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Background-subtraction in electroacoustic studies

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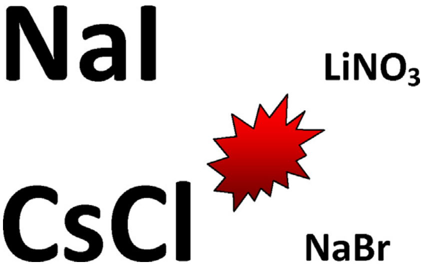
HIGHLIGHTS

- Overview of recent developments in high-ionic strength electroacoustics.
- New ideas (salts with negligible electroacoustic signal).
- New applications (multi-component dispersions).

GRAPHICAL ABSTRACT



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ABSTRACT

The background-subtraction procedure was used in electroacoustic measurements to determine the ζ potentials of various powders at electrolyte concentrations >0.1 M. At low concentrations, the contribution of the electrolyte to the overall signal is negligible, but at higher concentrations, the background-correction is necessary. More recently, the background-correction was used to analyze the electroacoustic signal of dispersions containing various types of particles.

1. Introduction

The electroacoustic method [1,2] offers an attractive alternative to electrophoresis in the measurements of the ζ potential. The electroacoustic method is especially suitable for the systems, in which electrophoretic measurements are not recommended, for example, in dispersions which are not transparent to light (high solid load, dark-colored solution) or unstable against coagulation and sedimentation (large particles, high specific density of the solid, high ionic strength). The electroacoustic phenomena can be considered as high-frequency (MHz range) analogs of classical electrokinetic phenomena. Electric sonic amplitude (ESA) is observed when applied electric field induces a vibration of colloidal particles. Colloid vibration current (CVI) is observed when applied acoustic wave induces an alternated electric field in a dispersion. Commercial instruments utilizing ESA or CVI to determine the ζ potential and particle size are available.

Ions present in solution induce effects similar to ESA or CVI, and the amplitude of the signal depends on the nature of the salt, and on its concentration. For example, the normalized ion vibration potential *IVP* of a simple binary electrolyte can be described by the following equation [1]:

$$\frac{IVP}{U_m} = \frac{c_m}{\mathrm{F}} \times (t^+W^+/z^+ - t^-W^-/z^-) \times (\omega^2/{\omega_{\mathrm{MW}}}^2 + 1)^{-1/2} \qquad (1)$$

where U_m is the oscillation velocity amplitude, c_m is the sound speed, F is the Faraday constant, t is the ion transport number, W is the ion apparent molar mass (molar mass minus a product of molar

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volume and specific density of the medium), z is the ion valence, ω is the frequency, and ω_{MW} is the Maxwell–Wagner frequency defined as conductivity of the medium divided by its permittivity. Incorrect definition of ion transport number is reported in [1]. In fact, the ion transport number is not defined by limiting conductances of the ions, but by their actual conductances (at given concentration), and this is why the ion transport number is concentration dependent. An expression similar to Eq. (1) was derived for ESA, as discussed in more detail elsewhere [3]. This is clear from Eq. (1) that the signal of salt solution is nearly proportional to the conductivity (which in turn is nearly proportional to salt concentration), and it strongly depends on the nature of the salt. Salts with large anions and small cations (as NaI) and salts with large cations and small anions (as CsCl) produce substantial signals even at relatively low concentrations). In certain salts, the signals of the anions and of the cations almost cancel out (the difference in brackets on r.h.s. of Eq. (1) is close to zero), and the overall signal of the salt is weak even at a relatively high concentration of the salt.

The overall signal of a dispersion is the sum of signals of salt (electrolyte) on the one hand, and of colloidal particles on the other. The signal of salt is negligible, and the overall signal is dominated by the signal of the colloidal particles when the solid load is high (>2% by mass), and the particles have high ζ potential (absolute value >20 mV) and high specific density (>2 g/cm^3), and the electrolyte concentration is low (<0.1 M). On the other hand with low solid loads, ζ potential close to zero, low specific density of the solid, and high electrolyte concentration, the overall signal is substantially affected (or even dominated) by the signal of the salt. Commercial instruments based on ESA and CVI have a built-in option of correction of the signal of dispersion by subtraction of (pre-measured and saved) signal of the salt. This feature offers a possibility of ζ potential measurements at very high ionic strengths.

Ten years ago Kosmulski and Rosenholm [3] reviewed the high-ionic-strength electroacoustic measurements obtained by the above-mentioned salt-background-subtraction method. Surprisingly, the ζ potential at high salt concentrations did not vanish (as it might be expected from extrapolation of low-ionic-strength behavior), but it assumed relatively high absolute values on the order of 20 mV in 1 M solutions. Moreover 1–1 salts (e.g., $LiNO_3$) at concentrations >0.1 M induced a shift in the IEP of metal oxides to high pH and even produced positive ζ potential over the entire pH-range. The shifts of the IEP and the sign-reversal were salt-specific. These affects are also surprising, because at lower concentrations the same salts are inert electrolytes, that is, they only affect the absolute value of the ζ potential, but not its sign. The recent studies of the ζ potential in high-ionic-strength systems are reviewed in the present paper.

