

## Coexistence curve exponent of a binary mixture with a high molecular weight polymer

Kiwing To

*Institute of Physics, Academia Sinica, Taipei, Taiwan 115, Republic of China*

(Received 21 September 2000; published 23 January 2001)

We studied the effects of a high molecular weight polymer (polyacrylic acid, PAA,  $M_w = 7.5 \times 10^5$ ) on the coexistence curve of a binary liquid mixture (2,6-lutidine + water, LW). A high precision refractometer was built to measure the temperature dependence of the refractive indexes of the two coexisting phases of phase separated LW samples containing less than 1 mg/cc of PAA. From the refractive indexes we mapped out the coexistence curve and obtained the refractive index difference  $\Delta n$  between the two coexisting phases. At temperature  $T$  close to the critical temperature  $T_c$ , the critical exponent  $\beta$  such that  $\Delta n \propto (T - T_c)^\beta$  was found to be  $0.41 \pm 0.02$  which is higher than ( $0.31 \pm 0.01$ ) that of pure LW.

DOI: 10.1103/PhysRevE.63.026108

PACS number(s): 64.60.Fr, 64.70.Ja, 61.41.+e

Binary liquid mixture at its critical point has been one of the model systems for studying critical phenomena in which composition fluctuation plays an important role. When a third component is added, the ternary mixture may be treated as a binary mixture if the amount of the third component is small. However, the third component, which can be considered as impurity, may couple to the composition fluctuation and may affect the critical behavior of the binary mixture. For example, quenched impurities such as a gel network in a binary mixture may act like a random field [1] to the binary mixture. In this case, frozen dynamics and suppression of phase transition have been observed [2,3]. If the impurities are small molecules, the local fluctuations of the impurity concentration may shift the critical temperature as well as the critical concentration, and may even modify the critical exponents [4,5]. For mobile impurities consist of macromolecules that dissolve in a binary solvent approaching its critical point, when the size of the macromolecules is comparable to the correlation length of the solvent [6], the correlation length critical exponents  $\nu$  has been found to be 0.44 which is smaller than the three-dimensional (3D) Ising value (0.60) measured in the pure binary solvent. So far there is no theoretical explanation for the measured  $\nu$  which is even smaller than the mean-field value (0.5) observed in binary mixture of polymer blends [7]. Hence, it is possible that a binary liquid mixture with dissolved macromolecules may belong to a new universality class with a different set of critical exponents from those predicted by 3D Ising model or mean-field model.

To check if the other critical exponents are indeed affected by the presence of the macromolecules, we built a precision refractometer to measure the coexistence curve of the binary liquid mixture (2,6-lutidine+water, LW) with minute amount (less than 1 mg/cc) of dissolved high molecular weight polymer (polyacrylic acid, PAA) [6]. We found that when we approached the critical point of LW, the critical exponent  $\beta$  was indeed changed from the Ising value of 0.31 to 0.41 due to the presence of PAA.

Polyacrylic acid (PAA) of molecular weight  $M_w = 7.5 \times 10^5$  with polydispersity 1.4 and 2,6-lutidine of 99% purity were purchased from Aldrich. They were used as received. LW sample of critical composition (30% lutidine volume fraction) and aqueous PAA solution in 1 mg/cc con-

centration was prepared using deionized water from a Barnstead NANOpure II purification system. We added appropriate amount of pure water and 2,6-lutidine to the aqueous PAA solution to obtain a near critical LW/PAA sample in which the PAA concentration was 0.70 mg/cc. Then a second LW/PAA sample of 0.35 mg/cc PAA was obtained by diluting the first sample using pure LW mixture.

