Solubility of Polymers in Supercritical Fluids[1]

E. Kiran,[2] V. P. Saraf,[2] and Y. L. Sen[2]

The phase separation of solutions of monodisperse polystyrene samples of molecular weight 9000 in pure and also binary mixtures of *n*-butane and *n*-pentane has been examined under both subcritical and supercritical conditions over the whole concentration range using a variable-volume view cell capable of operating at up to 100 MPa and 500 K. The phase behavior of these solutions is discussed in terms of the coexistence curves and the theoretical predictions based on the mean-field lattice-gas theory.

KEY WORDS: *n*-butane; demixing; lattice-gas theory; *n*-pentane; polymers; polystyrene; supercritical fluids.

1. INTRODUCTION

There is a growing interest in supercritical fluids as process solvents for the polymer industries. As discussed in recent monographs [1–3], the properties of supercritical fluids such as density, viscosity, and diffusivity which affect their dissolving power and transport characteristics can be readily manipulated by changes in either the pressure or the temperature. Because of the adjustable nature of their properties, these fluids are "tunable solvents" and offer flexibilities that are not easily attainable by ordinary solvents.

Unlike ordinary solvents, the literature on dissolution and transport properties of polymers and theoretical models for their predictions in supercritical solvents is not extensive and often does not cover the whole concentration range [4–14]. Effective utilization of supercritical fluids in polymer applications requires information on these aspects, especially equilibrium solubilities and the influence of factors such as the molecular

---

[2] Department of Chemical Engineering, University of Maine, Orono, Maine 04469, U.S.A.

weight and distribution of the polymer, the nature of the solvent, and the dependence of behavior on pressure and temperature.

We have recently reported the phase behavior of monodisperse polystyrene standards in n-butane and n-pentane at near-critical and super-critical conditions over the complete concentration range for two different molecular weight samples [15, 16]. This paper is a continuation of these studies and presents solubility data in a series of binary mixtures of n-butane with n-pentane. The results of theoretical predictions based on mean-field lattice-gas theory are also discussed.

2. EXPERIMENTAL

2.1. Materials

Monodisperse polystyrene samples of molecular weight 4000 (PS4000) and 9000 (PS9000) with $M_w/M_n \leqslant 1.06$ were obtained from Pressure Chemicals Co. The solvents n-butane (purity, $>99.9\%$) and n-pentane (purity, $>99\%$) were obtained from Matheson and Aldrich Chemical Co. and were used without further purification.

2.2. Apparatus and Operational Procedures

The details of the experimental system have been described elsewhere [16, 17]. Essentially it is a variable-volume view cell which can be operated at pressures and temperatures up to 100 MPa and 500 K. With the aid of an external pressure generator and a movable piston, the volume of the cell is varied and the pressure is controlled independently at any temperature. Two sapphire windows permit visual observation of the cell content or measurement of the intensity of the laser light passing through the cell.

In a typical experiment, after the cell is loaded with the polymer and the solvent (corresponding to a given polymer concentration), the temperature and pressure are adjusted to achieve a homogeneous solution. The demixing (binodal) points are then determined by following the transmitted light intensity either as a function of temperature at a constant pressure or as a function of pressure at a constant temperature. As the demixing envelope is approached from one phase region, the intensity of light passing through the cell decreases. The temperature and pressure corresponding to the demixing point, which is characterized by intense scattering, are measured with an accuracy of 0.5 K and 0.03 MPa, respectively. Demixing curves obtained for solutions with different polymer concentrations are then used to generate the complete phase information (in the form of coexistence curves) for the polymer–solvent system.

