RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 42, NUMBER 10 15 NOVEMBER 1990

Liquid-liquid phase separation and critical exponents in ionic fluid mixtures

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(Received 16 May 1990)

The critical exponents of model ionic fluid mixtures exhibiting liquid-liquid phase separation are calculated analytically through the mean-spherical approximation. Classical exponents β and γ are found in agreement with the available experimental data for ionic fluids. The phase diagram of molten tetra-*n*-butylammonium picrate-1-chloroheptane is also well reproduced through the same theoretical approach, with excellent agreement of the calculated exponent β with the experimental value. Possible applications to other multicomponent fluids are briefly discussed.

Critical exponents in classical fluids have been hitherto determined analytically in correspondence of the liquid-vapor critical point of two simple model fluids.[1,2] A number of calculations based on numerical solutions of integral equation theories have also been reported[3-10] for various systems of the same type. However, there is still some debate[3,6-8] on the accuracy of these numerical procedures in the critical region, especially as far as the nature of the critical exponents is concerned.

The critical behavior of two-component model ionic fluids has also been investigated by various authors.[11-14] However, to the best of our knowledge, no theoretical determination of critical exponents has been published for liquid-liquid phase separation in either neutral or charged fluid mixtures.

It appears from the cited work that the status of microscopic derivation of critical exponents in liquids is somewhat unsatisfactory. There are, actually, extensive theories on the critical behavior of systems with long-range forces,[15] or Ornstein-Zernike systems in the mean-spherical approximation;[16] however, the related theoretical treatments have been fully developed only for some particular cases.

The situation is even worse concerning the description of phase equilibria in two- (or more-) component fluids. In fact, in such a case, one needs to determine the Gibbs free energy at both constant pressure and temperature, a task probably prohibitive in the framework of the more refined approximate theories of liquids that are solvable, as is well known, only through iterative procedures.

On the other hand, one is presently faced with outgrowing experimental evidence on phase stability and equilibria in a variety of systems such as, e.g., simple-fluid mixtures, molten-salt mixtures, electrolyte solutions, micellar solutions, colloids, etc., so that the availability of some theoretical approach allowing one to investigate the correlations between the interaction mechanisms and the thermodynamics of the coexisting phases in these multicomponent fluids, seems particularly urgent.

Such a situation prompts us to examine the performances of a theory that although known to be defective from the point of view of the thermodynamic consistency, has the great advantage of being analytically solvable. This is the mean-spherical approximation (MSA) which, noticeably, turns out to be rather accurate when thermodynamics is constructed from the structure via the "energy route."

In this spirit one of us[17,18] has recently studied the properties of charged hard-sphere fluid mixtures within such an approximation, and in a previous paper[18] it is shown that the MSA predicts liquid-liquid phase separation for such a system. The resulting phase diagram presents three different consolution points, two of which delimit a closed solubility loop.

In this Rapid Communication we report MSA calculations of the critical exponents corresponding to those consolution points, and similar calculations for another model mixture described below. These calculations are performed by starting from the MSA analytic expressions for the pressure and for the Gibbs free energy. Classical values are found for the exponents β and γ in all the examined cases, in agreement with the indications of the available experimental data.

We also show that the theory is able to reproduce the phase diagram of a real system, that is, tetra-*n*-butylammonium picrate-1-chloroheptane, recently studied by Pitzer *et al.*,[19] and modeled by us as a mixture of charged and neutral hard spheres.

We finally discuss the applicability of our approach to other multicomponent systems of current interest.

We first study the case of a mixture of charged hard spheres of equal diameter R. This system is obtained by mixing two ionic fluids constituted of cations and anions with charge numbers $Z_1=+1$, $Z_3=-1$, and $Z_2=+2$, $Z_3=-1$, respectively. The relative proportion of the two components is fixed by the (cationic) concentration $c \equiv \rho_1/(\rho_1+\rho_2)$, where ρ_i is the number density of particles in the ith ionic species. We are thus considering a common anion mixture with three different ionic species.

Other parameters in use are the packing fraction $\eta \equiv (\pi/6)\sum_i \rho_i R^3$, and the coupling parameter $\Gamma \equiv e^2/k_B T \epsilon R = 1/T^*$, where T^* is a reduced temperature, and ϵ is the macroscopic dielectric constant of a medium in which the particles are supposed to be merged.

The phase separation conditions are obtained by imposing $(\partial^2 G_M/\partial c^2)_{T,P}=0$, where G_M is the Gibbs free energy of mixing. This condition defines the spinodal line for the mixture.