We put 2 cc of the LW/PAA sample together with a small teflon coated magnetic bar in a quartz couette cell (QC) of 1 cm<sup>2</sup> square cross section. The cell was then sealed and secured in a sample holder with a water submersible magnetic stirrer (MS) installed right below the quartz cell as shown in Fig. 1(a). The sample holder was placed in a temperature controlled water bath (WB) made of 2 cm thick transparent plexiglass with internal dimension of 36 cm×36 cm×36 cm. We mounted the sample holder such that it could be rotated about the vertical axis through the center of the couette cell. The bath temperature was sensed by a quartz probe ( $P$ ) of a precision thermometer (HP2804A) with an IEEE488 bus connected to a personal computer (PC). The PC read the temperature and sent back the appropriate heat to the water bath through a computer controlled power supply (PS) and an electric heater ( $H$ ). A stirrer ( $S$ ) was used to circulate the water in the bath to reduce the temperature gradient. With this setup the temperature of the water bath could be set as a designated value within  $\pm 0.0005$  °C.

Note that LW has a lower critical temperature  $T_c \approx 33.7$  °C. Hence our experiments were performed at temperatures above 33 °C when our samples had completely phase separated. At the beginning of an experiment, the magnetic stirrer was turned on for at least 30 minutes to thoroughly mix the two coexisting phases inside the quartz cell. Then the magnetic stirrer was turned off and the sample was let undisturbed until the two coexisting phases completely separated before the refractive indexes were measured.

In order to measure simultaneously the refractive indexes of both the water-rich phase and the lutidine-rich phase in the phase separated sample, a vertical laser sheet, obtained by a He-Ne laser beam passing through a line generator (LG), was directed to the sample cell as shown schematically in Fig. 1. Because of the difference in refractive index between the sample in the cell and the water in the

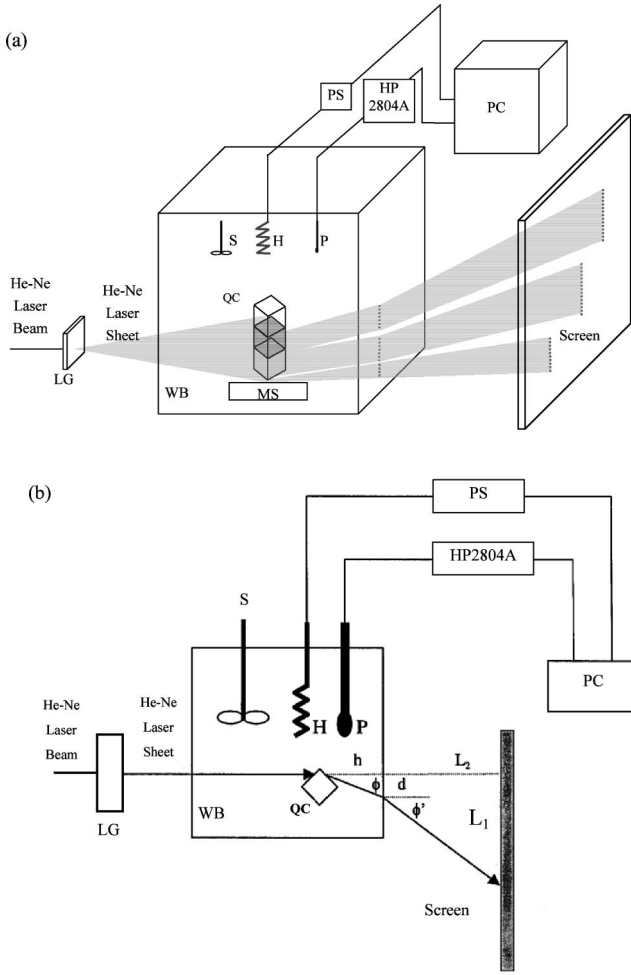


FIG. 1. Experimental setup: (a) schematic diagram of the precision refractometer and (b) schematic diagram showing the geometrical relations of the setup.

