

Lower Critical Solution Temperature in the Metastable Region of an Ionic Solution in a Non-Polar Solvent

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Previous studies of the critical behavior of ionic solutions in nonpolar solvents showed mainly upper critical solution temperatures. Now, we report for the solution of tetra-*n*-butyl ammonium bromide ($N_{4444}Br$) in toluene a nearly closed miscibility loop, where the lower critical solution temperature ($T_c = 297.75 \pm 0.05$ K, $x_c = 0.0270 \pm 5 \times 10^{-4}$) is located in the region, which is metastable in respect to crystallization of the salt. The new observation is in variance to the former findings according to which the phase separation of ionic solutions in nonpolar solvents is similar to that of the model of charged hard spheres in a dielectric continuum, termed restricted primitive model (RPM), which has an upper critical solution point.

1. Introduction

For a long time, the closed solubility loops and lower critical solution temperatures (LCST) were thought to be restricted to systems that could form hydrogen bonds^{1–4} and polymer systems with directional-specific interactions.⁵ Accordingly, nearly all previous studies on the critical behavior of binary ionic solutions in nonpolar solvents showed upper critical solution temperatures (UCST).^{6–9} In polar solvents other than water, mostly UCST were found.^{10–16} However, some exceptions should be mentioned. In 1903, a LCST was discovered by Walden for the solution of KI in SO_2 .¹⁷ More recent works report LCST for solutions in chloroform, fluoroform and other polar halo-carbons.^{18–21} For aromatic solutions, there were reported systems with an UCST at lower and indications of LCST at higher temperature.²²

A useful reference for analyzing electrolyte solutions is the so-called restricted primitive model (RPM). In this conceptual simple model the ions are regarded as hard sphere with the diameter σ and the charge q immersed in a continuum with the dielectric permittivity ϵ . Simulations that use finite size scaling techniques state Ising criticality and yield an UCST at the reduced temperature $T_c^* = kT_c\epsilon\sigma/q^2 = 0.059$ and the reduced density $\rho_c^* = \rho_c\sigma^3 = 0.05$,²³ where ρ is the number density of the ions. The figures of the critical data are about 1 order of magnitude below that of nonionic fluids.²⁴ Somewhat higher figures are obtained from analytical theories that are based on the Debye–Hückel theory and take ion-pairing into account.^{24,25} Investigation of the Landau–Ginzburg expansion of the theories shows that mean-field critical behavior cannot be expected in the vicinity of the critical point.²⁶

Although the solvent is not treated explicitly as a second component the model is useful for investigations of real solutions. In fact the RPM has proven to be a useful guide in finding phase-transitions in ionic solutions and to classify the systems into such where the phase transition is driven by

Coulomb interactions and such by solvophobic interactions.^{16,27} Phase transitions of which the critical data and the shape of the coexistence curve are in reasonable agreement with the RPM can be regarded as driven by Coulomb interactions and thus are termed Coulomb phase transitions. Simulations and analytical theories of the RPM yield an UCST.²⁸

By analyzing the phase diagrams of ionic solutions in terms of the reduced variables of the RPM, it turned out that the critical points of the solutions in nonpolar solvents are near but somewhat below the figures predicted by the RPM. Furthermore, the shape of the coexistence curve was shown to be in reasonable agreement with the RPM.^{6,7} For the solutions in chloroform and SO_2 ,^{17,18} the critical data are in the region predicted by the RPM. However, as mentioned above, LCST were found in variance to the RPM. This apparent contradiction can be resolved by using the reduced variables of the RPM taking into account the temperature dependence of the dielectric permittivity of the solvent.^{7,18} Then, the resulting scaled phase diagrams are in fair agreement with the RPM.

