

# Lower Critical Solution Temperature of Linear PNIPA Obtained from a Yukawa Potential of Polymer Chains

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**ABSTRACT:** The lower critical solution temperature (LCST) behavior of a linear poly(*N*-isopropylacrylamide) (PNIPA) in water is thought to result from the polymer–polymer attractive interaction. This polymer–polymer attraction is modeled by a temperature-dependent Yukawa attractive potential, with Yukawa parameters determined by fitting the theoretical phase diagram for a pure Yukawa fluid to the experimental lower consolute boundary for a PNIPA–water solution. The predicted coexistence curve for the PNIPA–water mixtures in the temperature–polymer volume fraction plane is reasonably close to the experimental cloud point data for the PNIPA–water system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1971–1976, 2000

**Key words:** poly(*N*-isopropylacrylamide) (PNIPA); lower critical solution temperature (LCST); Yukawa potential; polymer–polymer interaction; coexistence curve

## INTRODUCTION

Stimuli-responsive polymers are considered to have many potential applications, especially in the fields of medicine, biotechnology, and environmental problems.<sup>1–5</sup> Recently poly(*N*-isopropylacrylamide) (PNIPA) has been getting more attention because it has an attractive temperature-sensitive property.<sup>6–9</sup> Such temperature-sensitive PNIPA in an aqueous medium has a lower critical solution temperature (LCST) of 31°C for linear PNIPA and 34°C for PNIPA gel. At temperatures below the LCST, PNIPA is completely miscible or swells with water; at temper-

ature above the LCST, PNIPA become only partially miscible or it deswells.

It is well known that a PNIPA–water system exhibits an LCST because of that specific interaction (i.e., the hydrogen bond between the CONH(CH<sub>3</sub>)<sub>2</sub> groups in the polymer chain and the water). At temperatures below the LCST, the hydrogen bond is the major interaction, and the polymer is hydrophilic; but with an increase of temperature, the hydrogen bond becomes weak, and the hydrogen bond is then damaged when the temperature is above the LCST and the phase transition takes place, separating the system into two phases: the polymer-rich phase and the water-rich phase.

The thermodynamic characteristic of the LCST of PNIPA polymer and hydrogel has been studied in different ways in the past decade. Cussler<sup>10</sup>

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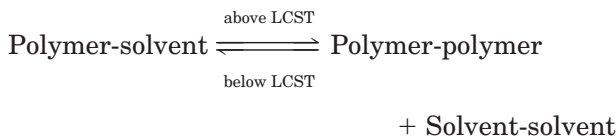
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considered the Helmholtz free energy of mixing,  $\Delta F$ , as described by the Sanchez and Lacombe extension of the Flory–Huggins theory of polymer–solvent systems. Prausnitz<sup>11</sup> obtained interaction energy parameters from liquid–liquid equilibrium (LLE) data by using an oriented quasi-chemical model that takes into account the strong specific or oriented interaction. Oh<sup>12</sup> modified Hu's<sup>13</sup> double-lattice model (MDL) by introducing an energy parameter and simplifying the expression for the Helmholtz energy of mixing. All of these approaches, which are based on treating the polymer–solvent system as a mixture and developing an approximation for the energy of mixing have yielded good results. In the research for our current study the PNIPA–water system is treated as a pseudo one-component system. The inter-chain attraction is described by a potential of mean force modeled as a temperature-dependent Yukawa attractive potential. This is similar to the approach introduced by Kenkare<sup>14</sup> to describe LCST phenomena for nonionic surfactant  $C_8E_5$  systems. The attractive Yukawa potential has the advantage that it can take into account the potential between the polymer chains, the polymer–polymer attraction increasing with temperature.

## EXPERIMENTAL

### Model and Potential of Interaction

The phase translation process of PNIPA can be described as following equilibrium:



There are three interactions in the PNIPA–water system. Below the LCST, the polymer–solvent interaction is the major one, and the polymer is hydrophilic. Above the LCST, the polymer–polymer and solvent–solvent interactions are major, and the polymer is hydrophobic, at which the LCST phase translation takes place. In order to get more information about the phase translation, every interaction must be discussed. In this article we discuss the polymer–polymer interaction by Yukawa potential. We take the subchain [group  $\text{CONH}(\text{CH}_3)_2$ ] of PNIPA as hard sphere.

