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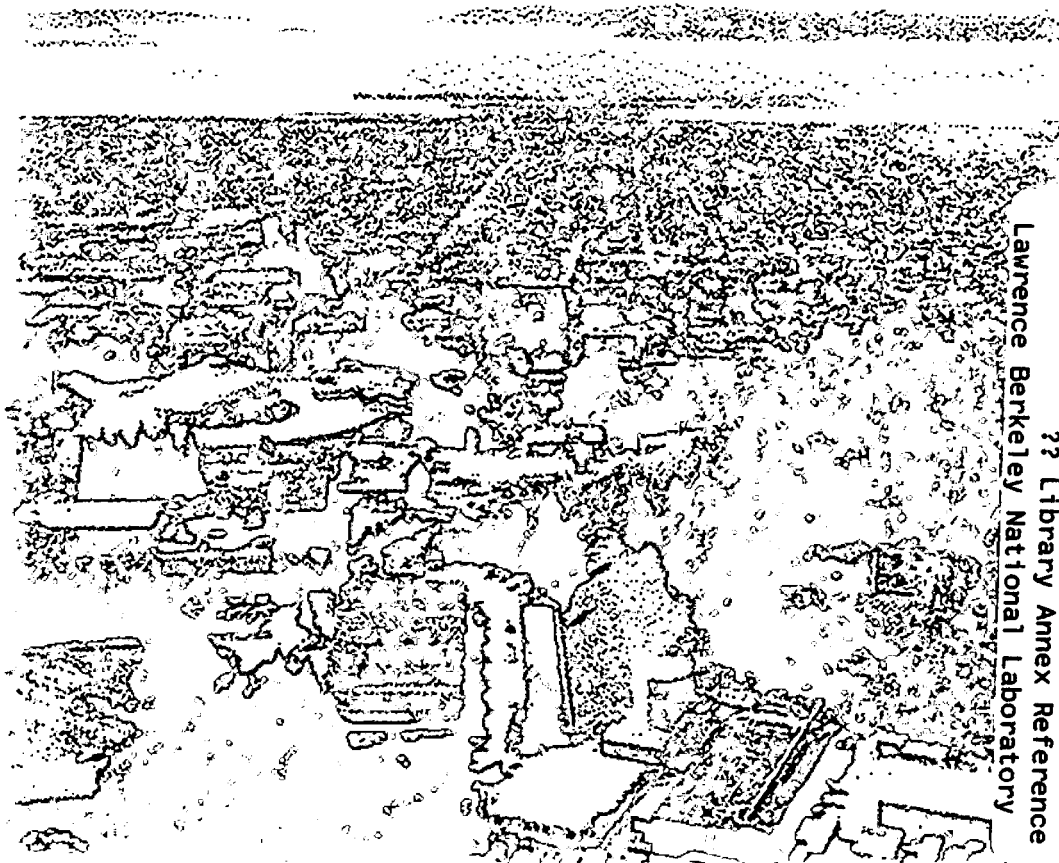
**Criticality and Phase Behavior
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Electrolyte: Effect of Ionic Association**

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and John M. Prausnitz

Chemical Sciences Division

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Criticality and Phase Behavior in the Restricted-Primitive Model Electrolyte: Effect of Ionic Association

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Criticality and phase behavior in the restricted-primitive model electrolyte: effect of ionic association

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Ionic association in the restricted-primitive model (RPM) electrolyte is incorporated to account for the strong attraction between unlike ions. Two methods are investigated within the McMillan-Mayer framework: first, the binding mean-spherical approximation (BIMSA) based on Wertheim's Ornstein-Zernike integral equation formalism; and second, combination of the BIMSA with a simple interpolation scheme (SIS) based on Wertheim's thermodynamic perturbation theory. The latter gives a better description. Four different association constants are used to calculate the degree of dissociation, the critical point and the vapor-liquid coexistence curve. A rising association constant leads to a lower critical temperature and a higher critical density, and thus, better agreement with computer simulations. When unlike ions are fully paired, corresponding to a charged hard dumbbell (CHDB) system, we obtain the best agreement with the most recent computer simulations of the RPM electrolyte.