3. RESULTS AND DISCUSSION

3.1. Experimental Results

Demixing curves for the polystyrene standard of molecular weight 4000 in *n*-butane and of molecular weight 9000 in *n*-butane and *n*-pentane have been determined at concentrations covering a range from 0.5 to 80.0 wt%. These data have been presented and the general trends with respect to solvent and molecular weight effects have been discussed in our earlier publications [15, 16]. In summary, demixing pressures are decreased upon changing the solvent from *n*-butane to *n*-pentane (a change from a relatively poor to a better solvent), but in a given solvent they are increased with an increase in the molecular weight of the polymer. Figure 1 shows the demixing pressures for the 9000 molecular weight sample in pure *n*-pentane and *n*-butane and in the binary mixtures of these solvents at different proportions, all at a fixed polymer concentration of 5 wt%. The region above each curve corresponds to the one-phase region. As shown in Fig. 1, with an increased fraction of *n*-butane in the binary solvent, the demixing pressures show a steady increase at each temperature. The temperature range that has been studied covers temperatures below and above the critical temperature of each solvent. At this polymer concentration, demixing pressures do not appear to be very sensitive to temperature, especially if the conditions are above the critical. The critical properties of the solvents are as follows: *n*-butane, $T_c = 425.2$ K and $P_c = 3.80$ MPa; *n*-butane, $T_c = 469.6$ K and $P_c = 3.37$ MPa; 3:1 (*n*-butane: *n*-pentane, by
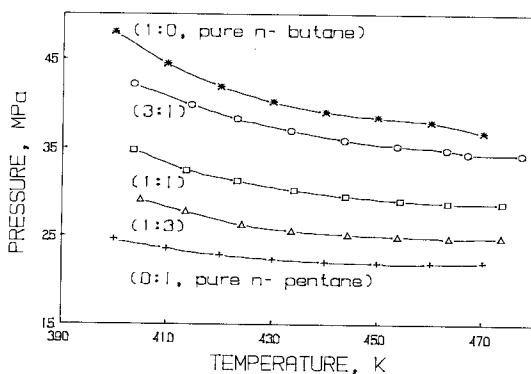

Fig. 1. Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 9000$; $M_w/M_n \leqslant 1.06$) in *n*-butane and *n*-pentane and their binary mixtures. The proportion of *n*-butane to *n*-pentane by weight is indicated. The polymer concentration is 5 wt%.

weight) binary mixture, $T_c = 436.4$ K and $P_c = 3.77$ MPa; 1:1 binary mixture, $T_c = 447.5$ K and $P_c = 3.71$ MPa; and 1:3 binary mixture, $T_c = 458.4$ K and $P_c = 3.58$ MPa. The mixture critical properties were evaluated from data in the literature [18].

Plots similar to Fig. 1 have been generated at other concentrations and the data have been used to obtain coexistence curves such as those shown in Figs. 2a and b, which compare the behavior of the polymer in pure solvents and their 50:50 binary mixture over the whole concentration range at two temperatures. As seen from these figures, the demixing pressure in the 1:1 binary solvent lies halfway between the demixing pressures in the pure solvents.
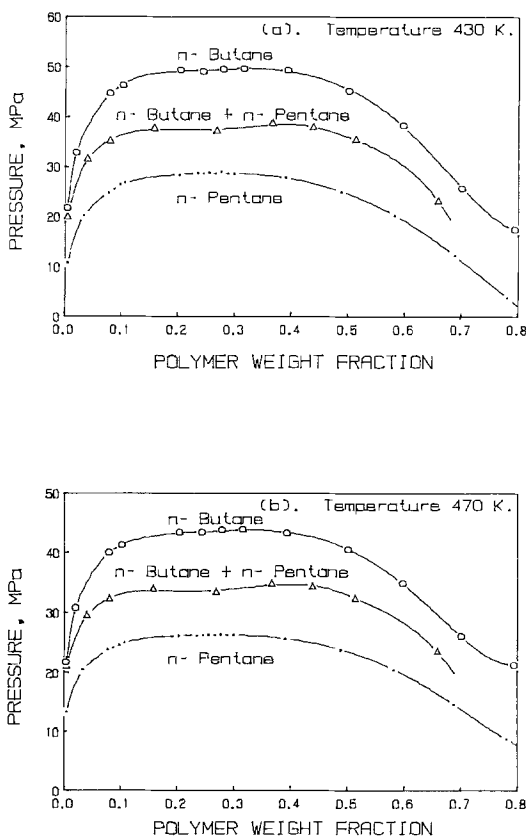

Fig. 2. Coexistence curves for solution of polystyrene ($M_w = 9000$; $M_w/M_n \leqslant 1.06$) in n-butane and n-pentane and their 1:1 binary mixture at (a) 430 K and (b) 470 K.

3.2. Theoretical Modeling

Using these data sets we have conducted theoretical predictive calculations using the mean-field lattice-gas model, which is based on the assumption that the lattice of a fluid consists of occupied and vacant sites. In the model, which has been discussed in detail in the literature [13], the volume per lattice site is taken to be the same for all kinds of sites, independent of the pressure and temperature. Each molecule, depending upon its size, is permitted to occupy more than one site. Changes in the pressure, temperature, and composition are accounted for by changes in the concentrations of the vacant and occupied sites. The model has been found to be suitable for the description of liquids as well as gases [13, 14].

