Temperature Induced Structural Changes of the Solute-Solvent Clusters and Demixing Phenomena in Aqueous Solutions [1]

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ABSTRACT

Demixing phenomena in the aqueous solutions of the organic molecules are considered in view of the temperature induced structural changes of the water-solute clusters. The main types of the clusters are discerned on their ability to be embedded in the network of the water hydrogen bonds. It was found that the concentration of the water-like clusters achieves maximum at some temperature. The lower and upper critical solution points are attributed to the appearance of some "critical" concentration of the water-like clusters. In accordance with this model of demixing both the lower and upper critical points are driven by hydrogen bonding and the immiscibility gap extends upon strengthening of the hydrogen bonds between water and solute molecules.

This approach is applied to the analysis of the demixing phenomena in the aqueous solutions of tetrahydrofuran. Experimentally observed changes of the lower and upper critical solution temperatures upon deuteration of water or tetrahydrofuran molecules, addition of salts are well reproduced in the framework of the proposed model .

KEY WORDS: aqueous solutions; critical solution points; hydrogen bonding; liquid-liquid phase separation.

1. INTRODUCTION

The temperature induced liquid-liquid phase separation are the result of the competition between energetic and entropy factors. Increasing temperature in general case promotes mixing of the two phases due to the growth of the positional entropy, therefore the phenomenon of the upper critical solution point (UCSP) is not surprising. The lower critical solution point (LCSP) corresponds to the phase separation with increasing temperature and may be understood only taking into account some microscopic details of the liquid structure. This phenomenon was attributed to the effect of the highly directional bonds (for example, hydrogen bonds, H-bonds) between unlike molecules of the mixture [1,2]. Increasing of the orientational entropy due to the breakdown of the H-bonds allows the homogeneous mixture to separate on two coexisting phases with decreasing of the positional entropy. This explanation connects appearance of the LCSP with existence of the two possible kinds of the pair interactions between unlike molecules: with H-bond (1H) and without H-bond (0H). The concentration of 1H pair clusters decreases whereas concentration of the 0H clusters increases with temperature due to the differences in the energies and orientational specifities of these states. Such dependencies mean breakdown of the H-bonds with temperature. It is obviously, that in this model lower critical solution temperature T_l increases with the strengthening of H-bonds whereas upper critical solution temperature T_u is not sensitive to the variations of the H-bonds. Therefore, some perturbations, which influence mainly on these H-bonds (such as deuteration or addition of salts), must essentially influence first of all on the T_l , at least the sensitivities of the T_l and T_u to the perturbations must be different since these critical points have different reasons. Besides, strengthening of the H-bonds must

result in the shrinkage of the immiscibility gap, which spreads between T_l and T_u, due to the increasing of the T_l.

The experimentally observed changes of the critical solution temperatures upon perturbations contradict to these predictions of the existing model of demixing. For example, in many solutions with hydrogen bonding the T_l and T_u have the similar sensitivities to such perturbations, as presence of the electron donating substituent groups in solute molecule, addition of salts, deuteration, pressure [3,4]. It is important, that strengthening of the H-bonds between unlike molecules due to these perturbations is accompanied by the extension of the immiscibility gap, in direct contradiction to the predictions of the existing model of demixing. These contradictions indicate on the necessity to find more reasonable mechanisms of the demixing processes in the aqueous solutions.

2. MODEL

Two-states presentation of the interaction between unlike molecules in the existing model of demixing [1,2] is oversimplificated approach for mixtures, containing molecules, able to form more than one H-bond (water, alcohol, etc.). The clustering processes in solution are not taken into account usually in lattice models [5], although they are of great importance for the liquids with H-bonds. On the other hand it is difficult now to take into account correctly fine details of the hydrogen bonding and clustering processes in the Monte Carlo simulations of the phase equilibrium [6]. So, another approach in the analysis of the demixing phenomena in the mixtures with H-bonds is necessary.

The closed-loop phase diagrams, temperature vs concentration, of the solutions of the organic molecules in the strongly associated solvents, such as water, usually have

the shape close to quadrangle. It means that the concentrations of the solute molecules in the coexisting phases are rather stable with temperature: there are 1 - 4 water molecules per one organic molecule in organic-rich phase, and a few dozens water molecules in the water-rich phase. These phases may be considered as two mixtures with different structures. In particular, in the aqueous solution of tetrahydrofuran (THF) there is approximately one water molecule per one THF molecule in organic-rich phase and there are 11 water molecules per one THF molecule in water-rich phase [7]. Note, that the stoichiometry of the water-rich phase may be considered as display of the stoichiometry of the solid clathrate hydrate $(H_2O)_{17}$ THF [8].

