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ANOMALOUS LIGHT SCATTERING IN AQUEOUS KCl SOLUTIONS

Molecular light scattering in dilute aqueous potassium chloride solutions has been studied. Anomalous (additional) molecular scattering of light is experimentally detected in the concentration interval from 0.001 to 0.004 mole fractions of the electrolyte. The obtained data are compared with the literature data on light scattering in aqueous and non-aqueous solutions of potassium chloride. The absence of additional scattering in the previous works was substantiated.

K e y w o r d s: light scattering, water, solutions, electrolytes.

1. Introduction

The researches of molecular light scattering (MLS) in dilute aqueous alcohol solutions with molar concentrations not exceeding 0.1, which were carried out more than half a century ago, made it possible to establish the existence of singular points [1–3]. In the vicinity of those points, the integral intensity of MLS increases by an order of magnitude [1–3], and the half-width of MLS spectra is several orders of magnitude narrower than the half-width of the spectra corresponding to the concentration light scattering [4]. In a cycle of works [5–11], we showed that the singular points of this kind almost exactly coincide with the points, at which the concentration curves of solution contraction measured at various temperatures intersect. This fact means that the physical nature of those points is identical or, more precisely, it is associated with the solution contraction (compaction), i.e. the emergence of a negative excess solution vol-

ume under the action of electrostatic fields created by admixture alcohol molecules. Here, the contribution of the molecular dipole moments dominates.

A similar contraction of the system should be observed in aqueous electrolyte solutions. In this case, the contraction effect should evidently be much stronger. Therefore, singular points should be observed at concentrations lower than the corresponding concentrations for aqueous alcohol solutions by about an order of magnitude.

In this work, the concentration dependence of the integral intensity of molecular light scattering in the aqueous potassium chloride solution is studied. The special attention is paid to the concentration dependence of the MLS intensity in the concentration interval of 0–0.004 mole fractions of the electrolyte.

2. Experimental Conditions and Results

The specimens were prepared, by using a KCl salt of the reagent grade and twice distilled water. Taking the experience of other researchers [12, 13] into ac-

count, as well as our own experience obtained from the previous works with aqueous alcohol solutions [10, 14–16], the specimens obtained after the salt dissolution were settled for several days. Before the measurement, the specimens were held at the measurement temperature for several hours until the steady MLS intensity was reached.

The intensity of scattered light was measured, by following classical methods [17]. An LGN-215 laser with the wavelength $\lambda = 633$ nm (a power of 60 mW, and the vertically directed radiation polarization vector) was used as a radiation source. The scattering angle was equal to 90° with an accuracy not less than 20″, which was provided by a goniometer G-1.5.

The light scattering intensity was measured with the help of the relative differential method. By means of a translucent plate, the laser radiation was divided into two beams (the probing and reference ones). The division was made in such a way that the probing beam intensity was significantly higher than that of the reference one. The intensity of scattered light was registered with the help of a photoelectronic multiplier (PEM) FEU-79 operating in the photon counter mode. The linearity of the sensitivity of a registration part of the installation was tested by means of neutral optical filters with the multiplicity varying from "×2" to "×100". The stability of the laser radiation intensity was observed by monitoring the intensity ratio between the scattered and reference beams, registered in sequence by the same PEM. The scattering coefficient of specimens was determined with respect to a benzene specimen, for which this parameter is well known: $R_b = 8.2 \times 10^{-6}$ cm^{-1} [17], and the scattering geometry for the reference and experimental specimens was identical. After the cuvette with benzene was replaced by a cuvette with the specimen, the scattering coefficient of the analyzed preparation was determined by the formula $R = R_b \frac{I}{I_b}$, where R_b is the coefficient of light scattering by benzene, and I and I_b are the intensities of scattering by the solution and benzene, respectively.

The specimen temperature was controlled with the help of a two-circuit thermostat system. The inner circuit was implemented on the basis of Peltier elements. The first circuit held a temperature of 25°C, and the specimen temperature was governed by the inner circuit and amounted to 20.0 ± 0.1°C.

The coefficient of MLS in the aqueous KCl solution was measured in the salt concentration interval
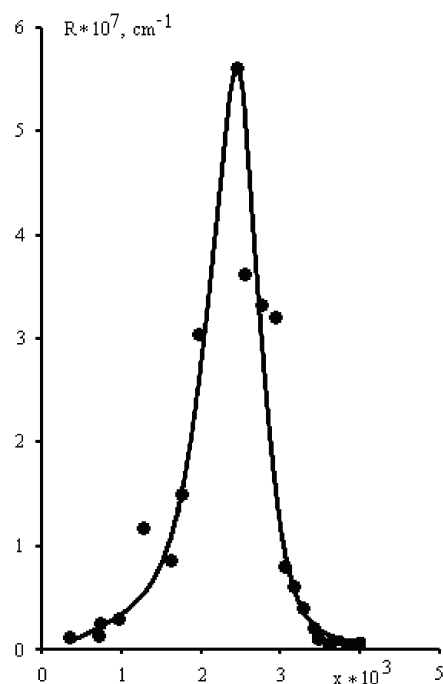
Concentration dependence of the coefficient of light scattering (the wavelength $\lambda = 682.8$ nm) in a KCl aqueous solution at a temperature of 20 °C

from 5×10^{-4} to 4×10^{-3} mole fractions with a step of 0.0001. The experimentally measured values of the scattering coefficient R are shown in Figure by symbols. The solid curve was fitted, by using the least-squares method. The left and right branches of the curve were fitted independently.

