$$

From the obtained expression it follows that the diagram's way with coordinates Z' and Z" at low frequencies will show the participation of the frequency dependent member R_x which we allowed with the opposite affirmation, in the measurable value of Z'. When $R_x \to 0$ only the frequency independent member $Z' \equiv R_x$ remains. Fig. 5 shows the dependance $Z' = f(Z'')$ obtained by us 11 for 1 10^{-1} mol dm^{-3} K with polarized geometrically and functionally nonsymmetric electrode system, at a potential of the indicator electrode E_i = - 1300 mV (SCE). In the area of low frequencies up to 15 kHz the dependence is a straight line, parallel to the axle Z". The angle coefficient

$k = -d(1/\omega C)/dR$ is a measure for the participation of R_x in Z'. When $k \rightarrow -\infty$ then $R_x \rightarrow 0$. For 1.10^{-1} mol/dm^{-3} KCL the value of the angle coefficient is $-7,210^3$ at E_i = - 1300 mV (SCE) and a frequency range of 300 Hz to 6 kHz. These results affirm the conclusion drawn above and the validity of the expression /4/ if the condition 1 is preserved.

At the emulsive dispersion systems of the type O/W the value R is a composite one. According to the ideas developed by Street-Masni-Duhin, the dependence $R=f(\varkappa^{\sigma},\varkappa)$ at nonconductive spherical particles and a highly conductive medium the expression is valid.

$$\frac{1}{R} = \varkappa - \frac{3}{2}\varkappa\cdot p + \frac{9}{2}\varkappa\cdot p\cdot\frac{\varkappa^{\sigma}}{\varkappa\cdot a + \varkappa^{\sigma}} \qquad /10/$$

where : R - general ohmic resistance of the system, $\Omega.cm^{-1}$

$\varkappa$ - relative electroconductivity of the medium, $S\,cm^{-1}$

$\varkappa^{\sigma}$ - surface electroconductivity, $S\,cm^{-1}$

p - a volumetric part of the oil phase.

a - average effective radius of the oil drops, cm^{-1}.

The first two members of this equation express the part of the volumetric current transmission corrected with the structural factor $F = 2/(2-3p)$, and the third member contains the part of the surface conductivity. The equation 10 can be written as

$$\frac{1}{R} = const.\,F^{-1} + const.(1-F^{-1}).\,\frac{3\varkappa^{\sigma}}{\varkappa.a + \varkappa^{\sigma}} \qquad /11/$$

Having in mind that $\varkappa^{\sigma}/\varkappa.a = R_{el}$ expresses the degree of influence of the double electric layer polarity on the local distribution of potential around the colloidal particles, while $2/(2-3p)$ is a structural coefficient F for the expression /10/.

$$\frac{1}{R} = \frac{\varkappa}{F} + \frac{9}{2}\varkappa.p\,\frac{R_{el}}{1+R_{el}} \qquad /12/$$

Fig. 7 shows the dependence $\varkappa = f(c)$ for electrolite solutions and for a dispersion system. The participation of $\varkappa^{\sigma}$ is best expressed at concentrations ofconcentrationon respective to the system C_{iso} state. At high electrolite concentrations the effect of the participation of $\varkappa^{\sigma}$ is screened by the high electroconductivity of the system.

Fig. 5. Dependence between the rea
imaginary part of the imp

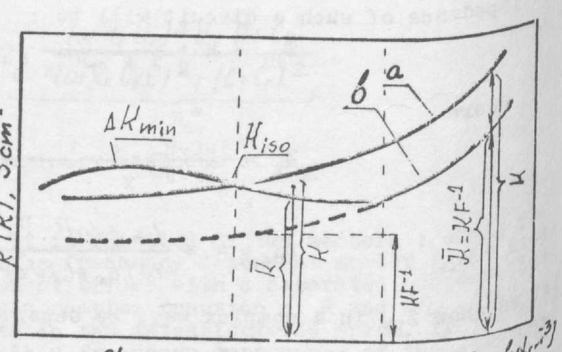

Fig. 6. Concentrational dependen
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persion system, cu
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curve "a".

General Conclusions

1. The utilization of low-frequency contact impedansometry for ageing kinetics and stability control of emulsion dispresion systems is built on the participation of the surface electroconductivity in the measurable real part of the impedance.

2. In order to make the contribution of greater in Z , it is necessary to operate by means of an alternating current bridge with a separated compensation on R and C and a conductometric sensor with a polarizationally geometric and functionally non-symmetric cell.

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