CRITICAL BEHAVIOR OF DILUTE ELECTROLYTE SOLUTIONS

A. R. Muratov[*]

Institute for Oil and Gas Research, Russian Academy of Sciences
117971, Moscow, Russia

A theory of the critical behavior of a dilute ionic solution is constructed. An expression for the susceptibility in a wide temperature region is obtained. It is shown that ionic solutions belong to the universality class of the Ising model. The Ginzburg parameter of the ionic solutions decreases with the increase of the solvent concentration. In the general case, the susceptibility critical exponent nonmonotonically depends on the temperature in the crossover region from the Ising-like to the mean-field behavior. In the vicinity of the transition point, the Debye–Hückel screening radius is proportional to the correlation length. As $T \to T_c$, it tends to infinity and the screening disappears. The voltage between the two phases of the ionic solution is proportional to the order parameter and changes as $|T/T_c - 1|^{\beta}$ in the vicinity of the phase transition point.

PACS: 61.20.Qg, 64.60.Fr, 05.70.Jk

1. INTRODUCTION

Critical phenomena in liquids and liquid mixtures are an extensively studied region of condensed matter physics [1, 2]. In general, the behavior of physical characteristics near the critical (consolution) point can be described sufficiently well as a crossover between the Ising-like asymptotic behavior and the mean-field behavior [3, 4, 5]. The Ising-like behavior occurs in a narrow vicinity of the critical point for

$$|T/T_c - 1| \ll G,$$

where T is the temperature, T_c is the critical temperature, and G is the so-called Ginzburg parameter. The mean-field behavior occurs for

$$|T/T_c - 1| \gg G.$$

For liquids, the parameter G is of the order 0.01–0.1.

Critical behavior of ionic solutions was discussed in a number of works (see [6, 7, 8, 9, 10]). Experimental studies show that the critical behavior of electrolyte solutions significantly differs from that of ordinary solutions. This difference occurs for both non-aqueous [11, 12, 13] and aqueous solutions [14]. The main feature of the electrolyte solutions is their mean-field behavior in the region

$$|T/T_c - 1| > t_x,$$

[*]E-mail: muratov@ogri.ru

where t_x varies from 1 to 10^{-4} for different solutions [15]. Numerous attempts to understand the ionic criticality have been made recently (see, e.g., [15, 16, 17]). In a recent experimental work [14], it was stated that the crossover behavior is not monotonic and the effective susceptibility exponent γ has its maximum value in the crossover region exceeding the asymptotic value $\gamma \sim 1.24$.

2. THEORY

We consider the electrolyte solution near the critical (or consolute) point of the solvent. We let $\varphi(\mathbf{r})$ be a field proportional to the order parameter (the solution density for the critical point or the concentration for the consolute point), $\phi(\mathbf{r})$ be the electric potential field, and $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ be the respective volume densities of the ion numbers with positive and negative charges. For simplicity, we assume that these charges are equal to e and $-e$ respectively.

Near the transition point, the ionic solution consists of two subsystems: the «fast» subsystem that depends on the ion densities ρ_1 and ρ_2 and the «slow» subsystem that depends on the order parameter φ and the electric potential ϕ. As in the standard Debye–Hückel (Hartree) approach, ions can be considered in the average long-wavelength field $\phi(\mathbf{r})$ and, in our case, $\varphi(\mathbf{r})$. We first evaluate the fluctuational corrections to the

Hamiltonian of the «slow» part of the system that are caused by the «fast» subsystem and then consider only the part of the Hamiltonian containing the density field φ and the electric potential field ϕ.

The main interaction terms of the fields ϕ, φ and ρ_1, ρ_2 can be written as

$$H_{int} = \int d\mathbf{r} \Big((e\rho_1(\mathbf{r}) - e\rho_2(\mathbf{r}))\phi(\mathbf{r}) + $$
$$+ (\gamma_1\rho_1(\mathbf{r}) - \gamma_2\rho_2(\mathbf{r}))\varphi(\mathbf{r}) \Big). \quad (1)$$

The first interaction term in Eq. (1) is the ordinary electrostatic interaction, the second term is some phenomenological interaction between the order parameter and the ion densities, and γ_1 and γ_2 are the interaction constants.

