Acta Chim. Slov. **2009,** *56,* 215–217

Short communication

The Relation Between Solvophobic Effects and Critical Phenomena in Solutions

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Received: 14-10-2008

Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

The relation between the solvophobic effects and the critical phenomena in ethylene glycol-tert-butanol and ethylene glycol-tetramethylurea diluted solutions were investigated by means of DSC analysis and exces molar partial volumes measurements.

Keywords: Solvophobic effect, critical phenomena, ethylene glycol, tert-butanol, tetramethylurea

1. Introduction

In diluted aqueous solutions of non-electrolytes (up to at most 0.1 mole fraction) the phenomena similar to those in the vicinity of critical immiscibility point can be observed: the existence of an anomalous low-concentration light scattering maximum, with no thermodynamic explanation, an giant increase in the level of concentration fluctuations, asymmetry of the indicatrix, narrowing the Rayleigh line wing, the appearance of concentration and anisotropy cross-fluctuations, and anomalous absorption and dispersion of sound.[1–5] The relations between the above-mentioned phenomena and the hydrophobic effects in the water – non-electrolyte systems, and the conception of the “unattainable” critical immiscibility point have been discussed in the literature already.[2–4]

In our previous investigations we have suggested an explanation of these phenomena from the point of view of the properties of the spatial network of H-bonds of water: its lability and elasticity.[6, 7] Lability, the broad distribution of H-bonds over angles and distances without their rupture, explains the easy formation of a cavity in the solvent, which is necessary for the entering of a non-electrolyte molecule, i.e. hydrophobic hydration. Elasticity is the tendency to preserve the initial configuration, the ability of pushing out the dissolved particles to the network defects and group them together. Therefore the hydrophobic interaction effect, i.e. the aggregation of non-electrolyte molecules in fairly dilute water solutions, can be explained as a consequence of the properties of the network built by the water molecules.

This approach to hydrophobic phenomena gives also a physical explanation of the “unattainable” critical immiscibility point. Hydrophobic phenomena strengthen the spatial network of H-bonds of water that pushes out the non-electrolyte molecules and forces them to group together. But this micro-immiscibility on the 3-dimensional network of H-bonds only occurs below a certain non-electrolyte concentration, beyond which the network is disturbed, hydrophobic effects decrease significantly, and the system never attains the critical immiscibility point. The system still can acknowledge the existence of this “unattainable” immiscibility point and thus displays the properties similar to those in the vicinity of the critical immiscibility point.

2. Method

One of the typical features of the hydrophobic effects is the appearance of the maximum of the heat capacity in the non-electrolyte solutions, which is most pronounced in the concentration dependence of excess molar heat capacity of the solution. Recently an analysis of the

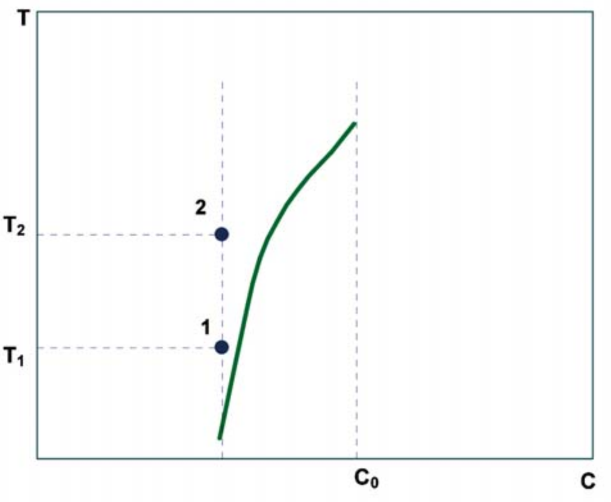

Figure 1. The conventional binodal and supposed points close to it; c_o is the concentration corresponding to the end of the binodal.

