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ELECTROSTATIC CHARACTERIZATION: DETERMINING THE ZETA POTENTIAL AND SURFACE CONDUCTIVITY

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ABSTRACT

In the procedures of preventing discharges and elimination of static electricity in a double-layer case the values of Zeta potential ($\zeta-$potential) and surface conductivity of the phases states contact are determined. For the liquid phases pH value of the liquid is also analyzed. This analysis is particularly important in the usage and work with dangerous and flammable liquids, so as with explosive dusts. In this paper the results of the conducted procedure are presented, obtained by the method of thermovision in the investigation of the minimum values of ignition energy. The application of the results is possible in pharmacy, chemical, petrol and gas industry.

Index Terms - Zeta potential, surface conductivity, electrostatic characterization

1. INTRODUCTION

For the adequate approach to the elimination of static electricity produced by the contact of two phases states in a double-layer and for the safe solution of that problem it is necessary to know the value of $\zeta-$potential. On the basis of this value static electricity can be eliminated in a passive way which enables safe technological process. Such approach leads to decreasing the value of minimum ignition energy or discharges that occur in a double-layer and can produce undesirable effects as flames and explosions [1].

2. $\zeta-$ POTENTIAL DETERMINATION

Does $\zeta-$potential characterize a certain substance, i.e., is it a property of material? The answer is negative, because if we describe a certain substance by the zeta potential value, indicating, for instance, $\zeta = -50\,\mathrm{mV}$ under predetermined conditions, we should know at least the following: its form (crystalline, amorphous, particulate, dispersions, macro-bodies e.g. discs, rods, spheres, capillaries, etc.); size of particles and purity of the substance; electrolyte (purity, concentration, conductivity); pH value; temperature; type of electrokinetic measurement and the corresponding conditions. Even if all the mentioned conditions were requested and defined by a convention, the absolute values of the zeta potential on most solid-liquid interfaces achieved in different laboratories are hardly reproducible. Also the comparison of absolute values of the zeta potential obtained by different techniques, e.g. micro electrophoresis or streaming potential or other, does not make much sense, even if the same class of substances (materials) is analyzed under the same basic conditions. On the other hand, in an isolated experiment, the zeta potential values obtained under the quite identical conditions could be highly reproducible and therefore very useful for the interpretation of the behavior of that particular investigated interface [1], [2].

3. $\zeta-$ POTENTIAL MEASUREMENTS

$\zeta-$potential measurements were conducted by laser Doppler electrophoresis using the Nano-S ZetaSizer (Malvern Instruments Limited, Malvern, Worcestershire, U.K.) equipped with a 2 mW Helium Neon laser with an output of 633 run. Zeta potential is a measure of the net charge on a particle and depends on the charge on the particle plus the charge associated with any ions that move along with the particle in an electric field. The applied potential of 150V and the modulation frequency of 250Hz were used. The instrument was calibrated with a standard carboxyl modified polystyrene latex solution, with a surface potential of 55mV, provided by Malvern Instruments.

$\zeta-$potential is calculated from the Helmholtz-Smoluchowski equation:

$$\zeta = 4\pi\mu\eta/\varepsilon \qquad (1)$$

where μ is the electrophoretic mobility or velocity at unit potential gradient, η is the viscosity of the liquid and ε is the dielectric constant. The dielectric constant and viscosity of water at 25°C were taken as applied. Samples were measured 20 times. The sample count rate was generally 2000 times higher than the background count for distilled and deionized water (filtered). For $\zeta-$potential determination, the results are expressed in absolute values (mV) [1], [3].

4. RESULTS

Using method of thermovision the events of discharges in double-layer phases states are registered with the discharge energies as noted (in Joules) and presented in Figs.1 and 2.