TABLE I. Critical parameters and critical exponents relative to the upper and lower consolution points of a charged hard-sphere mixture, and to the upper consolution point of a charged and neutral hard-sphere mixture. Results have been obtained by using a grid of 10^6 points (see text), except for the values in parentheses, which correspond to a grid of 10^4 points.

	$Z_1=+1,\ Z_2=+2,\ Z_3=-1,\ P_0=0.003$				
	$T^*_{\rm cr}$	$c_{\rm cr}$	$\eta_{\rm cr}$	β	γ
UCP	0.033 621 57	0.725 515	0.246 95	0.5 ± 0.001	1.00 ± 0.001
				(0.5 ± 0.05)	(1.00 ± 0.05)
LCP	0.136 518 11	0.787 467	0.031 523	0.5 ± 0.005	1.00 ± 0.009
UCP	0.174 067 79	0.654 085	0.020 799	0.5 ± 0.005	1.00 ± 0.001
	$Z_1=+1,\ Z_2=0,\ Z_3=-1,\ P_0=0.025$				
UCP	0.149 628 14	0.041 654	0.067 840	0.5 ± 0.005	1.00 ± 0.005
				(0.5 ± 0.07)	(1.00 ± 0.05)

As discussed in detail in Ref. 18, G_M is obtained by adding to the ideal mixing term, which has the standard form

$$G_M^{\rm id}=c\ln c+(1-c)\ln(1-c)\,,$$

the excess Gibbs free energy of mixing $G_M^{\rm ex}$. This, in turn, is obtained by first writing the excess Gibbs free energy per particle of the mixture $G_m^{\rm ex}$ as the sum of an excess hard sphere term, obtained from the Carnahan-Starling[20] equation of state, and an excess Coulombic term, obtained from the analytic solution of the MSA (Ref. 21) through the "energy route" (see Ref. 18 for details).

We have (in k_BT units)

$$G_m^{\rm ex}=\frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3}+\frac{1}{72\eta}[3x^2+3x-3x(1+2x)^{1/2}]\,, \tag{1}$$

with $x^2=24\eta\Gamma\sum_i c_iZ_i^2$.

$G_M^{\rm ex}$ is then calculated by subtracting from $G_m^{\rm ex}$ the concentration-weighted sum of the pure component Gibbs free energies, which correspond to the $c=0$ and $c=1$ limits of Eq. (1). $G_M^{\rm ex}$ so obtained is then transformed into the corresponding quantity per molecule, and finally added to $G_M^{\rm id}$ to obtain the Gibbs free energy of mixing G_M.

The condition of constant pressure, required in the calculation of $(\partial^2G_M/\partial c^2)_{T,P}$, is imposed, for each prefixed $\Gamma(T^*)$, through the calculation of the function $\eta(c;\Gamma)$ which makes the total pressure (expressed in e^2/R^4 units)

$$P=\frac{6\eta}{\pi\Gamma}\left[\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}+\frac{1}{72\eta}[3x+3x(1+2x)^{1/2}-2(1+2x)^{3/2}+2]\right], \tag{2}$$

equal to a prefixed value P_0 over the whole concentration range. The solution of Eq. (2) is obtained by an extended precision numerical routine to a very high accuracy (better than 10^{-30}). Once $\eta(c;\Gamma)$ is known, $(\partial^2G_M/\partial c^2)_{T,P}$ is calculated numerically by using grids of different spacings (10^4–10^6 points) for the 0–1 interval of concentrations.

As discussed in detail in Ref. 18, two upper consolution points (UCP) and one lower consolution point (LCP) are obtained. The related critical parameters are listed in Table I.

The critical exponents β and γ are then defined as follows:[22,23]

$$|c-c_{\rm cr}|\propto[(T^*_{\rm cr}-T^*)/T^*_{\rm cr}]^{\beta}\,,$$
$$S_{c\text{-}c}(0)\propto[(T^*-T^*_{\rm cr})/T^*_{\rm cr}]^{-\gamma}\,. \tag{3}$$

Here $c_{\rm cr}$ and $T^*_{\rm cr}$ indicate the critical concentration and temperature, respectively, while $S_{c\text{-}c}(0)$ is the $q=0$ limit of the concentration-concentration structure factor $S_{c\text{-}c}(q)$, which is obtained from G_M through the well-known relationship

$$S_{c\text{-}c}(0)=1\bigg/\left(\frac{\partial^2G_M}{\partial c^2}\right)_{T,P}\,;$$

$S_{c\text{-}c}(0)$ plays in the present context the role of an osmotic compressibility.

