# Interfacial Tension of a Decomposed Biopolymer Mixture

E. Scholten,[†,‡] R. Tuinier,*[,†,§] R. H. Tromp,[§] and H. N. W. Lekkerkerker[†]

*Van 't Hoff Laboratory, Debye Research Institute, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands, and NIZO food research, P.O. Box 20, 6710 BA Ede, The Netherlands*

*Received September 14, 2001. In Final Form: November 26, 2001*

Many biological systems as well as food products contain both proteins and polysaccharides, which are often thermodynamically incompatible. In this communication, measurements are presented of the interfacial tension in a segregated polysaccharide/protein mixture. The interfacial tension is an important quantity in determining the phase separation kinetics and the response to shear. As the protein/polysaccharide system, an aqueous gelatin/dextran mixture in 1.0 M sodium iodide was chosen to suppress gelation and achieve a low density difference between the coexisting phases. First, the phase threshold was determined by making dilution lines. From the relative volumes of the coexisting phases, the location of the critical point was estimated. Interfacial tensions of phase-separated mixtures, varying in distance from the critical point, were measured using the spinning drop method. The interfacial tension close to the critical point was less than 1 $\mu$N/m, and it increased, in a nonlinear fashion, to a value of up to 20 $\mu$N/m farther from the critical point. For the scaling relation of the interfacial tension with the density difference and the polymer concentration difference, we found scaling exponents of $2.7 \pm 0.3$ and $1.5 \pm 0.1$, respectively, which are in agreement with the critical mean-field scaling exponents of 3 and 3/2, respectively.

## 1. Introduction

In biological and food systems, polysaccharides and proteins are often jointly present. When a certain concentration of these biopolymers in the mixture is exceeded, phase separation often results.[1] When the polysaccharides are charged and the pH is such that the two biopolymers are oppositely charged, complexation can be responsible for decomposition. Alternatively, segregation of effectively repulsive biopolymers (equally charged or uncharged) can take place. In the latter situation, each phase becomes enriched in either polysaccharide or protein. During the past decade, a significant amount of work has been performed on studying the stability of polysaccharide/protein mixtures, as well as developing quantitative descriptions of the phase boundaries; see ref 2 for a recent review. These studies contribute to an understanding of the concentrations at which, and the conditions under which, phase separation processes are expected to occur. If phase separation takes place, the driving force for decomposition must overcome the accompanying increase in interfacial free energy, which equals the product of the interfacial tension and the total interfacial area associated with the phase separation. Therefore, the interfacial tension between the coexisting phases of the decomposed polysaccharide/protein system is of fundamental interest. The order of magnitude of the interfacial tension can be estimated from the scaling relation $\gamma = O(kT/\xi^2)$,[3−5] where $\gamma$ is the interfacial tension and $\xi$ is the width of the region in which the concentration of the components differ from their bulk values in the coexisting phases. The interfacial width is supposed to have a value of a few molecular diameters. Biopolymers usually have sizes in the range of 5−100 nm, corresponding to a range of interfacial tension of 1−100 $\mu$N/m. These values are extremely small in comparison with values for the interfacial tension between gases and liquids of atoms or low-molecular-mass substances, which lie between 1 and 100 mN/m. In addition to being a quantity that is of fundamental interest, the interfacial tension is also one of the key parameters that influences the phase separation rate.[6−9] Irrespective of whether one focuses on the spinodal decomposition,[6,7] the stability of a film between two droplets,[8] or the breakup of a liquid cylinder,[9] the interfacial tension always plays a central role.

Several studies[10−15] have been directed at analyzing and interpreting the interfacial tension in demixed polymer solutions. The magnitude of the interfacial tension depends on how far the system deviates from the critical point, near which values as small as 1 $\mu$N/m have been reported.[10,11] Critical exponents were determined and found to be quite reproducible for homopolymers, which led Heinrich and Wolf to propose a master curve for polystyrene.[11] Recently, however, for random copolymers,

* Corresponding author. Present affiliation: Forschungszentrum Jülich, Institut für Festkörperforschung, Weiche Materie, 52425 Jülich, Germany. Electronic mail: r.tuinier@fz-juelich.de.

† Debye Research Institute.

‡ Present affiliation: Food Physics, Department of Food Technology and Nutritional Sciences, Wageningen University, Bomenweg 2, 6703 HD Wageningen, The Netherlands.