The ionic solutions in alcohols mostly have UCST.^{10–16,29} However, representing their phase diagrams in the RPM variables the UCST become LCST,⁷ which indicates the contribution of hydrophobic interactions to the phase separation of ionic solutions in protic solvents. Some aqueous solutions show LCST and closed solubility loops already in the usual Kelvin temperature scale.^{27,30} Closed solubility loops are expected in general³ for aqueous ionic solutions with hydrophobic ions, although one of the branches may not be accessible experimentally. As for the classical examples of closed solubility loops of nonionic solution like nicotin in water or guajacol in glycerol² the directional forces of the hydrogen bonding can be expected to be responsible for the shape of the phase diagrams.

In the field of critical phenomena, closed solubility loops have been of interest because the size of the loops can be changed by changing the pressure or by adding a third component.^{4,31} In the limit, when the UCST and the LCST coincide the critical points become a double critical point, and the values of the critical indices are doubled.^{32,33} Quite generally, closed solubility

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loops can be obtained in mean field theories, for example, in the regular solution theory by allowing a temperature dependence of the interaction parameter. Beyond that, decorated lattice models have been developed to model the criticality demonstrating that such systems also belong to the Ising universality class.³⁴ In fact, it was shown that the analysis of the critical behavior may be carried out in the standard way using Wegner expansions³⁵ when the reduced temperature variable $\tau = |T - T_c|/T_c$ is replaced by $\tau_{UL} = |(T_U - T)(T_L - T)/T_U T_L|$ that depends on both the upper and the lower critical temperatures.³⁶

The LCST of the solution of tetra-*n*-butylammonium bromide ($N_{4444}\text{Br}$) in toluene reported in this work can neither be explained by the directional forces of hydrogen-bonds nor by the RPM taking into account the temperature dependence of the dielectric permittivity.

2. Experimental Procedure

The phase diagrams of solutions of hygroscopic salts like $N_{4444}\text{Br}$ in nonpolar solvents are extremely sensitive to humidity present in the atmosphere. Therefore the measurement of the LCST of $N_{4444}\text{Br}$ in toluene requires thorough drying of the components and working in a vacuum setup that is closed to the atmosphere. $N_{4444}\text{Br}$ puriss. >99% was purchased from Fluka and used without recrystallization. It was dried for 24 h at 373 K at a pressure of $<10^{-4}$ mbar. Toluene >99.5%, water <0.0075%, was purchased from Merck and dried over pulverized phosphorus pentoxide immediately before use. It was then condensed into the sample tube containing the salt by cooling with liquid nitrogen. Prolonged exposition of toluene to phosphorus pentoxide leads to unwelcome reactions. The samples were prepared in cylindrical Schlenk-vessels with a volume of about 6 mL. The mole fractions of the samples were determined gravimetrically using a precision balance (Sartorius A200S) with an accuracy of 2×10^{-4} g. However, due to electrostatic effects it was not possible to achieve an accuracy of the mol fractions better than $\pm 5 \times 10^{-4}$.

In order to reach the homogeneous one phase region, the samples were heated up to about 343 K in the first place. The mixture was held at this temperature and stirred with a magnetic bar for 15 min. In this way, the salt was completely dissolved in the two liquid phases and no seed crystals remained. Then the solution was gently shaken and cooled to room temperature, avoiding large temperature gradients within the sample. Notice that in the metastable region dilution can cause crystallization. In the last step, the homogeneous metastable solutions were heated up to the two phase region again. The demixing temperatures were determined visually via the cloud point method and could be reproduced with an uncertainty of less than ± 0.1 K.

For the ternary systems with traces of humidity or with 1,1,1-trifluoro-toluene the data are less precise (about ± 2 K). In those experiments, the different concentrations were obtained in simple dilution series without using the vacuum line so that humidity from the atmosphere was not fully excluded. Furthermore, because of the different volatilities of the solvents the relative concentration of the solvents may have been not strictly constant during the sample preparation and the dilution steps. The aim of those measurements was not a quantitative assessment of the influence of a third component but to demonstrate its qualitative effect.

In the screening experiments, the samples were prepared in the same way as the solutions in $N_{4444}\text{Br}$ and visually investigated in a thermostat filled with water. Measurements at higher temperatures were carried out in a bath of silicon oil.

