Supercritical fluid–polymer interactions: phase equilibrium data for solutions of polystyrenes in n-butane and n-pentane

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The phase separation of monodisperse polystyrene samples of different molecular weights in n-butane and n-pentane has been examined under both subcritical and supercritical conditions. A high-pressure variable-volume viewing cell capable of operating up to 100 MPa and 500 K permits the determination of phase separation points. A concentration range from 0.5 to 80% by weight has been studied. The phase behaviour of these solutions is discussed in terms of the demixing curves as well as the coexistence curves that are obtained from them. The demixing pressures depend upon the nature of the solvent and the molecular weight and concentration of the polymer in the solution.

(Keywords: supercritical fluids; polystyrene; n-butane; n-pentane; demixing; binodal temperature; high pressure; critical concentration)

INTRODUCTION

Supercritical fluids and their use as process solvents in a wide range of applications have been discussed in a number of recent review articles[1–3] and monographs[4–7]. Their use is becoming especially important in polymer science. They offer new possibilities for applications in polymer processing, synthesis and separations. This is because solvent characteristics of a given supercritical fluid can be readily regulated by manipulations of pressure or temperature. The effective use of these solvents in such applications requires information on the phase behaviour of polymers in these fluids. The present paper describes the phase behaviour of polystyrenes in supercritical n-butane and n-pentane.

The behaviour of polystyrenes in supercritical fluids with respect to their solubility, synthesis and fractionation has already received some attention in the literature[8–14]. Their separation by supercritical fluid chromatography has also been reported[15–24]. More specifically, Schroder and Arndt[8–10] studied the solubility of polystyrene of molecular weight 250000 in supercritical carbon dioxide at pressures up to 150 MPa. Lundberg and Ali[11] reported some data on the solubility of polystyrene in carbon dioxide, ethane and n-butane. Ali[12] further investigated the phase diagram of polystyrene of molecular weight 22000 in n-butane up to a pressure of 13 MPa at concentrations below 30%. Kumar *et al.*[13,14] have studied the synthesis and precipitation thresholds of polystyrenes in supercritical ethane, carbon dioxide and their mixtures in the pressure range 8–35 MPa and temperature range 313–333 K. Various investigators have studied the separation of oligomers and polymeric species of styrene (up to molecular weights of 600000) using carbon dioxide, alkanes and ethers (with or without secondary components) as mobile-phase fluids in supercritical fluid chromatography[15–24].

There has been no previous study showing the phase behaviour of polystyrenes in supercritical fluids over the complete concentration rate. The work by Ali[12] is limited to concentrations below 30%. Furthermore, the procedures of generating the phase separation points and the determination of polymer concentration were based on the assumptions of no polymer loss during pressure alterations (in bleeding the cell content with a capillary) and the assumption of applicability of solvent compressibility factors to the solutions, both of which introduce inaccuracies. An additional limitation in the study stems from the high polydispersity ($M_w/M_n = 1.24$) of the sample used, which can influence the determination of the demixing point. The higher-molecular-weight species would precipitate first upon pressure reduction, causing an overestimation of demixing pressures that can be assigned to the nominal (peak) molecular weight of the sample.

In a previous paper we have described an experimental system for accurate measurement of the demixing pressures and generation of coexistence curves for polymer solutions[25]. The present paper presents the phase behaviour of two monodisperse polystyrene samples of different molecular weights in n-butane and n-pentane.

EXPERIMENTAL

Apparatus

Figure 1 shows the schematics of the experimental set-up. It consists of one or more solvent delivery systems involving high-pressure liquid pumps, a high-pressure viewing cell, which can be operated at pressures up to 100 MPa and temperatures up to 500 K, an optical bench, an external pressure generator and the associated control, measurement and data storage units.

The main part of the system is the high-pressure viewing cell shown in greater detail in *Figure 2*. The basic design with respect to the use of a moveable piston is

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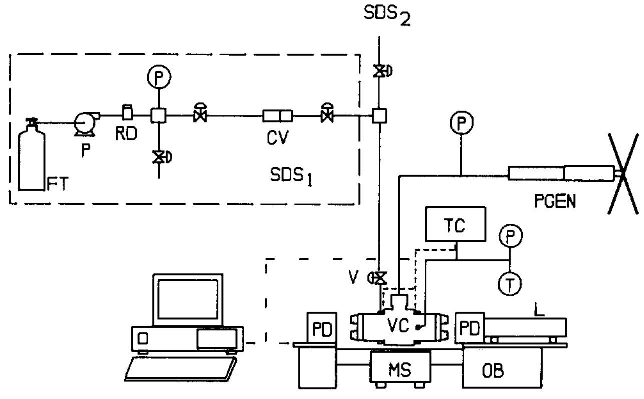