It is easy to see from Eq. (1) that the values

$$\Delta\mu_1(\mathbf{r}) = e\phi(\mathbf{r}) + \gamma_1\varphi(\mathbf{r}),$$
$$\Delta\mu_2(\mathbf{r}) = -e\phi(\mathbf{r}) - \gamma_2\varphi(\mathbf{r}) \quad (2)$$

can be considered as local additional corrections to the chemical potentials of the respective positive (μ_1) and negative (μ_2) ions. The Gauss distribution of the thermodynamic fluctuations of the chemical potential is given by (see [18])

$$w \propto \exp\left(-\frac{\Delta\mu\Delta\rho}{T}\right) = \exp\left(-\frac{\bar{\rho}}{2T^2}(\Delta\mu)^2\right), \quad (3)$$

where T is the absolute temperature in energy units and $\bar{\rho} = N/V$ is the average volume density of particles.

Inserting expressions (2) in Eq. (3), we obtain the fluctuation correction to the Hamiltonian of the «slow» part of the system,

$$\Delta H = \int d\mathbf{r} \times$$
$$\times \left(\frac{\bar{\rho}_1}{2T}(e\phi(\mathbf{r})+\gamma_1\varphi(\mathbf{r}))^2 + \frac{\bar{\rho}_2}{2T}(e\phi(\mathbf{r})+\gamma_2\varphi(\mathbf{r}))^2\right). \quad (4)$$

For the ionic solution, we must add expression (4) and the expression for the electrostatic energy

$$\int d\mathbf{r}\ (\mathbf{E}\cdot\mathbf{D}/8\pi)$$

(where $\mathbf{D} = \varepsilon\mathbf{E}$) to the standard Landau Hamiltonian of the system near the critical point. Taking into account that

$$\bar{\rho}_1 = \bar{\rho}_2 = \rho,$$

we obtain the effective Hamiltonian

$$H_{eff} = \int d\mathbf{r} \left(\frac{1}{2}\left(a+\frac{\rho}{T}(\gamma_1^2+\gamma_2^2)\right)\varphi^2 + \frac{1}{2}\alpha(\nabla\varphi)^2 +\right.$$
$$\left.+ \frac{\rho}{T}e^2\phi^2 + \frac{\varepsilon}{8\pi}(\nabla\phi)^2 + \frac{\rho}{T}e(\gamma_1+\gamma_2)\phi\varphi + \lambda\varphi^4\right). \quad (5)$$

There are three different fluctuation corrections in Hamiltonian (5). The correction proportional to ϕ^2 describes the Debye–Hückel screening. The correction proportional to φ^2 shifts the bare temperature of the phase transition. The correction proportional to $\phi\varphi$ couples the electric potential field to the order parameter. Far from the phase transition point, the parameter a is not small and the last two corrections to the Hamiltonian are not relevant. In the near-critical region, the parameter

$$a \propto |T/T_c - 1|$$

is small and we must take these corrections and the φ^4 term in the Hamiltonian into account.

In what follows, the angular brackets denote averaging over effective Hamiltonian (5). The quadratic part of effective Hamiltonian (5) determines the bare values of the correlation functions. The inverse correlation function is equal to

$$\begin{pmatrix} \langle\varphi(\mathbf{k})\varphi(-\mathbf{k})\rangle & \langle\varphi(\mathbf{k})\phi(-\mathbf{k})\rangle \\ \langle\phi(\mathbf{k})\varphi(-\mathbf{k})\rangle & \langle\phi(\mathbf{k})\phi(-\mathbf{k})\rangle \end{pmatrix}^{-1} = \frac{1}{T} \times$$
$$\times \begin{pmatrix} a+\alpha k^2+\rho(\gamma_1^2+\gamma_2^2)/T & e\rho(\gamma_1+\gamma_2)/T \\ e\rho(\gamma_1+\gamma_2)/T & \varepsilon(k^2+\kappa^2)/4\pi \end{pmatrix}, \quad (6)$$

where $\kappa = \sqrt{8\pi\rho e^2/T\varepsilon}$ is the inverse Debye–Hückel radius. Calculating the inverse matrix, we obtain

