LARGE-SCALE CONDUCTANCE FLUCTUATIONS IN SOLUTIONS OF ASSOCIATED ELECTROLYTES

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The study of conductance fluctuations in liquid ionic conductors is a subject of growing interest of investigators, due to, in particular, that very low level of $1/f$ noise was found in such systems [1]. The method of conductance fluctuation spectroscopy allows to obtain information about charge transfer processes in a system almost without perturbation of it by external force. In [2] we suggested the method of conductance fluctuation spectroscopy of liquid phase samples in flow. In this method the shape of fluctuation spectrum is defined by laminar flow of the liquid through a microcapillary. In [3] we applied the method for investigation of strong electrolyte solutions. The measuring accuracy of mean square conductance fluctuation approached by us allowed to show that in diluted solution of simple electrolyte this quantity is normalized to the full number of free ions in the volume under study. One would think that in the case of weak electrolyte its extent of dissociation may be obtained in this way.

However, in present work [4] devoted to measuring of conductance fluctuations in associated and weak electrolytes that form various kinds of ion pairs we found that in solutions of electrolytes which forms neutral ion pairs ($MgSO_4$, $H_2C_2O_4$) the fluctuation level is normalized to the full number of ions, as if these pairs were completely dissociated, though the fractions of neutral particles calculated from association constants are very high in these electrolytes (80% in 0.05 M $MgSO_4$). The explanation is that the lifetime of ion pair (maximum 10^{-5} s) is well below the time of its passage through a capillary in the flow ($2 \cdot 10^{-3}$ s in our experiments). In such a case the ion pairs during their presence in a capillary compose and decompose many times, and do this without any space and time correlation (due to the fact that in not too concentrated solutions ions collide numerously with solvent molecules until they form a new pair), and the fluctuation level is normalized to the full number of possible ions, not only to their dissociated fraction.

Let us now consider the case when the ion pair is a charge carrier itself. It is realized when association (or uncomplete dissociation) of unsymmetrical electrolytes (lanthanum chloride, sulfuric and oxalic acids) takes place. In all these systems in rather narrow concentration range we observed the transition from complete dissociation to complete ion pairing. The

qualitative explanation of the phenomena is clear: charged ion pair is a free charge carrier, and a weak unsymmetrical electrolyte should be considered as combined one, i.e. as forming two kinds of ions of equal charge sign and one kind of opposite one (in the case of sulfuric acid one can obtain the mixture of 1:2 and 1:1 — electrolytes, in the case of lanthanum chloride — 3:1 and 2:1). However, the picture of experimental concentration dependence of $\langle(\delta G)^2\rangle/\langle G\rangle^2$ differs from that expected from dissociation constants of these electrolytes (the renormalization of fluctuation level occurs in much more narrow concentration range, and for $LaCl_3$ even for much lower concentration). We explain such behaviour of fluctuations by the fact that for low electrolyte concentrations the relaxation time of ion atmosphere is greater than the lifetime of ion pair, i.e. the atmosphere can not react on appearance of ion pair, and the electroneutrality condition is valid for each of the ions separately. When the electrolyte concentration increases the relaxation time of the atmosphere reduces, and when it becomes lower then the lifetime of ion pair the ion atmosphere reconstructs to screen a new charge carrier, and the electroneutrality condition must include it too. The transition intervals defined using the literature data on kinetics of ion association reactions are in very good agreement with that founded in our experiments.

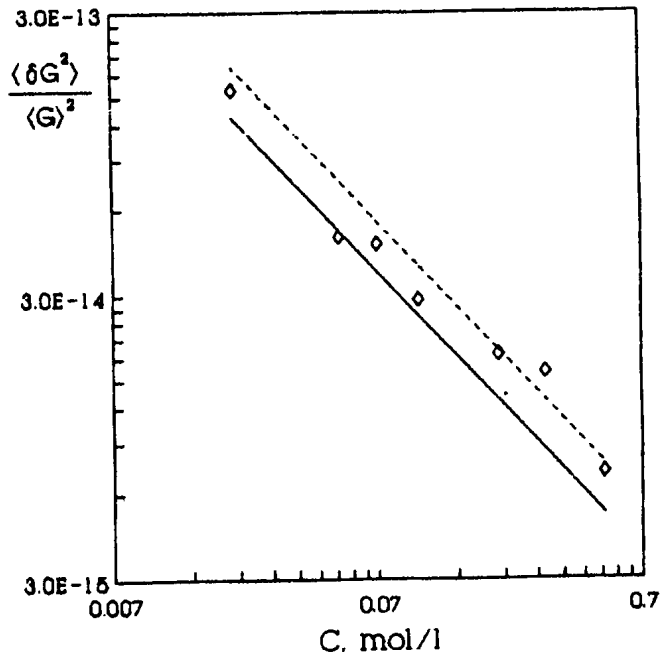

Fig. The dependence of mean square conductance fluctuation in aqueous solutions of $H_2C_2O_4$ on concentration for 25^{0}C. The solid line is theoretical dependence for strong 1:2 — electrolyte, the dashed one — for 1:1

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