ABNORMAL INCREASE OF THE LANDAU–PLACZEK RATIO NEAR THE PSEUDOSPINODAL IN DILUTED AQUEOUS-ALCOHOLIC SOLUTIONS

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UDC 544.164

The concentration dependences of the Landau–Placzek ratio in aqueous solutions of glycerol and γ-picoline have been studied. Cluster contributions to the central component of the polarized spectrum of molecular light scattering (MLS) have been analyzed. An elementary cluster was found to be composed of two-three γ-picoline molecules and approximately six water ones. In the concentration interval $0.02 < x < 0.09$, the system was considered as a solution of elementary clusters (pseudoparticles), the state of which can be described by the van der Waals equation. The most stable clusters were found to be formed in the vicinity of either the upper (water–glycerol) or the lower (water–γ-picoline) unattainable critical point. Theoretical estimations are in satisfactory agreement with experimental data.

1. Introduction

The Landau–Placzek ratio $R_{\rm LP}$ is an important characteristic of MLS in molecular systems. It is defined by the expression [1]

$$R_{\rm LP} = \frac{I_c}{2I_{\rm MB}}, \tag{1}$$

where I_c is the integral intensity of the central component of MLS, and $I_{\rm MB}$ is the integral intensity of one of the Mandelshtam–Brillouin components.

The integral intensity of the central component of MLS in single-component liquids is known [1, 2] to be caused by isobaric fluctuations δS of the entropy,

$$I_c(\mathbf{q}) \approx \langle|\delta S(\mathbf{q})|^2\rangle_p, \tag{2}$$

where $\delta S(\mathbf{q})$ is the Fourier transform of δS. At the same time, the Mandelshtam–Brillouin components are connected with isoentropic fluctuations of the pressure,

$$I_{MB}(\mathbf{q}) \approx \langle|\delta p(\mathbf{q})|^2\rangle_S. \tag{3}$$

With the help of thermodynamic expressions for root-mean-square values of entropy and pressure fluctuations [2, 3],

$$\langle|\delta S(\mathbf{q})|^2\rangle_p \approx k_{\rm B}T\beta_T\left(1-\frac{1}{\gamma}\right),$$

$$\langle|\delta p(\mathbf{q})|^2\rangle_S \approx \frac{k_{\rm B}T\beta_T}{\gamma}, \tag{4}$$

where β_T is the isothermal compressibility of a medium, $\gamma = c_p/c_v$ is the ratio between the specific heats c_p and c_v at constant pressure and volume, respectively, and neglecting the quantity $(\partial\varepsilon/\partial T)_\rho$, Landau and Placzek showed that

$$R_{\rm LP} = \frac{\langle|\delta S(\mathbf{q})|^2\rangle_p}{2\langle|\delta p(\mathbf{q})|^2\rangle_S} = \frac{c_p}{c_v} - 1. \tag{5}$$

In simple liquids, the Landau–Placzek ratio $R_{\rm LP}$ grows monotonously as the temperature T goes down [3]. But water demonstrates a more complicated behavior. Since the equality $c_p = c_v$ holds true at $T \approx 277.2$ K, one might expect – in agreement with Eq. (5) – that the Landau–Placzek ratio $R_{\rm LP}$ should tend to zero. However, experiments [4] testify that $R_{\rm LP}$ vanishes at $T \approx 275.5$ K. Moreover, an essential asymmetry of the temperature dependence $R_{\rm LP}(T)$ was observed. In work [5], an assumption was made that such a behavior of $R_{\rm LP}$ is explained by the formation of clusters in water; the cluster radius is about $5-10$ Å at the temperature $T = 263$ K, and it grows as the temperature reduces.

A similar dependence of the ratio $R_{\rm LP}$ should also be observed in water-alcohol solutions and solutions of the water-γ-picoline type which are subjected to clusterization as well. This conclusion is completely confirmed by experimental researches of MLS in a water-γ-picoline solution [6]. In work [6], the corresponding Landau–Placzek ratio was demonstrated to increase by two orders of magnitude in the temperature interval from 293 to 333 K while approaching the concentration interval $0.06 < x < 0.07$ in comparison with the values obtained beyond this range of states.

