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Authors

Gupta, R.B.
Prausnitz, John M.

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**Vapor-Liquid Equilibria of Copolymer/Solvent and
Homopolymer/Solvent Binaries: New Experimental
Data and Their Correlation**

Ram B. Gupta and John M. Prausnitz

Department of Chemical Engineering
University of California, Berkeley

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Ram B. Gupta and John M. Prausnitz

Department of Chemical Engineering, University of California,
and Chemical Sciences Division, Lawrence Berkeley Laboratory,
University of California, Berkeley, CA 94720-1462.

Abstract

Sixty-six isothermal data-sets for vapor-liquid equilibria (VLE) for polymer/solvent binaries have been obtained using a gravimetric sorption technique, in the range 23.5 to 80 °C. Solvents studied were: acetone, acetonitrile, n-butanol, 1,2-dichloroethane, chloroform, cyclohexane, n-hexane, methanol, octane, pentane, and toluene. Copolymers studied were: poly(acrylonitrile-co-butadiene), poly(styrene-co-acrylonitrile), poly(styrene-co-butadiene), poly(styrene-co-butyl methacrylate), poly(vinyl acetate-co-ethylene), and poly(vinyl acetate-co-vinyl chloride). All copolymers were random copolymers. Some homopolymers were also studied: polyacrylonitrile, polybutadiene, poly(butyl methacrylate), poly(ethylene oxide), polystyrene, and poly(vinyl acetate).

Composition of the copolymer may have a surprising effect on VLE. Normally, deviation from ideal behavior lies between those of the constituent homopolymers, according to the copolymer composition, as observed for cyclohexane/poly(ethylene-co-vinyl acetate) and chloroform/poly(styrene-co-butyl methacrylate). However, the strong non-ideal behavior observed for systems containing hydrocarbons and poly(butadiene-co-acrylonitrile) shows that the effect of acrylonitrile is in excess of that expected from the copolymer composition. The Perturbed Hard-Sphere-Chain (PHSC) equation of state was used to represent VLE of the copolymer solutions studied here.

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 an increasing amount of commercial interest because of their unique physical properties. World production of copolymers has been continuously rising over the last twenty years (Wohlfarth, 1993). However, published VLE studies for copolymer/solvent are rare. Some experimental results (Bonner and Prausnitz, 1974; Corneliussen et al., 1963; Iwai et al., 1990; Moore and Shuttleworth, 1963; Panayiotou and Vera, 1984) describe polymer/solvent VLE for finite solvent concentrations. By contrast, there are about 1000 data-sets published for homopolymer/solvent systems (Wohlfarth, 1994). There is a need for more experimental studies for copolymer solutions. This work contributes toward meeting that need.

The purpose of this work is to obtain VLE data for copolymer/solvent binaries and for some of their parent homopolymer/solvent binaries; and to examine the effect of copolymer composition on VLE. The experimental data are correlated using an equation of state based on molecular thermodynamics.

Experimental Apparatus and Procedure

Several experimental methods are available for measuring the vapor pressure of a solvent in a polymer solution (Danner and High, 1993). These include: inverse gas

chromatography, piezoelectric sorption, differential vapor pressure, gravimetric sorption, light scattering, and turbidimetry analysis. We have used a gravimetric sorption technique because it gives direct measurement of the VLE of polymer/solvent systems. This classic method has been described in detail by Panayiotou and Vera (1984). Figure 1 gives a schematic of the apparatus. A copolymer or homopolymer sample in an aluminum pan is suspended by a sensitive, calibrated quartz spring in an evacuated glass chamber. The glass chamber is kept in a constant-temperature air bath. In a typical experiment, a known amount (25 to 50 mg) of polymer is loaded on the pan and evacuated to remove any trace moisture, oligomers, or monomers present. Now the length of the spring is measured with a cathetometer to find the polymer mass, using a predetermined calibration curve. Solvent vapor is introduced into the evacuated system by quickly opening and closing the solvent valve. The system is left for equilibration for several hours; subsequent pressure and spring-length readings yield pressure as a function of polymer-phase composition. Readings are taken with increasing pressure. All experiments are at pressures below 90% of the saturation vapor pressure to avoid solvent condensation in the system.