Consideration of the possible liquid structures should be started from the analysis of the hydrogen bonding between unlike molecules. In general case the solute-solvent clusters of different compositions may be realized. From the point of view of the solution structure two characteristics of the clusters are important: its interaction with surrounding molecules (clusters) and their concentration. For the strongly associated liquids with H-bonds the interaction of the cluster with surroundings is determined mainly by its ability to form H-bonds and so different kinds of these clusters prefer solvent-like or solute-like phase of the mixture. So, all possible solute-solvent clusters must be sorted over this parameter. In general case increase of the number of H-bonds inside the cluster results in the lowering of its energy and entropy factor and in the lowering of its ability to form H-bonds with surroundings. The concentrations of the different kinds of clusters change with temperature in different manner and it may provoke structural changes of the solution, including its separation on two phases. At first approximation only pair solute-solvent clusters may be considered.

Many organic molecules contain more than one hydrophilic center. In this case pair clusters with two H-bonds (2H) between single water and single solute molecules must be considered parallel with 0H and 1H clusters. Due to the high directionality of the H-bonds, number of the possible pair configurations decreases in the sequence: 0H > 1H > 2H, whereas the average energies of the clusters decrease in the same sequence. As a result concentration of the 2H clusters decreases with temperature, concentration of the 0H clusters increases with temperature, and concentration of the 1H clusters achieves maximum at some temperature.

The 1H pair cluster correspond to the better embedding of the solute molecule in liquid water in comparison with the 0H and 2H clusters and may be considered as water-like cluster. It means that water molecules around the 1H cluster are associated stronger, than around 0H and 2H clusters. We suppose, that 1H clusters promote existence of the water-rich phase of the solution. In other words, solution separates on water-rich and organic-rich phases if concentration P_{1H} of the 1H clusters exceeds some "critical" value P_c . The equality $P_{1H} = P_c$ takes place at both lower and upper critical solution temperatures. It means that the both critical temperatures are driven by hydrogen bonding between water and solute molecules.

The temperature dependence of the concentration of the different pair clusters may be obtained from the calculations of the possible water-solute pair configurations using the method of atom-atom potentials, which allows to take into account fine details of the hydrogen bonding. In order to obtain the absolute values of the critical solution temperatures two fitting parameters must be used in the proposed approach: the value of the critical concentration P_c ("statistical" fitting parameter) and the highest possible energy of the pair configuration U_c ("energetic" fitting parameter,

which corresponds to the effect of the surroundings on the pair cluster). It allows to compare experimentally observed phase behavior of the aqueous solutions with the results of calculations.

The changes of the critical solution temperatures of the aqueous solutions of pyridines with deuteration of water, embedding of the alkyl-substituents in the pyridine molecule, addition of salt, are well reproduced in the framework of the proposed model [4]. In the present paper the changes of the critical solution temperatures of the aqueous solutions of THF upon such perturbations, as deuteration of water, deuteration of THF, addition of salts, are analyzed.

3. RESULTS

The energies of more than 10^8 pair configurations THF + H_2O were calculated using the method of atom-atom potentials. The potentials of the form (exp-6-1) with the set of parameters from [4] were used for non-bonding interactions. The special potentials for H-bonds of the form (10-12-1) were used. The initial parameters of these potentials were chosen as U_0 = -3.0 kcal/mol; R_0 = 1.9 A for stronger O-H...O bonds and U_0 = -1.5 kcal/mol; R_0 = 2.4 A for weaker C-H...O bonds. The distance in 2.7 A was chosen as “critical” for H-bonds distance between proton ant its acceptor.

The obtained energetic distributions of the 0H, 1H and 2H pair clusters are presented in Fig.1. The corresponding dependence of the concentrations of these clusters on temperature are presented in Fig..2. The “critical” concentration of the 1H clusters P_c is shown by horizontal line. The lower and upper critical solution temperatures correspond to the intersections of this line with the concentration line for

1H clusters. In order to fit experimentally observed critical temperatures of the THF - H_2O mixture [7] the “critical” concentration P_c was fixed at 33.9% and parameter U_c at -0.32 kcal/mol.