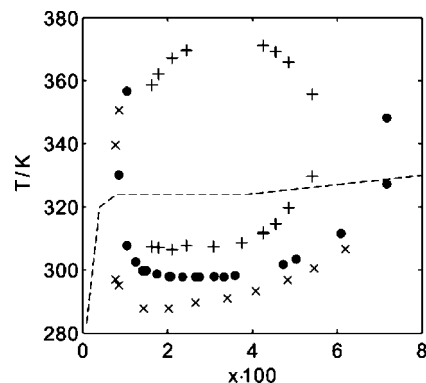


Figure 1. Liquid–liquid phase diagram of tetra-*n*-butylammonium bromide in toluene (●). The dashed line indicates the onset of the metastable region. The branch with the LCST is located in the metastable region. The branch of the UCST is not observable because it is cut off by the boiling curve of the mixture. The figure includes the data points (x) obtained with toluene, which was not dried over P_2O_5 and those of a ternary mixture (+) in which the mass ratio of 1,1,1-trifluoro-toluene to toluene was fixed to 0.02.

3. Results

The resulting coexistence curve is shown in Figure 1. The dashed line represents the saturation line, beyond which the mixture entered the metastable region. The UCST could not be measured at ambient pressure, because it lay above the boiling curve of the mixture. The branch with the LCST is located in the metastable region. Applying the equal volume criterion, the LCST was located at $T_c = 297.75 \pm 0.05$ K and $x_c = 0.0270 \pm 10^{-4}$, which coincides quite well with the observed minimum of the coexistence curve thus ensuring that no relevant contaminations were present in the samples. The data points that were obtained with toluene from the bulk (x) show that humidity changes the shape of the curve. It widens the two phase region and consequently lowers the LCST. 1,1,1-trifluoro-toluene (+) has an opposite effect. For a mass ratio of 0.06 the two-phase region vanishes. Benzene changes the phase diagram in a similar way as 1,1,1-trifluoro-toluene. A third component that solves equally well in the two phases reduces the size of the miscibility gap while water that goes preferable into the salt-rich phase increases the two phase region.

The observation of the almost closed solubility loop of the solution of $N_{4444}\text{Br}$ in toluene is a unique observation found out of a large set of screening experiments searching for liquid–liquid phase transitions allowing for investigation of critical properties. The size of the ammonium cation, the halide anion, and the aromatic solvent were varied. A list of screening experiments is given in the Supporting Information. Phase separations of ionic solutions in nonpolar solvents with observable critical points at ambient conditions are very rare. Mostly solid–liquid equilibrium was found near room temperature with complete mixing at higher temperatures. Less often liquid–liquid equilibrium was observed with a critical point at temperatures above that considered in the experiment. The salts $N_{5555}\text{Br}$, $N_{7777}\text{Br}$, and $N_{8888}\text{Br}$ yielded homogeneous solutions in toluene. Concerning the salt $N_{4444}\text{Br}$ equilibrium of a liquid and a solid phase was observed with benzene, while *o*-xylene, *p*-xylene, and ethylbenzene formed two liquid phases at temperatures above 350 K. A region with two liquid phases was also observed for the solution of $N_{4444}\text{I}$ in toluene above 375 K. UCST were found for the solutions of $N_{4444}\text{Cl}$ in *o*-xylene and ethylbenzene at $x_c = 0.038$, $T_c = 340.3$ K and $x_c = 0.056$, $T_c = 340.6$ K respectively.³⁷ Till now, no ionic solution in a nonpolar solvent with a LCST and a stable 2-phase region is known. The LCST

reported in this work is the only example, which however is observed in the region that is metastable in respect to crystallization of the salt. Attempts to see similar behavior in other solutions like $N_{4444}I$ /toluene, $N_{4444}Cl$ /o-xylene or in the solutions $N_{4444}Br$ in o-xylene, p-xylene, and ethylbenzene were not successful.