$$\langle\varphi(\mathbf{k})\varphi(-\mathbf{k})\rangle =$$
$$= \frac{T}{\tilde{a} + \alpha k^2(1 + b\kappa^2/(k^2+\kappa^2))},$$
$$\langle\varphi(\mathbf{k})\phi(-\mathbf{k})\rangle =$$
$$= -\frac{T(\gamma_1+\gamma_2)/2e}{\tilde{a} + (k/\kappa)^2(\tilde{a} + b\alpha\kappa^2 + \alpha(k^2+\kappa^2))},$$
$$\langle\phi(\mathbf{k})\phi(-\mathbf{k})\rangle =$$
$$= \frac{4\pi T/\varepsilon}{k^2 + \kappa^2(\tilde{a} + \alpha k^2)/(\tilde{a}+b\alpha\kappa^2 + \alpha k^2)},$$
$$\tilde{a} = a + \frac{\rho}{2T}(\gamma_1 - \gamma_2)^2,$$
$$b = \frac{\varepsilon}{16\pi\alpha e^2}(\gamma_1+\gamma_2)^2 = \frac{\rho}{2T\alpha\kappa^2}(\gamma_1+\gamma_2)^2. \quad (7)$$

The correlation function of the electric potential field in Eqs. (7) describes the Coulomb screening near the critical point of the ionic solution. It is easy to see that the screening has the ordinary form far from the critical point, where $a \gg \rho\gamma^2/T$. In the vicinity of the phase transition point $\tilde{a} = 0$ in the mean-field approximation, the screening radius behaves as

$$r_s = \frac{1}{\kappa}\sqrt{\frac{\tilde{a} + b\alpha\kappa^2}{\tilde{a}}}.$$

As $\tilde{a} \to 0$, the screening radius tends to infinity and the screening disappears.

The density correlation function in Eqs. (7) has the asymptotic behavior

$$\langle \varphi(k)\varphi(-k) \rangle \approx \frac{T}{\tilde{a} + \alpha(1+b)k^2}, \quad k \ll \kappa,$$

$$\langle \varphi(k)\varphi(-k) \rangle \approx \frac{T}{\tilde{a} + \dfrac{\rho}{2T}(\gamma_1+\gamma_2)^2 + \alpha k^2}, \quad k \gg \kappa. \tag{8}$$

The interaction between the mass density field (order parameter) and the charge density field redefines bare correlation function (4) in the long-wavelength region as

$$a \to \tilde{a}, \quad \alpha \to \alpha(1+b). \tag{9}$$

The asymptotic forms of correlation function (8) in the long and short wavelength regions are analogous to the ordinary form of the correlation function near the critical point. This means that the behavior of physical characteristics in the corresponding limits is the same as in the non-ionic case. The bare critical point

$$a = -\rho(\gamma_1^2 + \gamma_2^2)/T$$

and the real singularity point

$$a = -\rho(\gamma_1 - \gamma_2)^2/2T$$

are now different, both of them are less than the pure solvent transition point $a = 0$.

In the mean-field approximation, the correlation length in vicinity of the transition point is given by

$$r_c = \sqrt{\frac{\alpha(1+b)}{\tilde{a}}}.$$

In the vicinity of the transition point, the screening length is proportional to the correlation length and their ratio is

$$\frac{r_s}{r_c} = \sqrt{\frac{\tilde{a}/\alpha\kappa^2 + b}{1+b}}.$$

The mean-field aproximation does not correctly describe the behavior of the system near the transition point. It can be used in the region far from the transition point, where $\tilde{a} \gg G$. In a close vicinity of the transition point, the fluctuation effects must be taken into account.

3. RENORMALIZATION

We now calculate the expression for the susceptibility, which is an experimentally measured value [13, 14].

Fig. 1. One-loop corrections to the effective Hamiltonian parameters a and λ. The solid line corresponds to the field φ. The circle in the vertex is equal to λ

We must apply the standard renormalization procedure to effective Hamiltonian (5). The leading corrections to the coefficients $\tilde{a}$ and λ due to fluctuation effects can be represented by the diagrams in Fig. 1. The renormalization equations for these coefficients are given by

$$\frac{d\tilde{a}}{d\Lambda} = \frac{1}{3}K\frac{\tilde{a}(\Lambda)\lambda(\Lambda)\Lambda^{d-5}}{(1 + b\kappa^2/(\Lambda^2 + \kappa^2))^2},$$

$$\frac{d\lambda}{d\Lambda} = K\frac{\lambda^2(\Lambda)\Lambda^{d-5}}{(1 + b\kappa^2/(\Lambda^2 + \kappa^2))^2}, \tag{10}$$

where Λ is the renormalization equation parameter ($[\Lambda] = k$) and

$$K = \frac{18 T S_d}{(2\pi)^d \alpha^2},$$

with d being the space dimension and S_d the unit sphere surface. Equations (10) are written in the one-loop approximation, which corresponds to the first approximation in the parameter $\epsilon = 4 - d$. For simplicity, we do not use the ϵ-expansion but consider the one-loop renormalization equations directly for $d = 3$.