The critical exponents, calculated through the log-log plot of Eqs. (3) (displayed in Fig. 1 for the case of γ), are reported in Table I.

We see that classical values are quite accurately obtained for the two critical exponents, at the three consolu-

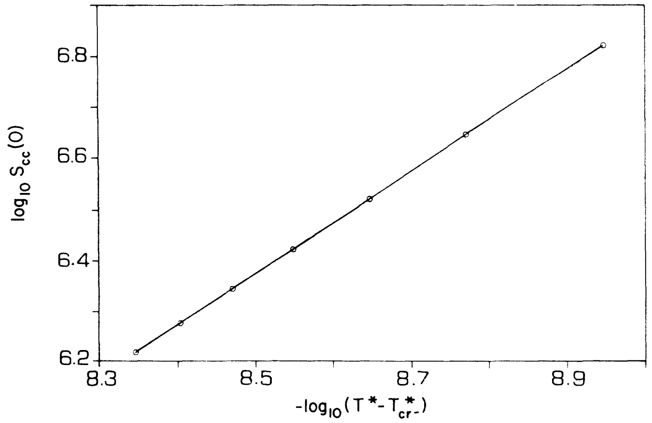

FIG. 1. Log-log plot of $S_{c\text{-}c}(0)$ vs $(T^*-T^*_{\rm cr})$ for a charged hard-sphere mixture corresponding to the UCP at low reduced temperatures.

tion points. However, the less fine grid leads to poorer estimates of β and γ. With reference to the recent numerical work on critical coefficients quoted above,[3-10] this effect of the grid further illustrates the difficulties inherent to any numerical determination of critical exponents, difficulties greatly simplified here by the knowledge of G_M in analytic form. For this proposal it is worth noting that, while unnecessary for the present purposes, calculations more accurate than shown here could be performed through the use of finer c grids.

Classical values for the critical exponent β have been obtained recently in experimental work on ionic fluids;[19,24] the predictions of the theory therefore look consistent with such previous results. We now consider, in particular, the case of tetra-*n*-butylammonium picrate–1-chloroheptane, cited above. Liquid-liquid phase separation and a critical point have been observed by Pitzer *et al.*[19] in this system, in which tetra-*n*-butylammonium picrate is present as a fused salt. The mixture contains three particle species, namely, positive tetra-*n*-butylammonium and negative picrate ions, and neutral chloroheptane molecules. The critical parameters reported in Ref. 19 are $T_{\rm cr}=414.4$ K, $x_{\rm cr}=0.08_5$ mole fraction of picrate, and $V_{\rm cr}=2300$ cm^{3}mol^{-1} picrate. The interionic distance is estimated to be approximately 7 Å.

We have modeled this system as a mixture of charged and neutral hard spheres. Specifically, we have considered a three component mixture with $Z_1=+1$, $Z_2=0$, $Z_3=-1$, and the concentration $c\equiv\rho_1/(\rho_1+\rho_2)$. $c=0$ thus corresponds to pure chloroheptane (species 2), and $c=1$ to pure tetra-*n*-butylammonium picrate (species 1 and 3).

The calculations of the phase stability conditions for this system is performed in the same manner as illustrated above; that is, for each applied pressure P_0 we obtain a phase diagram exhibiting, in this case, only one upper consolution point. By varying P_0 we then make the MSA critical concentration equal to $x_{\rm cr}^{\rm expt}=0.08_5$ pycrate (using Ref. 19 notation), that is $c_{\rm cr}=0.041$, using our notation. This fit is obtained at $P_0=0.025$ (e^2/R^4). The resulting critical consolution temperature $T_{\rm cr}^*=0.149\,628\,14$ (see Table I). Note that $c_{\rm cr}$ turns out to be only slightly dependent on P_0: e.g., at $P_0=0.004$ one has $c_{\rm cr}\simeq0.08$, and at $P_0=0.1$, $c_{\rm cr}\simeq0.03$.

The phase diagram, obtained from G_M through the common tangent procedure, is displayed in Fig. 2 together with the experimental result. We see that the overall pattern of the real system phase diagram, characterized by a marked asymmetry, is well reproduced by our approach.