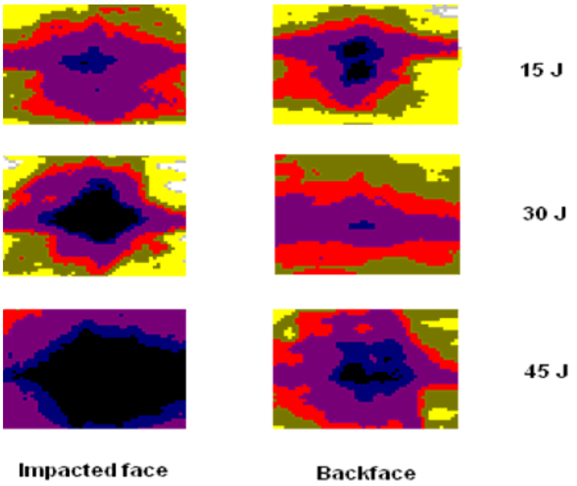

Figure 1 Typical IR thermograph images of impacted areas in 3D commingled laminates (40x32mm area) All the images acquired after 15 seconds transient[3].

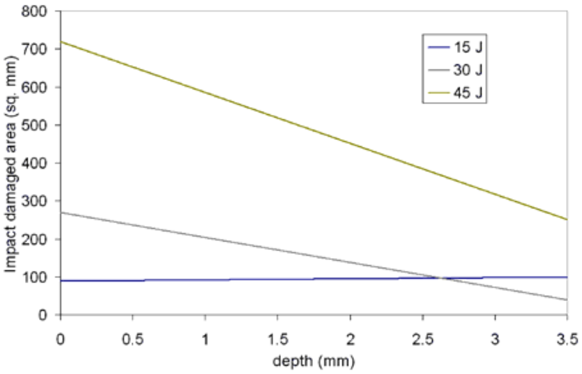

Figure 2 Linear interpolation of a typical evolution of impact-damaged area inside a sample of 3D commingled laminate. Agéma Thermovision 900 SW thermographic camera, thermo-electrically cooled), [3].

In the contact of phases states (in a double-layer) static electricity $q(t)$ is produced, which depends on the differential capacity $C_d = f(\partial U, \partial C, \partial t)$, where U is the established potential difference at the contact of phases states and C is the established capacity of the contact of phases states in a double-layer, determined per time unity. The value of the established differential capacity C_d at the interface of phases states in a double-layer can be determined from the expression $C_d = \frac{\partial U}{\partial C}\frac{\partial C}{\partial t}$ i.e. $C_d = \zeta\frac{\partial C}{\partial t}$. The term $\frac{\partial C}{\partial t}$ leads to the conclusion that at the interface of phases states there occurs the lifting of the charge $q(t)$ from one to another energetic level of the phases states, which is also the function of $\zeta-$potential. The phases states are characterized by the values of surface conductivity so as volume conductivity. For the analysis of the electrostatic characteristic of states and the $\zeta-$potential in this case is important the surface conductivity of the phases states examined together with the value of PH. Lifting of the charge $q(t)$ from one to another energetic level of the phases states occurs as an impulse for both positive and negative charge per time unit. The images presenting the process in the area of phases states contact are given in Fig.1. It is very important to determine critical values of the charge $q(t)$. Our investigations in petrol industry have given the following results [1]. Positive impulse discharges in a double-layer liquid/solid state (in the case of a partially filled reservoir with petrol) are denoted with V^+ and negative with V^-. We determined the discharge constant as $k_q = 50 \times 10^{-15} [\mathrm{C/mV}]$, so for

$$V^+ [\mathrm{mV}] = \frac{q_k^+ [\mathrm{C}]}{k_q} = 20 \times 10^{12} q_k^+ [\mathrm{C}] = 20 q_k^+ [\mathrm{pC}] \tag{2}$$

and

$$V^- [\mathrm{mV}] = \frac{|q_k^-| [\mathrm{C}]}{k_q} = 20 \times 10^{12} |q_k^-| [\mathrm{C}] = 20 |q_k^-| [\mathrm{pC}] \tag{3}$$

the following is obtained:

$$P(q_k^+) = 1 - \exp\{-0{,}116 \times 20 q_k^+ [\mathrm{pC}]\} = 1 - \exp\{-2{,}32 \times q_k^+ [\mathrm{pC}]\} \tag{4}$$

$$P(q_k^-) = 1 - \exp\{-0{,}168 \times 20 |q_k^-| [\mathrm{pC}]\} = 1 - \exp\{-3{,}36 \times |q_k^-| [\mathrm{pC}]\} \tag{5}$$

$$P(q_k^+ > q_{kg}^+) = \exp\{-0{,}116 \times 20 q_{kg}^+ [\mathrm{pC}]\} = \exp\{-2{,}32 \times q_{kg}^+ [\mathrm{pC}]\} \tag{6}$$

$$P(|q_k^-| > |q_{kg}^-|) = \exp\{-0{,}168 \times 20 |q_k^-| [\mathrm{pC}]\} = \exp\{-3{,}36 \times |q_k^-| [\mathrm{pC}]\} \tag{7}$$

where $P(q_k^+)$ and $P(q_k^+)$ represent the possibilities for the charges q_k^+ or q_k^- to be found in the reservoir in the corresponding intervals $q_k^+ \in (0, q_k^+)$ or $|q_k^-| \in (0, |q_k^-|)$, so $P(q_k^+ > q_{kg}^+)$ and $P(|q_k^-| > |q_{kg}^-|)$ are the possibilities for the charges q_k^+ and $|q_k^-|$ to be less than of the given values $\mathrm{q}_{\mathrm{kg}}^+$ or $|\mathrm{q}_{\mathrm{kg}}^-|$. The results of the calculations are given in the following table (Table 1) and the graphics are given in Figs.3 and 4.

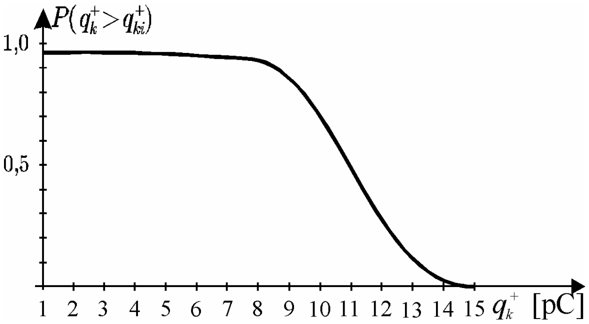

Figure 3 The possibility function obtained from the experiment for the interior of the reservoir in the experimental model [1], $P(q_k^+ > q_{ki}^+) = f(q_k^+)$.

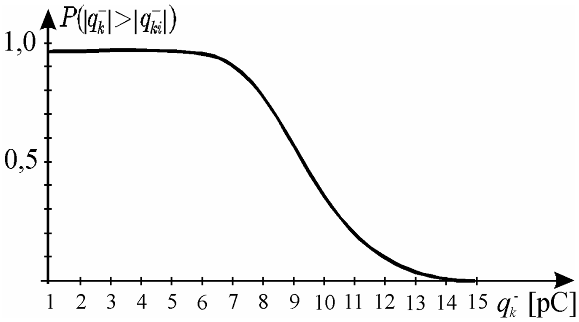

Figure 4 The possibility function obtained from the experiment for the interior of the reservoir in the experimental model [1], $P(|q_k^-| > |q_{ki}^-|) = f(q_k^-)$.

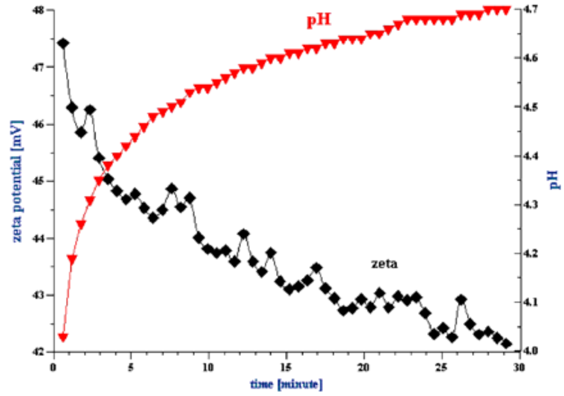

Figure 5 Equilibration of the 3%vl zirconia slurry prepared with KCl 10^{-2} with PH adjusted initially to 4. The equilibration takes about 2 hours, [3].