bath, the laser sheet was deviated by an angle  $\phi$  when it emerged from the sample cell. The laser sheet was further deviated to  $\phi'$  after refraction at the wall of the water bath. Finally it was intercepted by a screen placed at a distance  $L_2 = 36.5$  cm from the water bath. We rotated the sample holder until the deviation of the laser sheet was minimal at which  $\phi = \phi_m$  and then measured the location ( $L_1$ ) where the laser struck the screen. With a known value of the distance ( $h = 9$  cm) between the cell and the wall of the water bath, we can obtain the minimum angle of deviation  $\phi_m$  by solving the following geometrical relations numerically:

$$\frac{L_1 - d}{L_2} = \tan \phi',$$

$$d = h \tan \phi_m,$$

$$\sin \phi' = n_w \sin \phi_m,$$

Here  $n_w = 1.330$  is the refractive index of water in the bath and  $d$  is the distance between the locations where the refracted beam

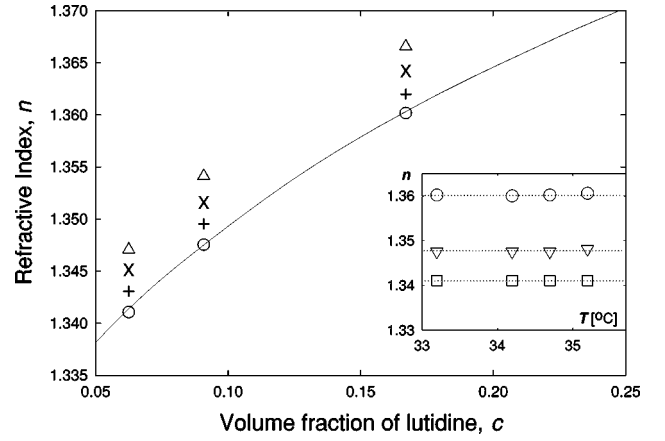


FIG. 2. The refractive index  $n$  for LW/PAA samples (approximately 1 mg/cc PAA) with different lutidine volume fraction  $c$  at  $T = 33.19$  °C ( $\circ$ ),  $34.19$  °C ( $+$ ),  $34.69$  °C ( $\times$ ), and  $35.19$  °C ( $\triangle$ ). For clarity,  $n$  for  $34.19$  °C,  $34.69$  °C, and  $35.19$  °C are shifted up by 0.002, 0.004, and 0.006, respectively. The inset shows the temperature dependence for samples with  $c = 0.06$  ( $\square$ );  $c = 0.09$  ( $\nabla$ );  $c = 0.17$  ( $\circ$ ). The lines in this figure are guide to the eyes only.

and the undeviated laser emerge from the bath as illustrated in Fig. 1(b). Then the refractive index of the sample is

$$n = \sqrt{2} n_w \sin \left( \frac{\phi_m}{2} + 45^\circ \right).$$

When the sample phase separated, the laser sheet passed through the coexisting phases of the sample so that the refractive indexes ( $n_1$  and  $n_2$ ) of both the coexisting phases (water-rich and lutidine-rich, respectively) could be measured simultaneously. Since part of the laser sheet did not pass through the sample cell at all, the reference point where the undeviated laser beam hit the screen could also be measured at the same time. Such arrangement reduced the systematic error due to the fact that the cross section of the couette may not be perfectly square [8]. We checked that the sensitivity of the refractometer on the change in refractive index was  $\pm 5 \times 10^{-4}$ .

Note that the refractive index  $n$  is a function of temperature  $T$ , the volume fraction of lutidine  $c$  and the concentration of PAA in the sample. Nevertheless, we found that the change in  $n$  due to increasing the concentration of PAA by 1 mg/cc is smaller than the sensitivity of our refractometer. Therefore we may consider  $n$  to be independent of the polymer concentration in our experiments. On the other hand,  $c$  depends on  $T$  also. Hence, the variation in  $n$  can be written as

$$\delta n = \frac{\partial n}{\partial c} \delta c + \frac{\partial n}{\partial T} \delta T = \left( \frac{\partial n}{\partial c} \frac{dc}{dT} + \frac{\partial n}{\partial T} \right) \delta T.$$

