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ABSTRACT

The role of intramolecular interactions in blend miscibility is well documented for polymer+copolymer mixtures (ten Brinke et al., 1983; Paul and Barlow, 1984). Some copolymer+polymer mixtures are miscible although their corresponding homopolymers are not miscible; for example, over a range of acrylonitrile content, styrene/acrylonitrile copolymers are miscible with poly(methyl methacrylate) but neither polystyrene nor polyacrylonitrile is miscible with poly(methyl methacrylate). Similarly, over a composition range, butadiene/acrylonitrile copolymers are miscible with poly(vinyl chloride) while none of the binary combinations of the homopolymers [polybutadiene, polyacrylonitrile, and poly(vinyl chloride)] are miscible. This behavior has been attributed to "intramolecular repulsion" between unlike copolymer segments.

We have observed similar behavior in vapor-liquid equilibria (VLE) of copolymer+solvent systems. We find that acrylonitrile/butadiene copolymers have higher affinity for acetonitrile solvent than do polyacrylonitrile or polybutadiene. We attribute this non-intuitive behavior to "intramolecular repulsion" between unlike segments of the copolymer. This repulsive interaction is weakened when acetonitrile molecules are in the vicinity of unlike copolymer segments, favoring copolymer+solvent miscibility. We find similar behavior when acetonitrile is replaced by methyl ethyl ketone. To our best knowledge, this effect has not been reported previously for VLE.

We have obtained VLE data for mixtures containing a solvent and a copolymer as a function of copolymer composition. It appears that, at a given solvent partial pressure, there may be copolymer composition that yields maximum absorption of the solvent. This highly non-ideal VLE phase behavior may be useful for optimum design of a membrane for a separation process.

1. INTRODUCTION

Vapor-liquid equilibria (VLE) in polymer+solvent systems are necessary for a variety of applications including surface acoustic-wave vapor sensors (Ballantine and Wohltjen, 1989; Grate et al., 1992); recovery of organic vapors from waste-air streams using a polymeric membrane (Baker et al., 1987; Matsumoto et al., 1991); pervaporation (Maeda et al., 1991), and other polymeric membrane-separation processes; polymer devolatilization (High and Danner, 1990); vapor-phase photografting (Kubota et al., 1990); and for optimum formulation of paints and coatings (Napper, 1983). For rational process and product design, we require experimental data and correlations based on molecular thermodynamics.

Copolymers are gaining increasing commercial interest because of their unique physical properties. Recently, we published sixty-six isothermal data-sets for VLE data for copolymer+solvent and homopolymer+solvent systems (Gupta and Prausnitz, 1995).

The purpose of this work is to examine the "intramolecular repulsion" effect on VLE of copolymer+solvent solutions. To our knowledge, such studies have not been previously reported in the literature. However, there have been many studies reporting the effect of "intramolecular repulsion" on polymer-blend miscibility.

It is well known that high-molecular-weight polymers are, in general, only miscible if there is a favorable specific interaction between them. Specific intermolecular interactions, such as hydrogen bonding (Brown and Obremski, 1984; Coleman and Painter, 1984; Coleman et al., 1991) and donor-acceptor complex formation, can lead to the negative enthalpy of mixing necessary to obtain miscible homopolymer blends (Olabisi at al., 1979). However, in copolymer-containing blends a different situation exists; miscible blends can be obtained without specific intermolecular interactions. Miscibility may be caused by an "intramolecular repulsion"

