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OPINION
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A comparative study of the different methods of electrokinetic spectroscopy

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The Electrokinetic Spectroscopy (EKS) combines the strengths of AC Electrokinetics and Spectroscopic AC Electric Field (EF) frequency response analyses. In the general case "Electrokinetic Phenomena (EKP) can be loosely defined as all those phenomena involving tangential fluid motion adjacent to a charged surface." Delgado et al. [1] in a broader definition, outside the AC EF, acoustic radiation and other directions of motion e.g., perpendicular fluid motion, adjacent to a charged or uncharged surface, respectively described by Maxwell-Wagner-O'Konski and Maxwell-Wagner theories [1] may be included. Thus, at present a new scientific area on the frontier of physics and chemistry is emerging, which is important both from scientific and application points of view [2, 3].

The practical applications of EKS starts from traditional industries (paper, china, water purification, etc.) and go to modern nanotechnology and microtechnology, microfluidic devices, etc. There High Frequencies (HF) (most often around and above 1 MHz) are mainly used. In science most investigations are made in a broader range of frequencies, including Low Frequencies (LF) (most often around and below 10 kHz). The LF polarization mainly depends strongly on the particle size and after its relaxation, the HF polarization remains. This relaxation mainly depends on the electric properties of the particles and the medium.

The EKS methods are based on nonequilibrium phenomena and are due basically to the formation of an Induced Dipole Moment (IDM) [2] of the particles.

In an "Opinion" it is difficult to enter in detail and consider more existing EKS methods. Therefore, I chose to present shortly only a part of the EKS methods as examples and gave general review references for those, who want to understand better the bases of some of the methods. In this "Opinion" the author's attention was mainly concentrated on Electro-Optic Spectroscopies (EOS) and especially on Electric Light Scattering Spectroscopy (ELSS). Thus, our investigations resulted in the unexpected hypothesis that probably EOS are the best way, at present, to study the mechanisms of the various electrokinetic relaxations (dispersions). Further I consider briefly some examples of EKS.

Interfacial Electric Spectroscopy (IES) Called also Dielectric Spectroscopy (DS)

DS is based on the interaction of the dispersed particles with applied AC electric field. This leads to redistribution (through translational and probably sometimes orientational movements of the particles) of all electric charges of the colloid dispersion including the charges of the particles, electric double layer and the media. In this case the dipole moments of the particles are calculated through the measurement of the permittivity and conductivity of the system. Here the relations of the "dielectric" data to Dipole Moment (DM) are used [4, 5]. The polarization of one particle is estimated indirectly from the measurements of the whole system, which is a weakness. Other weaknesses are probably related mainly to difficulties in measuring at low frequencies (below 100 Hz) connected mainly with electrode polarization. For example this method can not give direct information for the different relaxations' mechanisms, especially those related to the eventual participation of particle orientation, aggregation [6], deformation, etc.

The Electro-acoustic Spectroscopies (EAS)

EAS have similar weaknesses. These methods are based on coupling of the applied acoustic or AC electric fields on the system with the resulting respective electric or acoustic fields [7]. When an electric field is applied, a resulting acoustic field is measured and when an acoustic field is applied a resulting electric field is followed. Since the methods use HF electric fields and low electric field strengths, the electrode polarization is not a serious problem here. The big advantage of these methods (and IAS as well) is the possibility to study highly concentrated systems without dilution, near the conditions often met in colloids in various industries. Dynamic mobilities and sizes of the single particles are calculated and spectra rarely are followed outside the MHz range. Anyhow some studies at LF show that the results do not change considerably with the lowering of the frequency [7].

AC Dipolophoresis also Called "Dielectrophoresis" and AC Cell Electrorotation [Electrorotation Spectroscopy (ERS)]

In these methods the applied electric fields to the system are non-homogenous and rotating homogeneous. The dispersed particles are involved in translational and rotational motions, respectively. These methods are mainly applied to study biological particles and often direct visual observation is used for microscopic particles [6, 8]. These leads to some advantages, more direct, visual information and weaknesses, e.g., more time consuming.