2. High-ionic-strength systems

2.1. 2.1 1-1 electrolytes

The shift in the IEP of anatase to high pH in 0.5 M NaI, and positive ζ potential over the entire pH-range in 1 M NaI were observed by means of 3 different instruments using ESA and CVI [4]. The numerical values of the ζ potential observed by means of 3 different instruments were consistent at a low ionic strength, but much less consistent at high ionic strengths (e.g., 1 M NaI). The surprisingly high (>20 mV) ζ potentials in 1 M electrolytes (discussed in Section 1) were confirmed with ESA, while CVI produced much lower values (up to 4 mV).

Positive ζ potential of anatase over the entire pH-range in 0.5 M NaI was reported [5]. The salt specificity was also confirmed, that is, 0.5 M NaCl and NaBr caused only a shift in the IEP to high pH by about 0.5 pH unit.

A shift in the IEP of alumina to high pH in the presence of 0.3 M $LiNO_3$ originally observed by means of ESA was recently confirmed by CVI [6]. However, the maximum absolute values of the ζ potential (15 mV) were lower than those observed by ESA at the same salt concentration.

A shift in the IEP of hematite to high pH in the presence of 0.1 M $NaNO_3$ and a sign reversal of the ζ potential to positive at pH 11–14 in 0.2–5 M $NaNO_3$ were reported [7,8]. Dispersions of hematite in NaOH (in the absence of any salt) were also studied and positive ζ potentials in 1–10 M NaOH were observed. The studied range of ionic strengths (up to 10 M) was broader than in previous publications. Only very basic (pH > 11) high-ionic-strength dispersions were studied.

An apparent shift in the IEP of magnetite to high pH at NaCl concentration as low as 0.05 M was reported [9]. Yet, natural magnetite was used, which has a very low IEP at a low ionic strength, probably due to insufficient purity.

An apparent shift in the IEP of manganite to high pH at NaCl concentration as low as 0.1 M was reported [10]. Yet, background correction was not explicitly addressed in the Experimental part, and this is not clear if the ζ potentials were salt-background-corrected.

An apparent shift in the IEP of hematite to high pH at NH_4Cl concentration as low as 0.005 M, and the positive ζ potential over the entire pH-range at NH_4Cl concentration of 0.25 M were reported [11]. Yet, background correction was not explicitly addressed in the Experimental part, and this is not clear if the ζ potentials were salt-background-corrected. Moreover, the specimen of hematite used in that study had a very low IEP at a low ionic strength (5.6 instead of 9 typically reported for pure hematite), probably due to insufficient purity.

Kosmulski and Rosenholm [12] reported several compositions of mixed electrolytes (e.g., $LiNO_3$-LiCl, $NaNO_3$-NaBr, and $LiNO_3$-KNO_3), which produced very weak (negligible) electroacoustic signals in spite of their high ionic strengths. In other words the electroacoustic signals of both salts (components of mixed electrolyte) cancel out. These mixed electrolytes can be used to prepare dispersions of various powders, which do not require salt-background-subtraction in ζ potential measurements at high ionic strengths. This should be emphasized that at electrolyte concentrations on the order of 1 M, the signal of the electrolyte is not proportional to the salt concentration [13], and this is why each composition has to be determined experimentally, and simple scaling up or down is not applicable. The electrokinetic behavior of alumina [12] and titania [14] was studied in such mixes electrolytes at total salt concentrations up to 1.7 M, and similar shifts in the IEP, sign reversal to positive, and salt-specificity were observed, as previously reported for simple electrolytes.

A shift in the IEP of melamine-formaldehyde latex to low pH in 0.1 M KCl and $LiNO_3$, and in 0.3 M $LiNO_3$ was observed [15]. This shift was confirmed by electrophoresis [16] for 0.1 M solutions of seven sodium and potassium salts. The IEP observed in 0.1 M solutions was rather insensitive to the nature of the salt. The shift in the IEP observed for latex was in opposite direction than the shift in the IEP observed for metal oxides. This difference is explained by soft character of latex and hard character of metal oxides in terms of hard-soft acid-base theory.

A shift in the IEP of kaolin to high pH in 0.3 M KCl and CsCl (but not for $LiNO_3$) was observed by means of electroacoustic method [17], and this result was confirmed by electrophoresis. The character of the salt-specificity for kaolin is similar to that previously observed for silica (Cs induces a shift, and Li does not), but opposite to the salt-specificity observed for metal oxides (Li induces a shift, and Cs does not). This difference is explained by soft character of kaolin (and silica) and hard character of metal oxides.