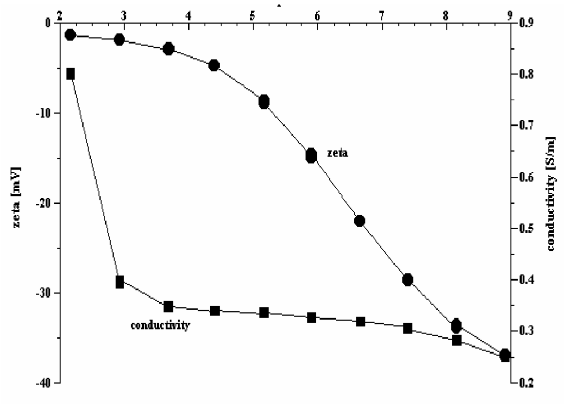

Figure 6 Titration of the 10%wt silica Ludox using 1NHCl and KOH, [3].

Table 1 The classification of calculated values of the possibilities for the charges q_k^+ and q_k^- to occur inside the area of the experimental model of the reservoir [1].

i	1	2	3	4	5	6	7
q_{ki}^+ $[pC]$	$\frac{1}{4096}$	$\frac{1}{2048}$	$\frac{1}{1024}$	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$
$P(q_k^+ > q_{ki}^+)$	0,999	0,999	0,997	0,995	0,991	0,982	0,964
$\lvert q_{ki}^-\rvert$ $[pC]$	$\frac{1}{4096}$	$\frac{1}{2048}$	$\frac{1}{1024}$	$\frac{1}{512}$	$\frac{1}{256}$	$\frac{1}{128}$	$\frac{1}{64}$
$P(\lvert q_k^-\rvert > \lvert q_{ki}^-\rvert)$	0,999	0,998	0,997	0,993	0,987	0,974	0,949
i	8	9	10	11	12	13	14
q_{ki}^+ $[pC]$	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
$P(q_k^+ > q_{ki}^+)$	0,930	0,865	0,748	0,560	0,313	0,098	0,010
$\lvert q_{ki}^-\rvert$ [pC]	$\frac{1}{32}$	$\frac{1}{16}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{2}$	1	2
$P(\lvert q_k^-\rvert > \lvert q_{ki}^-\rvert)$	0,900	0,811	0,657	0,432	0,186	0,035	0,001

Table 2 Zeta potential, surface conductivity and PH values[1] for the petrol.

zeta potential [mV]	+30	+22	+12	0	-15	-35	-30	-38	-40
conductivity [S/m]	500	380	380	380	380	380	380	400	680
pH	3	4	5	6	7	8	9	10	11

The results of the experimental investigation carried out for [1] are also numbers of positive impulse discharges of the static electricity registered with an oscilloscope $N^{+} = 297$, and the number of negative discharges $N^{-} = 181$, so the total number of impulses is then $N = N^{+} + N^{-} = 478$, registered with the duration time of one second during the interval of 15 minutes, i.e. in the total time period of 15 seconds. Thus, the average values of the impulse frequencies are:

$$f_{sr}^{+} = \frac{N^{+}}{t\,[\mathrm{s}]} = \frac{297}{15\,[\mathrm{s}]} = 20\,[\mathrm{Hz}], \tag{8}$$

$$f_{sr}^{-} = \frac{N^{-}}{t\,[\mathrm{s}]} = \frac{181}{15\,[\mathrm{s}]} = 12\,[\mathrm{Hz}], \tag{9}$$