Figure 1 Experimental system: SDS, solvent delivery system; FT, fluid tank; P, pump; RD, rupture disc; CV, check valve; PGEN, pressure generator; V, valve; VC, viewing cell; TC, temperature controller; L, laser; OB, optical bench; PD, photoelectric detector; MS, magnetic stirrer

similar to that of Liphard and Schneider[26]. Other variable-volume cells operable at lower temperatures and pressures have also been reported[27,28]. The present cell is made of 316 stainless steel and has a variable volume in the range 16–24 cm^3. The contents are mixed with an external magnetic stirrer and a Teflon-coated stir bar inside the cavity of the cell. The cell has five 1/16 inch connections, one of which is used in the present study to charge the solvent into the cell under pressure. The temperature of the cell is controlled with an Omega controller connected to four cartridge heaters inserted into the cell body.

Two sapphire windows (1/2 inch thick and 1 inch in diameter supported at 1/2 inch diameter) provide access for the visual observation of the cell contents. The sapphire windows are sealed with gold foil on the inside (wetted side) and copper washers on the outside. The windows are secured with 5/16 inch bolts and a stack of Belleville spring washers.

The variable-volume assembly (made of 410 stainless steel) consists of a snug-fitting brass piston inside a cylindrical cavity. The assembly is secured onto the cell using a copper washer for seal. The 5/8 inch o.d. piston carries a Teflon O-ring. The assembly is connected to a pressure generator (High Pressure Equipment). Using compressed carbon dioxide in the pressure generator, alteration of cell pressures by as low as 0.01 MPa is possible. The snug-fitting piston with its Teflon O-ring assures that the pressurizing fluid does not mix with the cell contents.

The optical device consists of a Uniphase He–Ne laser with a beam splitter and two photoelectric detectors. The optical path length through the cell is about 12 cm. The intensity of the light passing through the cell is compared with the reference, amplified and stored on a microcomputer along with the time, temperature and pressure signals.

The cell pressure is measured with an accuracy of ±0.03 MPa using a Dynisco flush mount type transducer. The readings are frequently checked against a calibrated Heise gauge. The temperature is read with an Omega Digicator with an accuracy of ±0.5 K.

The binodal points are established by following the change in transmitted light intensity either as a function of temperature at constant pressure or as a function of pressure at constant temperature. For a given concentration of polymer the demixing curve is established by determining the binodal points in a given temperature or pressure range. The complete phase information is generated from demixing data obtained at different concentrations without the need for sampling of the phases.

Materials

Monodisperse polystyrene samples ($MW = 4000$ and 9000 both with $M_w/M_n \leq 1.06$, batch numbers 30525 and 80314 respectively) were obtained from Pressure Chemicals. The solvents n-butane (purity >99.5%) and n-pentane (purity >99%) were obtained from Matheson and Aldrich, respectively. The critical temperature and pressure for n-butane are 425.2 K and 3.93 MPa and for n-pentane 496.6 K and 3.38 MPa, respectively.

RESULTS AND DISCUSSIONS

Figures 3 and *4* show the demixing curves for the solution of polystyrene of molecular weight 4000 in n-butane. Data are presented for solutions of 0.5, 3.0, 6.0, 11.5 and 17.1 wt% polymer in *Figure 3* and for 22.7, 49.1, 60.1, 69.7 and 80.0 wt% solutions in *Figure 4*. In

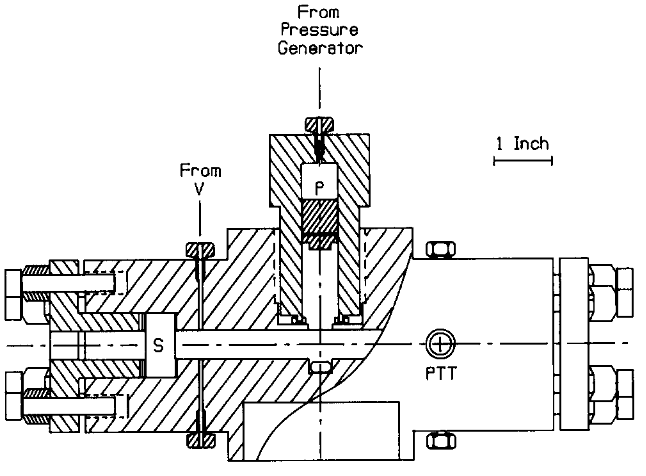

Figure 2 Variable-volume viewing cell: S, sapphire window; P, piston; PTT, pressure–temperature transducer; V, valve connection to fluid line