We note that the Mandelshtam–Brillouin components remain almost constant in water and a water–γ-picoline solution. In particular, the shifts of peaks'

maxima $\Delta\omega/\omega_{\rm MB}$ do not exceed the value of $0.012 \div 0.043$ [6]. The same order of magnitude is typical of the integral intensity variation of the Mandelshtam–Brillouin components as well. Qualitatively, such a behavior of $R_{\rm LP}$ can be naturally explained in the framework of the cluster model, but the quantitative analysis of the phenomenon requires a more detailed study.

This work aimed at studying the anomalous dependence of the Landau–Placzek ratio in water-glycerol and water-γ-picoline solutions. We emphasize that just the effective value of this ratio was a matter of concern, because the central component is a sum of the thermal and cluster contributions. We were going (i) to make the qualitative analysis of clusterization processes, (ii) to determine the magnitude of cluster contribution to the central component intensity of MLS, and (iii) to study the dependence of the $R_{\rm LP}$-ratio on the solution concentration.

2. clusterization Effects

clusterization of water and water-alcohol solutions is a consequence of the formation of strong hydrogen bonds between water molecules or between water and alcohol molecules. For instance, in a water-glycerol solution, the energies of hydrogen bonds between water molecules (≈ 0.19 eV [7]) and between glycerol ones ($0.22 \div 0.25$ eV [8]) are lower than the binding energy between water and glycerol molecules (≈ 0.29 eV [7]). In a water-picolinee solution, the binding energy of the $\rm N-H\ldots O$ bond falls within the interval of $0.20 \div 0.22$ eV [8], which is also a precondition for the formation of clusters.

Picoline $\rm CH_3-C_5H_4N$ is an isomer of pyridine. The basis of a molecule consists of a benzene ring, where one of the carbon atoms is substituted by a nitrogen atom. The actual isomeric form (α-, β-, or γ-picoline) depends on where the methyl groups $-\rm CH_3$ are located in the benzene ring. The nitrogen atom has an unshared electron pair; if the atom approaches the ring, the pair interacts with a hydrogen ion, and it can form a hydrogen bond N–H... O. The hydrogen bonds are the most stable in the case of aqueous solutions of α- and γ-picolines. It is caused by the fact that the methyl groups that are located in positions 2 and 4 (see Fig. 1) saturate the unshared electron pair of the nitrogen, thus increasing chances for the creation of a hydrogen bond with a water molecule.

In work [9], the anomalous growth of the MLS intensity in dissolved water-alcohol solutions ($x \approx 0.05$) was associated with processes of clusterization.

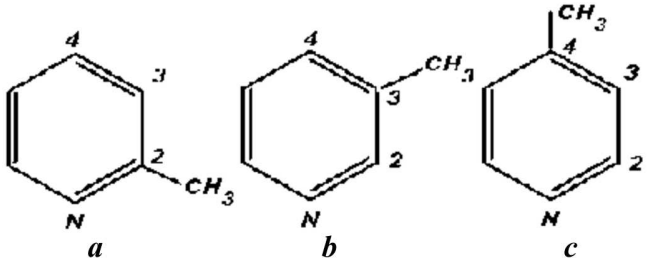

Fig. 1. Structures of α- (a), β- (b), and γ-picolines (c)

Similarly to that, we also connect the anomalous behavior of the Landau–Placzek ratio in a water-γ-picoline solution with the generation of clusters, owing to the formation of hydrogen bonds between the nitrogen atom and the hydroxyl groups of water molecules.