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effect that originates from unfavorable interactions between different segments of the random copolymer (ten Brinke et al., 1983; Paul and Barlow, 1984; Kammer, 1986). Thus, miscibility may occur in a homopolymer+copolymer blend even if all three respective homopolymer pairs are immiscible. All these cases have one thing in common: at least one of the components is a random copolymer. Styrene/acrylonitrile (SAN's) copolymers are miscible with poly(methyl methacrylate) PMMA (Stein el al., 1974) and with poly(ethyl methacrylate) PEMA (Chiou et al., 1982) over a range of acrylonitrile content but neither polystyrene nor polyacrylonitrile is miscible with PMMA or PEMA (Paul and Barlow, 1984). Ethylene/vinyl acetate copolymers (EVA's) are miscible with poly(vinyl chloride) PVC over a range of vinyl acetate content (Hammer, 1971) but neither polyethylene nor poly(vinyl acetate) is miscible with PVC. Over a composition range, butadiene/acrylonitrile copolymers are miscible with PVC while the corresponding homopolymers are not (Zakrzewski, 1973). Likewise, α-methyl styrene/acrylonitrile copolymers are miscible with PMMA and PEMA but the homopolymers are not (Goh et al., 1982). Finally, a blend where both components are copolymers is poly(butadiene-co-styrene) and poly(vinyl chloride-co-vinyl acetate) (Krause, 1978). These copolymers are miscible for a range of copolymer composition. However, none of the binary combinations of the homopolymers [polybutadiene, polystyrene, poly(vinyl chloride), and poly(vinyl acetate)] are miscible, indicating that there is no specific interaction between them.

There have been some studies toward fundamental understanding of intramolecular repulsion. For example, Janarthanan et al. (1993) have used Fourier transform infrared spectroscopy to detect intramolecular interaction in blends of poly(ϵ-caprolactone) and poly(styrene-co-acrylonitrile). This system displays a miscibility window as a function of copolymer composition (Chiu and Smith, 1984). The shift of the γ-CH out-of-plane deformation band of styrene to higher frequencies shows that miscibility in this system is mainly due to the dilution of the unfavorable intramolecular interaction between styrene and acrylonitrile segments by poly(ϵ-caprolactone). The miscibility window observed from measurements of the integrated intensity ratio of the γ-CH out-of-plane vibration is consistent with the miscibility window reported by differential scanning calorimetry.

Pfennig et al. (1985) showed that intramolecular repulsion can lead to an exothermic heat of mixing. An experimental simulation was performed using low-molecular-weight liquids that approximately model the monomers in the blend poly(methyl methacrylate)+poly(styrene-co-acrylonitrile). Three liquids selected for this study were 1, methyl cyanide; 2, toluene; 3, methyl isobutyrate. Mixing any two liquids always gave an endothermic heat of mixing. However, mixing 3 with a premix of 1 and 2 gave an exothermic heat of mixing over a composition range. This composition range corresponds closely to the acrylonitrile content in the copolymer in the miscible region for poly(methyl methacrylate)+poly(styrene-co-acrylonitrile) blends. The exothermic heat of mixing 3 with a premix of 1 and 2, was due to the decrease in the number of the strongly repulsive 1-2 contacts, relative to 1-3 and 2-3 contacts. A similar study was also performed by Cruz-Ramos and Paul (1989).

Polymer-blend miscibility studies, suggest that the same "intramolecular repulsion" effect may be observed in VLE of solvent+copolymer systems. Therefore, VLE data were obtained for solutions of poly(butadiene-co-acrylonitrile) where two dissimilar segments are incompatible and have repulsive interactions. Studies were made for two solvents: acetonitrile and methyl ethyl ketone. The experimental data are correlated using an equation of state based on molecular thermodynamics.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental methods for measuring the vapor pressure of a solvent in a polymer solution are discussed by Danner and High (1993). We have used a gravimetric sorption technique. This classical method has been described in detail by Panayitou and Vera (1984) and in our earlier publication (Gupta and Prausnitz, 1995).

Experiments were performed at temperatures higher than the glass-transition temperature of the polymer. All polymers used here are high-molecular-weight (molecular weights > 100,000) homopolymers or random copolymers. The composition of the copolymer is in weight percent.

3. BRIEF SUMMARY OF THEORY FOR CORRELATION

To model VLE of copolymer solutions, we have used a perturbed hard-sphere-chain (PHSC) equation of state (Song et al., 1994a, 1994b, 1994c). For ordinary VLE at low pressures, it is often possible to use Flory-Huggins theory for a reasonable correlation of polymer/solvent VLE data. But we would like to use a model that can describe both upper and lower critical solution temperatures, VLE phase diagrams at high pressures, and

account for solvent compressibility. For binary polymer solutions, the PHSC theory can reproduce all types of observed LLE phase diagrams, including upper or lower critical solution temperatures (UCST or LCST), or both, including closed partial-miscibility loops (Song et al., 1994c).