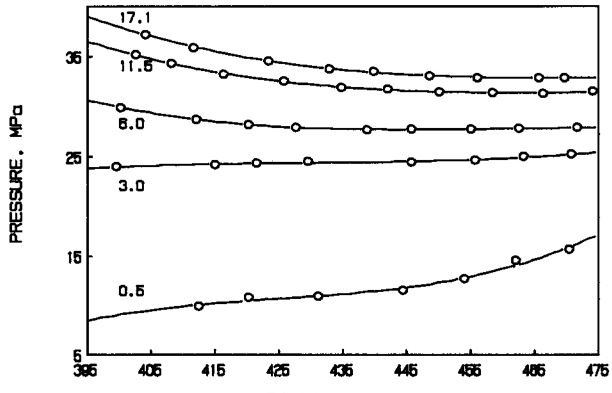

Figure 3 Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 4000$, $M_w/M_n = 1.06$) in n-butane. The polymer concentration in percent by weight is indicated

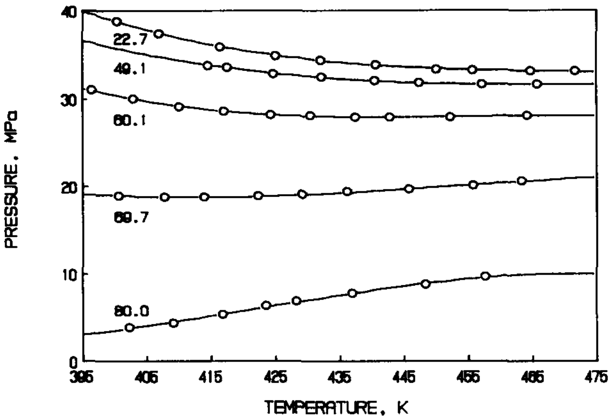

Figure 4 Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 4000$, $M_w/M_n = 1.06$) in n-butane. The polymer concentration in percent by weight is indicated

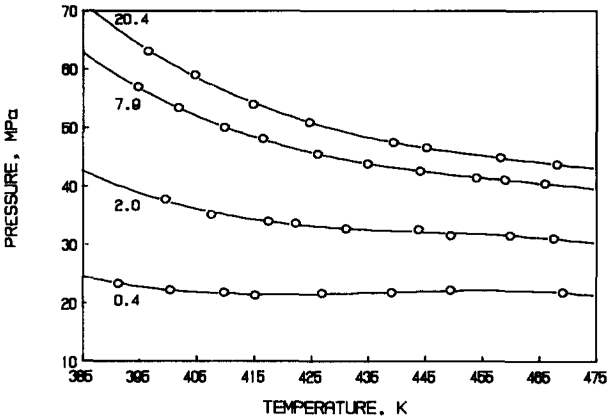

Figure 5 Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 9000$, $M_w/M_n = 1.06$) in n-butane. The polymer concentration in percent by weight is indicated

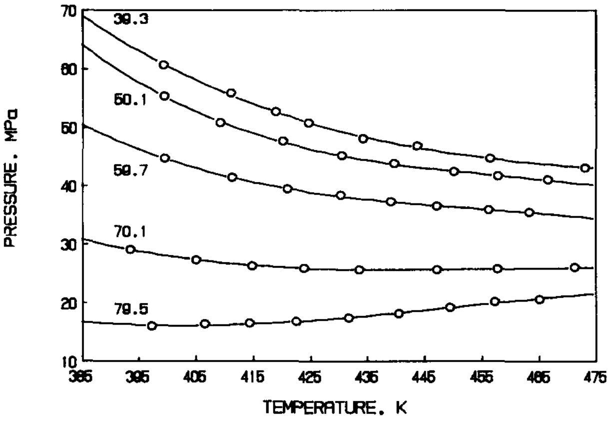

Figure 6 Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 9000$, $M_w/M_n = 1.06$) in n-butane. The polymer concentration in percent by weight is indicated

these figures, the region above each curve (corresponding to a given concentration) is the homogeneous one-phase region. These curves show that the binodal pressures generally decrease with temperature, the decrease being more significant in the subcritical range, i.e. below 425 K. However, at very low and very high polymer concentrations (i.e. 0.5 and 80%) the slope is positive and binodal pressures tend to increase with temperature. In other words, at very low and very high concentrations at a fixed pressure, with an increase in temperature, the system transforms from one-phase to two-phase regions. On the other hand, at intermediate concentrations, one-phase regions are approached upon an increase in temperature which is typical of systems showing an upper critical solution temperature.