3. Cluster Contributions to the Integrated Intensity of Light Scattering

In molecular solutions, the central section of the MLS spectrum is formed by (i) thermal fluctuations which are of the same character as those occurring in single-component systems, and (ii) concentration fluctuations. In such solutions, the spectrum of the diffusion component looks like

$$I_c(\omega) \sim \frac{D_s k^2}{\omega^2 + (D_s k^2)^2}, \tag{6}$$

where D_s is the self-diffusion coefficient, and $\mathbf{k}$ is the wave vector ($|\mathbf{k}| \approx 10^5$ cm^{-1}). The self-diffusion coefficient is described with a satisfactory accuracy by the Einstein formula

$$D_s = \frac{k_{\rm B}T}{6\pi\eta r_{\rm eff}}, \tag{7}$$

where η is the shear viscosity, and the value of the parameter $r_{\rm eff}$ is close to the radius of dissolved molecules in ordinary molecular solutions. However, in diluted ($x \approx 0.05$) water-alcohol solutions and solutions of the water-γ-picoline type, $r_{\rm eff}$ should be identified as either the radius of elementary clusters or the correlation length between them. The essential difference between them arises, if the consideration approaches the so-called pseudospinodal of the system (see work [9]). In work [10], it was demonstrated that the halfwidth of the central peak in the MLS intensity spectrum in a water-glycerol solution, $\Gamma_c^{(\rm w-gl)}$, is of the order of 10^4 s^{-1}, which brings about the effective correlation length $r_{\rm eff} \approx 65$ Å. The latter value is an order of magnitude larger than the

molecular radius of glycerol and the radius of elementary clusters composed of glycerol molecules.

Due to the clusterization, the intensity I_c of the central spectral section becomes a sum of two contributions, namely, a standard one, I_s, caused by thermal fluctuations, and another one, $I_{\rm cl}$, having the cluster origin:

$$I_c = I_s + I_{\rm cl}. \tag{8}$$

The temperature and concentration dependences of the integral intensity $I_{\rm cl}$ in a water-glycerol solution were studied in work [9]. It was shown that

$$I_{\rm cl} \approx \frac{T}{A}, \tag{9}$$

where

$$A = L_0 + L_1(x - x_s(T))^2 + L_2(x - x_s(T))^4 + \ldots \tag{10}$$

Here, the coefficients L_0, L_1, and L_2 are associated with the cluster-induced osmotic pressure $p_{\rm osm}$ through the relation

$$A = \frac{\partial p_{\rm osm}(v)}{\partial v}. \tag{11}$$

The osmotic pressure is supposed to obey the van der Waals equation (see work [9])

$$\tilde{p}_{\rm osm}(x) = \frac{x\tilde{T}}{1 - \tilde{b}x} - \tilde{a}x^2, \tag{12}$$

where the dimensionless temperature $\tilde{T}$ and coefficients are defined as follows:

$$\tilde{T} = \frac{T}{T_m}, \qquad \tilde{a} = \frac{a}{a_0}, \qquad \tilde{b} = \frac{4\tilde{n}_{\rm w}}{z_{\rm g}},$$

$$\tilde{p}_{\rm osm}(x) = \frac{p_{\rm osm}(x) z_{\rm g}}{n_{\rm w} k_{\rm B} T_m}, \qquad a_0 = \frac{k_{\rm B} T_m z_{\rm g}}{n_{\rm w}}, \tag{13}$$

T_m is the crystallization temperature of water, $v_{\rm cl}$ is the volume of an elementary cluster; $z_{\rm g}$ and $\tilde{n}_{\rm w} = n_{\rm w} v_{\rm cl}$ are the numbers of glycerol and water molecules, respectively, in a cluster; and $n_{\rm w}$ is the concentration of water molecules. In work [9], the coefficients L_0, L_1, and L_2 were shown to look like

$$L_0 = \frac{1}{(1 - \tilde{b}x)^2}\tau_s, \qquad L_1 = 2\left[\frac{\tilde{b}}{(1 - \tilde{b}x_s)^3} - \tilde{a}_1\right],$$

$$L_2 = \frac{3\tilde{b}^2}{(1 - \tilde{b}x_s)^4}, \qquad \tilde{a}_1 = \frac{\tilde{a}}{k_{\rm B} T_s(x)}. \tag{14}$$