The PHSC equation of state is applicable to fluid mixtures containing any number of components over the entire range of fluid conditions. Since the PHSC equation-of-state uses molecular parameters that have physical significance, it provides a potentially useful method for predicting thermodynamic properties outside the range of available data.

The PHSC equation-of-state for heteronuclear chains is

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \left[\sum_{k=1}^{r_i} \sum_{l=1}^{r_j} b_{ij,kl} g_{ij,kl} \right] - \sum_{i=1}^{m} x_i \sum_{k=1}^{r_i-1} \left[g_{ii,k,k+1} - 1 \right] - \frac{\rho}{k_B T} \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \left[\sum_{k=1}^{r_i} \sum_{l=1}^{r_j} a_{ij,kl} \right] \quad (1)$$

where, p = pressure; T = absolute temperature; ρ = number density; m = number of components; x = mole fraction; k_B = Boltzmann constant; a = attractive energy parameter; b = second virial coefficient of hard spheres; r = number of hard spheres per chain; and g = pair radial distribution function of hard spheres at contact. Subscript ij,kl denotes the pair containing k^{th} segment of component i and l^{th} segment of component j. Parameters a and b are temperature-dependent as given by the Song-Mason (1989) method. For pure solvents and homopolymers, these are:

$$a = \frac{2}{3} \pi \sigma^3 \varepsilon F_a (k_B T / \varepsilon) \quad (2)$$

$$b = \frac{2}{3} \pi \sigma^3 F_b (k_B T / \varepsilon) \quad (3)$$

where, σ = distance of separation at minimum potential energy; ε = well depth of pair potential; F_a, and F_b are universal functions given by Song et al. (1995).

For a pair of dissimilar segments A and B, parameters a and b are given by:

$$a_{AB} = \frac{2}{3} \pi \sigma_{AB}^3 \varepsilon_{AB} F_a (k_B T / \varepsilon_{AB}) \quad (4)$$

$$b_{AB} = \frac{2}{3} \pi \sigma_{AB}^3 F_b (k_B T / \varepsilon_{AB}) \quad (5)$$

where

$$\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B)(1 - \lambda_{AB}) \quad (6)$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} (1 - \kappa_{AB}) \quad (7)$$

Parameters σ_A, ε_A pertain to segment A; κ_{AB}, λ_{AB} are adjustable inter-segmental parameters.

The pair correlation function at contact is

$$g_{ij,kl} = \frac{1}{(1-\eta)} + \frac{2}{3} \frac{\xi_{ij,kl}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij,kl}^2}{(1-\eta)^3} \quad (8)$$

where the packing fraction is

3

$$\eta = \frac{\rho}{4} \sum_{i=1}^{m} x_i \sum_{k=1}^{r_i} b_{i,k} \tag{9}$$

and

$$\xi_{ij,kl} = \frac{\rho}{4} \left[\frac{b_{i,k} b_{j,l}}{b_{ij,kl}} \right]^{1/3} \sum_{i=1}^{m} x_j \sum_{k=1}^{r_i} b_{i,k}^{2/3} \tag{10}$$

In summary, each pure solvent or homopolymer is characterized by three molecular constants: r, segment number per molecule; σ, segment size; and ε, non-bonded segment pair interaction energy. Each copolymer is characterized by the molecular constants of the parent homopolymers and the copolymer composition. Molecular constants are obtained from readily available pure-component data for thermodynamic properties such as vapor pressures, densities, and compressibilities (Song et al., 1994b). Pure-component parameters for 77 solvents and for 22 polymers have been collected by Song et al. (1995). For each unlike pair of segments, usually one and only rarely two binary parameters, (κ and λ) are needed for the mixture; these can be determined from experimental mixture properties.