The deuteration of proton donor molecule leads to the slight elongation of H-bonds [9]. It may be simulated in our calculations by small increase of the parameter R_0 in the potential of the corresponding H-bond. In order to reproduce experimentally observed extension of the immiscibility gap upon deuteration of water [7] it was necessary to increase parameter R_0 in the potential for O-H...O bonds on 0.004 A (Fig.3,a), assuming linear changes of the R_0 with the fraction of heavy water in total water.

The deuteration of THF molecules leads to the unusual shrinkage of the immiscibility gap [7]. This effect was reproduced in our calculations by increase of the corresponding parameter R_0 in the potential for C-H...O bonds on 0.005 A (Fig.3,b), assuming linear changes of the R_0 with the fraction of deuterons in total number of deuterons and protons of the THF molecules in solution.

The addition of salts changes essentially critical solution temperatures of the aqueous solutions [3]. The decrease of the T_l was observed for the set of the salts, containing anions Cl^- [7]. These anions act as strong proton acceptors and their effect is spreaded over some region of the solution due to the collective character of H-bonds in water. As was obtained by NMR investigations [7], presence of the salt KCl in the aqueous solution of the THF leads to the increase of the activation energy of the reorientational motion of the THF molecule without noticeable changes for water molecules. It evidences that the H-bonds between water and THF molecules strengthen due to the presence of anions Cl^-. Therefore, addition of the anions Cl^-

may be simulated in our model by increase of the parameter $|U_0|$ in the potential for the O-H...O bond. The critical line was calculated, assuming linear dependence of the U_0 on the "mole" fraction X of Cl^- anions from 0 to $4*10^{-3}$ (Fig.4). The deviation of the calculated curve from experimental points [7] we attribute to the worsening of the linear correlation between U_0 and X when fraction of salt increases. As can be seen from Fig.4, the effect of the cations on the critical solution temperatures is insignificant in comparison with the effect of the anions.

So, the experimentally observed changes of the critical solution temperatures of the aqueous solutions of THF [7] upon deuteration of water, deuteration of THF molecules, addition of salts, are well reproduced in the framework of the proposed model of demixing. The value of the fitting parameter U_c for the aqueous solutions of THF (-0.32 kcal/mol) practically coincides with the value, obtained for the aqueous solutions of pyridines (-0.34 kcal/mol [4]). It displays similar effect of the surroundings on the water-solute clusters in both cases. The obtained value of the parameter P_c for the aqueous solutions of THF (33.9%) is lower in comparison with the aqueous solutions of pyridines (42% [4]), that displays the lower critical concentration of the solute molecules in latter case [3,7].