Electro-optic Spectroscopy (EOS)

EOS is a new part of the EKS. Here three of the most often used EOS will be considered: Electric Birefringence Spectroscopy (EBS), Electric Light Scattering Spectroscopy (ELSS) and Electric Dichroism Spectroscopy (EDS). Some of the advantages of EOS are the simple experiment and the possibilities to work even with low molecular systems at high enough concentrations and appropriately high electric field strengths. Here, especially, when studying also the optical properties of the particles it should not be forgotten that most of the existing theory is fully correct only for Rayleigh particles, i.e., for which particle size is much smaller than the wavelength of used light in the medium [10]. This might be one of the most unpleasant weaknesses related in a different degree to the optics of all EOS methods. Further EBS and ELSS will be considered for more details.

The aggregation effect, which is a big problem for all EKS methods can be studied or detected in the case of all EOS methods. That is done simply by directly following the Rotational Diffusion Coefficients of the particles that is obtained from the decay of the Electro-Optic Pulses.

Electric Birefringence Spectroscopy (EBS)

EBS is discussed as an electrokinetic spectroscopy method by Bellini and Mantegazza [9] and Stoylov [10]. This spectroscopy mainly studies the orientation of nonspherical particles leading to optical birefringence of colloid systems subjected to a pulsed AC homogeneous electric field. More details can be found by the next EOS method-the ELSS.

AC Electric Light Scattering spectroscopy (ELSS)

The method is one of the EOS methods and investigates mainly the orientational motion of nonspherical (or in special cases of high electrically and optically anisotropic particles) due to the Dipole Moments such as Permanent (PDM) or/and IDM of the particles upon the action of applied homogenous AC electric field pulses. This method gives the possibility also to experimentally study (and/or to detect) processes of: (1) aggregation (both reversible and/or irreversible) [10, 11]; (2) deformation; (3) conformation [12]; (4) strong nonlinearity and cooperativity of optical and electro-optical effects. However, it seems that only the ELSS can distinguish deformation from size growth, conformation etc. This can be done by changing the geometry of the experiment, e.g., through variation of the angle between the directions of the applied electric field and the bisector line (bisectrix) of the angle of observation. [10, 12] For ELSS studies of the optical properties of the particles there are two options: study very small (Rayleigh [10]) particles at high concentrations and high electric field strengths or study bigger paricles comparable to the wavelength of the incident light with refraction index close to that of the medium (Rayleigh-Debye-Gans particles [10]) at low number concentrations and low electric field strengths, which is by far the more often case [9]. It should be noted that for both EBS and ELSS the violations of the optical approximations (wavelength/particle size ratios) and refraction indices (particle/medium ratios) do not affect considerably the correctness of the final results [9].

Generally the EOS may be considered as pure electro-orientational methods. Except for the "mysterious" slow electric polarizability [13] relaxation that hypothetically might be related also to an increase of the Stern Layer electric charges' mobility with the increase of the frequency of the applied EF [1] and not to particles' orientation.

Another "mystery" is the Electro-optic anomaly (EOA) [14, 15] that is observed by EBS and ELSS at concentrations near the beginning of the semi-dilute regime, where the sign of the electro-optic effect changes. These are probably the two most appropriate methods for the direct and detailed investigation of the mechanisms of the different EKS relaxations. On the other side, non-EOS methods could also essentially contribute to the investigation of the mechanism of the EOA if systematic studies are done with nonspherical particles and/or electrically anisotropic particles. Further progress in EKS and especially in EOS studies might bring the broader utilization of EKS, EDS, ELSS, etc. for particles with appropriate absorbance and/or fluorescent groups, better designed measuring cells, as well as better lasers, amplifiers and electric generators [10].

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