The subchains are modeled as hard spheres interacting via a temperature-dependent attractive Yukawa potential. According to the mean spherical approximation (MSA) model, Yukawa potential is the major interaction of hard spheres when the distance between two hard spheres is greater than their hard core<sup>14</sup>; In our research the range and depth of the Yukawa potentials were adjusted so that the theoretically predicted PNIPA–water spinodal line matched the experimentally determined cloud point data.

The work of Hayter, Zulauf, and coworkers<sup>15–17</sup> and of Reatto and Tau<sup>18</sup> shows that the potential between the micellar species can be modeled by using a temperature-dependent attractive Yukawa potential. The intermicellar attraction is thought to increase with temperature. Here we analyze PNIPA's LCST by the polymer subchain–subchain interaction. This can be understood by considering how the shell of structured water surrounding the polymer subchains screens the van der Waals attraction between them. As temperature is increased, the size of this shell diminishes, causing the attraction between the subchains to increase. So as temperature is increased, the tendency to phase-separate into polymer-rich and polymer-poor phases increases, and hence the system exhibits an LCST behavior.

There are three interactions in binary Yukawa mixtures: solvent–solvent interaction ( $U_{11}$ ); polymer–solvent interaction ( $U_{12}$ ), and polymer–polymer interaction ( $U_{22}$ ). The intersubchains' attraction is modeled by using an attractive Yukawa potential,  $U_{22}(r)$ , of the form<sup>14</sup>

$$\begin{aligned} U_{22} &= \infty \quad r \leq d_2 \\ &= -\frac{\varepsilon}{(r/d_2)} \exp\left[-z\left(\frac{r}{d_2} - 1\right)\right] \quad r > d_2 \end{aligned} \quad (1)$$

where  $r$  is the distance between the center of subchains,  $d_2$  is the diameter of subchain particle [ $-\text{CONH}(\text{CH}_3)_2$ ] (by the MSA),  $\varepsilon$  is the depth of the attractive well, and  $z$  is the range of the potential. The increase in interchain attraction with increasing temperature is modeled by making the well depth,  $\varepsilon$ , an increasing function of temperature,  $T$ .

$$\varepsilon = k_B T / (A - BT) \quad (2)$$

where  $A$  and  $B$  are constants and  $k_B$  is Boltzmann's constant. In our research the constants  $A$ ,

$B$ , and  $z$  are fit to make the theoretically predicted temperature-polymer volume fraction coexistence curve match the experimentally observed temperature-polymer volume fraction of the LCST for PNIPA–water solution. A similar approach has been used successfully by other investigators in modeling phase separation in nonionic micellar solutions.<sup>18–19</sup>

Following Ginoza,<sup>20</sup> they have an equation

$$\Gamma(\Gamma + z)(1 + \Gamma\psi(z))^2 + xw(z) = 0 \quad (3)$$

where  $x = \varepsilon/k_B T = 1/T^*$  is the inverse reduced temperature, or potential strength parameter.

$$w(z) = \frac{6\eta}{(\Phi_0(z))^2} \quad (4)$$

$$\Phi_0 = \frac{e^{-z}L(z) + S(z)}{z^3(1 - \eta)^2} \quad (5)$$

$$\psi = z^2(1 - \eta)^2 \frac{1 - e^{-z}}{e^{-z}L(z) + S(z)} - 12\eta \frac{1 - z/2 - (1 + z/2)e^{-z}}{e^{-z}L(z) + S(z)} \quad (6)$$

and

$$\eta = \pi\rho\sigma^3/6 \quad (7)$$

where  $\rho = N/V$  is the number of molecules divided by the volume. The polynomials  $L(z)$  and  $S(z)$  are given by

$$L(z) = 12\eta[(1 + \eta/2)z + 1 + 2\eta] \quad (8)$$

and

$$S(z) = (1 - \eta)^2 z^3 + 6\eta(1 - \eta)z^2 + 18\eta^2 z - 12\eta(1 + 2\eta) \quad (9)$$