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FIGURE CAPTIONS

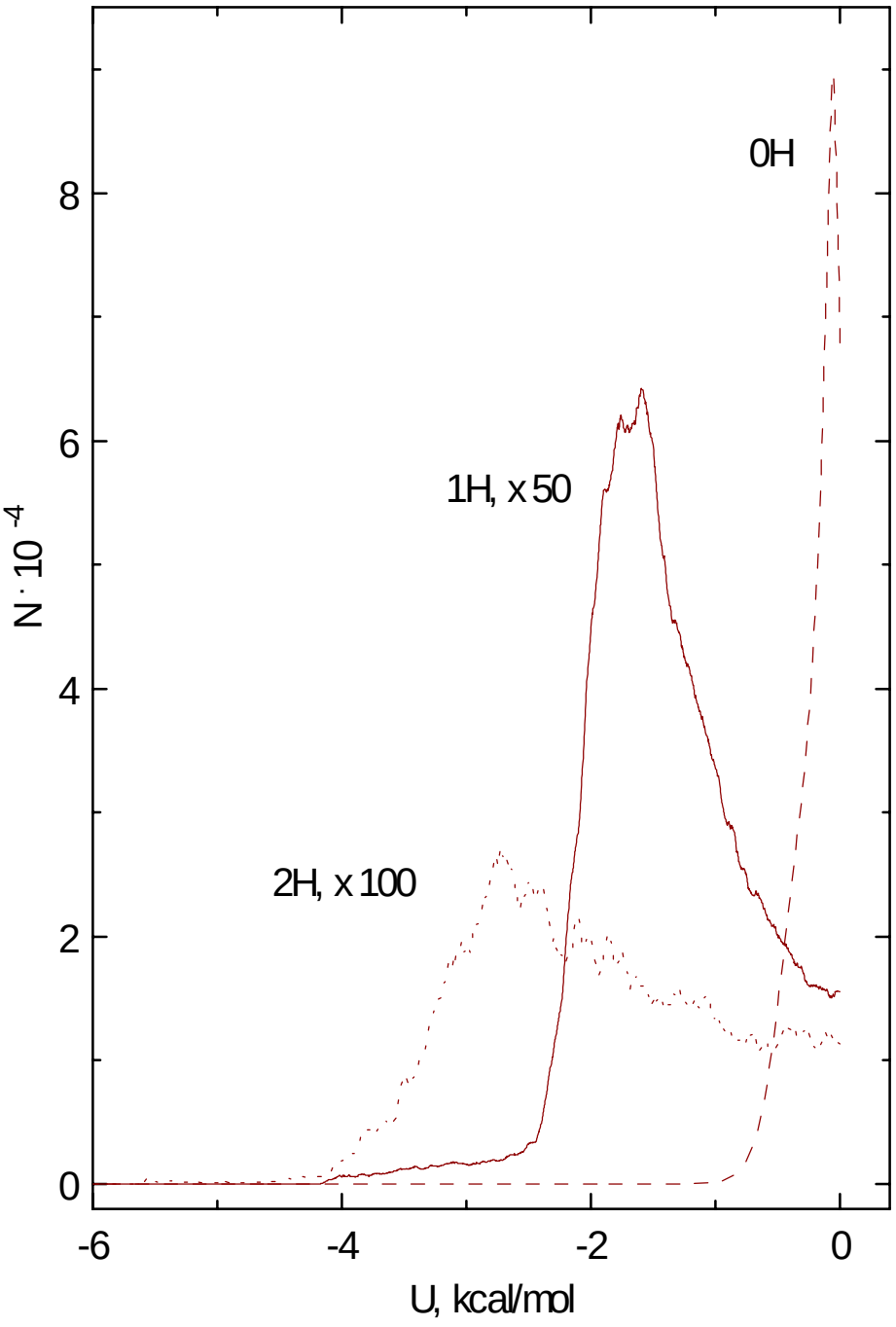
Fig. 1. Energetic distributions of the 0H, 1H and 2H pair clusters THF + H_2O. N - number of the clusters, U - energy of the cluster.

Fig. 2. Temperature dependence of the concentrations P of the clusters 0H, 1H and 2H, obtained from the energetic distributions, presented at Fig.1. P_c is the "critical" concentration of 1H clusters, T_l and T_u are the lower and upper critical solution points.

Fig. 3. a) Calculated dependence of the critical solution temperatures T_l and T_u on the parameter R_0 in the potential for O-H...O bonds. Experimental critical temperatures [7] for the solutions THF + H_2O and THF + D_2O are shown by open and solid circles, respectively.

b) Calculated dependence of the critical solution temperatures T_l and T_u on the parameter R_0 in the potential for C-H...O bonds. Experimental critical temperatures [7] are shown for the solutions: THF-h_8 + D_2O (circles), THF-h_4d_4 + D_2O (squares), 75% THF-d_8 + 25% THF-h_8 (triangle). The cross corresponds to the value of R_0, estimated for the THF-d_8 , which is miscible in D_2O.

Fig. 4. Calculated dependence of the critical solution temperatures T_l and T_u on the mole fraction of the anions Cl^- in the solution THF-h_8 + D_2O. Experimental critical temperatures [7] are shown for the solution without salt (solid circles) , with salts NaCl, Kcl, RbCl, CsCl (open circles), with salt $CaCl_2$ (solid squares) and $AlCl_3$ (open squares).


