LIQUIDS AND LIQUID CRYSTALS

STUDIES OF THE SELF-DIFFUSION OF ALCOHOL IN ALCOHOLIC ELECTROLYTE SOLUTIONS BY QUASIELASTIC SCATTERING OF SLOW NEUTRONS

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The method of quasielastic scattering of slow neutrons has been used to study the influence of a solvent on the self-diffusion processes in the aqueous and alcoholic solutions of LiCl and CoCl₂ electrolytes with various concentrations. Values of the molecular self-diffusion coefficient of the solvent in the indicated solutions have been determined, and the decomposition of the self-diffusion coefficient into the one-particle and collective contributions has been made. It has been found that the self-diffusion coefficients in the LiCl—ethanol and CoCl₂—ethanol systems are much lower than those in the corresponding aqueous solutions within the whole range of concentrations. A substantial growth of the collective contribution to the self-diffusion coefficient with increase in the ion concentration in alcoholic solutions has been detected. It evidences for a substantial enhancement of the short-range orientational order in the solvent, which is caused by the introducion of ions into alcohol, in comparison with analogous aqueous electrolyte solutions.

1. Selection of Experimental Objects

The scientific interest in aqueous electrolyte solutions is caused by the vital importance of water. That is why a great number of experimental and theoretical works is devoted to their studying. Nevertheless, studying only aqueous electrolyte solutions cannot provide the full knowledge of the properties and structure of electrolyte solutions. Self-diffusion in electrolyte solutions depends obviously not only on the ion geometry and charge, but also on the nature of a solvent. In order to trace the influence of the solvent on the properties of electrolyte solutions, we selected solvents with a well-investigated molecular structure such as methyl and ethyl alcohols. Making use of the method of quasielastic slow-neutron scattering (QESNS), the studies of self-diffusion in the

alcoholic solutions of uni- and bivalent salts, LiCl and CoCl₂ with various concentrations have been carried out.

The comparison of ion hydration in aqueous electrolyte solutions with ion solvation in alcoholic ones revealed the chemical individuality of the latter. The choice of liquid methanol and liquid ethanol as solvents was not casual. First, a methanol molecule, by its structure, reminds a water molecule, with one proton being substituted by an inert, more bulky group CH₃. The methanol structure forms long hydrogen chains connected by linear hydrogen bonds. Nevertheless, the regular structures which are typical of the tetrahedral grid of water at room temperature were not observed in alcohols. No doubt, these features of the alcohol structure should strongly affect the physical properties of electrolyte solutions, and, first of all, the self-diffusion coefficients. Secondly, the substances that include hydrogen are especially convenient objects for studying the self-diffusion by the QESNS method, because the cross-section of scattering by hydrogen atoms is approximately 20 times that of scattering by other atoms. Therefore, when the alcoholic solutions of LiCl and CoCl₂ are studied, slow neutrons are scattered mainly by alcohol molecules, which enables one to observe the thermal motion of molecules in alcohol solutions directly.

2. Experimental Part

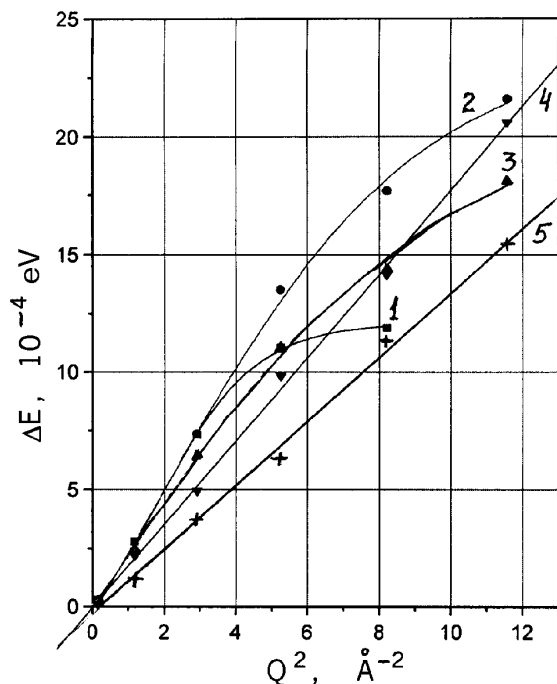The measurements of slow neutron scattering in electrolyte solutions were carried out using a