In the model, equation of state for a pure substance which is regarded as a binary system of occupied and vacant sites is given by

$$- Pv_0/RT = \ln \phi_0 + (1 - 1/m_1)\, \phi_1 + \phi_1^2\{\alpha_1 + g_{11}(1 - \gamma_1)^2/(1 - \gamma_1\phi_1)^2\} \qquad (1)$$

where v_0 is the volume per lattice site equal for all sites, ϕ_0 and ϕ_1 are the volume fractions of the vacant and occupied sites, m_1 is the number of lattice sites occupied by the molecule (chain length), α_1 is the empirical entropy correction term (for mixing the vacant and occupied sites), g_{11} is the interaction energy parameter for a 1–1-type contact, and γ_1 is a parameter related to surface areas of occupied and vacant sites. The volume fraction of the occupied sites ϕ_1 is related to the density ρ_1 and the molecular weight M_1 of the substance by

$$\phi_1 = \rho_1 m_1 v_0/M_1 \qquad (2)$$

Equation (1) involves v_0 (or m_1), γ_1, g_{11}, and α_1 as adjustable parameters. In the treatment of pure fluids these parameters are evaluated by using the critical properties of the fluid and the vapor–liquid equilibrium data.

In the model, binary mixtures are treated as ternary systems involving vacant sites and the sites occupied by components 1 and 2. The relationships now involve, in addition to pure-component parameters, a new interaction parameter, g_{12}, reflecting the 1–2-type interactions, and a new empirical entropy correction factor, α_{12}, for mixing of components 1 and 2. In the treatment of binary mixtures, the parameters are adjusted using values of the pure-substance parameters derived from pure-substance critical data and experimental data on binary phase equilibria. The model has been used recently for cases where pure-component critical data for one of the constituents in a binary mixture are not available such as those involving inorganic salts [19]. In such cases optimization procedures are

used to evaluate simultaneously the pure substance parameters and the binary parameters.

Similar to salts, since the data on critical properties of polymers are not accessible, in our mean-field lattice-gas treatment of polymer solutions, we have also used [20] an optimization procedure involving the equation of state for the binary fluid

$$
\begin{aligned}
-Pv_0/RT = &\ln \phi_0 + (1 - 1/m_1)\,\phi_1 + (1 - 1/m_2)\,\phi_2 \\
&+ (\alpha_1\phi_1 + \alpha_2\phi_2)(\phi_1 + \phi_2) \\
&- \phi_1\phi_2\{\alpha_{12} + g_{12}(1 - \gamma_1)(1 - \gamma_2)/Q^2\} \\
&+ \{g_{11}(1 - \gamma_1)\,\phi_1 + g_{22}(1 - \gamma_2)\,\phi_2\}(Q - \phi_0)/Q^2
\end{aligned}
\tag{3}
$$

and equality of the chemical potential of the species i in both phases at equilibrium,

$$
\begin{aligned}
(1/m_i)\ln \phi_i'/\phi_i'' \\
= \varDelta\{&(1 - 1/m_i)\,\phi_i + (1 - 1/m_j)\,\phi_j \\
&+ (\alpha_i\phi_0 + \alpha_{ij}\phi_j)(\phi_0 + \phi_j) - [\alpha_j + g_{jj}(1 - \gamma_j)(1 - \gamma_j)/Q^2]\,\phi_0\phi_j \\
&+ [g_{ii}\phi_0(1 - \gamma_i) + g_{ij}(1 - \gamma_i)(1 - \gamma_j)\,\phi_j][\phi_0 + (1 - \gamma_j)\,\phi_j]/Q^2\}
\end{aligned}
\tag{4}
$$

where $Q = 1 - \gamma_1\phi_1 - \gamma_2\phi_2$ and $\varDelta$ indicates the difference of values in the curly braces between the vapor (″) and the liquid (′) phases.