§ NIZO food research.

(1) Grinberg, V. Y.; Tolstoguzov, V. B. *Food Hydrocolloids* **1997**, *11*, 145.

(2) Doublier, J.-L.; Garnier, C.; Renard, C.; Sanchez, C. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 184.

(3) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(4) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon Press: Oxford, U.K., 1984.

(5) Vrij, A. *Physica A* **1997**, *235*, 120.

(6) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.

(7) Verhaegh, N. A. M.; Lekkerkerker, H. N. W. Phase transitions in colloidal suspensions. In *Proceedings of the International School of Physics 'Enrico Fermi'*; IOS Press: Amsterdam, 1997.

(8) Ivanov, I. B.; Kralchevsky, P. A. *Colloids Surf. A* **1997**, *128*, 155.

(9) de Hoog, E. H. A.; Lekkerkerker, H. N. W. *J. Phys. Chem. B* **2001**, *105* (47), 11636 Lekkerkerker, H. N. W.; de Hoog, E. H. A. *Physica A* **2001**, *298*, 69.

(10) Shinozaki, K.; van Tran, T.; Saito, Y.; Nose, T. *Polymer* **1982**, *23*, 728.

(11) Heinrich, M.; Wolf, B. A. *Polymer* **1992**, *33*, 1926.

(12) Heinrich, M.; Wolf, B. A. *Macromolecules* **1992**, *25*, 3817.

(13) Enders, S.; Huber, A.; Wolf, B. A. *Polymer* **1994**, *35*, 5743.

(14) Enders, S.; Wolf, B. A.; Binder, K. *J. Chem. Phys.* **1995**, *103*, 3809.

(15) Schneider, A.; Wolf, B. A. *Polymer* **2000**, *41*, 4089.

10.1021/la0114373 CCC: $22.00 
Published on Web 02/21/2002

significant differences in the critical exponents of various systems have been found.[15]

The interfacial tension of decomposed polysaccharide/protein mixtures is, in contrast to the phase stability of these systems, an aspect to which limited attention has yet been paid. Tolstoguzov et al.[16] measured the interfacial tension of gelatin/dextran aqueous mixtures using a capillary rise method and reported a value of 27 $\mu$N/m. Wolf et al.[17] applied shear to a phase-separated aqueous gellan/$\kappa$-carrageenan mixture, and from the shape of the droplets, they estimated an interfacial tension of 7.5 $\pm$ 1.4 $\mu$N/m. Using the same method, Stokes et al.[18] measured the interfacial tension of the interface in a phase separated gelatin/maltodextrin system, resulting in values in the range of 50$-$100 $\mu$N/m. These reported values correspond to the expected order of magnitude.

Here, we present measurements of the interfacial tension of the interface between the phases in a decomposed gelatin/dextran mixture in 1.0 M sodium iodide. Recent investigations suggest[19] that the phase separation in gelatin/dextran mixtures is mainly entropy-driven. The protein gelatin is frequently used in low fat products or as a binder in yogurt, and it is a material that makes it possible to encapsulate (pharmaceutical) ingredients in capsules having a neutral taste. Gelatin is obtained from the fibrous protein collagen, extracted mainly from bones or hides of various animals, using chemical/thermal processing. It is able to undergo a conformational coil/helix transition, where chains in the helix conformation can form reversible gels.[20] Dextran is a polysaccharide produced by the bacterium *Leuconostoc mesenteroides*, which, after its discovery in the 19th century, became of significance as a thickener in the food industry. Most dextrans mainly consist of $\alpha(1\rightarrow6)$ linked glucoses and a small fraction of the glucoses linked via $\alpha(1\rightarrow3)$ bonds. Both gelatin and dextran are approved food ingredients.

Sodium iodide was used as a salt to suppress gelatin gelation as well as to achieve a small density difference between the coexisting phases; iodide has a higher affinity to bind to gelatin than to dextran, thereby making the (upper) gelatin-rich phase heavier. We used the spinning drop method for measuring the interfacial tensions. It has been demonstrated that this method is well-suited for measuring very low interfacial tensions.[21] The spinning drop method has been used successfully in recent years to determine the interfacial tensions in demixed colloid/polymer mixtures,[22$-$24] yielding tensions with values of a few micronewtons per meter.