The parameter  $\Gamma$  is the fundamental quantity in Ginoza's analysis. If  $\Gamma$  is expanded in powers of  $x$ ,

$$\Gamma = \sum x^n \Gamma_n \quad (10)$$

it was found that

$$\Gamma_0 = 0 \quad (11)$$

$$\Gamma_1 = -w/z \quad (12)$$

$$\Gamma_2 = -w^2(1 + 2z\psi)/z^3 \quad (13)$$

$$\Gamma_3 = -w^3(w + 6z\psi + 7z^2\psi^2)/z^5 \quad (14)$$

and

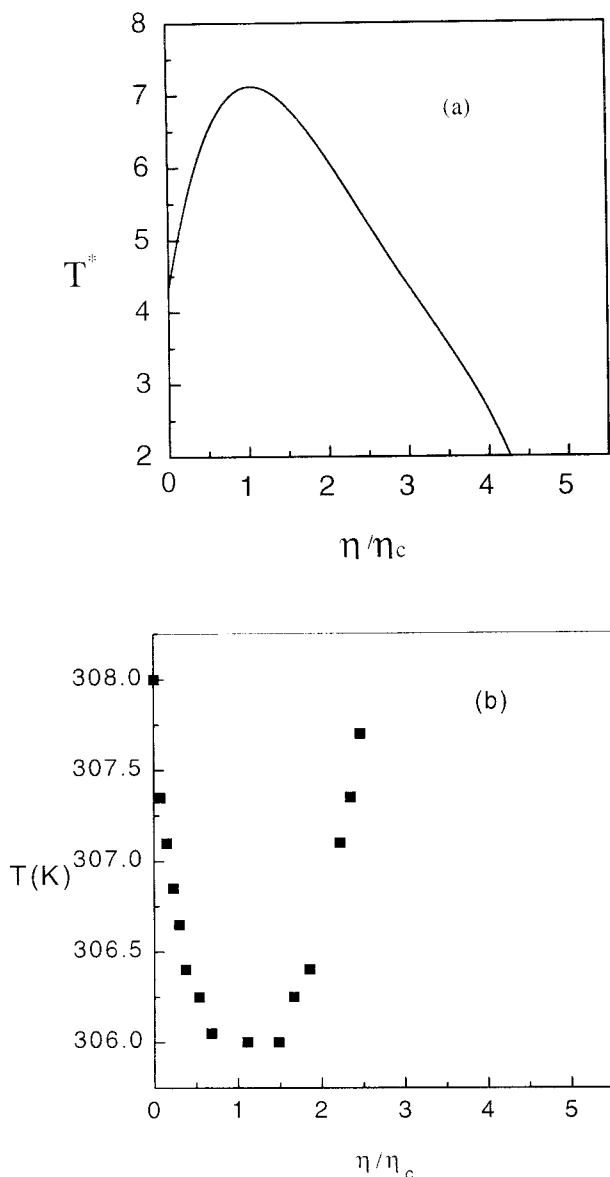
$$\Gamma_4 = -w^4(5 + 20z\psi + 36z^2\psi^2 + 30z^3\psi^3)/z^7 \quad (15)$$

Using those results, we find that eq. (3) can have only three parameters,  $x$ ,  $\eta$ , and  $z$ . That means  $T^*$  has a relationship with  $\eta$  at different  $z$  values. As a result, the plane of relation of  $T^* \sim \eta/\eta_c$  or  $T^* \sim \rho\sigma^3$  were given with different  $z$  values in Duh et al.<sup>21</sup>

## RESULTS AND DISCUSSION

We determined the values of Yukawa range parameter  $z$  and the parameters  $A$  and  $B$  (which govern the temperature-dependence of  $\varepsilon$ ), which make the theoretical temperature-volume fraction coexistence curve agree with the experimental LCST for the PNIPA–water mixture. Figure 1(b) plots the experimental lower consolute boundary (or LCST) for a PNIPA polymer–water mixture in the  $T$ – $\eta/\eta_c$  plane, where  $\eta$  is the volume fraction of the PNIPA, and  $\eta_c$  is the critical volume fraction. Figure 1(a) shows the phase diagram of a pure Yukawa fluid with a range  $z = 0.5$  plotted in the  $T^*$ – $\eta/\eta_c$  plane where  $T^* \equiv k_B T/\eta$ ,  $\eta = \sum_{i=1}^2 \pi\rho_i d_i^3/6$  and  $\eta_c (= 0.134$  for  $z = 0.5)$  is the critical volume fraction.<sup>14</sup> We compromise here by choosing  $z = 0.5$ ; at this value the coexistence curve exhibits a critical volume fraction,  $\eta_c = 0.134$ , which is reasonably close to the experimental value of  $\eta_c = 0.135$  for a PNIPA–water mixture. After the analysis of the experimental data, we find that the experimental value for  $\eta_c$ , 0.135, is nearly same as the value of pure Yukawa fluid. Since the  $\varepsilon$  used in obtaining the curve in Figure 1(a) has no functional dependence on temperature, the coexistence curve ends in an upper critical solution temperature. This can be converted into a curve ending in a lower critical solution temperature by introducing temperature dependence into  $\varepsilon$  of the form shown in eq. (2).