Fig. 1. Dependence $\Delta E = \Delta E(Q^2)$ of the quasielastic peak broadening on the square of the transferred wave vector for the LiCl solutions in ethyl alcohol at various concentrations $C = 0.1$ (*1*), 0.6 (*2*), 1.1 (*3*), 2.2 (*4*), and 4.4 mol/l (*5*)

Fig. 2. The same as in Fig. 1 but for the $CoCl_2$ solutions in ethyl alcohol at various concentrations $C = 0.1$ (*1*), 0.5 (*2*), 1 (*3*), 1.5 (*4*), and 3 mol/l (*5*)

multidetector neutron spectrometer by the time-of-flight method. Slow neutrons were generated by a VVR-M nuclear reactor at the Institute for Nuclear Researches of the National Academy of Sciences of Ukraine, Kyiv. A monochromatic beam of neutrons with the energy $E_0 = 13.26$ meV was scattered by a solution in a flat 140×60-mm^2 container windowed with a 0.07 mm titanium foil for neutrons to pass. The thickness of the electrolyte layer under investigation was about 1 mm. The energy resolution of the spectrometer was 0.66 meV. Neutrons scattered by a specimen at various angles were registered by the system consisting of eight detectors arranged in a vertical circle with the radius $R = 2.82$ m and with a specimen at the center. The energy spectra of scattered neutrons were measured by the time-of-flight method simultaneously at several angles in the range $9 - 117°$. The experimental procedure was described in detail in work [1].

Every scattering angle corresponds to a certain value of the transferred wave vector $\mathbf{Q} = \mathbf{k}_0 - \mathbf{k}$, where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors which describe the neutron states before and after the scattering, respectively. The experimental dependences of the broadening of quasielastic peaks ΔE on the square of the transferred
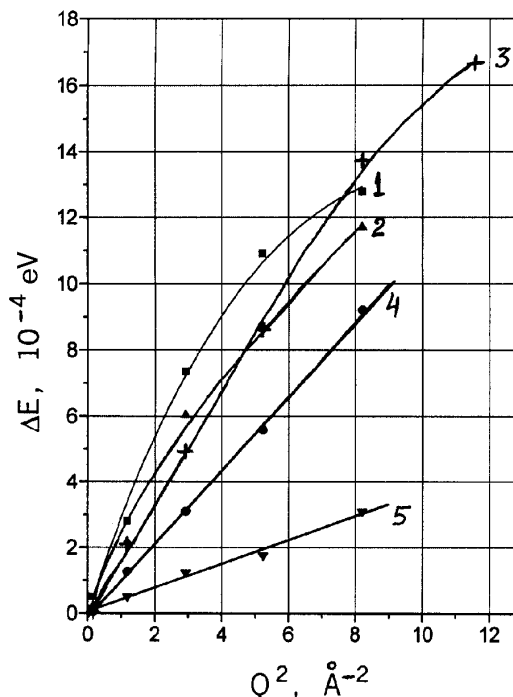
wave vector Q^2 were analyzed in the framework of certain models of self-diffusion [2], namely,

$$\Delta E = 2\,\hbar Q^2 D \tag{1}$$

for the model of continuous diffusion,

$$\Delta E = \frac{2\,\hbar}{\tau_0}\left[1 - \frac{\exp\left(-2\,W\right)}{1 + D\,Q^2\,\tau_0}\right] \tag{2}$$

for the Singwi–Sjölander model of jump diffusion, and

$$\Delta E = \frac{2\,\hbar}{\tau_0}\left[1 + D_0\,Q^2\,\tau_0 - \frac{\exp\left(-2\,W\right)}{1 + D\,Q^2\,\tau_0}\right] \tag{3}$$

for the Oskotskii–Ivanov model, where, in addition to the jumps of molecules from one center of oscillations to another one, the continuous diffusion of the very centers of oscillations is also taken into account.

While analyzing the experimental dependences $\Delta E = \Delta E\left(Q^2\right)$, the self-diffusion coefficient can be decomposed into a one-particle contribution, D_0, and a collective, D_K, one, and the dwell time τ_0 of the solvent molecule in the equilibrium position can be estimated. For this purpose, we used a special method [1,3]. In order

to determine the indicated parameters, experimental data were approximated by the theoretical curve

$$\Delta E = 2\,\hbar\,D_{\mathrm{K}}Q^2 + \frac{2\hbar}{\tau_0}\left[1 - \frac{\exp\left(-2W\right)}{1 + Q^2(D - D_K)\tau_0}\right] \qquad (4)$$

within the whole range of variations of the square of the transferred wave vector. Further, the roles of the fast one-particle and slow collective motions in the general picture of molecular thermal motion in solutions were estimated quantitatively.