## 2. Experimental Section

**Materials.** A purified low-molar-mass fraction of gelatin was a gift from DFG-Stoess, Germany, and dextran was purchased from Fluka. The molar mass (distribution) of the samples was determined using a combination of size-exclusion chromatography (SEC) and multi-angle laser light scattering (MALLS) at NIZO Food Research, as described in refs 25 and 26. The gelatin had a number-average molar mass, $M_n$, of 24 kg/mol and a weight-averaged molar mass, $M_w$, of 41 kg/mol, resulting in a polydispersity, expressed as $M_w/M_n$, of 1.7. The investigated dextran sample had a number-average radius of gyration ($R_g$) in aqueous solution of 20 $\pm$ 1 nm, a $M_n$ of 260 kg/mol, and a $M_w$ of 387 kg/mol ($M_w/M_n$ = 1.49).

**Methods.** *Preparation of the Polysaccharide/Protein Mixtures.* Both gelatin and dextran were simultaneously dissolved in 1.0 M sodium iodide (NaI). Sodium azide (0.03%) was added as an antimicrobial agent. The mixtures, which had a pH of 6.0, were kept at room temperature for at least 1 h, after which the samples were heated to 60 °C and kept at that temperature for 30 min. They were then vigorously shaken to obtain a homogeneous mixture. All subsequent experiments were made at room temperature.

*Spinning Drop Method.* To measure the interfacial tension of the gelatin/dextran mixtures, a spinning drop tensiometer was used,[22,23] which included a spinning drop tube with a diameter of 4 mm and a length of 4 cm (see ref 23 for details). The high-density (dextran-rich) phase, with a volume of ~1 mL, was injected into the spinning drop tube, which was closed on one side with a Teflon stopper, using a glass capillary. The volume of the low-density droplets, injected with a microsyringe, was 1$-$2 $\mu$L. Subsequently, the tube was inserted into the tensiometer and rotated about its axis. Thus, a centrifugal field was applied to deform the low-density droplet in the high-density matrix. The applied spinning frequency was high enough that the drop was spinning sufficiently fast about its horizontal axis to neglect acceleration due to gravity. In the centrifugal field, the drop was elongated along the rotational axis until a certain equilibrium deformation was achieved where the Laplace pressure over the interface was balanced by the centrifugal pressure. At sufficiently high rotational speeds, the length of the droplet will exceed four times the droplet diameter, and it follows[27] that the droplet will closely resemble a cylinder with spherical caps. In that case, the Vonnegut equation will be valid[28]

$$\gamma = \frac{\Delta\rho\omega^2 R^3}{4} \qquad (1)$$

where $\omega$ is the spinning frequency, $R$ is the radius describing the curvature on the outside of the elongated droplet, and $\Delta\rho$ is the density difference between the coexisting phases. It was always verified during the measurements that the droplet had a length that exceeded 8$R$. To determine the interfacial tension, at least three droplets were spun several times at five or six frequencies. The rotational speeds were measured with an optical sensor, and the observed dimensions (length and diameter) of the elongated droplets were measured with a micrometer. As a result of the curvature of the tube, the dimensions of the droplet are slightly different from its actual size.[29] The actual droplet radius, $R_d$, was calculated from the apparent drop radius, $R_{da}$, as $R_d = R_{da}n_a/n_1$, where $n_1$ and $n_a$ are the refractive indices of the liquid surrounding the drop and of the phase outside the tube, respectively. The refractive index of the high-density phase was determined using a refractometer. After each measurement, the rotational speed was increased, and the droplet was allowed to deform for about 1 h, after which the shape of the droplet no longer changed. Compared to previous reports,[22,23] the equilibration time required here was very small. This allowed the measurements at different rotational speeds to be carried out within a relatively short period of time.