It is easy to see from Eqs. (10) that

$$\frac{d\tilde{a}}{d\lambda} = \frac{\tilde{a}}{3\lambda}, \quad \frac{\tilde{a}^3(\Lambda)}{\lambda(\Lambda)} = \text{const.} \tag{11}$$

The solution of the equation for the interaction vertex is given by

$$\frac{1}{\lambda(\Lambda)} - \frac{1}{\lambda} = K \int\limits_0^{1/\Lambda} dx \left(\frac{1 + \kappa^2 x^2}{1 + (1+b)\kappa^2 x^2}\right)^2. \tag{12}$$

Calculating the integral in (12) and taking Eq. (11) into account, we find

$$\lambda(\Lambda) = \frac{\lambda(\infty)}{1 + F(\Lambda)}, \quad \tilde{a}(\Lambda) = \frac{\tilde{a}(\infty)}{(1 + F(\Lambda))^{1/3}}, \tag{13}$$

where

$$F(\Lambda) = \frac{K\lambda(\infty)}{2\kappa(1+b)^{5/2}} \times$$

$$\times \left(t(2 + \frac{b^2}{1+t^2}) + b(b+4)\arctan t\right), \tag{14}$$

$$t = \frac{\kappa}{\Lambda}\sqrt{1+b}.$$

To obtain the expressions for physical quantities valid in a wide region near the transition point, it is neccesary to choose a mathching point Λ^* for solutions (13). The matching point can be chosen in the same way as in [3] (see also [19]),

$$\Lambda^* = \sqrt{\frac{\tilde{a}(\Lambda^*)}{\alpha}}. \qquad (15)$$

Inserting this in Eq. (13), we obtain the equation for the susceptibility,

$$\tilde{a}(\Lambda^*) \left(1 + \frac{K\lambda(\infty)}{2\kappa(1+b)^{5/2}} \left(t^* \left(2 + \frac{b^2}{1+t^{*2}} \right) + \right. \right.$$
$$\left. \left. + \; b(b+4) \arctan t^* \right) \right)^{1/3} = \tilde{a}(\infty), \quad (16)$$

where

$$t^* = \sqrt{\frac{(1+b)\alpha\kappa^2}{\tilde{a}(\Lambda^*)}}.$$

Equation (16) determines the susceptibility in a wide temperature region in the one-loop approximation. The critical exponent γ is equal to $6/5$ in this approximation. It is neccesary to modify this expression in order to apply it to experimental data. The simplest way is to replace the exponent $1/3$ in (16) with $2 - 2/\gamma$, where $\gamma = 1.24$.

4. DISCUSSION

The expressions obtained can be used for electrolyte solutions (strong or weak) if the ion density ρ is small. As $\rho \to 0$, all the expressions transform to the ordinary form valid for non-ionic liquids. The pure solvent limit can also be obtained as $b \to 0$, i.e., if the density is weakly coupled to the charge density.

The Debye–Hückel screening radius in the vicinity of the transition point is proportional to the correlation length. As $T \to T_c$, the screening radius tends to infinity and the screening disappears.

The asymptotic forms of the density correlation function for $k \gg \kappa$ and $k \ll \kappa$ are the same as for the non-ionic liquid, and therefore, the corresponding (mean-field or Ising-like) asymptotic behavior is the same. The value of $F(\Lambda^*)\sqrt{\tilde{a}^*}$ in the ionic solution is similar to the Ginzburg parameter G for the ordinary liquids. It decreases as the salt concentration increases, and the Ising-like region of ionic solutions therefore decreases as the concentration increases, which agrees with the experimental data.

