ELECTRONEUTRALITY PRINCIPLE AND CONDUCTANCE FLUCTUATIONS IN SOLUTIONS OF STRONG ELECTROLYTES

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The electroneutrality principle allows to reduce the number of independent variables in many problems of physical kinetics. It can easily be shown that this principle must be also valid for ion concentration fluctuations in electrolyte solutions if linear dimensions of volumes under study are much greater then the Debye screening length $\varkappa^{-1}$. What is the effect of electroneutrality on large-scale conductance fluctuations?

Using the method of conductance fluctuation analysis of liquid-phase samples in the flow /1/ we have studied large-scale fluctuations in solutions of strong electrolytes with an accuracy exceeding by an order of magnitude previously reported results /2,3/. Measurements of the space average square value (single-time correlator) of these fluctuations were done with a cylindrical capillary of 13μ radius in a 408μ plate of fused quartz. The electrolyte flow through the capillary was maintained by a $1.4 \cdot 10^3$ Pa external pressure difference and determined the spectra of excess noise (fig. 1).

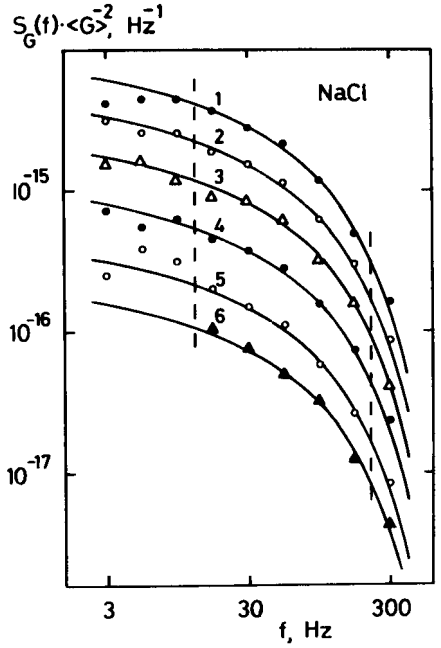

Fig. 1. Spectra of relative conductance fluctuations fitted by «laminar flow spectrum» /1/ (solid lines) for NaCl aqueous solutions of varied concentrations: 0.01M (*1*), 0.02M (*2*), 0.04M (*3*), 0.1M (*4*), 0,3M (*5*), 1.0M (*6*). The spectra are 1/f — noise-free in accordance with earlier reported results /1—3, 6/

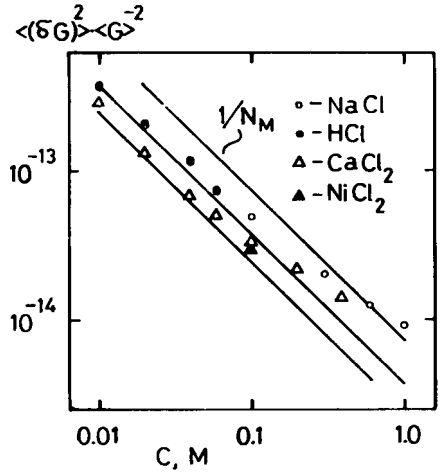

Fig. 2. Relative mean square value of conductance fluctuations as function of electrolyte concentration and type. Solid lines indicate the inverse total, double total and triple total numbers of dissolved electrolyte molecules

We found that the relative value of conductance fluctuations at low concentrations of simple electrolytes equals, within a few per cent, the inverse total number of ions in the volume under study (fig. 2) and does not depend on electrolyte nature or on the relationship between cation and anion mobilities. On the contrary, for combined electrolytes this normalization is violated even for dilute solutions (fig. 3).

Our experimental findings are supported by a simple theory /4/ that is based on the method of correlation functions and is a generalization of the classical result of Lax & Mengert /5/ for multicharge carriers and combined systems. Using the Debye-Huckel approximation one may arrive at

$$\langle (\delta N_\alpha)^2 \rangle \cdot \langle N_\alpha \rangle^{-1} = 1 - n_\alpha z_\alpha^2 [1 - \chi_\alpha(\varkappa)] \left(\sum_j n_j z_j^2 \right)^{-1}, \qquad (1)$$

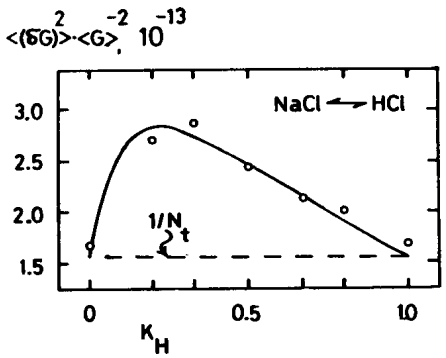

Fig. 3. Relative mean square value of conductance fluctuations for dilute NaCl/HCl electrolyte mixture vs. composition. Solid line is drawn according to Eqs. (3) and (4); interrupted line corresponds to the inverse total number of ions, that was held constant during the experiment

where z_α, n_α, N_α are charges, concentrations and total numbers of α-type ions,

$$\varkappa_\alpha(\varkappa)=\frac{e_2 z_\alpha^2}{16\pi\varepsilon kT}\,\varkappa+\left(\frac{r_0^2}{2}-\frac{e^2 z_\alpha^2 r_0}{8\pi\varepsilon kT}\right)\varkappa^2+\ldots, \tag{2}$$

r_0 is the minimum distance between ions; all other symbols are conventional. For a dilute mixture of two 1:1-electrolytes with common anion *a* and cations c1, c2 this results in

$$\langle(\delta G)^2\rangle \cdot \langle G\rangle^{-2}=\Theta\cdot\Big(\sum_j N_j\Big)^{-1}, \tag{3}$$

where Θ is a multiplier that characterizes the deviation from normalization to the total number of ions and may be written as

$$\Theta = 1+\frac{2K_{c2}(1-K_{c2})(u_{c1}-u_{c2})^2}{[u_a+u_{c1}-K_{c2}(u_{c1}-u_{c2})]^2}. \tag{4}$$

Here K_{c2} denotes the relative concentration of c2 cation, that is $K_{c2}=n_{c2}/(n_{c1}+n_{c2})$. For differing cation mobilities ($u_{c1}\neq u_{c2}$) Θ is always larger than unity except the points $K_{c2}=0$ and $K_{c2}=1$ that correspond to simple electrolytes. This observation is in good agreement with the data in fig. 2 and fig. 3.

So it is exactly the long-range Coulomb interactions between ions, responsible for macroscopic electroneutrality, that bring about the normalization of conductance fluctuations in dilute solutions of simple electrolytes to the total number of ions as well as the violation of this normalization for combined electrolytes.

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