Quartz springs (Ruska Instruments Corp., Houston, TX) have a sensitivity of 1 mg/mm with the maximum load limit of 250 milligrams. These springs are equipped with reference pointers on the top and bottom of the spring. Quartz spring calibration (length versus weight, a linear correlation) is independent of temperature in the range of interest (23 to 80 °C). The buoyancy effect on the calibration was also negligible. Spring length was measured using a cathetometer with a precision of 0.05 mm.

Pressure was measured using a mercury manometer kept at the same temperature as that of the polymer solution. There was no solvent condensation on the mercury meniscus as the system pressure was always lower than the solvent saturation pressure. The pressure was measured with a precision of 1 Torr, except in the cases of cyclohexane

(23.5 °C), octane (60 °C), and toluene (23.5 °C) where the precision was 0.1 Torr. The temperature of the air bath was controlled within 0.5 °C of the set point.

Materials

All polymers were supplied by Scientific Polymer Products (SPP), Ontario, NY, except poly(butyl methacrylate) which was from Aldrich. These polymers are listed in Table I along with their molecular weight (Mw), polydispersity (Mw/Mn), and glass-transition temperature (T_g). All the copolymers used here were random copolymers.

Glass-transition temperatures for copolymers were calculated from the Fox-Flory equation:

$$1/T_g = F_1/T_{g1} + F_2/T_{g2} \quad (1)$$

where T_g = glass transition temperature of the copolymer; T_{g1} , T_{g2} = glass-transition temperatures of parent homopolymers; and F_1 , F_2 = weight fraction of monomers 1 and 2 respectively. All temperatures are in Kelvins.

Both copolymers and homopolymers had polydisperse molecular weights. These were used without further fractionation because polymer molecular weight has negligible influence on the VLE behavior provided the molecular weight is above about 10,000 (see for example, Kun et al., 1993; Bonner and Prausnitz, 1974).

Solvents were used after degassing by a freeze/thaw procedure described by Panayiotou and Vera (1984).

Experimental Data

Table I gives a summary of all the new data obtained in this study. Table II gives experimental VLE data for polymer/solvent binary systems. Most of the experiments were performed at a temperature higher than the glass-transition temperature of the

polymer. A total of sixty-six data-sets were obtained by varying solvent, copolymer composition, and temperature.

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., 1993, 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 successfully reproduces 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

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{i=1}^m \sum_{j=1}^m x_i x_j \left[\sum_{k=1}^{r_i} \sum_{l=1}^{r_j} b_{ij,kl} g_{ij,kl} \right] - \sum_{i=1}^m x_i \sum_{k=1}^{r_i-1} [g_{ii,k,k+1} - 1] - \frac{\rho}{k_B T} \sum_{i=1}^m \sum_{j=1}^m x_i x_j \left[\sum_{k=1}^{r_i} \sum_{l=1}^{r_j} a_{ij,kl} \right] \quad (2)$$

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:

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

$$b = \frac{2}{3} \pi \sigma^3 F_b(k_B T / \epsilon) \quad (4)$$

where, σ = distance of separation at minimum potential energy; ϵ = well depth of pair potential; F_a , and F_b are universal functions.