We chose values for parameters  $A$  and  $B$  to make the theoretical coexistence curve in Figure 1(a) agree with the experimental lower consolute bound-

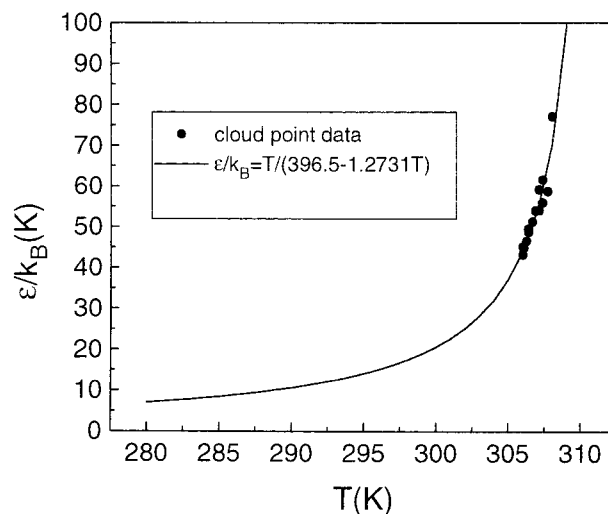


**Figure 1** (a) Coexistence curve in the temperature-reduced volume fraction plane for a Yukawa fluid with attractive well depth,  $\varepsilon$ , and range of  $z = 0.5$ . The temperature is expressed in dimensionless units,  $T^* = k_B T/\varepsilon$ ;  $\eta$  ( $= \pi \rho d^3/6$ ) is the hard sphere volume fraction, and  $\eta_c$  ( $= 0.134$ ) is the critical volume fraction. (b) Lower consolute phase boundary in the temperature-reduced volume fraction plane for a PNIPA-water solution. The data were obtained from the article of Oh et al.<sup>3</sup> The phase boundary has a critical volume fraction,  $\eta_c = 0.135$ .

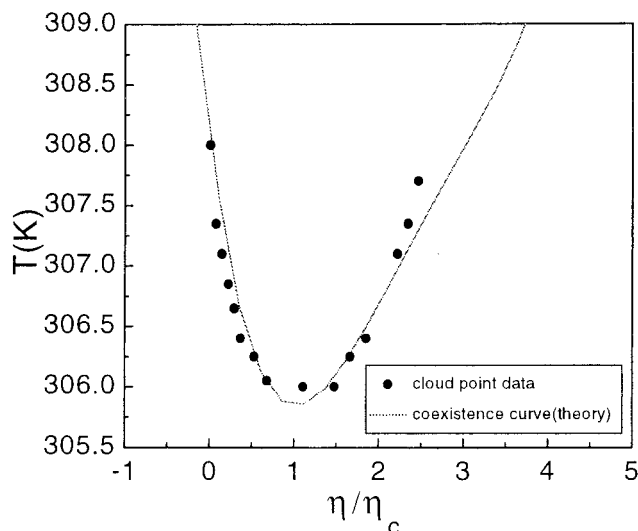
ary in Figure 1(b). At each data point ( $\eta/\eta_c$ ) appearing in Figure 1(b), we determined the associated value of  $T$  from Figure 1(b) and the value of

$T^* \equiv k_B T/\eta$  from Figure 1(a). In Figure 2 we plot the resulting relationship (filled circle) between  $\varepsilon/k_B$  ( $= T/T^*$ ) and  $T$  for each of the data points in Figure 1(b). We obtained values for  $A$  and  $B$  such that the functional dependence of  $\varepsilon/k_B$  on  $T$ , given by  $\varepsilon/k_B = T/(A - BT)$ , passes through these data points.