*Construction of the Phase Diagram.* Samples were prepared that segregated and diluted with solvent (1.0 M NaI). In this way, the gelatin/dextran ratio was held constant. After dilution, the solution was mixed and shaken, and it was then investigated whether the samples still phase-separated. Below a certain total

(16) Tolstoguzov, V. B.; Mzhel'sky, A. I.; Gulov, V. Ya. *Colloid Polym. Sci.* **1974**, *252*, 124.
(17) Wolf, B.; Scirocco, R.; Frith, W. J.; Norton, I. T. *Food Hydrocolloids* **2000**, *14*, 217.
(18) Stokes, J. R.; Wolf, B.; Frith, W. J. *J. Rheol.* **2001**, *45*, 173.
(19) Edelman, M. W.; van der Linden, E.; de Hoog, E.; Tromp, R. H. *Biomacromolecules* **2001**, *2*, 1148.
(20) Normand, V.; Muller, S.; Ravey, J.-C.; Parker, A. *Macromolecules* **2000**, *33*,1063.
(21) Kegel, W. K.; van Aken, G. A.; Bouts, M. N.; Lekkerkerker, H. N. W.; Overbeek, J. Th. G.; de Bruin, P. L. *Langmuir* **1993**, *9*, 252.
(22) Vliegenthart, G. A.; Lekkerkerker, H. N. W. *Prog. Colloid Polym. Sci.* **1997**, *105*, 27
(23) de Hoog, E. H. A.; Lekkerkerker, H. N. W. *J. Phys. Chem. B* **1999**, *103*, 5274.
(24) Chen, B.-H.; Payandeh, B.; Robert, M. *Phys. Rev. E* **2000**, *62*, 2369.
(25) Hoffmann, M. A. M.; Sala, G.; Olieman, C.; de Kruif, C. G. *J. Agric. Food Chem.* **1997**, *45*, 2949.
(26) Tuinier, R.; Ten Grotenhuis, E.; de Kruif, C. G. *Food Hydrocolloids* **2000**, *14*, 1.
(27) Vonnegut, B. *Rev. Sci. Instrum.* **1930**, *13*, 6.
(28) Princen, H. M.; Zia, I. Y. Z.; Mason, S. G. *J. Colloid Interface Sci.* **1967**, *23*, 99.
(29) Coucoulas, L. M. *J. Colloid Interface Sci.* **1983**, *93*, 281.

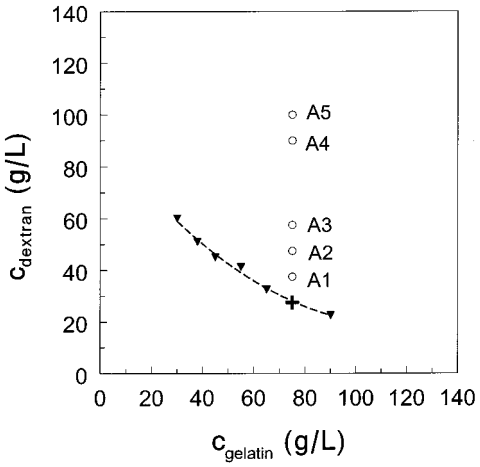


**Figure 1.** Phase diagram of mixture of gelatin and dextran in 1.0 M NaI. Solid triangles indicate the estimated phase threshold values along a dilution line. The estimated critical point is identified by the cross (+). The open circles refer to mixtures for which, after phase separation, the interfacial tension has been measured.

**Table 1. Interfacial Tension, Concentration, and Density Difference for the Gelatin/Dextran Phase-Separated Mixtures Presented as Open Circles in Figure 1**

| sample number | gelatin concentration (g/L) | dextran concentration (g/L) | $\Delta\rho$ (g/L) | $\gamma$ ($\mu$N/m) |
|---|---|---|---|---|
| A1 | 75.1 | 37.6 | $1.1 \pm 0.1$ | $0.5 \pm 0.1$ |
| A2 | 74.8 | 47.5 | $1.8 \pm 0.1$ | $2.4 \pm 0.3$ |
| A3 | 75.2 | 57.6 | $2.7 \pm 0.1$ | $5.9 \pm 0.5$ |
| A4 | 75.2 | 90.0 | $4.0 \pm 0.1$ | $15.7 \pm 0.7$ |
| A5 | 75.0 | 100.0 | $4.1 \pm 0.1$ | $19.3 \pm 0.8$ |

biopolymer concentration, the mixtures remained homogeneous. The threshold concentrations were then taken to be situated halfway between the lowest separating and highest nonseparating compositions. In the dilution series, steps of 5−10 g/L were made.

*Density Measurements.* The densities of the both phases of the decomposed system were determined with an Anton Paar DMA 5000 density meter. The difference in density between the two phases is required for the interfacial tension to be calculated, as well as for the (critical) scaling behavior to be studied. The densities of the samples were measured at least four times to also determine the statistical error.