Running Title: Ionic association in the RPM electrolyte

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I. INTRODUCTION

It is well recognized that ionic association is of significant importance in determining criticality and phase behavior of an electrolyte. This is a result of the strong electrostatic attraction between ions of unlike charges. This effect is far from linear in terms of the strength of electrostatic interaction. The Debye-Hückel (DH)¹ theory and the mean-spherical approximation (MSA)^{2,3} theory for electrolyte are essentially linearized Poisson-Boltzmann theories and yield the correct Coulomb screening but cannot capture the effect of ionic association. Since the early days of last century, various methods have been suggested to take ionic association into account. In 1926, Bjerrum⁴ incorporated chemical association of ions to the DH theory in a meaningful way. In the 1980s, Ebeling and Grigo (EG)⁵ combined ionic pairing with the MSA through the mass action law (MAL) and the second ionic virial coefficient. In EG's method, the ionic pair is assumed to be an ideal component, i.e., its activity coefficient is unity. Years later, in the same spirit, Gillan⁶, Tani and Henderson⁷, and Pitzer and Schreiber⁸ evaluated the effect of ionic association including pairs and higher-mers. For a detailed historic account, see recent reviews⁹⁻¹³.

In recent years, several theoretical methods were proposed where ionic pairing is based on the *ad hoc* chemical association model of Bjerrum and EG for size-symmetric electrolytes, i.e., the restricted-primitive model (RPM) electrolytes. Fisher and Levin^{14,15} extended DH theory by considering the solvation of dipolar ionic pairs in an ionic fluid (dipole-ion interaction). When the hard core of ions is neglected, the resulting Debye-Hückel-Bjerrum-Dipole-Ion (DHBjDI) theory gives a fairly good critical point and coexistence curve upon comparison with Monte Carlo (MC) simulation data¹⁸. DHBjDI is probably quantitatively the most successful theory for the RPM electrolyte presently available. Careful studies¹², however, found that the hard core contribution plays an important role in determining the phase coexistence of electrolytes. Indeed, inclusion of the hard core into DHBjDI, the resulting Debye-Hückel-Bjerrum-Dipole-Ion-Hard-Core (DHBjDIHC) destroys agreement with MC simulation. Upon comparison with the latest high precision MC simulation data¹⁹, large deviations are found for both DHBjDI and DHBjDIHC.

Stell and coworkers^{16,17} proposed pairing MSA on the basis of a simple interpolation scheme (SIS)²⁰. In the SIS the cavity correlation function of an associating fluid remains nearly the same as that of a dissociating fluid. This approximation is equivalent to Wertherim's first order

thermodynamic perturbation theory²¹ that has been widely used to study thermodynamic properties of associating fluids and chain-like macromolecules. The pairing MSA was extended by the authors combining ion-dipole interaction to model the RPM electrolyte. Because in the MSA the excluded-volume is treated correctly, we expect that this method will give better results than DHBjDI. Unfortunately, the calculated critical point and coexistence curve are less satisfactory. Stell and coworkers concluded that the agreement of DHBjDI with MC simulation was largely fortuitous.

Recently, Guillot and Y. Guissani¹², and Schröer and coworkers^{22,23} incorporated dipole-dipole interaction and dipolar screening to account for the dielectric effect. But unhappily, worse results were obtained; the calculated critical temperature is too high, critical density is too low and the coexistence curve is too narrow when compared with MC simulation results.

In this work, we present two methods to investigate criticality and phase behavior in the RPM electrolyte. First, the effect of ionic association is calculated with the binding mean-spherical approximation (BIMSA) developed earlier^{24,25}. The salient feature of the BIMSA is that it satisfies the exact fully associated zero density DH limit, that is, if two ions associate, the limiting osmotic coefficient is given by the DH expression for an ion with charge equal to the sum of the two associating ions. Similarly, the associative mean-spherical approximation (AMSA), basically the BIMSA, was briefly described by Raineri *et al.*²⁶ to study the size-asymmetric primitive model electrolytes. We use first the analytical solution of the BIMSA expressed by a screening parameter Γ^B that is a function of the degree of dissociation. When Γ^B is substituted by Γ without association, the BIMSA reduces to the SIS. Second, we use a combination of the BIMSA with the SIS, which gives a better critical point and a better coexistence curve. Sec. II presents the basic model and theoretical framework. Sec. III shows calculated results for four versions of the association constant, including full association corresponding to the charged hard dumbbell (CHDB) system²⁷. Sec. IV gives discussion and concluding remarks.