4. Discussion

The physical explanation for the closed solubility loop in the $N_{4444}Br$ /toluene system is an open question. One would have thought that the ions of the salt $N_{4444}Br$ are much better approximated by spheres than e.g. the rather asymmetric ions of typical ionic liquids so that the RPM might be a particular good model for the investigated system. The observation of an almost closed solubility gap appears to be in contradiction to this presumption. However, it might well be that the RPM, when investigated at lower temperatures than considered till now in theory and simulations may lead to a closed loop in the phase diagram. One could speculate that nonpolar associates as quadrupoles or higher aggregates may be solved better than the ion pairs and free ions.^{38,39} The aggregation of the ions⁴⁰ may be broken, when the temperature rises or when water molecules are present. This could explain the observed lowering of the LCST with increasing humidity of the samples.

Alternatively, interactions between the ions and toluene might turn out to be relevant. It is well-known that various low melting salts form clathrate-like inclusion compounds when crystallized from simple aromatic hydrocarbons such as benzene, toluene or xylenes.^{41–44} At ambient temperatures these binary ionic solutions often undergo liquid–liquid phase separations with a salt-rich lower phase, denoted as liquid clathrate.⁴⁵ Despite their fluidity liquid clathrates develop a certain degree of distant molecular order, determined by Coulomb forces and interactions between the ions and the aromatic solvents.⁴⁶ The importance of cooperative CH- π interactions for clathrate formation has been discussed.⁴⁷ Crystal structures have been reported for very similar systems suggesting a coordination of tetraalkylammonium cations by the aromatic solvent, which apparently leads to the formation of chains and three-dimensional networks.⁴⁸

The broad metastable region of aromatic $N_{4444}Br$ solutions appears to be quite a special feature of this salt. Extensive screening with other symmetric tetraalkyl-ammonium halides did not reveal further examples of LCST. Thus, some special properties of $N_{4444}Br$ may also be relevant for understanding the phase behavior of the solutions. Other than the chloride, $N_{4444}Br$ can be denoted as plastic crystal. It undergoes three phase transitions from the solid to the liquid state.⁴⁹ N_{4444}^+ -salts with higher melting points, for example, the iodide, have more rigid crystal lattices and their solutions cannot be super cooled as much as the solution of $N_{4444}Br$ in toluene.

5. Conclusion

We have reported the observation of a closed solubility loop in the solution of $N_{4444}Br$ in toluene. The UCST is above the boiling temperature of the solution and hence could not be investigated. The LCST is found in the region which is metastable in respect to crystallization of the salt. The separation between the UCST and the LCST is increased by water while it is decreased by trifluoro-toluene and benzene. It would be interesting to investigate if the properties of the expected double critical point of this ionic solution are the same as that observed in the nonionic systems. The $N_{4444}Br$ /toluene/benzene ternary system would be the first example of an ionic solution in nonpolar solvents with a double critical point.

The explanation of the almost closed solubility loop of the solution of $N_{4444}Br$ in toluene is a challenge for further work. The question if the closed solubility loop is a general feature of the phase diagrams of ionic solutions in nonpolar solvents, which is usually not observable because of crystallization of the salt or special property of the system investigated, cannot be decided at this stage. Maybe those simple models like the RPM or such that take the granular structure of the solvent into account can already provide an explanation. However, interactions between the ions and the aromatic rings may also turn out to be relevant.