4. RESULTS AND DISCUSSION

Figure 1 shows VLE data for poly(butadiene-co-acrylonitrile)+acetonitrile. At a given pressure, solvent absorption in polyacrylonitrile is higher than that in polybutadiene because polar acetonitrile prefers polar segments of polyacrylonitrile to hydrocarbon segments of polybutadiene. Intuitively, one might expect that the copolymer curve should lie in-between the two homopolymer curves, as reported for many copolymer+solvent systems including poly(butadiene-co-acrylonitrile)+hydrocarbon (Gupta and Prausnitz, 1995). However, Figure 1 shows that the copolymer curves lie beyond the bound of the two homopolymer curves. At a given pressure, acetonitrile solubility in a copolymer is much higher than that in the corresponding homopolymers. In Figure 1, the solubility of acetonitrile is unexpectedly high in poly(butadiene-co-51% acrylonitrile).
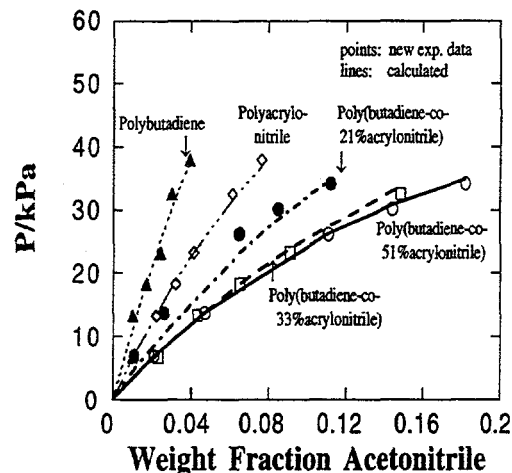

Figure 1. Vapor-liquid equilibria for acetonitrile with cis-1,4-polybutadiene, polyacrylonitrile, and poly(butadiene-co-acrylonitrile) solutions at 60 °C. PHSC parameters: acetonitrile + polyacrylonitrile, κ = 0.0; λ = 0.018; acetonitrile + cis-1,4-polybutadiene, κ = 0; λ = 0.095; cis-1,4-polybutadiene + polyacrylonitrile, κ = 0.129; λ = 0.239.
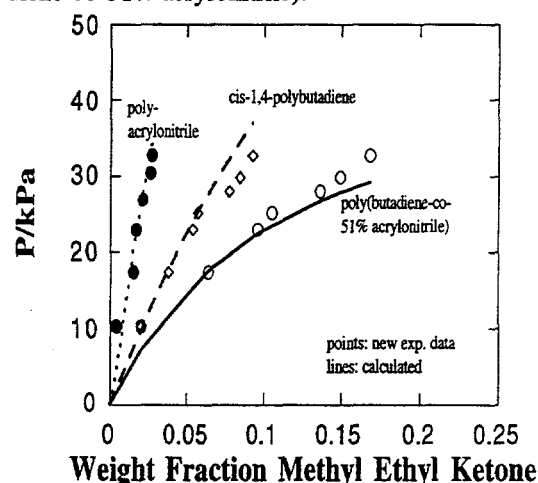
Figure 2. Vapor-liquid equilibria for methyl ethyl ketone with cis-1,4-polybutadiene, polyacrylonitrile, and poly(butadiene-co-acrylonitrile) solutions at 60 °C. PHSC parameters: methyl ethyl ketone + polyacrylonitrile, κ = 0.0; λ = -0.005; methyl ethyl ketone + cis-1,4-polybutadiene, κ = -0.003; λ = 0.016; cis-1,4-polybutadiene + polyacrylonitrile, κ = 0.129; λ = 0.239.

Similar behavior was observed for poly(butadiene-co-acrylonitrile)+methyl ethyl ketone as shown in Figure 2. At a given pressure, solubility of methyl ethyl ketone in poly(butadiene-co-51% acrylonitrile) is much higher than that in the corresponding homopolymers, polybutadiene, and polyacrylonitrile.

These two examples show unexpected VLE behavior. However, that behavior can be explained by "intramolecular repulsion" between the unlike segments of the random copolymer. Higher affinity of the solvent for a copolymer that exhibits "intramolecular repulsion" may find applications in sensor technology, or in separation of organic molecules using a polymeric membrane.

In Figures 1 and 2, data were correlated using the PHSC equation of state. The butadiene-acrylonitrile segment interaction parameters were the same in both cases. Only one or at most two binary interaction parameters are used for each dissimilar segment pair.