II. MODEL AND THEORY

At the McMillan-Mayer level, the RPM electrolyte is represented by charged hard spheres with identical diameter σ in a continuous dielectric medium with permittivity ϵ . The number

density of the hard sphere is $2\rho_0$; one half of the species carries charge $+ze$ and the other half $-ze$ ($e=1.602\times 10^{-19}$ C is the elementary charge). Interactions between two particles are hard sphere repulsion and electrostatic potential:

$$u_{ij}(R) = \begin{cases} \infty & R < \sigma \\ \frac{z_i z_j e^2}{4\pi\epsilon R} & R \geq \sigma \end{cases}, \quad (1)$$

where R is center-to-center distance. Ionic association between unlike ions is modeled using Baxter's sticky point potential inside the hard core σ^- . Only pairs are allowed (no trimers no higher).

Suppose α is the degree of dissociation then the number density of free ions is $\rho_+ = \rho_- = \rho_0\alpha$ and that of neutral ionic pairs is $\rho_p = \rho_0(1-\alpha)$. The mass action law (MAL) is:

$$K = \frac{\rho_p}{\rho_+\rho_-} = \frac{1-\alpha}{\rho_0\alpha^2}, \quad (2)$$

or

$$\rho_p = \frac{2K\rho_0^2}{1+2K\rho_0 + \sqrt{1+4K\rho_0}} = \frac{1+2K\rho_0 - \sqrt{1+4K\rho_0}}{2K}, \quad (3)$$

where the stoichiometric association constant K depends on density at given temperature. K can be separated into two parts: $K = K^0 K^\gamma$. $K^\gamma = \gamma_+\gamma_-/\gamma_p$ is the ratio of the activity coefficients of the free ions to that of the neutral pair. The thermodynamic association constant K^0 , a constant at given temperature, is the infinite-dilute limit of K . We chose an approximation given by Ebeling²⁸ for K^0 such that the second ionic virial coefficient is recovered:

$$K_{\text{Eb}}^0 = 8\pi\sigma^3 \sum_{m=2}^{\infty} \frac{(T^*)^{-2m}}{(2m)!(2m-3)} = 4\pi\sigma^3 \int_0^1 dt [e^{t/T^*} + e^{-t/T^*} - (t/T^*)^2 - 2]/t^4, \quad (4)$$

where $T^* = 4\pi\epsilon\sigma/\beta e^2 z^2$ is the reduced (dimensionless) temperature. The degree of dissociation near the critical point, calculated by K_{Eb}^0 is too large^{5,16,17}. As suggested by Raineri *et al.*²⁶, two alternative thermodynamic association constants K_{OS}^0 ²⁹ and K_{Fu}^0 ³⁰ may be used to repair this deficiency. Following Raineri *et al.*²⁶, we choose:

$$K_{\text{OS}}^0 = 3K_{\text{Fu}}^0 = 12K_{\text{Eb}}^0. \quad (5)$$

Figure 1 shows the effect of reduced temperature T^* on these thermodynamic association constants; from bottom to top, they are K_{Eb}^0 , K_{Fu}^0 and K_{Os}^0 . They are large at low T^* and fall with rising T^* , indicating strong ionic association at low T^* .

As found from MC simulation^{19,31,32} in both vapor and liquid phases structure of the RPM electrolyte is largely that of the CHDB. They have a similar critical point and similar phase behavior suggesting that we can assume full association between anion and cation ($\alpha = 0$, $K_{\text{fa}}^0 = \infty$) by ignoring free ions as a first approximation to model the RPM, as shown earlier²⁷.

The model above, called the sticky electrolyte model (SEM), was studied extensively using the Ornstein-Zernike (OZ) integral equation with a hybrid approximation PY/MSA or HNC/MSA.³³⁻³⁵ Recently^{24,25}, we reported an analytical solution of the BIMSA by solving Wertheim's Ornstein-Zernike (WOZ) integral equation²¹. Unlike the usual OZ derived from Mayer density expansion, the WOZ is derived from an activity/fugacity expansion. WOZ can account properly for saturation effects where only one bond is allowed between ions. This formalism includes the fraction of bonded sites, which is obtained from the MAL.