## 3. Results and Discussion

**Phase Behavior of Gelatin/Dextran Mixtures.** Aqueous systems of gelatin/dextran in 1.0 M NaI at sufficient concentrations show phase separation into two clear fluid phases, separated by a sharp interface.[19,30] The upper phase is (relatively) concentrated in gelatin, and the lower phase is enriched in dextran. The interface can be described as appearing sharp to the eye. The phase-diagram was constructed along the dilution lines by determining the concentrations above which phase transition takes place. For gelatin/dextran mixtures in 1.0 M NaI, the resulting phase diagram is plotted in Figure 1. In this figure, the solid triangles refer to those points on the dilution line where the stability threshold is crossed. The cross (+) refers to the estimated critical point, determined from the position at the threshold where the volumes of the coexisting phases are equal. An estimation of the overlap concentration, $c^*$, of dextran can be made using the weight-average molar mass of 387 kg/mol and the average radius of gyration of 20 nm to give $c^* \approx 19$ g/L. The dextran concentration at the phase line in Figure 1 lies above this value for the samples investigated which indicates that phase separation takes place in the semidilute range of dextran concentrations. The phase diagram was constructed to determine the critical point, which is required to study the density difference and concentration dependence of the interfacial tension.

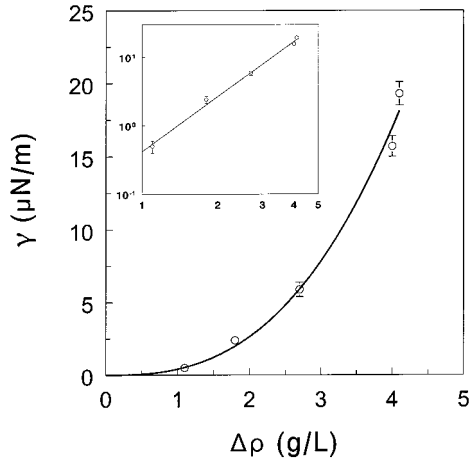


**Figure 2.** Interfacial tension of the systems referred to in Figure 1 as a function of the density difference. The drawn curve is the best fit to the scaling relation $\gamma = q(\Delta\rho)^p$ (see text). The scaling relation is plotted logarithmically in the inset.

**Interfacial Tension Data.** To determine the interfacial tension, samples were allowed to phase separate, and the coexisting phases were then put into the spinning drop tensiometer, as described in section 2. An overview of the results of the measurements made, including the statistical error in the measured quantities, is given in Table 1. The interfacial tensions were calculated with eq 1.

Because $\Delta\rho \equiv 0$ at the critical point, the value for the density difference, $\Delta\rho$, is indicative of the quench depth, i.e., how far the system is from the critical point. For the gelatin/dextran system, the gelatin concentration was kept constant, and only the dextran concentration was varied to simplify the analysis. Because the density differences were small (on the order of grams per liter), the rotational speeds had to be very high (at least 250 rad/s) to deform the droplets such that they were sufficiently elongated. As can be seen in Table 1, the interfacial tension close to the critical point is very small, namely, $0.5 \pm 0.1$ $\mu$N/m for system A1 in Table 1. This value increases to values of $\sim$20 $\mu$N/m farther from the critical point. These values are smaller than those reported by Stokes et al.[18] and can be explained by the fact that the maltodextrin they used had a relatively low molar mass. Theoretically, an estimate of the interfacial tension can be obtained from the scaling relation $\gamma \sim kT/\xi^2$.[3−5] For the size of the molecules involved here, we can take the dextran radius of gyration to estimate the order of magnitude of the interfacial tension. For $R_g = 20$ nm (the average value for dextran), we find at 298 K an estimate for the interfacial tension of $\sim$10 $\mu$N/m, which corresponds to the magnitude of the values found in the gelatin/dextran systems investigated, as reported in Table 1.

**Interfacial Tension, Scaling Behavior.** The set of data we obtained allows us to investigate the scaling behavior of the gelatin/dextran system. The effect of deeper quenching was studied by increasing the overall dextran concentration while keeping the overall gelatin concentration constant. In Figure 2, we plot the interfacial tension

(30) Tromp, R. H.; Rennie, A. R.; Jones, R. A. L. *Macromolecules* **1995**, *28*, 4129.