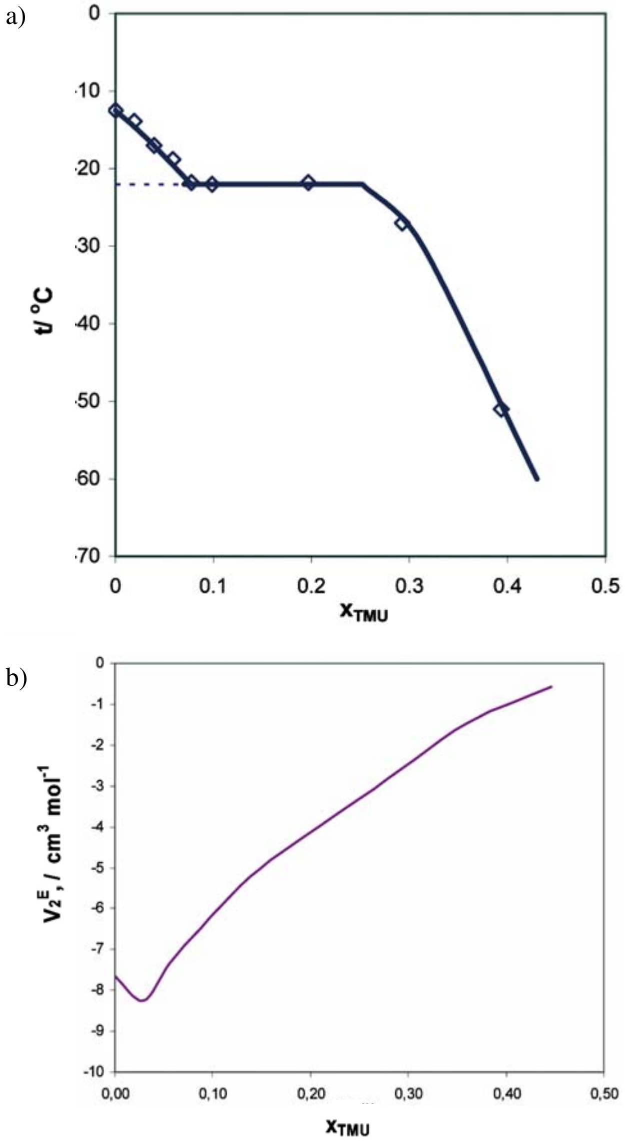

Figure 2. a) A fragment of the phase diagrams of the system ethylene glycol – TMU and b) the dependence of the V^E of TMU on the mole fraction of TMU in this system at 25 °C, where the mimumum at $x_{TMU} \approx 0.03$ is visible.

excess molar heat capacity of the aqueous solution of the tert-butanol, as a function of concentration at several different temperatures has been performed.[8] It has been shown that the major part of the heat capacity peak at low concentrations of the non-electrolyte is due to the critical concentration fluctuations in the proximity of the binodal as it is shown in Figure 1. These fluctuations and an appearance of conventional binodal are the result of micro-immiscibility on the network of H-bonds in aqueous solutions of non-electrolytes with hydrophobic molecules.

3. Results and Discussion

In this work[8] it was shown that maximum in the excess heat capacity is observed close to the concentration where the anomalous light scattering maximum is attained.

Similar phenomena are observed not only in aqueous but also in other solutions of non-electrolytes in solvents with spatial networks of H-bonds, such as ethylene glycol. Thus, in low concentration ethylene-glycol solutions of tert-butanol[9] nd tetramethylurea[10] anomalous light scattering maxima were found: they appear at higher concentrations than in aqueous solutions and their scattering intensities are reduced considerably. At approximately the same concentrations the solvophobic effects were stated, i.e. the minimums of excess molar partial volumes (V^E) of tert-butanol and tetramethylurea in these systems.

By means of differentially-scanning calorimetry the fragments of the phase diagrams of the systems ethylene glycol-tert-butanol (t-BuOH) and ethylene glycol tetramethylurea (TMU) in the low concentration range of the second component has been investigated. The liquid phase immiscibility in the concentration ranges of 0.10–0.17 mole fraction of t-BuOH at –37 °C and of 0.08–0.25 mole fraction of TMU at –22 °C in the mentioned ethylene glycol systems has been found (Figures 2 and 3). The presence of the liquid phase immiscibility in these ethylene glycol solutions has been confirmed by visual examination at keeping the system at –37 °C and –22 °C respectively.[12]

The analysis of the presented experimental facts clearly shows the relation between the solvophobic effects and the critical phenomena in solutions, and states a rather interesting question: at what distance (on concentration and temperature) from the critical immiscibility point the system acknowledges this point, discovering the phenomena proper to pre-critical ranges.

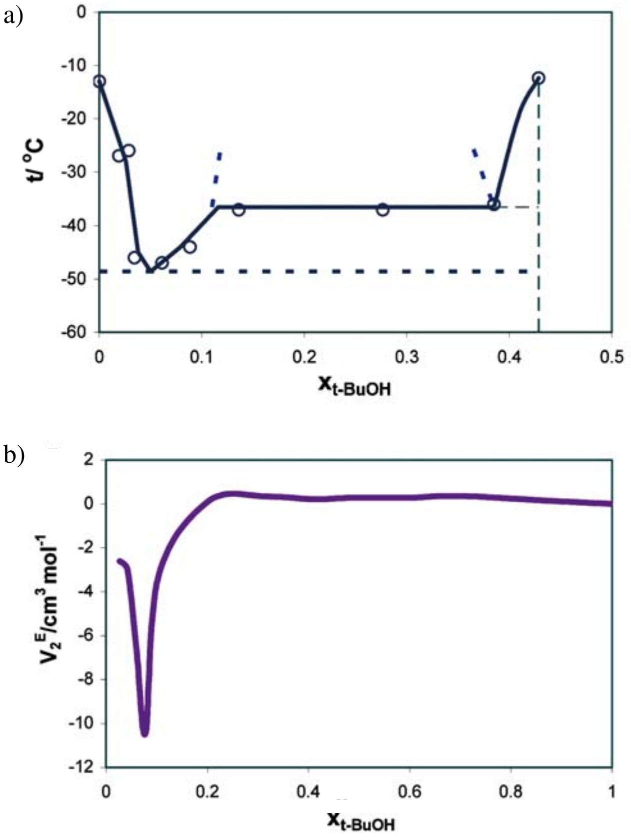

Figure 3. a) A fragment of the phase diagrams of the system ethylene glycol –t-BuOH and b)) the dependence of the V^E of t-BuOH on the mole fraction of t-BuOH in this system at 25 °C, where the mimumum at $x_{t\_BuOH} \approx 0.08$ is visible.

4. Acknowledgement

This work was financially supported by the Russian Foundation for Basic Research (project nos. 06-03-32605) and by a grant from the Department of Chemistry and Materials Science of RAS nos 2.4.

5. References

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Povzetek

Z meritvami presežnih toplotnih kapacitet ter presežnih molskih volumnov smo raziskovali zvezo med solvofobnim efektom in kritičnimi pojavi v razredčenih raztopinah etilen glikola v t-butanolu ter etilen glikola v tetrametilurei.