The demixing curves for the sample of molecular weight 9000 in n-butane are shown in *Figures 5* and *6*. Data are presented for solutions of 0.4, 2.0, 7.9 and 20.4 wt% polymer in *Figure 5* and for 39.3, 50.1, 59.7, 70.1 and 79.5 wt% solutions in *Figure 6*. *Figures 7* and *8* show the demixing curves or the same polymer in n-pentane. The data are presented for solutions of 0.5, 3.3, 7.8, 9.8 and 20.3 wt% polymer in *Figure 7* and for 29.9, 48.9, 58.3, 68.9 and 78.1 wt% solutions in *Figure 8*. By selecting n-butane and n-pentane, neither of which are solvents for polystyrenes under normal conditions, the sensitivity of dissolution with pressure at different concentrations is conveniently illustrated by these demixing curves.

From *Figures 3*, *5* and *7*, it is seen that, as the polymer concentration is increased, the demixing curves are shifted to higher pressures. This increase in pressure continues up to a concentration range where the demixing pressures remain practically constant and then with

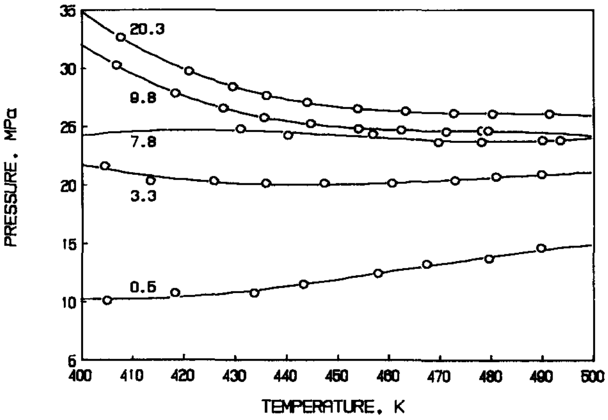

Figure 7 Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 9000$, $M_w/M_n = 1.06$) in n-pentane. The polymer concentration in percent by weight is indicated

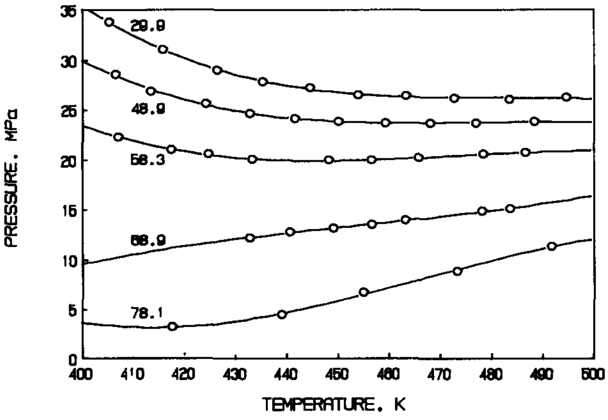

Figure 8 Variation of binodal (demixing) pressure with temperature for solutions of polystyrene ($M_w = 9000$, $M_w/M_n = 1.06$) in n-pentane. The polymer concentration in percent by weight is indicated

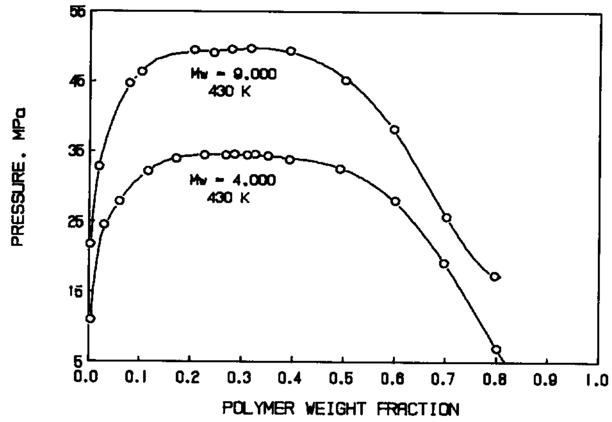

Figure 9 Comparison of coexistence curves for solutions in n-butane at 430 K for two samples of polystyrenes differing in molecular weight ($M_w = 9000$ and 4000)