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Supporting Information Available: Tables containing the data of the phase diagrams and a list of other solutions investigated in screening experiments are available in the electronic supplement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Hirschfelder, J.; Stevenson, D.; Eyring, H. *J. Chem. Phys.* **1937**, 5, 896.
- (2) Narayanan, T.; Kumar, A. *Phys. Rep.* **1994**, 249, 135.
- (3) (a) Glasbrenner, H.; Weingärtner, H. *J. Phys. Chem.* **1989**, 93, 3378. (b) Weingärtner, H. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, 93, 1058.
- (4) Weingärtner, H.; Klante, D.; Schneider, G. M. *J. Sol. Chem.* **1999**, 28, 435.
- (5) ten Brinke, G.; Karasz, F. E. *Macromolecules* **1984**, 17, 815.
- (6) Schröer, W.; Kleemeier, M.; Plikat, M.; Weiss, V.; Wiegand, S. *J. Phys.: Condens. Matter* **1996**, 8, 9321.
- (7) Butka, A.; Vale, V. R.; Saracsan, D.; Rybarsch, C.; Weiss, V. C.; Schröer, W. *Pure Appl. Chem.* **2008**, 80, 1613.
- (8) Domańska, U.; Marciniak, A. *Fluid Phase Equilib.* **2006**, 260, 9.
- (9) Domańska, U.; Paduszynski, K. *J. Phys. Chem. B* **2008**, 112, 11054.
- (10) Wagner, M.; Stanga, O.; Schröer, W. *Phys. Chem. Chem. Phys.* **2003**, 5, 3943.
- (11) Heintz, A.; Lehmann, J. K.; Wertz, C. *J. Chem. Eng. Data* **2003**, 48, 472.
- (12) Domańska, U.; Zolek-Tryznowska, Z.; Królikowski, M. *J. Chem. Eng. Data* **2007**, 52, 1872.
- (13) Crosthwaite, J. M.; Aki Sudhir, N. V. K.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2004**, 108, 5113.
- (14) Ferreira, R.; Blesic, M.; Trindade, J.; Marrucho, I.; Canongia Lopes, J. N.; Rebelo, L. P. N. *Green Chem.* **2008**, 10, 918.
- (15) Wu, C. T.; Marsh, K. N.; Deev, A. V.; Boxall, J. A. *J. Chem. Eng. Data* **2003**, 48, 486.
- (16) (a) Weingärtner, H.; Merkel, T.; Maurer, U.; Conzen, J. P.; Glasbrenner, H. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, 95, 1579. (b) Käshammer, S. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, 95, 1579.
- (17) Walden, P.; Centnerszwer, M. *Z. Phys. Chem.* **1903**, 42, 432.
- (18) Wiegand, S.; Kleemeier, M.; Schröder, J. M.; Schröer, W.; Weingärtner, H. *Int. J. Thermophys* **1994**, 15, 1045.
- (19) Lachwa, J.; Szydłowski, J.; Najdanovic-Visak, V.; Rebelo, L. P. N.; Seddon, K. R.; Nunes da Ponte, M.; Esperanca, J. M. S. S.; Guedes, H. J. R. *J. Am. Chem. Soc.* **2005**, 127, 6542.
- (20) Yokozeki, A.; Shiflett, M. B. *AIChE J.* **2006**, 52, 3952.
- (21) Shiflett, M. B.; Yokozeki, A. *J. Phys. Chem. B* **2006**, 110, 14436.
- (22) Lachwa, J.; Szydłowski, J.; Makowska, A.; Seddon, K. R.; Esperanca, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N. *Green Chem.* **2006**, 8, 262.
- (23) (a) Orkoulas, G.; Panagiotopoulos, A. Z. *J. Chem. Phys.* **1999**, 110, 1581. (b) Panagiotopoulos, A. Z. *J. Chem. Phys.* **2002**, 116, 3007. (c) Orkoulas, G.; Panagiotopoulos, A. Z.; Fisher, M. E. *Phys. Rev. E*, **2000**, 61, 5930. (d) Caillol, J.-M.; Levesque, D.; Weiss, J.-J. *J. Chem. Phys.* **2002**, 116, 10794. (e) Yan, Q. L.; de Pablo, J. J. *J. Chem. Phys.* **1999**, 111, 9509.
- (24) Fisher, M. E. *J. Stat. Phys.* **1994**, 75, 1.
- (25) (a) Levin, Y.; Fisher, M. E. *Physica A* **1996**, 225, 164. (b) Weiss, V. C.; Schröer, W. *J. Chem. Phys.* **1998**, 108, 7747.
- (26) (a) Leote de Carvalho, R. J. F.; Evans, R. J. *Phys.: Condens. Matter* **1995**, 7, L 575. (b) Lee, B. P.; Fisher, M. E. *Phys. Rev. Lett.* **1996**, 76, 29069. (c) Schröer, W. W.; Weiss, V. C. *J. Chem. Phys.* **1998**, 109, 8504. (d) Schröer, W. W.; Weiss, V. C. *J. Chem. Phys.* **1999**, 110, 4687.