The variable $\tau_s(x) = [T - T_s(x)]/T_s(x)$ describes a deviation of the temperature from its value on the pseudospinodal given by either the curve $T_s(x)$ or the curve $x_s(T)$. It is easy to see that the temperature dependence $T_s(x)$ is described by the equation

$$\tilde{T}_s(x) = 2\tilde{a}(\tilde{T}_s) x (1 - \tilde{b}x)^2. \tag{15}$$

As was shown in [9], the pseudospinodal coincides with the left-hand branch of the van der Waals spinodal in the concentration region $x < x_p$, where x_p is the percolation threshold which corresponds to the packing of elementary clusters. In addition, the pseudospinodal is limited by the temperatures ($T_{\rm cr} < T < T_p$), which correspond to intersections of the spinodal with the solution crystallization curve and the straight line $x = x_p$.

Concentration fluctuations grow, if one approaches the solution pseudospinodal; contrary to the spinodal and due to the cluster destruction, the pseudospinodal possesses only one branch. The pseudospinodal becomes destroyed, if the solution concentration reaches the threshold of the formation of a percolation cluster (see work [9]).

In accordance with the aforesaid, the Landau–Placzek ratio looks like

$$R_{\rm LP} = \frac{I_c}{2I_{\rm MB}} = \frac{I_s + I_{\rm cl}}{2I_{\rm MB}} = R_{\rm LP}^{(0)} + \frac{I_{\rm cl}}{2I_{\rm MB}} \tag{16}$$

for diluted clustered solutions, where $R_{\rm LP}^{(0)}$ is the contribution to the Landau–Placzek ratio given by thermal fluctuations. Since the shift of Mandelshtam–Brillouin components is insignificant in a water-glycerol solution, the integral intensity of those components is supposed to be same as it is in pure water, namely, $I_{\rm MB} \approx 0.04$ cm^{-1}.

In work [9], the parameters $\tilde{a}$ and $\tilde{b}$ for glycerol were demonstrated to lie within the intervals 0.2−1.9 and 63−173, respectively. The concentration dependences of the Landau–Placzek ratio $R_{\rm LP}$ for a water-glycerol solution at isotherms $T = 276, 278$, and 283 K, which are depicted in Fig. 2, were plotted just using this assumption. As the temperature decreases, one should expect for the growth of $R_{\rm LP}$ maxima and their shift into the $0.045 < x < 0.09$ concentration interval. The halfwidth Γ of the integral intensity peaks should diminish with the temperature reduction and get equal to the following values:

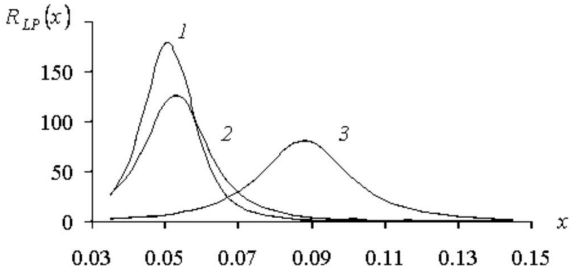

Fig. 2. Concentration dependences $R_{\rm LP}(x)$ calculated by formulas (9)–(12) for a water-glycerol solution at the temperatures $T = 276$ (*1*), 278 (*2*), and 283 K (*3*)

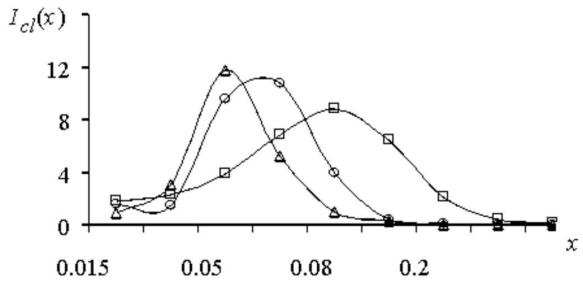

Fig. 3. Concentration dependences $I_{\rm cl}(x)$ calculated for a water-γ-picoline solution at the temperatures $T = 333$ (triangles), 313 (circles), and 291 K (squares)

$\Gamma = 3.4 \times 10^4$ cm^{-1} at $T = 283$ K, $\Gamma = 1.6 \times 10^4$ cm^{-1} at $T = 278$ K, and $\Gamma = 0.9 \times 10^4$ cm^{-1} at $T = 276$ K.