Toward obtaining a picture on the molecular level, Figure 3 gives a schematic representation of interactions in poly(butadiene-co-acrylonitrile)+acetonitrile. Acetonitrile has a polar end (CN) and a nonpolar end (CH_3). The polar end of acetonitrile is repulsed by the non-polar hydrocarbon segments of polybutadiene; while the non-polar end of acetonitrile is repulsed by polyacrylonitrile; therefore, both homopolymers show poor absorption of acetonitrile. However, in the copolymer poly(butadiene-co-acrylonitrile), acetonitrile is able to find both type of sites, polar and non-polar, giving higher solvent absorption. A similar argument can be made for VLE for poly(butadiene-co-acrylonitrile)+methyl ethyl ketone.
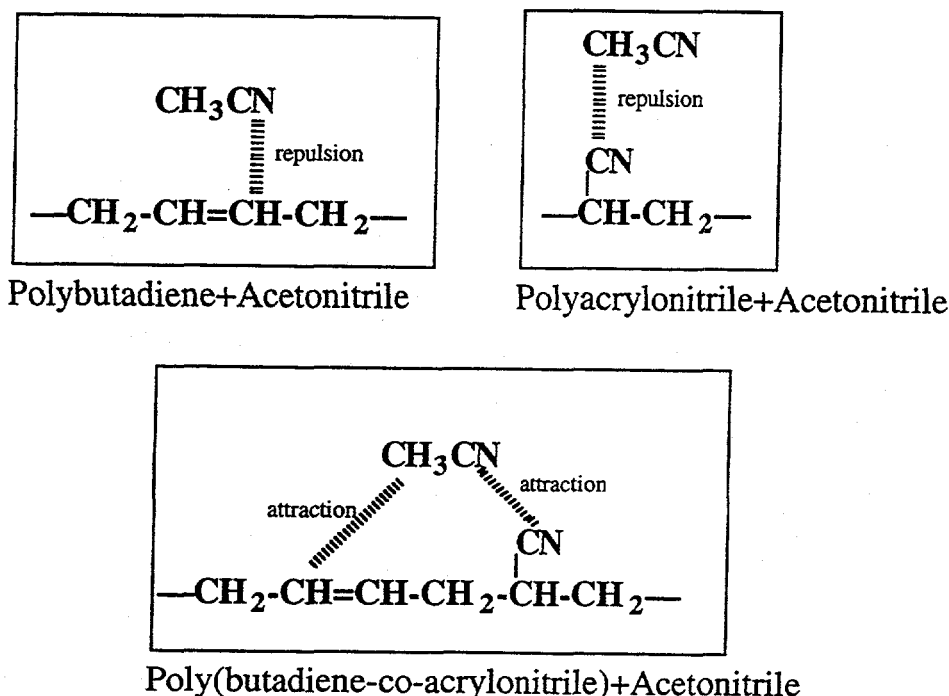

Polybutadiene+Acetonitrile   Polyacrylonitrile+Acetonitrile

Poly(butadiene-co-acrylonitrile)+Acetonitrile

Figure 3. Schematic of molecular interactions between acetonitrile with cis-1,4-polybutadiene, polyacrylonitrile, and poly(butadiene-co-acrylonitrile). Repulsive interactions are shown in cis-1,4-polybutadiene (and in polyacrylonitrile)+acetonitrile systems. However, intractions are attractive in poly(butadiene-co-acrylonitrile)+acetonitrile system.

5. CONCLUSIONS

We have observed unusual VLE for poly(acrylonitrile-co-butadiene)+acetonitrile (and for methyl ethyl ketone). For both solvents, the solvent is better liked by the copolymer than by either of the homopolymers due to "intramolecular repulsion" between the two dissimilar segments of the copolymer.

To our best knowledge this is the first study reporting the "intramolecular repulsion" effect for VLE in copolymer+solvent systems.

The Perturbed Hard-Sphere-Chain (PHSC) equation of state for mixtures of heteronuclear chains can represent this unexpected vapor-liquid equilibria using one or at most two binary parameters for each pair of unlike segments.

6. ACKNOWLEDGMENT

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