3. Experimental Results

Experiments with alcoholic electrolyte solutions confirm the assumption about the availability of the short-range order in them and the coordination of solvation spheres. Figs. 1 and 2 show the experimental dependences $\Delta E = \Delta E(Q^2)$ for the LiCl and CoCl$_2$ solutions, respectively, in ethyl alcohol at various concentrations. As one can see from the figures, the Oskotskii–Ivanov model describes diffusive processes in the investigated alcoholic solutions only at low concentrations ($C < 1$ mol/l). At higher concentrations, a linear dependence of ΔE on the square of the transferred wave vector, which corresponds to the model of continuous diffusion, is observed. Confronting these experimental data with similar dependences for the aqueous solutions of LiCl and CoCl$_2$ (Fig. 3), a conclusion can be drawn that the alcoholic solutions are much more ordered under the influence of dissolved ions in comparison with similar aqueous systems. For example, in the case of the aqueous solutions, a continuous character of self-diffusion is observed only for the solutions LiCl–H$_2$O with high concentrations ($C > 5$ mol/l). In the LiCl–H$_2$O and CoCl$_2$–H$_2$O solutions in the concentration range $C < 5$ mol/l, the self-diffusion processes are combinations of collective and individual motions. A strong orienting influence of ions on solvent molecules becomes observed in the LiCl and CoCl$_2$ aqueous solutions at concentrations not higher than 1 mol/l. At the same time, the character of the self-diffusion of solvent molecules in the alcoholic solutions of the same salts still corresponds to the model of continuous diffusion at solution concentrations above 1 mol/l.

It is obvious that, when ions of strong electrolytes are introduced, the solvation processes that regulate the system structure dominate in alcoholic solutions, contrary to aqueous systems, over those leading to a destruction of the primary structure of the liquid. The absence of such regular structures, which are characteristic of the tetrahedral grid of water, in ethanol
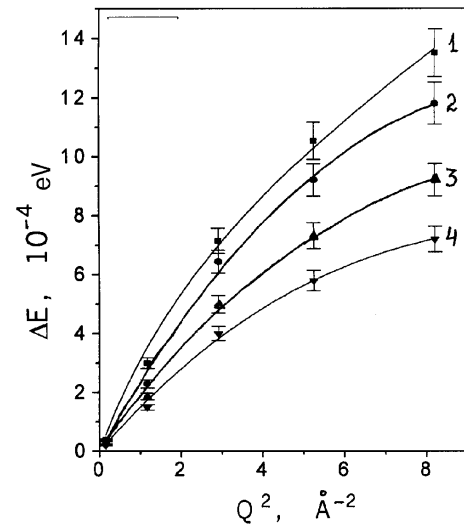

Fig. 3. The same as in Fig. 1 but for the CoCl$_2$ solutions in water at various concentrations $C = 1$ (*1*), 2 (*2*), 3 (*3*), and 4 mol/l (*4*)

and methanol and a significant violation of ordering in their liquid phase result in that the inclusion of ions into these systems cannot bring about such a disorder enhancement that would be inevitable in case of the water solvent. It is the first portions of ions penetrating into water that most strongly influence water; afterwards, a mutual compensation of various effects takes place. This scenario is not true for alcohols. Therefore, the ordering activity of the solvation has to prevail here as it does.

Thus, the structure of ethyl alcohol becomes much stronger under the influence of dissolved ions than the structure of water. The higher the solution concentration, the higher the system ordering. The self-diffusion coefficients of alcohol molecules quoted in the table give evidence for that.