As one can see, the MLS ratio in the aqueous electrolyte solution increases at its maximum by about two orders of magnitude. The MLS maximum is located at about $x = 0.0024$ mole fraction, and the half-width of the peak is about 0.001 by the order of magnitude. Such a considerable growth of the scattering coefficient is completely untypical of the ordinary scattering at density and concentration fluctuations. The same can be said about the peak half-width. Those facts make us assume that microscopic heterogeneities, whose size is comparable with the light wavelength, are formed in a very dilute aqueous electrolyte solution.

3. Possible Origins of the Anomalous Peak

The appearance of a peak in the scattering coefficient can be explained by the following qualitative

consideration: i) every ion forms a hydration shell (or the so-called elementary cluster) [18]; ii) at a certain concentration, the elementary clusters can form a macroscopic structure like a percolation cluster; and iii) from the equation of state for an ensemble of elementary clusters, it follows that the system may become unstable at certain concentrations and temperatures, and, as a result, the intensity of large-scale fluctuations may drastically increase (see work [19]).

Note that a hydration shell may include several molecular layers. At salt concentrations of about $x \approx$ $\approx 2 \times 10^{-3}$, there are approximately 250–300 water molecules per one ion. The size of this hydrated complex is approximately 1–1.2 nm, i.e. the number of molecular layers reaches a value of 3–4, which seems quite reasonable [20]. In this case, elementary clusters can really form a percolation cluster, whose specific volume is equal to

$$\phi \approx \left(\frac{4\pi}{3} R_{cl}^3 n_w \right) x_M \approx 0.23,$$

where n_w is the water density, and x_M the concentration, at which the MLS intensity is maximum. A characteristic value in the size distribution of such clusters becomes proportional to the probing light wavelength, because, according to the results of work [17], the intensity of scattered light in the same case was not proportional to λ^{-4}, but to $\lambda^{-1.5}$.

The formation of a percolation cluster from a set of elementary clusters (ions with their hydration shells) is similar to the formation of snowflakes from ice crystals, a typical illustration of the fractal structure emergence. A similar mechanism giving rise to the formation of an MLS intensity maximum in aqueous alcohol solutions was considered in works [20–22]. We face the same situation near the critical point, where the equation of state for a system with conjugate phase inclusions is modeled by the van der Waals equation [23, 24].

It is not impossible that the emergence of macroscopic structures of the described type takes a lot of time. A stationary value of the light scattering intensity was observed in our experiments in a few hours after the solution preparation. For the sake of comparison, the same process of attaining the light scattering equilibrium in aqueous glycerol solutions takes about 24 h [25]. The same and longer time intervals were observed for non-aqueous alcohol solutions [13] and aqueous solutions of more complex substances [26].

The generation of hydration complexes is accompanied by an increase in the local system density and the extrusion of gases dissolved in water, first of all, carbon dioxide. This process is really observed and becomes the most pronounced, if the solution concentration corresponds to the MLS intensity maximum. In this connection, one could identify the origin of the MLS peak with the presence of gas bubbles, different in size, in the solution volume. In time, those bubbles should eventually leave the solution, so that the intensity of light scattering would decrease. However, the intensity of MLS changes non-monotonically in time, reaches a maximum value, and remains constant afterward.

4. Discussion

Let us make a comparison with the research results concerning the intensities of polarized and depolarized light scatterings in aqueous and alcohol electrolyte solutions.

According to experimental data obtained by G.P. Roshchina [13], the concentration dependences of the intensity of isotropic MLS in the systems LiCl-methanol, LiCl-ethanol, and LiCl-propanol had a non-monotonic character with a minimum at the salt mole fraction $x \approx 0.1$. The available experimental points covered a solution concentration interval starting from a salt mole fraction of 0.005.

In work [27], the isotropic MLS in the KCl-water system was studied. A monotonic growth of the scattering intensity with the solution concentration was registered. The available experimental points covered a solution concentration interval starting from a salt mole fraction of 0.0055.

Our measurements of the MLS intensity show that the peak of anomalous scattering in the aqueous KCl solutions is observed at the salt mole fraction $x \approx 0.0022$, and its half-width does not exceed $\Delta x \approx 0.001$.

A comparison of experimental conditions allows us to assume that the absence of the anomalous MLS peak in works [13, 28] is associated with the lack of measurements with steps smaller than $\Delta x \approx 0.001$. As a certain feature testifying that the MLS peak can exist at such low solution concentrations, there can be the initial sections of the concentration dependences of the light scattering intensity for alcohol electrolytes solutions [13]. In those sections, the intensity of light

scattering decreases and passes through a minimum, which can be interpreted as the right-hand side of the additional MLS peak.