Parameters a and b for a pair of dissimilar segments A and B are given as:

$$a_{AB} = \frac{2}{3} \pi \sigma_{AB}^3 \epsilon_{AB} F_a(k_B T / \epsilon_{AB}) \quad (5)$$

$$b_{AB} = \frac{2}{3} \pi \sigma_{AB}^3 F_b(k_B T / \epsilon_{AB}) \quad (6)$$

where

$$\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B) (1 - \lambda_{AB}) \quad (7)$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} (1 - \kappa_{AB}) \quad (8)$$

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

The pair correlation function is

$$g_{ij,kl} = \frac{1}{(1-\eta)} + \frac{2}{3} \frac{\xi_{ij,kl}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij,kl}^2}{(1-\eta)^3} \quad (9)$$

where the packing fraction is

$$\eta = \frac{\rho}{4} \sum_{i=1}^m x_i \sum_{k=1}^{r_i} b_{i,k} \quad (10)$$

and

$$\xi_{ij,kl} = \frac{\rho}{4} \left[\frac{b_{i,k} b_{j,l}}{b_{ij,kl}} \right]^{1/3} \sum_{i=1}^m x_j \sum_{k=1}^{r_i} b_{i,k}^{2/3} \quad (11)$$

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. These 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 Lambert (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.

Results and Discussion

The PHSC equation-of-state has been applied to some data sets from the experimental section. The experimental molecular weights of the polymers were used in the calculations; however, if these were not available, a 100,000 molecular weight has been assumed because molecular weight has negligible effect on the VLE for high-molecular-weight polymer solutions. Pure-component molecular parameters (r , ϵ , and σ) were obtained from pure-component properties (Lambert 1995).

Figure 2 shows pressure versus weight fraction solvent in the polymer phase for the system cyclohexane/poly(ethylene-co-vinyl acetate) at 80 °C. At a given pressure, solvent absorption in the copolymer increases as its ethylene content rises. This rise is expected because the hydrocarbon segments of cyclohexane are better liked by the similar

hydrocarbon segments of ethylene, whereas polar segments of vinyl acetate are disliked by the solvent molecules. The solubility of cyclohexane falls in proportion to the vinyl-acetate concentration in the copolymer. All binary parameters κ were set equal to zero, whereas three λ binary parameters were regressed using the experimental data. The PHSC equation of state can accurately correlate the experimental data.

Figure 3 shows VLE for a system containing chloroform and a copolymer poly(styrene-co-butyl methacrylate), and chloroform with the parent homopolymers, polystyrene and poly(butyl methacrylate). Figure 3 shows relative pressure P/P_{sat} (P_{sat} = saturation pressure of the solvent at the given temperature) instead of P because data at 50 °C are compared with data at 70 °C; normalizing pressure with P_{sat} tends to eliminate the temperature effect in a small temperature range such as here. Going from polystyrene to poly(styrene 50%-co-butyl methacrylate) to poly(butyl methacrylate), increases the solubility of chloroform because of favorable polar interaction between chloroform and butyl methacrylate segments. Chloroform also has some polar interaction with styrene segments, but these are not as strong as those with the butyl methacrylate segments. Solubility of chloroform rises in proportion to butyl methacrylate content in the polymer.

For the system shown in Figure 3, all binary parameters κ were set equal to zero. Solvent/homopolymer λ parameters were obtained from their VLE experimental data. The polystyrene/poly(butyl methacrylate) λ parameter was obtained from the copolymer/solvent VLE data. With only one adjustable parameter for each data set, the PHSC equation of state can correlate the VLE behavior.

Figures 4-6 show VLE data for hydrocarbons with poly(butadiene-co-acrylonitrile). For these systems, solubility is not a simple function of copolymer composition.

Figure 4 compares VLE data for cyclohexane/poly(butadiene-co-butyl methacrylate) with theory. At a given pressure, progressing from polybutadiene to poly(butadiene-co-12% acrylonitrile) to poly(butadiene-co-51% acrylonitrile), the

solubility of cyclohexane decreases dramatically with the acrylonitrile content in the copolymer. Cyclohexane has negligible solubility in polyacrylonitrile due to strong repulsion between non-polar cyclohexane segments and highly polar acrylonitrile segments. Binary parameters for the PHSC equation of state were regressed from the VLE data for cyclohexane in polybutadiene and poly(butadiene-co-21% acrylonitrile) as shown in Figure 4. VLE for cyclohexane in poly(butadiene-co-51%acrylonitrile) were predicted; the prediction is in excellent agreement with the experimental data.