The parameters for the pure solvents are first determined by the usual procedure. They are given in Table I. The optimization procedure evaluates the polymer parameters (m_2, α_2, and γ_2) and the temperature-dependent binary parameters (α_{12}, g_{12}) in the form

$$
\alpha_{12} = \alpha_{12a} + \alpha_{12b}\exp(\alpha_{12c}/T)
\tag{5}
$$

$$
g_{12} = g_{12a} + g_{12b}\exp(g_{12c}/T)
\tag{6}
$$

which introduces additional parameters. In the procedure, we have used nine data points for each system and optimized the values of the parameters in a way to give a minimum total error between the predictions and the experimental values. The first step in the optimization procedure is to start with some assumed values for the nine variables and determine ϕ_0' and ϕ_0'' using the equation of state for the binary [Eq. (3)] and Newton–Rhapson procedure. In the process, the interaction parameter for the polymer g_{22} is evaluated as a dependent variable using the equation of state [Eq. (1)] and the densities of the polymer [which gives ϕ_1 with Eq. (2)], which were taken from the literature [21]. Knowing all the

Table I.   Parameters for the Systems ($v_0 = 36 \text{ cm}^3 \cdot \text{mol}^{-1}$)

Pure solvent	m_1	α_1	γ_1	g_{11}	
n-Butane	2.178	1.1335	-2.4217	$-1.9305 + 1.5291$ $\times \exp(132.04/T)$	
n-Pentane	2.543	1.1026	-2.8142	$-2.2053 + 1.8544$ $\times \exp(106.19/T)$	

Binary system	m_2	α_2	γ_2	α_{12}	g_{12}
PS4000 $+ n$-butane	88.75	1.9344	-0.1987	$0.00948 + 0.0682$ $\times \exp(396.54/T)$	$0.0745 + 0.01322$ $\times \exp(402.8/T)$
PS9000 $+ n$-butane	202.74	1.9150	-0.3897	$0.1515 - 0.0257$ $\times \exp(-515.87/T)$	$0.4915 + 0.0075$ $\times \exp(966.97/T)$
PS9000 $+ n$-pentane	139.06	3.2891	-2.1506	$0.3613 - 0.8818$ $\times \exp(-787.80/T)$	$0.0015 + 0.0455$ $\times \exp(-2921.15/T)$
PS9000 $+ n$-butane $+ n$-pentane	132.49	3.5146	-1.9202	$0.1760 + 0.1039$ $\times \exp(-443/41/T)$	$0.0835 - 0.3485$ $\times \exp(-672.88/T)$

variables, they are substitued in Eq. (4) and the error is determined. This is repeated with all the data points and the total error is obtained. Optimization is done by minimizing the total error while keeping the parameter values realistic. This is achieved using unidirectional DSC search for minimum and Powell's method for acceleration [22]. The parameters evaluated are also given in Table I. In the system involving the binary solvent mixture, the solvent was treated as a pseudosolvent, its parameters being derived by compositional averaging.

It is noted that the chain lengths of the polymeric components in all cases are of the right order of magnitude compared to the chain lengths of the solvents. In fact, the chain lengths of the polystyrenes of molecular weights 4000 and 9000 evaluated in n-butane solutions are at the same ratio as their molecular weights. The chain length of polystyrene of molecular weight 9000 in n-pentane and its binary mixture with n-butane, however, is substantially lower than that in n-butane. The solvent constitutent in principle is not expected to affect the chain length of the polymer, as the same lattice size has been used. The solvent dependence of the chain length may reflect the limitations of the theory. The correct order of magnitude of the parameters, however, may still be regarded as a very satisfactory result.

The predictions of the phase diagram using the evaluated parameters are shown in Fig. 3. There is some overshoot in the predicted pressure at compositions close to the critical composition of the solutions, but
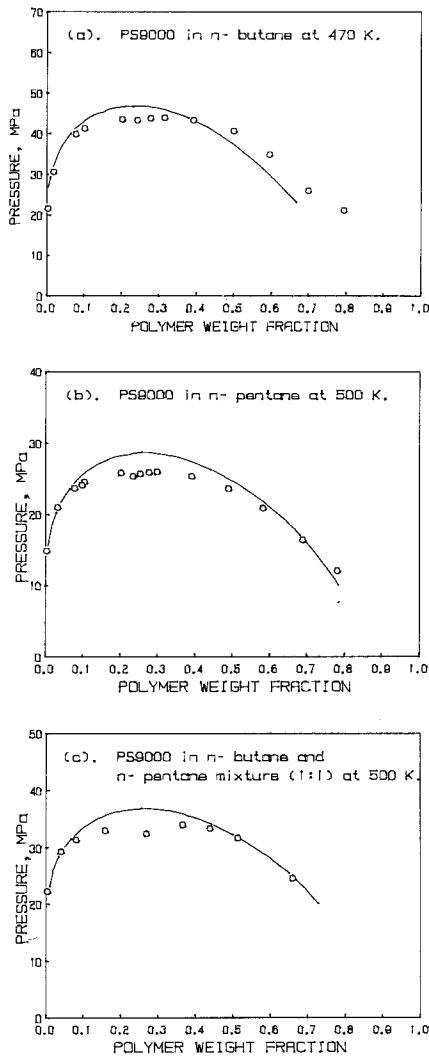
Fig. 3. The experimental points on the coexistence curve and the predictions with mean-field lattice-gas theory for the solution of polystyrene $(M_w = 9000;$ $M_w/M_n \leqslant 1.06)$ in different solvents: (a) n-butane at 470 K, (b) n-pentane at 500 K, and (c) 1:1 binary mixture of n-butane and n-pentane.