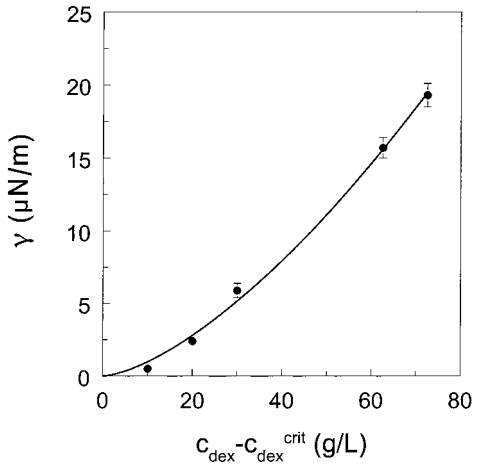


**Figure 3.** Interfacial tension of the systems referred to in Figure 1 as a function of the difference of the dextran concentration from that at the critical point. The full curve is a best fit of the scaling relation $\gamma = a(c_{dex} - c_{dex}^{crit})^b$ (see text).

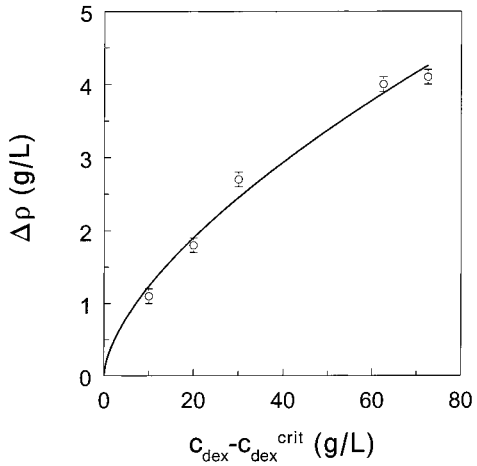


**Figure 4.** Density difference as a function of the difference of the dextran concentration from that at the critical point.

as a function of the density difference, $\Delta\rho$, between the coexisting phases. The dependence of $\gamma$ on $\Delta\rho$ is nonlinear. The data were fitted to the relation $\gamma = a(\Delta\rho)^b$, for which $a = 0.4 \pm 0.2$ and $b = 2.7 \pm 0.3$ were found as best-fit parameters (see the fit in Figure 2). The scaling exponent of $2.7 \pm 0.3$ is close to that given by the mean-field relation[4]

$$\gamma \sim (\Delta\rho)^3 \tag{2}$$

The Ising model predicts a value of 3.88,[4] which is significantly larger than the value we found. For a demixed polystyrene solution, Shinozaki et al.[10] and Heinrich and Wolf[11] reported values of 3.3−3.9 for the critical exponent, which agrees well with the Ising model. Schneider and Wolf, however, recently found[15] for random copolymers that the critical exponent can vary from 2.5 to 4.6. These latter findings were explained in terms of a more suitable way of arranging the copolymer monomeric units in the interface. Because gelatin is a copolymer as well, deviations from the Ising critical exponent are to be expected.

For the case of depletion-induced phase separation of a colloid/polymer mixture, Brader and Evans[31] performed density functional theory calculations of the interface. In their osmotic equilibrium theory, the investigated system was held in equilibrium with a hypothetical reservoir that contained only polymer. Their results for the interfacial tension correspond to eq 2.

They also investigated the scaling of the interfacial tension with the polymer concentration in the reservoir and found the relationship

$$\gamma \sim (c_p^R - c_p^{R,crit})^{3/2} \tag{3}$$

where $c_p^R$ ($c_p^{R,crit}$) is the (critical) polymer concentration in the reservoir. In our experimental system, it is hard to determine the effective free volume for the polymers. Therefore, we can only compare these scaling results for the polymer reservoir concentration ($c_p^R - c_p^{R,crit}$) with ($c_{dex} - c_{dex}^{crit}$), where $c_{dex}^{crit}$ is the concentration of dextran in the critical point, for the data points in the phase diagram of Figure 1. Results for the interfacial tension as a function of ($c_{dex} - c_{dex}^{crit}$) are plotted in Figure 3. Obviously, the dependence is again rather nonlinear. The curve was fitted to the scaling relation $\gamma = q(c_{dex} - c_{dex}^{crit})^p$, for which the best-fit values are $q = 0.033 \pm 0.002$ and $p = 1.5 \pm 0.1$ (the fit is plotted as the full curve). The exponent of 1.5 matches the theoretical result of 3/2.