From the BIMSA, the Helmholtz energy density f has four contributions from, respectively, ideal gas, hard-sphere repulsion, MAL and electrostatic interaction:

$$f = f^{\text{id}} + f^{\text{hs}} + f^{\text{mal}} + f^{\text{ele}}. \quad (6)$$

The ideal-gas contribution is:

$$\beta f^{\text{id}} = 2\rho_0 \ln \rho_0 - 2\rho_0, \quad (7)$$

where $\beta = 1/k_{\text{B}}T$ ($k_{\text{B}} = 1.38 \times 10^{-23} \text{ JK}^{-1}$ is the Boltzmann constant and T is temperature).

The hard-sphere repulsion contribution is obtained from the well-known Carnahan-Starling³⁶ equation of state:

$$\beta f^{\text{hs}} = \frac{2\rho_0 \eta(4-3\eta)}{(1-\eta)^2}, \quad (8)$$

where $\eta = \rho^* \pi/6$ ($\rho^* = 2\rho_0 \sigma^3$, the reduced density) is the packing fraction of ions before association.

The MAL contribution is:

$$\beta f^{\text{mal}} = 2\rho_0 \ln \alpha + \rho_0(1-\alpha). \quad (9)$$

The electrostatic-interaction contribution is obtained from the BIMSA²⁴. However, to obtain the correct limit for a very dilute solution the BIMSA was closed by the exponential approximation (BIMSA-EXP)²⁵ that gives:

$$\beta f^{\text{ele}} = -2\ell_B \rho_0 z^2 \frac{\Gamma^B}{1 + \Gamma^B \sigma} + \frac{(\Gamma^B)^3}{3\pi}, \quad (10)$$

where $\ell_B = \beta e^2 / 4\pi\epsilon$ is the Bjerrum length characterizing the dielectric property of the continuous medium. Γ^B is the unique screening parameter calculated from:

$$4(\Gamma^B)^2 (1 + \Gamma^B \sigma)^3 = \kappa^2 (\alpha + \Gamma^B \sigma), \quad (11)$$

where κ is the inverse Debye screening length defined by $\kappa = \sqrt{4\pi\ell_B \sum \rho_k z_k^2}$. Without association, $\alpha = 1$, Γ^B reduces to $\Gamma = (\sqrt{1 + 2\sigma\kappa} - 1) / 2\sigma$, which is the screening parameter in the usual MSA^{2,3}. In this case, eq. (10) reduces to:

$$\beta f^{\text{ele}} = -2\ell_B \rho_0 z^2 \frac{\Gamma}{1 + \Gamma \sigma} + \frac{\Gamma^3}{3\pi}. \quad (12)$$

From the BIMSA^{25,37} K^r is given by:

$$K^r = g_{+-}(\sigma) / g_{+-}^0(\sigma), \quad (13)$$

where $g_{+-}(\sigma)$ is the anion cation contact pair correlation function and $g_{+-}^0(\sigma)$ is the corresponding infinite-dilute limit,

$$g_{+-}(\sigma) = g^{\text{hs}}(\sigma) \exp\left[-\frac{\ell_B z_+ z_-}{\sigma (1 + \Gamma^B \sigma)^2}\right], \quad (14)$$

where $g^{\text{hs}}(\sigma) = (1 - \eta/2) / (1 - \eta)^3$ is the contact pair correlation function for hard sphere fluid from the Carnahan-Starling equation of state³⁶. With eq. (14), eq. (13) reads:

$$K^r = g^{\text{hs}}(\sigma) \exp\left[\frac{\ell_B z_+ z_- \Gamma^B (2 + \Gamma^B \sigma)}{(1 + \Gamma^B \sigma)^2}\right]. \quad (15)$$

Equations (6-15) complete the BIMSA scheme for ionic pairing in the RPM electrolyte based on the Wertheim's Ornstein-Zernike integral equation. On the other hand, however, we can use the pair MSA as proposed from the SIS. In the SIS the cavity correlation function of an associating fluid remains almost the same as that of a dissociating fluid. This approximation is

equivalent to Wertheim's first order thermodynamic perturbation theory²¹. In the SIS, electrostatic interaction is calculated from eq. (12) and K^γ is given by:

$$K^\gamma = y_{+-}^{\text{ref}}(\sigma), \quad (16)$$

where $y_{+-}^{\text{ref}}(\sigma)$ is the contact anion-cation cavity correlation function evaluated at $\alpha=1$, the reference ionic fluid without association.