otherwise the agreement is quite good. It must be noted, however, that the predictions were found to be not as good at the lower extreme of the temperatures studied [20]. The same data set has been treated by other theoretical procedures such as the corresponding-state theory [16, 20]. Similar trends with respect to poor predictions at lower temperatures have been observed. Even when more data points at the low-temperature end of the range were used in optimization, not much improvement could be realized since a large temperature range (e.g., 400–500 K) is involved. The predictions can be made better by optimizing on a narrower temperature range or using more data points. In general, the predictions are more satisfactory in the supercritical region.

4. CONCLUSION

The demixing pressures for the solutions of polystyrenes in n-butane, n-pentane and their binaries show a strong dependence on the nature of the solvent and decrease with the n-pentane content of the solvent. The phase diagrams can be predicted with reasonable accuracy with the mean-field lattice-gas theory.

ACKNOWLEDGMENT

REFERENCES

1. M. E. Paulaitis, J. M. L. Penninger, R. D. Grey, and P. Davidson (eds.), *Chemical Engineering at Supercritical Fluid Conditions* (Ann Arbor Science, Ann Arbor, Mich., 1983).
2. J. M. L. Penninger, M. Radosz, M. A. McHugh, and V. J. Krukonis (eds.), *Supercritical Fluid Technology* (Elsevier, New York, 1985).
3. M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction* (Butterworth, Boston, 1986).
4. P. Ehrlich, *J. Polym. Sci.* A3:131 (1965).
5. P. Ehrlich and J. J. Kurpen, *J. Polym. Sci.* A1:3217 (1963).
6. T. W. de Loos, W. Poot, and G. A. M. Diepen, *Macromolecules* 16:111 (1983).
7. T. W. de Loos, R. N. Lichtenthaler, and G. A. M. Diepen, *Macromolecules* 16:117 (1983).
8. E. Schroder and K.-F. Arndt, *Faserforsch. Textiletech.* 27:135, 141, 159 (1976).
9. S. Ali, *Z. Phys. Chem.* 137:13 (1983).
10. S. K. Kumar and U. W. Suter, *Polym. Preprints* 28:286 (1987).
11. D. C. Bonner, D. P. Maloney, and J. M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.* 13:91 (1974).
12. J. R. Schmidt and B. A. Wolf, *Macromolecules* 15:1192 (1982).
13. L. A. Kleintjes, Ph.D. thesis (University of Essex, Essex, 1979).

14. L. A. Kleintjens and R. Koningsveld, *Coll. Polym. Sci.* **258**:711 (1980).
15. V. P. Saraf and E. Kiran, *Polymer* **29**:2061 (1988).
16. V. P. Saraf and E. Kiran, *J. Supercrit. Fluids* **1**:37 (1988).
17. V. P. Saraf and E. Kiran, *Polym. Preprints* **28**:397 (1987).
18. C. P. Hicks and C. L. Young, *Chem. Rev.* **75**:119 (1975).
19. H. Morouschek and S. Peter, *Fluid Phase Equil.* **21**:61 (1985).
20. V. P. Saraf, Ph.D. thesis (University of Maine, Orono, 1988).
21. H. Hocker, G. J. Blake, and P. J. Flory, *Trans. Faraday Soc.* **67**:2251 (1971).
22. G. S. G. Beveridge and R. S. Schechter, *Optimization Theory and Practice* (McGraw–Hill, New York, 1970).