For the interface of a critical mixture, there is also a scaling relation for the concentration difference with the critical point concentration (denoted as $\Delta c$) and the density difference, $\Delta\rho$, namely, $\Delta\rho \sim (\Delta c)^z$, with $z = 0.5$ in a mean-field approach (combining eqs 2 and 3) and $z = 0.32$ for the Ising model. In Figure 4, we plot $\Delta\rho$ as a function of $c_{dex} - c_{dex}^{crit}$, which we take as $\Delta c$. From the experimental data, it follows that $z = 0.55 \pm 0.10$, which is in agreement with the mean-field value but above the Ising model prediction. For all determined scaling exponents, we thus find that the experimental results agree with mean-field critical scaling predictions. Odijk[32] argued that, for a mixture of small proteins and large polymers, a mean-field description suffices. This might explain why the results presented for the interface can be described by a mean-field theory as well.

Care should be taken, however, when comparing the measured scaling exponent data with theoretical values. First, there is some uncertainty in the location of the critical point; it is not certain whether there is a well-defined critical point for a decomposed mixture of two polydisperse biopolymers. The critical point will be a projection of a critical line in the phase diagram with a high dimensionality onto a two-dimensional plot. Further, the determination of the critical point was made using an operational definition: the location at the threshold where the volumes of the coexisting phases are equal. Another issue that might explain discrepancies is that the quench depth at which the exponent is determined might differ from the region that is sufficiently close to the critical point to expect critical (scaling) behavior.

The dependence of the interfacial tension on the density difference differs from the results obtained using a model colloid/polymer mixture by De Hoog and Lekkerkerker.[23] They found an approximately linear dependence of $\gamma$ on $\Delta\rho$, which can be explained by the fact that the relative density difference was very large in their system, indicating that their system is relatively farther from the critical point. From the results of Chen et al.,[24] it follows that the exponent is close to 3.5, which is between the mean-field (3) and Ising model predictions (3.88). An important issue here is determining which system is closest to the critical point. To quantify the distance from the critical point, the density difference $\Delta\rho$ can be normalized by the density at

(31) Brader, J. M.; Evans, R. *Europhys. Lett.* **2000**, *49*, 678.

(32) Odijk, T. *Macromolecules* **1996**, *29*, 1842; *Physica A* **2000**, *278*, 347.

the critical point, $\rho^{crit}$. The densities of dextran, gelatin, and the 1.0 M NaI solvent could be estimated from the density measurements as 1605, 1367, and 1110 g/L, respectively, giving an estimation for the density at the critical point of ~1150 g/L. This means that $\Delta\rho/\rho^{crit}$ is always smaller than 0.005, whereas the values for $\Delta\rho/\rho^{crit}$ in the systems of both De Hoog and Lekkerkerker[23] and Chen et al.[24] were in the range from about 0.1 to 0.4. The measurements on the decomposed gelatin/dextran mixture reported here are, therefore, relatively closer to the critical point. The determination of the scaling exponents allows the scaling relations to be used to describe, for instance, the phase separation kinetics and response to shear of (phase-separating) gelatin/dextran mixtures.

## 4. Conclusions

Using the spinning drop method, the interfacial tension of phase separated gelatin/dextran mixtures was determined. The interfacial tension close to the critical point was determined to be close to 1 $\mu$N/m, and it increased to values of 20 $\mu$N/m farther from the critical point. From these measurements, we can conclude that the magnitudes of the interfacial tension can be compared with those found in phase-separated model colloid/polymer and polymer mixtures and that these values are low compared to those for an atomic gas/liquid interface (1−100 mN/m). The scaling behavior of the interfacial tension close to the critical point was compared with theoretical predictions. Experimental scaling exponents were in reasonable agreement with critical mean-field values.

**Acknowledgment.** This work was sponsored by the NWO-Unilever program. Special purified gelatin fractions were kindly supplied by DFG-Stoess. We are indebted to M. W. Edelman, E. H. A. de Hoog, and A. Vrij for useful discussions and to S. R. Williams and E. ten Grotenhuis for a critical reading of the manuscript. E. Sallomons, C. Pathmamanoharan, and J. Suurmond are thanked for technical assistance. R.T. thanks H. J. Klok and C. G. de Kruif for helpful discussions on the gelatin/dextran system.

LA0114373