0H
1H, x 50
2H, x 100
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6
4
2
0
-6
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-2
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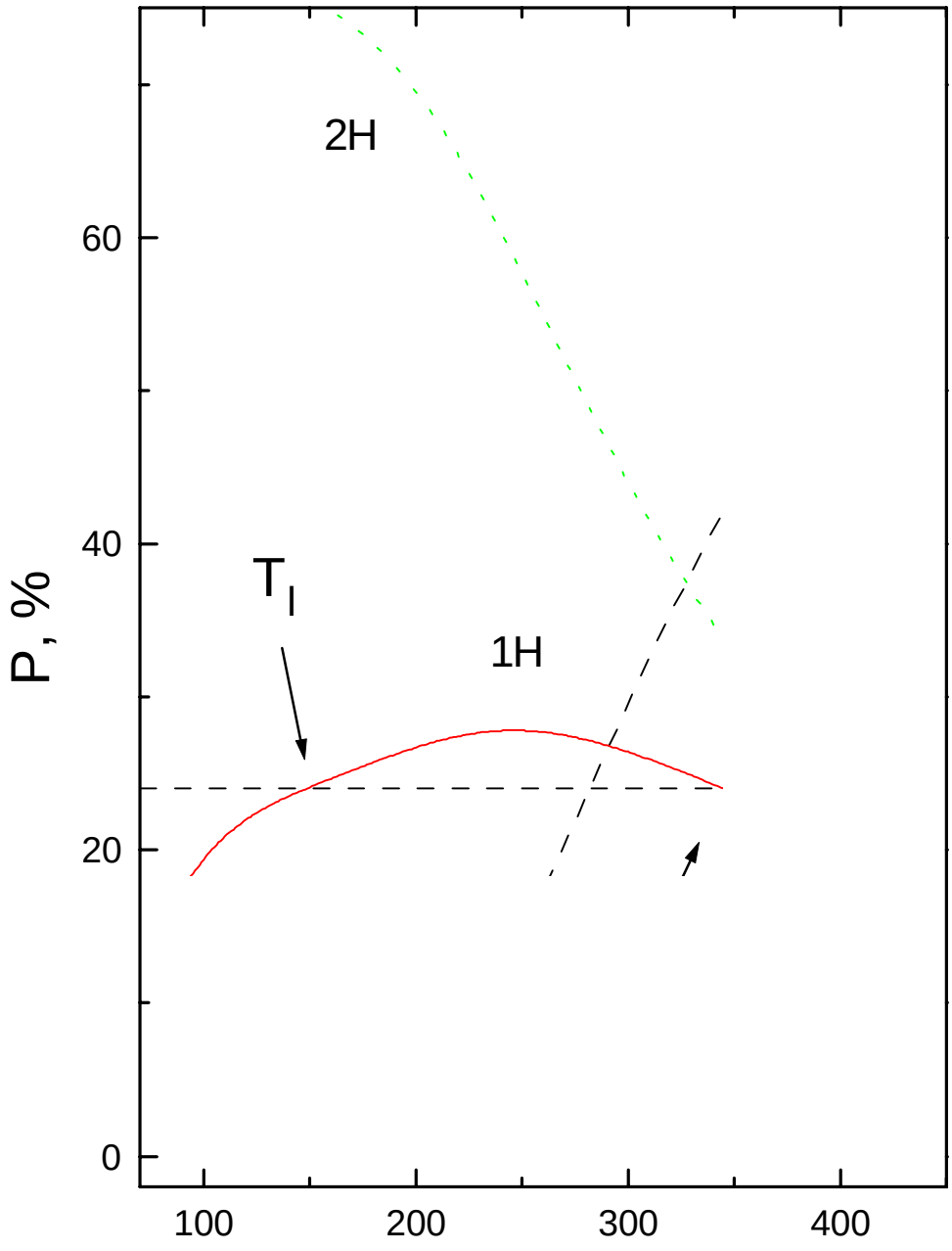
U, kcal/mol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1H