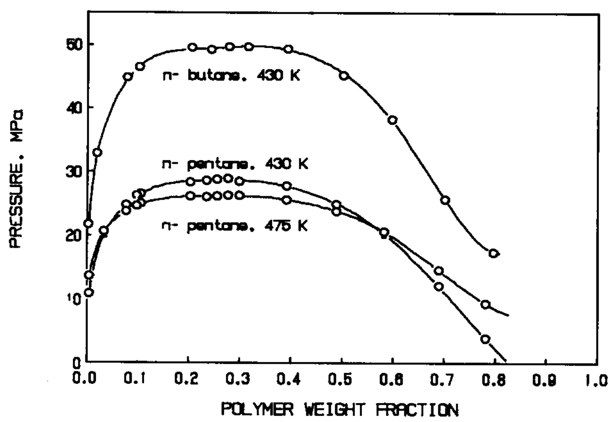

Figure 10 Comparison of coexistence curves for solutions in n-butane and n-pentane for a sample of polystyrene ($M_w = 9000$) at same absolute (430 K) and reduced ($T_r = 1.011$) temperature.

further increase in concentration show a rapid decrease as seen in *Figures 4, 6* and *8*. This behaviour can be followed much more readily by examining the variation of demixing pressure with concentration at any temperature. Such a dependence is readily extracted from the demixing curves by taking constant temperature cuts and noting the concentration dependence. *Figure 9* is such a plot for 4000 and 9000 molecular-weight samples in n-butane generated at 430 K. *Figure 10* is a similar plot for the 9000 molecular-weight sample in n-butane and n-pentane (430 and 475 K curves). At temperatures above the critical temperature of the solvent, the demixing curves are not very sensitive to temperatures and the corresponding coexistence curves show only minor differences.

The coexistence curves thus generated provide ready information on the dependence of minimum pressures needed to achieve one-phase conditions. As seen from *Figures 9* and *10*, upon doubling the molecular weight, demixing pressures are almost doubled. In going from a poor to a better solvent (i.e. from n-butane to n-pentane), demixing pressures are significantly lowered. In *Figure 10*, the solvents are compared at identical absolute (430 K) and reduced ($T_r = 1.011$; i.e. 430 and 475 K) temperatures. As noted earlier, because of the low sensitivity of the coexistence curves to temperature, the relative magnitudes of the demixing pressures are not altered significantly.

The coexistence curves for these systems are relatively flat around the critical concentration. The critical concentrations were determined by observing the adjacent compositions on the dew-point and bubble-point curves. If the concentration is less than the critical, the polymer-rich phase decreases in volume during equilibration to one-phase solution. If, however, it is more than the critical, the polymer-rich phase swells and occupies the whole cell volume. The observations are similar to those on one-component systems. For those systems, at densities less than the critical, the vapour phase (but at higher than the critical the liquid phase) occupies the whole volume of the cell as the system goes from subcritical to supercritical region. The method of determining the critical concentration is also in principle equivalent to the phase volume ratio method[29,30]. In that method, as the precipitation temperature approaches the cloud point, the ratio of dilute to polymer-rich phase goes to infinity if the concentrations are lower than the critical but to zero if the concentrations are higher. At the critical concentration, this ratio approaches 1. The critical concentrations were determined to be 32.0 wt% for $M_w = 4000$ and 25.0 wt% for $M_w = 9000$ in n-butane and 26.6 wt% for $M_w = 9000$ in n-pentane. The shift to lower concentration with increasing molecular weight is in accord with general expectations.

Even though the coexistence curves shown in *Figures 9* and *10* are relatively flat over a considerable range around the critical concentrations, for both systems, within the limits of measurements, the maxima of the curves are taken to coincide with the critical point. Considering that the systems are pseudobinaries (with monodisperse polystyrenes in n-butane or n-pentane) this would be expected. A further note is the observation that the coexistence curves become sharper as the molecular weight increases, which is noted in *Figure 9*.

Information on coexistence curves and critical concentrations are valuable in the assessment of predictive models. The current data, having been obtained on monodisperse samples over the full composition range, are especially useful for testing theoretical models. A model that correlates the experimental observations is currently under development.

CONCLUSIONS

This study has shown that polystyrenes can be dissolved in n-butane and n-pentane under pressure. The demixing pressures are shown to depend upon the molecular weight, temperature and the type of solvent involved. Critical concentrations were found to depend strongly on the polymer molecular weight but did not differ much with the solvents studied.

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