The solid line in Figure 2 shows that for values of  $A = 396.5$  and  $B = 1.2731$ , the  $\varepsilon/k_B$ -versus- $T$  plot (solid line) passes through the data points (filled circles). From Figure 2 it might at first seem that a linear line passing through the data points would provide the best fit. However, a linear plot through the data points would intersect the  $x$  axis at  $T \approx 302$  K, for which it can be inferred that for  $T \leq 302$  K the well depth  $\varepsilon/k_B = 0$ , or that there is no attraction between the subchains. In reality, at temperatures below the critical point, the attraction between the subchains decreases but does not become zero. We found that the fit of  $\varepsilon/k_B = T/(A - BT)$  incorporates the essential features of phase separation in PNIPA-water systems. At temperatures above the critical temperature there is a steep rise in  $\varepsilon/k_B$ , signifying a strong attraction between the CONH(CH<sub>3</sub>)<sub>2</sub> groups leading to phase separation, and at temperatures below the critical point there is a gradual decrease in  $\varepsilon/k_B$ , signifying a weaker attraction between the polymer chains because of increased hydrogen bonding between the —CONH(CH<sub>3</sub>) group and the water.



**Figure 2** The filled circles give the correspondence between  $\varepsilon/k_B$  and  $T$  (or alternatively between  $T^*$  and  $T$ ) for each data point in Figure 1 (b). The solid line is fitted to pass through the points and is used to represent the functional dependence of well depth,  $\varepsilon/k_B$ , on temperature,  $T$ .



**Figure 3** The circles represent the experimental lower consolute boundary [Fig. 1(b)], and the solid line represents the coexistence curve for a model Yukawa fluid obtained using the parameters  $z = 0.5$  and  $\varepsilon = k_B T / (396.5 - 1.2731T)$

The values for  $A$  and  $B$  determined above are used to obtain the theoretical  $T-\eta/\eta_c$  coexistence curve corresponding to the  $T^* = \eta/\eta_c$  coexistence curve shown in Figure 1(a). This is done by recognizing that the relationship  $\varepsilon/k_B = T/(A-BT)$  is equivalent to setting  $T^* = A-BT$  and then rescaling the  $T^* = \eta/\eta_c$  diagram by determining the  $T$  corresponding to each value of  $T^*$  in Figure 1(a). Figure 3 shows the resulting theoretical  $T$ -versus- $\eta/\eta_c$  coexistence curve, along with the experimental cloud point data for the PNIPA-water mixture. The fit between the theoretical phase diagram and experimental data is good except near the critical region, where the theory cannot predict the flattening of the cloud point data. This is probably because of the competition between the thermal and configurational entropies<sup>22</sup> or the strong specific interaction between polymer and solvent.<sup>23</sup>

Bae et al.<sup>24-25</sup> did similar researches for binary systems containing polymers. However, in their studies an extended Flory-Huggins equation is applicable to both vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE). They studied mainly the polymer-solvent interaction. In our present research, we mainly investigated the polymer-polymer interaction.

Since the critical volume fraction ( $\eta_c = 0.135$ ) of a PNIPA-water system is nearly similar to the

value of pure Yukawa fluid ( $\eta_c = 0.134$  for  $z = 0.5$ ), we chose  $z = 0.5$  for the PNIPA-water system. Therefore, the Yukawa potential of intersubchain attraction between PNIPA can be modeled as:

$$U_{22} = -\frac{\varepsilon}{(r/d_2)} \exp\left[-0.5\left(\frac{r}{d_2} - 1\right)\right] \quad r > d_2$$

$$\varepsilon = k_B T / (396.5 - 1.2731T)$$

The value of  $d_2$  can be determined by neutron scattering.

## CONCLUSIONS

The LCST behaviors of PNIPA were analyzed by the polymer-polymer attractive interactions, which were calculated by the temperature-dependent Yukawa potential according to the MSA model. After fitting the theoretical phase diagram for a pure Yukawa fluid to the experimental cloud point data, Yukawa parameters were determined. A new method to analyze the phase separation of PNIPA is suggested by this research.

The approach taken here was suggested by the work of Kenkare et al.<sup>14</sup>

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