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P, %
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300
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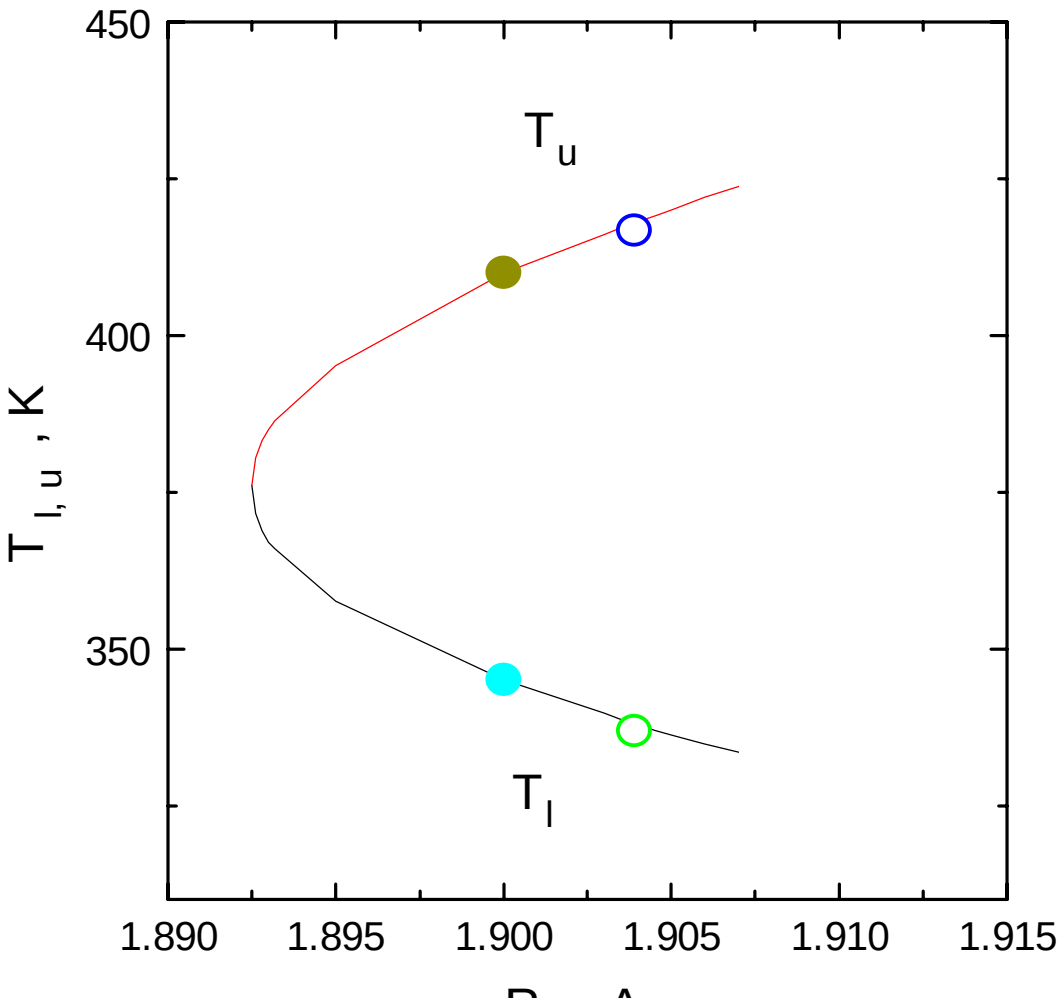
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T_l