As an improvement for the SIS, we propose a simple interpolation between the SIS and the BIMSA; we denote this interpolation SIS/BIMSA. Electrostatic interaction, similar to the SIS, is calculated by eq. (12); however K^γ is from eq. (15). We find that this combination gives better results.

III. RESULTS

Table I lists critical temperature T_c^* , critical density ρ_c^* in the RPM electrolyte and degree of dissociation α_c at the critical point estimated from the BIMSA and the SIS/BIMSA with four versions of thermodynamic association constant K^0 ; included for comparison are those from DH¹, DHBjDI¹⁴, DHBjDIHC¹⁴, MSA^{2,3} and MC simulation¹⁹. Figure 2 shows the corresponding diagram for T_c^* and ρ_c^* . For either BIMSA or SIS/BIMSA, with rising K^0 ($K_{\text{Eb}}^0 < K_{\text{Fu}}^0 < K_{\text{OS}}^0 < K_{\text{fa}}^0$), α_c decreases as expected, leading to lower T_c^* and higher ρ_c^* . Given K^0 , SIS/BIMSA gives lower T_c^* , higher ρ_c^* and larger α_c , compared with BIMSA. As linearized theories, no ionic association ($\alpha_c=1$) is incorporated in DH and MSA; as a consequence, they give too high T_c^* but too low ρ_c^* , far from the exact critical point. DHBjDI and DHBjDIHC both give fairly good T_c^* but too low ρ_c^* . When $K^0 = K_{\text{fa}}^0 = \infty$, that is, when anion and cation fully associate into neutral pairs, SIS/BIMSA-fa gives the best prediction (0.0525, 0.0640) for the critical point, very close to MC simulation (0.0496, 0.0792)¹⁹. This favorable results support the assumption that the RPM electrolyte may be modeled as the CHDB without taking free ions into account, as shown in recent MC simulations^{19,31,32}.

Figure 3 shows the vapor-liquid coexistence curve in the RPM electrolyte calculated from MSA, BIMSA (a), SIS/BIMSA (b) and MC simulations (open squares)¹⁹. From top to bottom, the corresponding thermodynamic association constant K^0 rises. For either BIMSA or

SIS/BIMSA, with rising K^0 , the slopes of both vapor and liquid phases decrease. At low temperature T^* , for BIMSA, the vapor and liquid phases change little with K^0 ; in contrast, for SIS/BIMSA, the liquid phase decreases with rising K^0 . Given K^0 , both vapor and liquid phases from SIS/BIMSA are flatter than those from BIMSA, i.e., with lower slopes, because SIS/BIMSA gives lower T_c^* .

Figure 4 shows the vapor-liquid coexistence curve in the RPM electrolyte calculated from MSA, BIMSA-fa, SIS/BIMSA-fa, DHBjDI¹⁴, DHBjDIHC¹⁴ and MC simulation (open squares)¹⁹. Upon comparison with MC simulation, the slope of vapor phase from MSA, BIMSA-fa, DHBjDI and DHBjDIHC is too steep; nevertheless, SIS/BIMSA-fa gives much better results. In the liquid phase, DHBjDI gives a density that is too high while DHBjDIHC gives a density that is too low. Similar to the prediction for critical point, SIS/BIMSA-fa gives the most successful prediction for the coexistence curve when the RPM electrolyte is modeled as the CHDB.

IV. DISCUSSION AND CONCLUSIONS

In this work, two approximations, the BIMSA and the SIS/BIMSA are presented to study the RPM electrolyte. Ionic pairing between unlike ions is found to be a very important factor to determine criticality and vapor-liquid phase equilibrium. With rising association constant, critical temperature T_c^* decreases and critical density ρ_c^* increases. Compared with the BIMSA, in general, the SIS/BIMSA gives a better critical point and coexistence curve. When unlike ions are fully paired, i.e., the RPM electrolyte turns to the CHDB, SIS/BIMSA-fa gives the most successful quantitative prediction for the critical point and for the coexistence curve, consistent with the observation from computer simulation that the critical point and phase equilibrium of the RPM electrolyte are very similar to those from the CHDB.

The nature of criticality in the RPM electrolyte — whether of classical (mean field or van-der-Waals type, $\alpha_{\text{classical}} = 0$) or Ising type ($\alpha_{\text{Ising}} = 0.11$) or crossover — remains a controversial. Experimentally, both classical^{38,39} and Ising type⁴⁰ have been reported; other possible scenario entails a crossover from classical to Ising type⁴¹. On the other hand, by analyzing heat capacity C_v near the critical point, MC simulation⁴² pointed to classical criticality in the RPM electrolyte.