In Fig. 4, for comparison, the concentration dependences of the self-diffusion coefficient for the LiCl and CoCl$_2$ solutions in either ethyl alcohol or water are presented. One can see that these dependences are qualitatively similar by shape and can be described by the expression of the type $D = D_p \exp\left(kC\right)$, where D_p is the molecular self-diffusion coefficient of the pure solvent and C the solution concentration. The introducion of uni- and bivalent ions results, in both cases, in an appreciable reduction of the self-diffusion coefficient, with the self-diffusion coefficients in the LiCl–ethanol and CoCl$_2$–ethanol systems being considerably lower at all concentrations than those in the corresponding aqueous solutions. A similar situation is observed for the
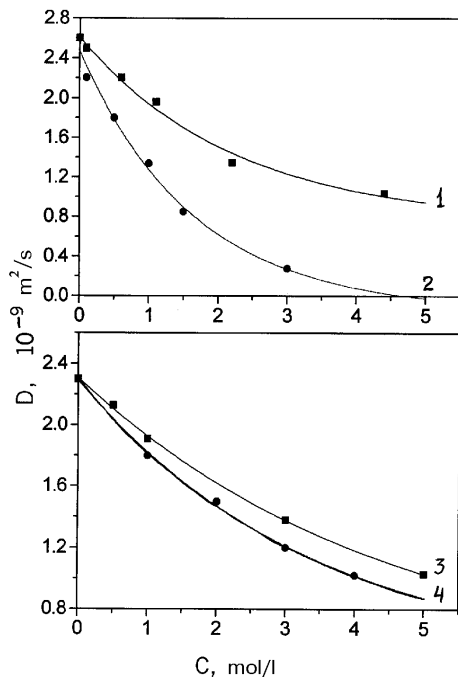
Fig. 4. Concentration dependence of the self-diffusion coefficient for aqueous and alcoholic solutions of LiCl and CoCl$_2$: (1) LiCl–ethyl alcohol, (2) CoCl$_2$–ethyl alcohol, (3) LiCl–H$_2$O, and (4) CoCl$_2$–H$_2$O

testifies to that the interaction energy between salt ions and solvent molecules changes regularly when changing from aqueous to alcoholic electrolyte solutions. The explanations should be searched for in the modification of the molecular structure of solutions and their dielectric characteristics. Along with the electrostatic interaction between ions and alcohol molecules, the donor-acceptor bond of the type either

$$R - O - H \ldots Cl^- \quad \text{or} \quad R - O - H,$$
$$\vdots$$
$$Li$$
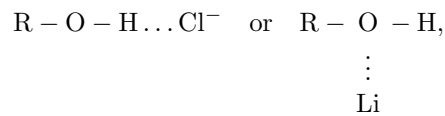
arises, which is imposed onto the ion–dipole interaction. Just this circumstance results in a substantial growth of the short-range orientational order when ions are introduced into alcohol.

According to the analysis of X-ray diffraction data [3], a Li$^+$ ion is co-ordinated tetrahedrically in alcohol and is positioned at the intersection of hydrogen bonds between alcohol molecules, bending these bonds strongly.

The most probable model of the bivalent cation solvation in alcohols is an octahedron which is formed owing to the cations that become located at the center of mass of triangles made up of three OH$^-$ groups of the top layer and three OH$^-$ groups of the bottom layer with the alcohol structure. Anions Cl$^-$ are supposed to be located on the opposite faces of octahedrons, in the

CoCl$_2$ solutions in methyl alcohol. The trend of the experimental dependences $D = f(C)$ is much more abrupt for the LiCl and CoCl$_2$ alcoholic solutions than that for the corresponding aqueous ones (see Fig. 3). This

The self-diffusion coefficient of solvent molecules in the aqueous and alcoholic solutions of LiCl or CoCl$_2$ with various concentrations

Substance	Concentration C, mol/l	Self-diffusion coefficient $D \times 10^9$, m^2/s	Collective contribution coefficient to the self-diffusion $D_k \times 10^9$, m^2/s	$D_k/D \times 100$ %
LiCl—ethanol	0.1	2.50 ± 0.1	—	~ 0
	0.6	2.21 ± 0.09	0.85 ± 0.05	38
	1.1	1.96 ± 0.08	1.02 ± 0.05	52
	2.2	1.35 ± 0.09		~ 100
	4.4	1.04 ± 0.09		~ 100
CoCl$_2$—ethanol	0.1	2.2 ± 0.1	0.41 ± 0.05	19
	0.5	1.8 ± 0.1	0.69 ± 0.03	38
	1	1.34 ± 0.09	0.95 ± 0.05	71
	1.5	0.85 ± 0.09		~ 100
	3	0.28 ± 0.08		~ 100
LiCl—H$_2$O	0.5	3.13 ± 0.09	0.36 ± 0.05	17
	1	1.91 ± 0.10	0.63 ± 0.03	33
	3	1.38 ± 0.10	0.97 ± 0.10	71
	5	1.03 ± 0.05		~ 100
	10	0.61 ± 0.05		~ 100
CoCl$_2$—H$_2$O	1	1.80 ± 0.10	0.74 ± 0.03	41
	2	1.52 ± 0.09	0.63 ± 0.02	42
	3	1.23 ± 0.10	0.48 ± 0.02	40
	4	1.05 ± 0.10	0.42 ± 0.02	41