M.F. Vuks *et al.* [3] observed a maximum of the additional MLS in aqueous ethanol solutions at an alcohol mole fraction of about 0.1. On the basis of thermodynamic data, the cited authors calculated the concentration dependence of the scattering coefficient in those solutions. The obtained result testified to a monotonic character of the dependence, which did not contain any specific features. This fact confirmed that no substantial concentration scattering should be observed in aqueous ethanol solutions. On this basis, the cited authors concluded that the maximum of the additional MLS was not directly related to the concentration fluctuations.

In work [28] made by G.P. Roshchina in 1960, a maximum was observed in the MLS concentration interval near the alcohol mole fraction of about 0.2. On the basis of the data presented in work [3] for the same solutions, we may assume that the indicated position of the MLS maximum in work [28] is erroneous. Really, on the basis of the materials of work [28], we may assume that the concentration, at which additional scattering was observed, was indicated in weight percent, whereas the data along the ordinate axis were reckoned in molar percent. The corresponding recalculation completely eliminates the misunderstanding between the concentration positions of the additional MLS maximum in works [3] and [28].

It should be noted that M.F. Vuks marked that the additional MLS maximum was detected for the first time by G.P Roshchina [28], who had attributed it to the concentration MLS. However, either the mistake or any other factor did not allow her to classify the observed MLS peak as a new phenomenon.

Work [29] is a similar indirect confirmation of our assumption that the absence of literature data on the anomalous peak of MLS in dilute solutions takes place due to errors or a distrust of the data obtained. The corresponding concentration dependence of MLS obtained in work [29] was similar to that calculated in work [3]. But there were no scattering data in the interval of solution concentrations corresponding to the observation of the additional MLS, although the data to the left and right sides from this interval were available. We may assume that the results obtained in this concentration interval were estimated by the cited authors as erroneous. Really, such a large growth of the

light scattering intensity (see Figure) in such a narrow concentration interval may seem amazing.

Additional MLS was also observed in solids, e.g., in quartz at its transition between the α and β modifications [30, 31]. In work [4], I.L. Fabelinskii marked that this phenomenon "... could have been detected almost immediately after the molecular light scattering was detected in crystals in general. ... However, as often happens, it did not take place" [4]. Actually, this phenomenon occurs at a temperature of 846 K and in a temperature interval of about 0.1 K, so that it can be detected only in a purposeful experiment. The same can be said about the additional MLS in solutions. The governing factor of the phase transition in crystals is the temperature; in solutions, this is the solution concentration. Thus, the additional peak of MLS in aqueous solutions was detected by us in a rather narrow concentration interval of salt mole fractions (0–0.004). For aqueous alcohol solutions, this interval is about 0.03–0.1 in terms of alcohol mole fractions [17, 32, 33].

We would like to make some remarks about the physical origin of MLS in dilute solutions of electrolytes in water and alcohols. Let us demonstrate that if a component of the MLS intensity had been associated with density or concentration fluctuations, it would not have been consistent with experimental data. Really, the intensity ratio for the MLS of this type should be proportional to the ratio between the squared isotropic components of the molecular polarizability:

$$\frac{I_{VV}^{(e)}}{I_{VV}^{(m)}} \sim \left(\frac{\alpha_0^{(e)}}{\alpha_0^{(m)}} \right)^2 .$$

Since the isotropic components of the molecular polarizability are proportional to the molecular volume, this ratio can be rewritten in the form

$$\frac{I_{VV}^{(e)}}{I_{VV}^{(m)}} \sim \left(\frac{v_{\text{eff}}^{(e)}}{v_{\text{eff}}^{(m)}} \right)^2 .$$

From the data obtained by Roshchina [13], it follows that

$$I_{VV}^{(e)}/I_{VV}^{(m)} \approx 0.7,$$

whereas the square of the ratio between the molecular volumes equals

$$\left(v_{\text{eff}}^{(e)}/v_{\text{eff}}^{(m)}\right)^2 \approx 1.9.$$

This means that the contribution of the anisotropic MLS dominates. Unfortunately, we have no information concerning the anisotropy of the polarizability of methanol and ethanol molecules.

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АНОМАЛЬНЕ (ДОДАТКОВЕ)
РОЗСІЯННЯ СВІТЛА У ВОДНИХ РОЗЧИНАХ KCl

Р е з ю м е

В роботі вивчається молекулярне розсіяння світла в розведених водних розчинах хлориду калію. Експериментально показано наявність аномального (додаткового) молекулярного розсіяння світла в інтервалі від 0,001 до 0,004 мольних часток електроліту. Проведено зіставлення отриманих даних з літературними даними по розсіянню світла в водних і неводних розчинах хлориду калію. Обґрунтовано відсутність додаткового розсіяння в опублікованих раніше роботах.