We found that when no phase transition occurred, i.e.,  $c$  remained constant, the temperature dependence of  $n$  was very weak and  $\partial n / \partial T < 10^{-3} \text{ } ^\circ\text{C}^{-1}$  as shown in the inset of Fig. 2. On the other hand, the refractive index measurement in Fig. 2 gives  $\partial n / \partial c \approx 0.2$ . Furthermore, the temperature dependence of composition is  $dc/dT \propto (T - T_c)^{\beta-1}$  which

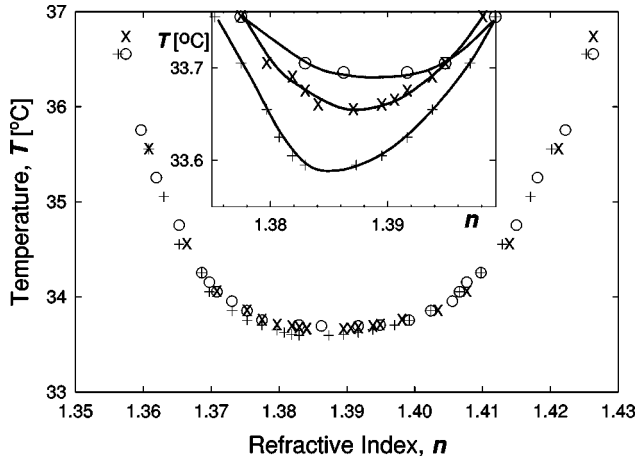


FIG. 3. Temperature dependence of the refractive indexes of the coexisting phases for pure LW ( $\circ$ ); LW/PAA with 0.35 mg/cc PAA ( $\times$ ); and LW/PAA with 0.70 mg/cc ( $+$ ). The inset shows the data close to the critical point in a finer scale. The lines in the inset are guide to the eyes only.

diverges towards the critical temperature because  $\beta - 1 < 0$ . Hence  $(\partial n / \partial c)(dc/dT) \gg (\partial n / \partial T)$  so that  $\delta n = (\partial n / \partial c)(dc/dT) \delta T$ . Therefore, the refractive index  $n$  can be taken as a direct measure of the composition  $c$  and the coexistence curve of our samples can be obtained by measuring the refractive indexes of the coexisting phases.

Let  $n_1, n_2$ , and  $c_1, c_2$  be the refractive indexes and the lutidine volume fractions of the lutidine-rich phase and the water-rich phase, respectively. Then the composition contrast  $c_1 - c_2$  will be proportional to the refractive index contrast  $n_1 - n_2$ . To check the validity of the above argument, we used the refractometer to measure the coexistence curve of a pure LW sample. From the temperature variation of the refractive index contrast between the coexisting phases we found the coexistence curve exponent  $\beta$  to be  $0.31 \pm 0.01$  which is consistent to the 3D Ising value. Hence, the refractometer indeed measures the temperature dependence of the composition for our samples.

Figure 3 summarizes the results of our experiments for the LW samples with 0.70 mg/cc and 0.35 mg/cc PAA. This figure shows the refractive indexes of the two coexisting phases of the LW/PAA sample. The data for the pure LW sample (i.e., 0 mg/cc PAA) measured by the same apparatus were also included for comparison. To see the differences of refractive indexes among samples of different PAA concentrations, we plotted the same data in a finer scale as shown in the inset of Fig. 3. From this figure, one can clearly see that the critical temperature of LW was shifted down approximately by  $0.03^\circ\text{C}$  and  $0.1^\circ\text{C}$  by adding 0.35 mg/cc and 0.70 mg/cc PAA, respectively. In addition, the critical composition  $c_c$  of LW was changed as indicated by the shift of the minima of the coexistence curves toward smaller  $n$  when PAA was added. Since the refractive index of water (1.330) is smaller than that (1.497) of 2,6-lutidine, the addition of PAA causes  $c_c$  to shift towards higher water fraction. Presumably, a water-rich wetting layer is formed close to the PAA molecules because water is a better solvent of PAA than lutidine. This would reduce the amount of water that