plane of CH$_3$ methyl groups belonging to two trios of alcohol molecules, so that an "ion–pair" complex emerges.

The growth of the ion concentration is probably accompanied by a gradual modification of the solution structure. In strongly diluted alcoholic solutions, an ion is surrounded only by solvent molecules. Therefore, the experimental dependence $\Delta E = \Delta E\left(Q^2\right)$ has to possess an aqueous-like character at small concentrations, which is the case. As the ion concentration grows, the dependence $\Delta E = \Delta E\left(Q^2\right)$ straightens and, within a certain concentration range, looks like a straight line, which corresponds to the model of continuous diffusion (Figs. 1 and 2). It can be explained by the extension of the regions with the ion short-range order with increase in the concentration and by the emergence of "ion–pair" complexes, which stick together and, beyond the threshold of full solvation, form something like a crystalline structure. It should be noted that the threshold of full solvation in alcoholic solutions becomes attainable at much lower concentrations than that in the case of hydration.

As the concentrations of LiCl and CoCl$_2$ in ethyl alcohol increase, the one-particle contribution to the self-diffusion coefficient gradually decreases and, at concentrations $C > 1.5$ mol/l, tends to zero. At concentrations $C > 1.5$ mol/l, alcohol molecules participate only in the collective mechanism of diffusion (see the table). Therefore, if the concentration of alcoholic solutions increases, the regions of local ordering compose a strongly correlated system with the characteristic length greater than the average interionic distance.

4. Conclusions

On the basis of the experimental comparison between the hydration of ions and their solvation in alcoholic solutions, the following conclusions can be drawn.

1) The variation of the self-diffusion coefficient of solvent molecules, which accompanies the introduction of ions into various solvents (water, alcohols), is very sensitive to the character of the interaction between ions and solvent molecules.

2) The introduction of LiCl or CoCl$_2$ molecules into both aqueous and alcoholic solvents reduces the mobility of solvent molecules. The higher the ion concentration, the more ordered is the structure of the considered solutions under the influence of dissolved ions.

3) Comparing the analogous aqueous and alcoholic solutions of the salts in question, the self-diffusion coefficient of alcohol molecules turns out much lower than that of water molecules, which testifies to that the enhancement of the short-range orientational order induced by ions is higher in the case where the latter have been introduced into alcohol rather than water.

4) Ions in alcoholic electrolyte solutions are solvated; the more the ion charge, the higher the solvation.

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2. *Gurevich I.I., Tarasov L.V.* Physics of Low-Energy Neutrons. — Moscow: Nauka, 1965 (in Russian).

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ДОСЛІДЖЕННЯ САМОДИФУЗІЇ СПИРТУ
В СПИРТОВИХ РОЗЧИНАХ ЕЛЕКТРОЛІТІВ
МЕТОДОМ КВАЗІПРУЖНОГО РОЗСІЯННЯ
ПОВІЛЬНИХ НЕЙТРОНІВ

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Р е з ю м е

Методом квазіпружного розсіяння повільних нейтронів проведено дослідження впливу розчинника на процеси самодифузії у водних та спиртових розчинах електролітів LiCl та CoCl$_2$ різних концентрацій. Визначено коефіцієнти самодифузії молекул розчинника в указаних розчинах, проведено розділення коефіцієнта самодифузії на одночастковий та колективний внески. Встановлено, що для всіх концентрацій в системах LiCl—етанол і CoCl$_2$—етанол коефіцієнт самодифузії значно менший, ніж для відповідних розчинів у воді. Відмічено також значне зростання колективного внеску в коефіцієнт самодифузії з ростом концентрації іонів у спиртових розчинах. Це свідчить про значне збільшення близького орієнтаційного порядку при введенні іонів до спирту в порівнянні з аналогічними водними розчинами електролітів.