and the corresponding time intervals T_{sr}^{+} and T_{sr}^{-}:

$$T_{sr}^{+} = \frac{1}{f_{sr}^{+}} = 50\,[\mathrm{ms}], \tag{10}$$

$$T_{sr}^{-} = \frac{1}{f_{sr}^{-}} = 83\,[\mathrm{ms}]. \tag{11}$$

For each positive voltage V^{+} or negative voltage V^{-} impulse there are positive q_k^{+} or negative q_k^{-} charges determined by the discharge constant $k_q = 50\times 10^{-15}[\mathrm{C/mV}]$. The possibilities for the charges to occur are transformed into the possibilities for the voltages to occur, as the following:

$$P(V^{+}) = P(q_k^{+}) = 1 - e^{-0{,}116 V^{+}[\mathrm{mV}]} = 1 - e^{-2{,}32 q_k^{+}[\mathrm{pC}]}, \tag{12}$$

$$P(V^{-}) = P(q_k^{-}) = 1 - e^{-0{,}168|V^{-}|[\mathrm{mV}]} = 1 - e^{-3{,}36|q_k^{-}|[\mathrm{pC}]}, \tag{13}$$

$$P(V^{+} < V_g^{+}) = P(q_k^{+} < g_{kg}^{+}) = e^{-0{,}116 V_g^{+}\ \mathrm{mV}} = e^{-2{,}32 q_{kg}^{+}\ \mathrm{pC}}, \tag{14}$$

$$P(|V^{-}| < |V_g^{-}|) = P(|q_{kg}^{-}| < |g_{kg}^{-}|) = e^{-0{,}168|V_g^{-}|\ \mathrm{mV}} = e^{-3{,}36|q_{kg}^{-}|\ \mathrm{pC}}. \tag{15}$$

For the maximum values of amplitudes of the $\zeta-$potential at the established differential capacity C_d, as the consequence of the break-down voltage $u_{k\,\max} = 1\ \mathrm{kV}$ in the reservoir [1] as the following

$$\zeta = V^{+}{}_{\max} = \left|V^{-}{}_{\max}\right| = 173\mathrm{mV}, \tag{16}$$

so the following is obtained:

$$q_k^{+} = |q_k^{-}| = \frac{0{,}116}{2{,}32}173 = \frac{0{,}168}{3{,}36}173 = 8{,}65\ \mathrm{pC}, \tag{17}$$

and

$$V_{\max}^{+} = |V_{\max}^{-}| \geq 173\,[\mathrm{mV}] \wedge q_k^{+}(V_{\max}^{+}) = |q_k^{-}(V_{\max}^{-})| \geq 8{,}56\,[\mathrm{pC}], \tag{18}$$

so that

$$P(V^{+} \geq 173\,[\mathrm{mV}]) = P(q_k^{+} \geq 8{,}65\,[\mathrm{pC}]) = 1{,}93\times 10^{-9}, \tag{19}$$

$$P(|V^{-}| \geq 173\,[\mathrm{mV}]) = P(|q_k^{-}| \geq 8{,}65\,[\mathrm{pC}]) = 2{,}39\times 10^{-13}. \tag{20}$$

For the conditions [1]:

$$P(V^{+} \geq V_{sr}^{+}) = P(q_k^{+} \geq q_{ksr}^{+}) = 0{,}5, \tag{21}$$

$$P(|V^{-}| \geq |V_{sr}^{-}|) = P(|q_k^{-}| \geq |q_{ksr}^{-}|) = 0{,}5, \tag{22}$$

the following is obtained:

$$e^{-0{,}116 V_{sr}^{+}} = e^{-2{,}32 q_{ksr}^{+}} = 0{,}5, \tag{23}$$

$$e^{-0{,}118|V_{sr}^{-}|} = e^{-2{,}32|q_{ksr}^{-}|} = 0{,}5, \tag{24}$$

so afterwards the following values are obtained:

$$V^{+}(P = 0{,}5) = V_{sr}^{+} = \frac{\ln 0{,}5}{-0{,}116} = 5{,}98\,[\mathrm{mV}], \tag{25}$$

$$q_k^{+}(P = 0{,}5) = q_{ksr}^{+} = \frac{\ln 0{,}5}{-2{,}32} = 0{,}299\,[\mathrm{pC}], \tag{26}$$

$$|V^{-}|(P = 0{,}5) = |V^{-}|_{sr} = \frac{\ln 0{,}5}{-0{,}168} = 4{,}13\,[\mathrm{mV}], \tag{27}$$

$$|q_k^{-}|(P = 0{,}5) = |q_k^{-}|_{sr} = \frac{\ln 0{,}5}{-3{,}36} = 0{,}206\,[\mathrm{pC}]. \tag{28}$$

From the graphics given in Figs. 3 and 4 it can be noticed that at the points $q_k^+(P = 0,5)$ and $|\,q_k^-\,|(P = 0,5)$ we obtain the fastest changes of possibilities $P\left(q_k^+ \;{}^3\; q_{ki}^+\right)$ and $P\left(q_k^+ \;{}^3\; q_{ki}^+\right)$. As for each value of the charge q_k^+ or q_k^- there is a value of the voltage V^+ or V^-, the same diagrams can be used for the determination of possibilities $P\left(V^+ \;{}^3\; V_i^+\right)$ or $P\left(|V^-| \;{}^3\; |V_i^-|\right)$ for the voltages, the distribution of the positive and negative impulse amplitudes, so as for the intervals of reliabilities $V^+(P)$ or $|V^-|(P)$ of these impulse amplitudes [1]. If we suppose that the charged drops are condensing above thin film of the uncharged petrol at the metallic walls of the reservoir, whereas each of charged drops has an average charge equal to the q_{ksr} which is $q_{ksr} = q_k(P = 0,5) = 0,299\ [\mathrm{pC}]$, than for the case of ignition of the charged petrol layer it is necessary to calculate the number of charges that is obtained as the ratio of the critical charge for the ignition $q_{kr} = 0,5\ [m\mathrm{C}]$ and the average value of generated charges $q_{ksr} = q_k(P = 0,5) = 0,299\ [\mathrm{pC}]$. The investigations carried out for analysis of the established value of the electrokinetic or the Zeta potential available in literature [3] for other phases states, where the values of PH and conductivity are taken into account, are given in Figs. 5 and 6.

The electroacoustic $\zeta-$potential probe is a convenient tool for determining the optimal surfactant concentration corresponding to the saturated surface. This characterization can be performed also in the intact concentrated dispersion eliminating dilution. The classical equation, relating the electrophoretic velocity v and the $\zeta-$potential, ignores the retardation and relaxation forces, and thus it is only approximation in natural conditions, where ε is the relative permittivity, E is the strength of the electrical field and η is the viscosity of the fluid.

The flow of a liquid through a capillary tube induces a convection current in the direction of flow. Conduction current is induced by the potential difference at the ends of the capillary. At the stationary state, the conduction current is equal to the convection. Evaluation of the currents gives $v = \zeta\varepsilon E / 4\pi\eta$ and $E/P = \zeta\varepsilon / 4\pi K_w$, where K_w the specific conductance of the liquid is and P is the applied pressure drop in the capillary per unit length. The results for the $\zeta-$potential and surface conductivity obtained from measurements [1] are presented in Table 2.

5. CONCLUSION

On the basis of $\zeta-$potential the value of electrostatic field can be estimated, so as the charge per unit volume. There is also a relation of this potential to the differential capacity C_d of a double-layer and the conductivity of the cloud formed in the contact of the states phases.

Results for the $\zeta-$potential and surface conductivity obtained from measurements and presented in this paper can be applied in passive elimination of the static electricity [1] in different industrial processes in order to prevent fires and explosions.

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