- (27) Weingärtner, H.; Kleemeier, M.; Wiegand, S.; Schröer, W. *J. Stat. Phys.* **1995**, *78*, 169.
- (28) Weingärtner, H.; Schröer, W. *Adv. Chem. Phys.* **2001**, *116*, 1.
- (29) Kleemeier, M.; Wiegand, S.; Schröer, W.; Weingärtner, H. *J. Chem. Phys.* **1999**, *110*, 3085.
- (30) Yan, P.; Huang, J.; Lu, R.; Jin, C.; Xiao, J.; Chen, Y. *J. Phys. Chem. B* **2005**, *109*, 5237.
- (31) Prafulla, B. V.; Narayanan, T.; Kumar, A. *Phys. Rev. A* **1992**, *46*, 7456.
- (32) Johnston, R. G.; Clark, N. A.; Wiltzius, P.; Cannell, D. S. *Phys. Rev. Lett.* **1985**, *54*, 49.
- (33) Schröer, W.; Wiegand, S.; Staude, W.; Peters, T. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 1126.
- (34) Walker, J. S.; Vause, C. A. *J. Chem. Phys.* **1983**, *79*, 2660.
- (35) Anisimov, M. A. *Critical Phenomena in Liquids and Liquid Crystals*; Gordon and Breach: Philadelphia, 1991.
- (36) Wang, J.; Anisimov, M. A.; Sengers, J. V. *Z. Phys. Chem.* **2005**, *9*, 1273.
- (37) Dittmar, H.; Butka, A.; Vale V. R.; Schröer, W. *J. Mol. Liq.*, in press. Available online at <http://dx.doi.org/10.1016/j.molliq.2008.11.015>.
- (38) Stern, K. H.; Richardson, E. A. *J. Am. Chem. Soc.* **1960**, *82*, 1296.
- (39) Sawada, K.; Takahashi, E.; Horie, T.; Satoh, K. *Monatsh. Chem.* **2001**, *132*, 1439.
- (40) Davies, M.; Williams, G. *Trans. Faraday Soc.* **1960**, *56*, 1619.
- (41) Lachwa, J.; Bento, I.; Duarte, M. T.; Canongia Lopes, J. N.; Rebelo, L. P. N. *Chem. Comm.* **2006**, *23*, 2445.
- (42) Hrnčir, D. C.; Barden, L. M.; Wells, M. R.; Stark, P. C. *J. Inclusion Phenom.* **1988**, *6*, 233.
- (43) Coleman, A. W.; Means, C. M.; Bott, S. G.; Atwood, J. L. *J. Crystallogr. Spectrosc. Res.* **1989**, *20*, 199.
- (44) Christie, S.; Dubois, R. H.; Rogers, R. D.; White, P. S.; Zaworotko, M. J. *J. Inclusion Phenom.* **1991**, *11*, 103.
- (45) Atwood, J. L.; Steed, J. W. *Encyclopedia of Supramolecular Chemistry*; CRC-Press: Cleveland, 1984; pp 804–807.
- (46) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction: Evidence, Nature, and Consequences*; Wiley-VCH: Weinheim, 1998.
- (47) Suezawa, H.; Yoshida, T.; Hirota, M.; Takahashi, H.; Umezawa, Y.; Honda, K.; Tsuboyama, S.; Nishio, M. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 2053.
- (48) Harder, S. *Chem.—Eur. J.* **1999**, *5*, 1852.
- (49) Pajak, Z.; Szafranska, B. *Phys. Status Solidi A* **1993**, *136*, 371.

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