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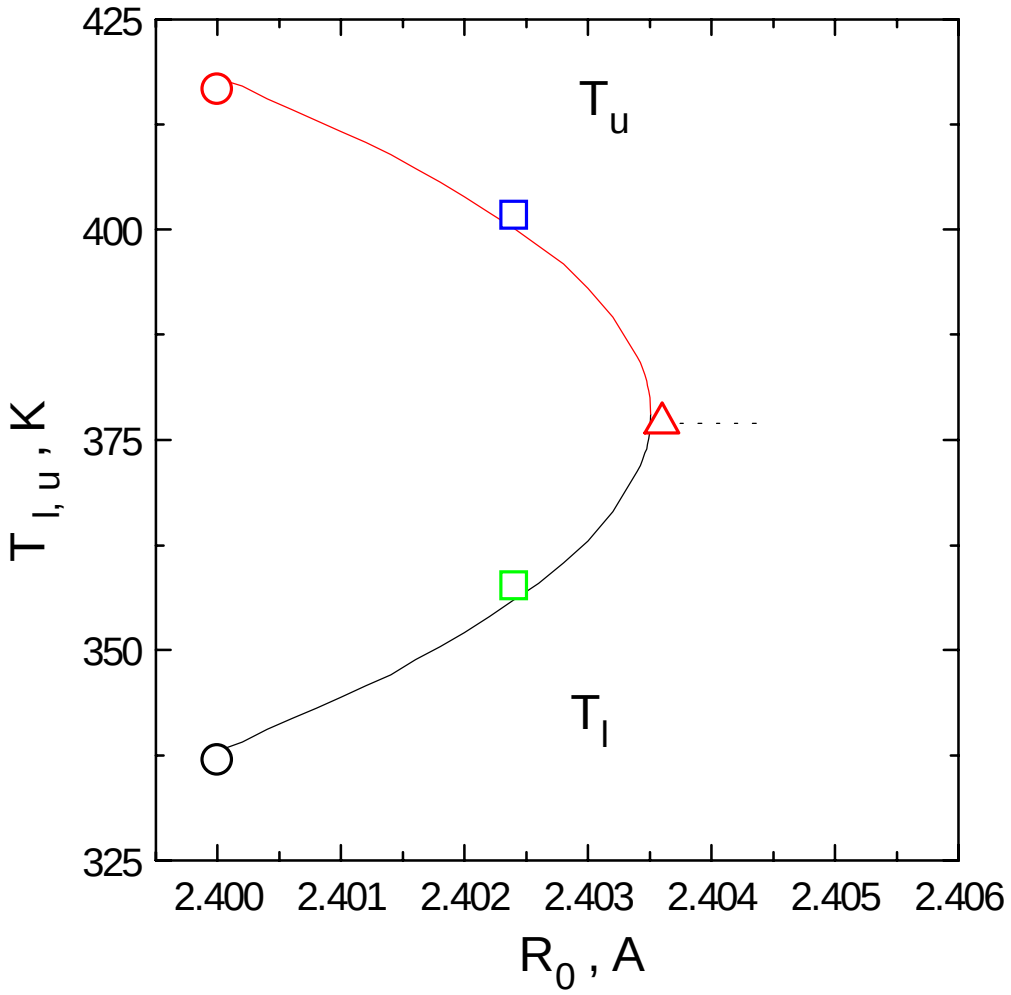
1.910
1.915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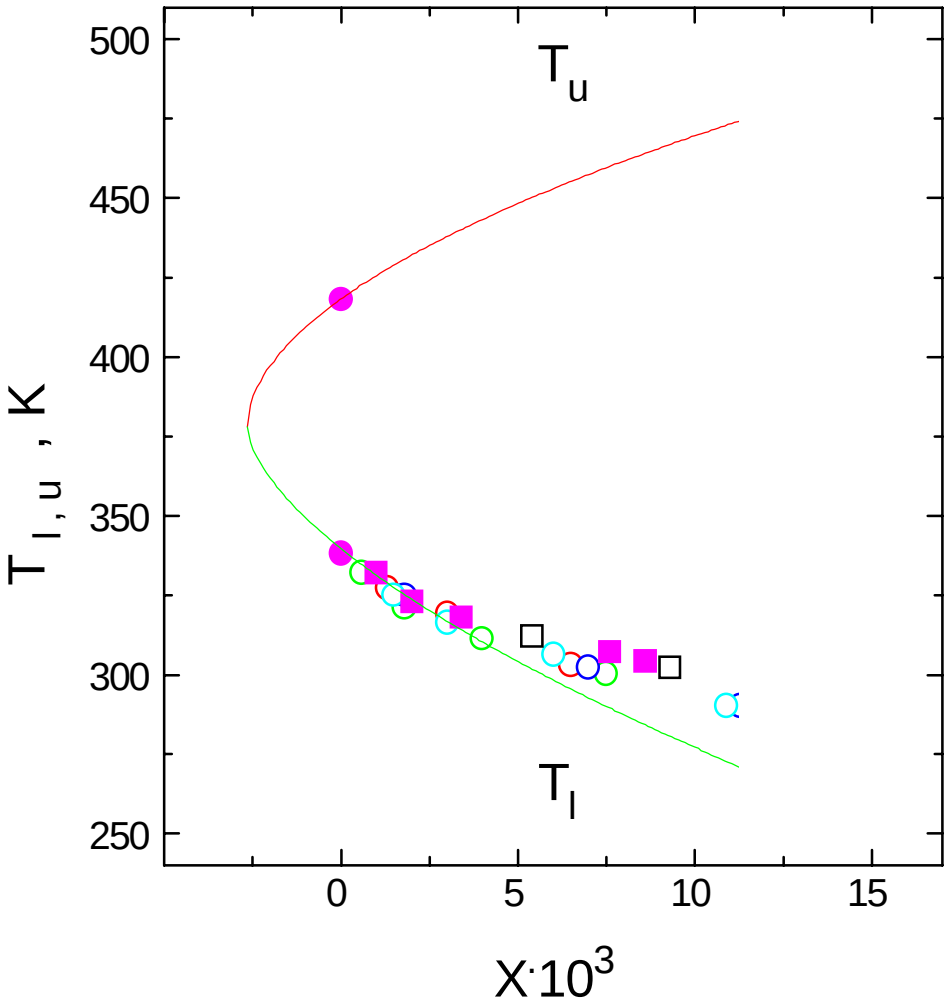
T_u
T_l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T_u
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$T_{l,u}$, K
$X \cdot 10^3$