Since Γ-values are directly associated with the characteristic dimensions of elementary clusters that are formed in the system, it is possible to assert that a reduction of the cluster concentration is accompanied by the growth of cluster sizes. This conclusion agrees with the conclusions drawn in work [9].

Taking into account the similarity between the clusterization processes in water-γ-picoline and water-glycerol solutions, the approach developed by us in work [9] can be applied to the former as well. The concentration dependence of $R_{\rm LP}$ in this solution was experimentally studied in work [6]. Taking advantage of formula (16), the values obtained for $R_{\rm LP}$ in work [6] can be applied to find the behavior of $I_{\rm cl}$ as a function of the concentration at the temperatures $T = 293$, 313, and 333 K (Fig. 3). Now, it is evident that, unlike the case of a water-glycerol solution, the maximal value of the cluster contribution $I_{\rm cl}$ to the intensity decreases with decrease in the temperature. Such a behavior of the $I_{\rm cl}$-intensity is a manifestation of the fact that the pseudospinodal position corresponds to the unattainable upper critical point (see work [9]) for a water-glycerol solution and to the unattainable lower critical point for a water-γ-picoline solution.

The left-hand branches of pseudospinodals for a water-γ-picoline solution were calculated by formula (15) for clusters with various dimensions, and they are exhibited in Fig. 4. In all the variants, the lower critical points are unattainable, because the corresponding concentration values exceed percolation thresholds. The

r_0, Å	T_c, K	$\tilde{a}$	$\tilde{b}$
5.21	284	1.39	39.5
6.36	309	2.75	71.9
6.57	323	3.16	79.1

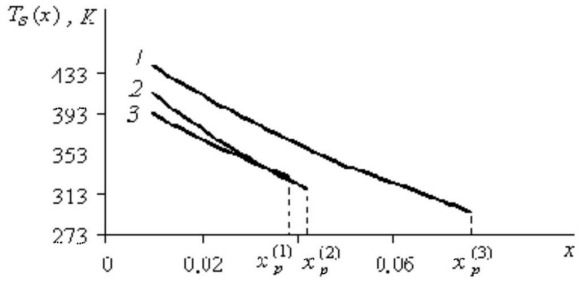

Fig. 4. Locations of the pseudospinodal $T_s(x)$ in the water-γ-picoline solution case for clusters with various radii: 5.21 (*1*), 6.36 (*2*), and 6.57 Å (*3*)

value of the percolation threshold x_p was calculated by the formula

$$x_p = \frac{\varphi_p}{v_{\rm cl} n_w} \tag{17}$$

derived in work [9]. One can easily see that $x_p \approx 0.075$, 0.042, and 0.038 at $r_0 \approx 5.2$, 6.4, and 6.6 Å, respectively.

The dimension of a γ-picoline molecule is approximately equal to 3.4 Å. The values of the parameters $\tilde{a}$ and $\tilde{b}$ in the van der Waals equation were calculated by formulas (14) in the same way as in work [9]; they are quoted in Table. Let us put those the quantities $\tilde{a}$ and $\tilde{b}$ into agreement with the parameters z_p and n_w which determine the numbers of γ-picoline and water molecules, respectively, in an elementary cluster, by using the simplest geometric model of elementary cluster. In such a way, we come to the conclusion that a cluster contains two γ-picoline molecules and about six water molecules. An elementary cluster in a water-γ-picoline solution contains the smaller number of water molecules in comparison with that in an aqueous solution of glycerol. It stems from the fact that, in γ-picoline, hydrogen bonds are formed only owing to one nitrogen atom which possesses two unshared electronic

pairs. In glycerol, such a possibility is inherent to three hydroxyl groups (−OH), which results in an increase of the number of hydrogen bonds between water and glycerol molecules.

The most probable is the formation of clusters, the radius of which amounts to 5–7 Å.