The mapping of the experimental temperatures onto T^* values depends on the values of ϵ and R, which are fixed by the request that $T_{\rm cr}^{\rm expt}$ (in reduced units) $=T_{\rm cr}^*$. Now, no experimental estimate of ϵ seems available for our particular system; Pitzer *et al.*, estimate $\epsilon T_{\rm cr}\sim1500$ on the basis of a corresponding state argument while in, e.g., tetra-*n*-butylammonium picrate in buthanol, one has $\epsilon=9.4$.[25]

If we assume $\epsilon=8.6$, then in order that the reduced $T_{\rm cr}^{\rm expt}=0.149\,628\,14$ we need to have $R=7$ Å (which is the experimental interionic distance); in this case $P_0=0.025$ (e^2/R^4) will correspond to 240 atm $(e^2/R^4\simeq9600$ atm), while from $\eta_{\rm cr}\sim0.068$, we deduce $V_{\rm cr}\sim3250$ cm^{3}mol^{-1} picrate, which compares fairly well with the experimental result. A smaller ϵ would lead to a greater R, with an improvement of the pressure ($P_0\sim37$ atm, if we take, e.g., $\epsilon T_{\rm cr}=1500$); however, the critical volume turns out to be sensibly overestimated in this case.

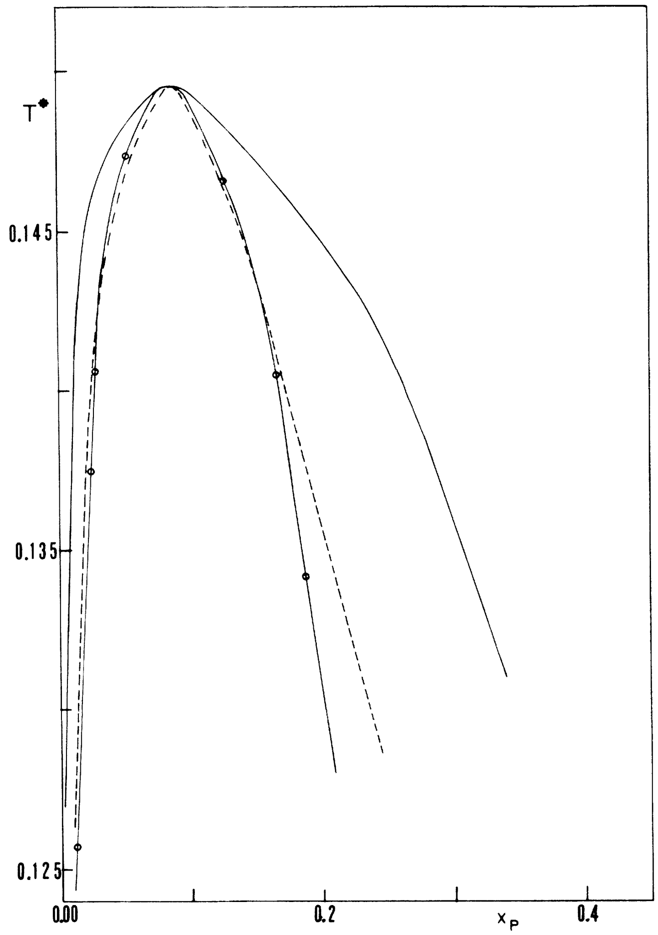

FIG. 2. Phase-coexistence diagram and spinodal line for a mixture of charged and neutral hard spheres. Solid line and dashed line: MSA phase coexistence and spinodal line, respectively. Open circles: experimental data from Ref. 19 for tetra-*n*-butylammonium picrate–1-chloroheptane, with experimental temperatures rescaled as explained in the text.

Finally, we have calculated the critical exponent β, reported in Table I. The classical value obtained is to be compared with the experimental result $\beta\sim0.5$ reported by Pitzer *et al.*[19] The theory appears to correctly reproduce the experimental classical result.

We see that a very simplified model, as the one used here, is capable of satisfactorily describing the critical behavior of a fluid of highly structured molecules, as tetra-*n*-butylammonium picrate–1-chloroheptane is. This constitutes a clear indication that "elementary" interactions, such as harsh repulsion at short-range and long-range Coulombic forces, play a dominating role in this system, at least as far as its critical behavior is concerned.

One can then reasonably expect this type of calculation to be successfully applicable to the determination of phase diagrams of, e.g., charged micellar solutions. In fact, a model such as the one we have proposed here is generally considered realistic for such systems, and we have already reported some preliminary results of this type in Ref. 18, where the case of a charged hard sphere mixture with both asymmetric charges and sizes was considered. It is, however, evident that more experimental evidence would be necessary at this stage in order to get a more complete test of the predictions of the theory.

It is also worth mentioning that the MSA solution is known in an essentially analytic form for an arbitrary number of components. It would then be possible to study multiple phase equilibria in mixed charged and neutral fluids through the present approach.

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