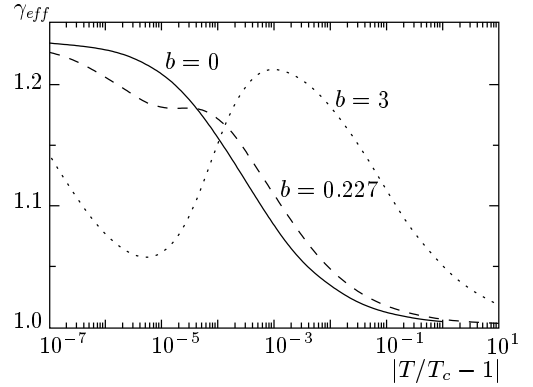Equation (16) determines the behavior of the susceptibility in the crossover region. The dependence of

Fig. 2. The dependence of the effective susceptibility critical exponent γ_{eff} on the value of b for the model system. The curve where $b = 0$ corresponds to the non-ionic solution

the effective exponent γ on the temperature for the model system is presented in Fig. 2. For small values of b, this dependence has the usual shape, but it becomes nonmonotonic for $b \sim 1$. For the real experimental situation in [14], this specific behavior occurs in a close vicinity of the transition point and it is difficult to reveal it. The authors of [14] state that they see this peculiarity.

The shape of the crossover curve depends on the dimensionless parameter b (Eqs. (7)), i.e., on $\gamma_1 + \gamma_2$. This quantity can be estimated from a simple electric measurement. In the mean-field approximation, Eq. (5) gives

$$\langle \phi \rangle = -\frac{\gamma_1 + \gamma_2}{2e} \langle \varphi \rangle = -\frac{\gamma_1 + \gamma_2}{4e} \sqrt{\frac{-\tilde{a}}{\lambda}} \qquad (17)$$

for the two-phase state. Therefore, the voltage between the two phases of the ionic solution is determined by $\gamma_1 + \gamma_2$. Near the transition point, this voltage is proportional to the order parameter and behaves as $(T/T_c - 1)^\beta$.

The detailed comparison of the expressions obtained with the experimental data is not a simple task. The data presented in [11–13] have significant error bars. The ionic solutions in [14, 20] were ternary and their behavior was studied near the consolute points. These solutions had a high concentration (10%), and there were additional problems due to the clustering and the vicinity of double critical and tricritical points. The data for a fixed concentration can be easily fitted in accordance with Eq. (16). Unfortunately, this fit is not informative, and further experimental studies are necessary.

REFERENCES

1. C. Domb and M. S. Green, Phase Transitions and Critical Phenomena, Academic, NY (1974), Vol. 3.

2. A. Z. Patashinskii and V. L. Pokrovskii, *Fluctuational Theory of Phase Transitions* [in Russian], Nauka, Moscow (1982).

3. J. Rudnick and D. R. Nelson, Phys. Rev. B **13**, 2208 (1976).

4. J. F. Nicoll and P. C. Albright, Phys. Rev. B **31**, 4576 (1985).

5. S. Tang, J. V. Sengers, and Z. Y. Chen, Physica A **179**, 344 (1991).

6. M. E. Fisher, J. Stat. Phys. **75**, 1 (1994).

7. G. Stell, J. Stat. Phys. **78**, 197 (1994).

8. J. M. H. Levelt Sengers and J. A. Given, J. Mol. Phys. **80**, 899 (1993).

9. K. S. Pitzer, Acc. Chem. Res. **22**, 333 (1990).

10. H. Weingartner, M. Kleemeier, S. Wiegand, and W. Schroer, J. Stat. Phys. **78**, 169 (1995).

11. T. Narayan and K. S. Pitzer, Phys. Rev. Lett. **73**, 3002 (1994).

12. T. Narayan and K. S. Pitzer, J. Phys. Chem. **98**, 9170 (1994).

13. T. Narayan and K. S. Pitzer, J. Chem. Phys. **102**, 8118 (1995).

14. J. Jacob, A. Kumar, M. Anisimov, A. Povodyrev, and J. V. Sengers, Phys. Rev. E **58**, 2188 (1998).

15. B. P. Lee and M. E. Fisher, Phys. Rev. Lett. **76**, 2906 (1996).

16. M. E. Fisher and B. P. Lee, Phys. Rev. Lett. **77**, 3561 (1996).

17. B. P. Lee and M. E. Fisher, Europhys. Lett. **39**, 611 (1997).

18. L. D. Landau and E. M. Lifshitz, Statistical Physics, Vol. 5 [in Russian], Nauka, Moscow (1976).

19. M. Yu. Belyakov, S. B. Kiselev, and A. R. Muratov, Zh. Eksp. Teor. Fiz. **77**, 279 (1993).

20. M. A. Anisimov, J. Jacob, A. Kumar, V. A. Agayan, and J. V. Sengers, Phys. Rev. Lett. **85**, 11, 2336 (2000).