Conversely, Ising type criticality was suggested from more recent MC simulation⁴³. Indeed in many studies by computer simulation such as Ref. 19, *a priori* Ising type criticality is supposed to estimate the critical point with a mixed-field finite-size scaling method. Ultimately, the renormalization group theory may be required to describe this system properly.

At present, in this field, computer simulation studies are well ahead of the theories. From cluster analysis, there appears to be an appreciable amount of neutral pairs and linear alignment (chain-like) of alternatively charged ions. Theories based on the *ad hoc* chemical association model of Bjerrum and EG describe ionic association only at the pairwise level only; they cannot account for geometries and interactions in larger clusters. More efforts should be made toward offering further physical insight into the nature of electrolytes.

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Table I. Critical temperature, critical density and degree of dissociation from theories and MC simulation in the RPM electrolyte. ^{a)} In Ref. 12, $T_c^* = 0.0521$ and $\rho_c^* = 0.0243$ if the hard core repulsion uses the Carnahan-Starling equation of state.

Theory	T_c^*	ρ_c^*	α_c	Date source
DH	1/16	1/64 π	1	Ref. 1
DHBjDI	0.0574	0.0280	0.207	Ref. 14
DHBjDIHC	0.0554 ^{a)}	0.0260 ^{a)}	0.144	Ref. 14
MSA	0.0786	0.0144	1	Ref. 2,3
BIMSA-Eb	0.0723	0.0293	0.317	This work
BIMSA-Fu	0.0684	0.0375	0.149	This work
BIMSA-OS	0.0662	0.0415	0.082	This work
BIMSA-fa	0.0627	0.0471	0	This work
SIS/BIMSA-Eb	0.0707	0.0355	0.329	This work
SIS/BIMSA-Fu	0.0632	0.0511	0.155	This work
SIS/BIMSA-OS	0.0587	0.0590	0.084	This work
SIS/BIMSA-fa	0.0525	0.0640	0	This work
MC	0.0496	0.0792		Ref. 19

Figure Captions:

FIG.1. Effect of the reduced temperature on the thermodynamic association constant. From bottom to top: K_{Eb}^0 , K_{Fu}^0 and K_{OS}^0 .

FIG.2. Critical temperature T_c^* and density ρ_c^* from theories and MC simulation in the RPM electrolyte. Lines are drawn to guide the eye.

FIG.3. Vapor-liquid coexistence curve from theories and MC simulation in the RPM electrolyte. (a) BIMSA; (b) SIS/BIMSA.

FIG.4. Vapor-liquid coexistence curve from theories and MC simulation in the RPM electrolyte.