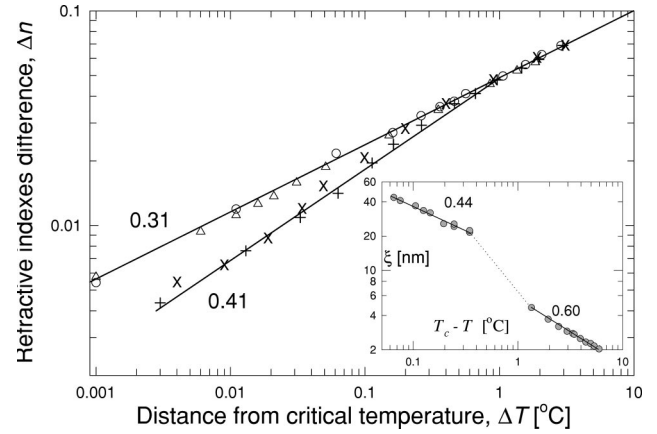


FIG. 4. Change of refractive index difference  $\Delta n$  between the two coexisting phases with respect to the distance from the critical temperature  $\Delta T$  for pure LW ( $\circ$ ); LW/PAA with 0.35 mg/cc PAA of  $M_w = 7.5 \times 10^5$  ( $\times$ ); LW/PAA with 0.70 mg/cc PAA of  $M_w = 7.5 \times 10^5$  ( $+$ ); and LW/PAA with 0.70 mg/cc PAA of  $M_w = 2 \times 10^3$  ( $\triangle$ ). The slopes of the straight lines in the plot are 0.31 and 0.41, respectively. The inset (data obtained from Ref. [6]) shows the correlation length  $\xi$  measured in LW with 0.7 mg/cc PAA. The slopes of the straight lines in this inset are 0.44 and 0.60, respectively.

take part in the phase separation of LW and hence, would explain the shift in  $c_c$  towards higher water fraction. Nevertheless, the shift in  $c_c$  by adding 0.35 mg/cc PAA was only of the order  $\delta n (\partial n / \partial c)^{-1} \sim 0.002/0.2 \sim 0.01$ . Such small shift in  $c_c$  and  $T_c$  was an indirect evidence that the amount of PAA added to LW was only small perturbation so that the LW/PAA samples in our experiments can be regarded as binary mixtures instead of a ternary mixtures.

When we plotted the refractive index difference  $\Delta n \equiv n_1 - n_2$  between the two coexisting phases with respect to the distance from the critical temperature  $\Delta T \equiv T - T_c$ , we found  $\Delta n \propto \Delta T^\beta$  with  $\beta = 0.31 \pm 0.01$  for pure LW as mentioned before. On the other hand, when PAA is added, one sees a crossover at  $\Delta T \approx 1^\circ\text{C}$  where  $\beta$  changes from 0.31 to  $0.41 \pm 0.02$  as shown in Fig. 4. Note that when the salt gadolinium nitrate is added to the binary mixture isobutyric acid+water, not only the critical temperature and the critical composition are shifted, the critical exponent  $\beta$  is also changed to 0.36 [5]. This is consistent with the Fisher renormalization [4] which predicts  $\beta$  to be increased by the factor  $1/(1 - \alpha)$ . Here  $\alpha = 0.11$  is the specific heat exponent. However, in our sample the increase in  $\beta$  due to Fisher renormalization is not large enough to explain the 33% increase in the critical exponent  $\beta$  of our high molecular weight LW/PAA sample. In order to confirm that the change in  $\beta$  is really due to the large molecular size of PAA, we repeated our experiment using LW/PAA sample containing the same amount (0.7 mg/cc) of PAA of smaller molecular weight ( $M_w = 2000$ ). The results are also plotted in Fig. 4 for comparison. We found that  $\beta$  for this sample with smaller molecular weight PAA is the same as that for the pure LW sample.