4. Conclusions

Therefore, the formation of clusters and the direct influence of clusters on the anomalous growth of concentration fluctuations in the dissolved aqueous solutions of alcohols and picolines compose a basis for our approach to the description of peculiarities of MLS in those solutions, as well as their other properties. In the framework of our approach, the features in the behavior of the Landau–Placzek ratio $R_{\rm LP}$ find their quite natural explanations. In particular, it was established that an anomalous growth of the Landau–Placzek ratio is to be expected in a water-glycerol solution, if one approaches the left pseudospinodal branch with an unattainable upper critical point. For this solution, the maximal values of $R_{\rm LP}$ are expected to be at concentrations of about 0.05.

In contrast to this case, in a water-γ-picoline solution, there emerge the conditions that favor the appearance of an unattainable lower critical point of lamination; depending on the dimensions of an elementary cluster, this point is located somewhere within the temperature interval $T_c \approx 284 - 323$ K. The $R_{\rm LP}$-maxima should be observed at that within the concentration range $0.03 < x < 0.06$. Beyond this range, clusters are unstable. We showed that an elementary cluster includes two or three γ-picoline molecules and about six water molecules. The radius of such a cluster amounts to $5 - 7$ Å, which is in qualitative agreement with its most simple geometric model.

The authors are grateful to the State Foundation for Fundamental Researches for the financial support of this work (grant No. F25.2/111).

1. I.L. Fabelinskii, *Molecular Scattering of Light* (Plenum Press, New York, 1968).
2. L.D. Landau and E.M. Lifshits, *Statistical Physics, Part 1* (Pergamon Press, Oxford, 1980).
3. D. McIntyre and J.V. Sengers, in *The Physics of Simple Liquids,* edited by H.N.V. Temperley, G.S. Rushbrooke, and J.S. Rowlinson (North Holland, Amsterdam, 1968), p. 447.
4. G. Maisano, D. Majolino, F. Mallamace, P. Migliardo, F. Aliotta, C. Vasi, and F. Wandeligh, J. Mol. Liq. **57**, 1083 (1986).
5. T.V. Lokotosh and N.P. Malomuzh, J. Mol. Str. **432**, 43 (2004).
6. L.M. Sabirov, D.I. Semenov, and Kh.S. Khaidarov, Opt. Spektr. **102**, 955 (2007).
7. Yu. Efimov and Yu. Naberukhin, Zh. Strukt. Khim. **41**, 532 (2002).
8. L. Pauling, *General Chemistry* (W.H Freeman/Dover Publications, San Francisco, 1970).
9. N.P. Malomuzh and E.L. Slinchak, Zh. Fiz. Khim. **81**, No. 11, 1 (2007).
10. V.Eu. Chechko, V.Ya. Gotsul'sky, and V.G. Zaremba, J. Mol. Liq. **105**, 211 (2003).

Received 25.06.08.
Translated from Ukrainian by O.I. Voitenko

АНОМАЛЬНЕ ЗРОСТАННЯ ВІДНОШЕННЯ ЛАНДАУ–ПЛАЧЕКА ПОБЛИЗУ ПСЕВДОСПІНОДАЛІ РОЗБАВЛЕНИХ ВОДНО-СПИРТОВИХ РОЗЧИНІВ

М.П. Маломуж, О.Л. Слинчак

Р е з ю м е

Досліджено концентраційну залежність відношення Ландау–Плачека у водних розчинах гліцерину та γ-піколіну. Проаналізовано кластерні внески у центральну компоненту поляризованого спектра молекулярного розсіяння світла. Встановлено, що дві-три молекули γ-піколіну з приблизно шістьма молекулами води утворюють елементарний кластер. У діапазоні концентрації $x \in (0,02;\ 0,09)$ система розглядається як розчин елементарних кластерів (псевдочастинок), стан яких моделюється рівнянням Ван-дер-Ваальса. Показано, що найстійкіші кластери утворюються в околі як верхньої (вода–гліцерин), так і нижньої (вода–γ-піколін) недосяжної критичної точки. Показано, що теоретичні оцінки задовільно узгоджуються з експериментальними даними.