FIG.1

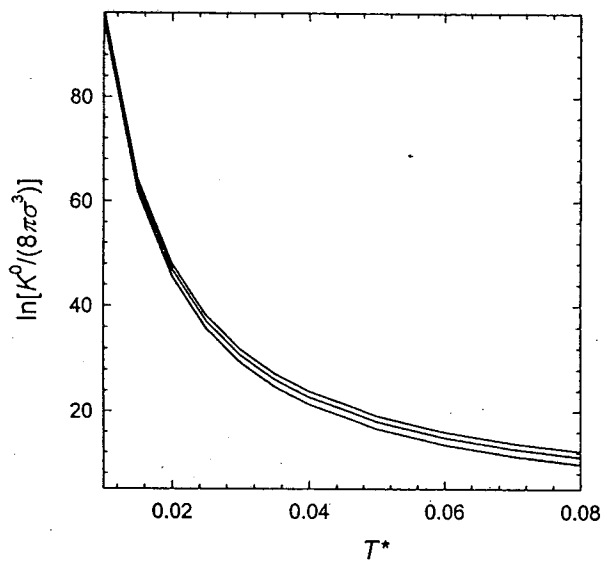


FIG.2

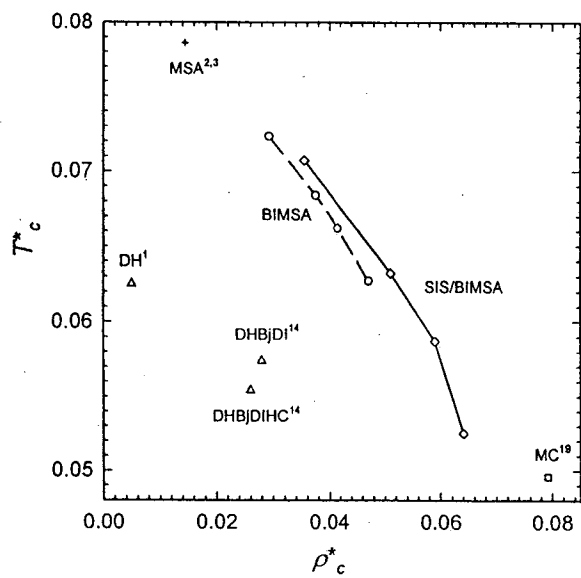


FIG.3

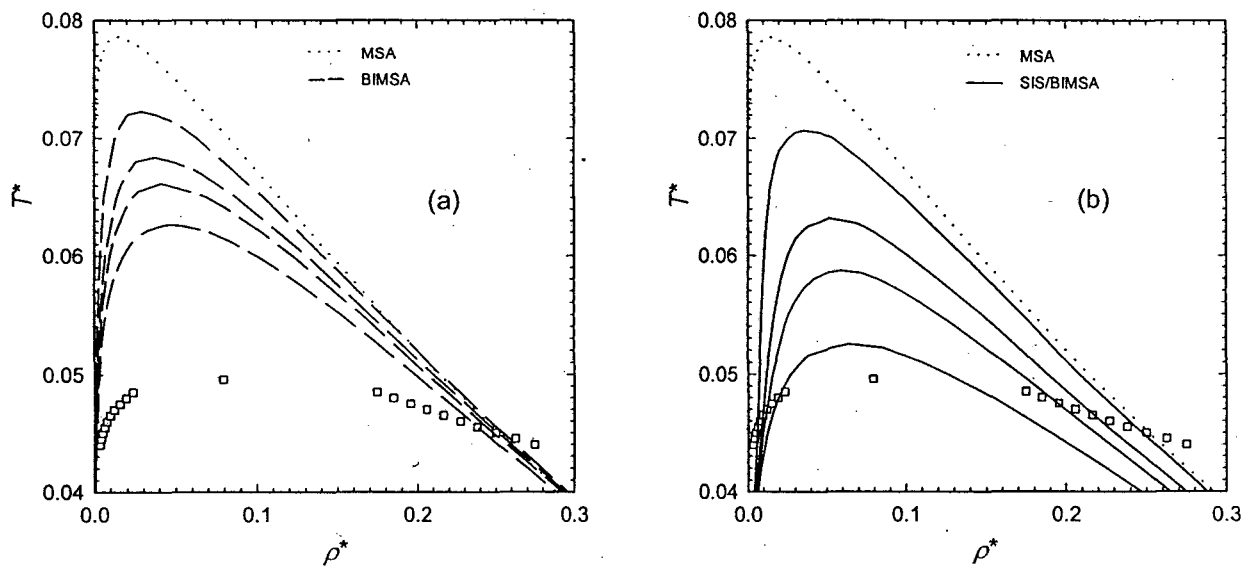
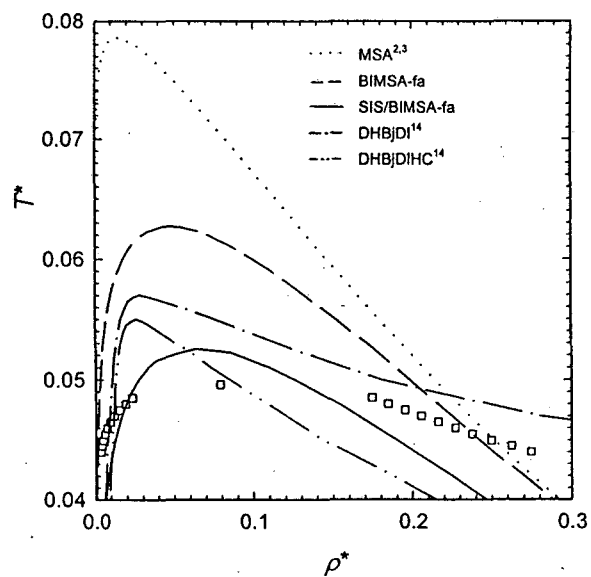


FIG.4



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