The crossover temperature at  $\Delta T \approx 1^\circ\text{C}$  can be understood if we consider the PAA molecules as fluctuations to the composition of LW. Then the length scale of such com-

position fluctuation should be the same order of the molecular size (the hydrodynamic radius,  $R_h$ ) of the PAA molecules. In fact, To and Choi [6] have already pointed out that it is the coupling between the critical composition fluctuation (with correlation length  $\xi$ ) of LW to the PAA molecules that lead to the change in the critical exponent  $\nu$  as shown in the inset of Fig. 4. Therefore, the effect will be most significant when  $\xi$  is comparable to  $R_h$ . Their work on the same system revealed that  $\xi \sim R_h$  when  $T_c - T \sim 1$  °C. This is consistent to our observation that a different value of the critical exponent  $\beta$  for the LW/PAA samples was obtained from data measured at temperature less than 1 °C from the critical temperature. For temperatures farther away from  $T_c$ , the refractive index differences of the two coexisting phases are the same for LW samples with and without PAA as shown in Fig. 4.

It is worth comparing the phase separation of our LW/PAA sample to that of polymer blends. In a study of the coexistence curve of polystyrene/poly(2-chlorostyrene) blends, Chu *et al.* [7] found that  $\beta=0.5$  which is the mean-field value. Intuitively a high molecular weight molecule, because of its large spatial extent, may be able to interact with a significant number of other molecules in a polymer blend. Such a mean-field-type interaction may be expected to give rise to the mean-field-type critical exponents. In the renormalization group theory, the Ising model will become mean-field type when the spatial dimension is 4 or higher. This can be interpreted as higher connectivity in higher di-

mension so that a molecule can interact with a large number of other molecules even with nearest neighbor interaction. On the other hand, the large PAA molecules in our LW/PAA sample may induce an indirect interaction between the water molecules and the lutidine molecules. Because of the large spatial extent of the macromolecules, such an indirect interaction will enable a water or a lutidine molecule to interact with a large number of other water and lutidine molecules. Hence,  $\beta$  increases towards the mean-field value when macromolecules (PAA) are added to the binary mixture (LW). Since a universality class in critical phenomenon is characterized by a set of critical exponents, different values of  $\beta$  and  $\nu$  implies that the binary mixture LW with dissolved macromolecules PAA may belong to a different universality class than that (3D Ising) of the pure LW. Hence, further works should be done towards this direction.

To summarize, we report our experimental studies on the critical exponent  $\beta$  of the coexistence curve for a binary liquid mixture (2,6-lutidine and water, LW) in the presence of dissolved macromolecules (polyacrylic acid, PAA). We found that the critical exponent  $\beta$  of LW changes from 0.31 to 0.41 when PAA of  $M_w = 7.5 \times 10^5$  was added.

The authors thank Dr. C. K. Chan and Dr. K. T. Leung for valuable discussions. This work has been supported by the National Science Council of Republic of China under Grant No. NSC88-2112-M-001-010.

- 
- [1] P.G. de Gennes, *J. Phys. Chem.* **88**, 6469 (1984).  
 [2] J.V. Maher, W.I. Goldberg, D.W. Pohl, and M. Lanz, *Phys. Rev. Lett.* **53**, 60 (1984).  
 [3] K.-Q. Xia, Ph. D. thesis, University of Pittsburgh, Pittsburgh, PA, 1987 (unpublished).  
 [4] M.E. Fisher, *Phys. Rev.* **176**, 1 (1968).  
 [5] M. Bouanz and D. Beysens, *Chem. Phys. Lett.* **231**, 105 (1994).  
 [6] K. To and H.J. Choi, *Phys. Rev. Lett.* **80**, 536 (1998).  
 [7] B. Chu, K. Linliu, Q. Ying, T. Nose, and M. Okada, *Phys. Rev. Lett.* **68**, 3184 (1992).  
 [8] K.-Q. Xia, *J. Chem. Phys.* **105**, 6018 (1996).