Figure 5 shows results for hexane/poly(butadiene-co-acrylonitrile). In this case, VLE behavior is similar to that for cyclohexane/poly(butadiene-co-acrylonitrile) shown in Figure 4. The solubility of hexane decreases dramatically with the acrylonitrile content in the copolymer. PHSC can successfully correlate this behavior with adjustable binary parameters given in Figure 5. The predicted VLE for hexane-poly(butadiene-co-51% acrylonitrile) is in good agreement with experiment.

Finally, Figure 6 shows results for pentane with poly(butadiene-co-acrylonitrile). Results are similar to those for hexane (Figure 5) and cyclohexane (Figure 4). The solubility of pentane decreases dramatically with acrylonitrile content in the copolymer. The PHSC equation of state can successfully correlate the data for pentane with only one binary parameter for each pair as shown in Figure 6. Polybutadiene/polyacrylonitrile binary interaction parameters were the same as those used in Figures 4 and 5.

Conclusions

New VLE data have been obtained for 44 copolymer/solvent binaries and for 15 homopolymer/solvent binaries, using a gravimetric absorption technique. "Expected" non-ideal behavior has been obtained for systems such as cyclohexane/poly(ethylene-co-vinyl acetate), and chloroform/poly(styrene-co-butyl methacrylate). However, strong non-linear non-ideal behavior has been observed for systems containing hydrocarbons and poly(butadiene-co-acrylonitrile).

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

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Table I. Summary of new experimental vapor-liquid equilibrium data for polymer/solvent binaries.

Polymer (weight % copolymer composition)	Polymer Characteristics				Solvent (temperature, °C)										
	Mw	$\frac{M_w}{M_n}$	T _g (°C)	Catalog No. (SPP)*	Acetone	Acetonitrile	n-Butanol	1,2Dichloroethane	Chloroform	Cyclohexane	n-Hexane	Methanol	n-Octane	n-Pentane	Toluene
Polyacrylonitrile	150,000		85	134		60		70, 80		60	60			60	
Poly(acrylonitrile 21%-co-butadiene)			-64	523		60				60	60		60	60	
Poly(acrylonitrile 33%-co-butadiene)			-50	528		60			60		60			60	
Poly(acrylonitrile 51%-co-butadiene)			-25	530		60			60	60	60		60	60	
cis 1,4-Polybutadiene	250,000		-85	206		60			60	60	60			60	
Poly(butyl methacrylate)			27						70						
Poly(ethylene oxide)	5x10 ⁶		-67	345					60						
Polystyrene	110,000	1.1	100	580				70, 80							
Poly(styrene 70%-co-acrylonitrile)	185,000		95	495				70, 80							
Poly(styrene 5%-co-butadiene)			-80	199	50				50	60					35
Poly(styrene 23%-co-butadiene)			-60	200	50, 60				50	23.5, 60	70			60	35
Poly(styrene 45%-co-butadiene)			-30	201	50, 60				50	23.5, 60	70			60	
Poly(styrene 50%-co-butyl methacrylate)	200,000	1.9	56	595	60				70			80			
Poly(vinyl acetate)	194,000	3.1	30	024C			80		60						
Poly(vinyl acetate 9%-co-ethylene)			-118	506			80		60						
Poly(vinyl acetate 25%-co-ethylene)	88,000	4.4	-103	245					60	80					
Poly(vinyl acetate 50%-co-ethylene)	250,000	4.2	-74	785					60	80					
Poly(vinyl acetate 70%-co-ethylene)	280,000	5.6	-42	786					60	80					
Poly(vinyl acetate 12%-co-vinyl chloride)	30,000	2.1	75	063			80								
Poly(vinyl acetate 10%-co-vinyl chloride)	115,000		76	068								80			

*SPP = Scientific Polymer Products, Ontario, NY.

Table II. New experimental vapor/liquid equilibrium data for polymer/solvent binaries.

(W_1 = weight fraction solvent in polymer phase; T = temperature; and P = pressure)

Acetone/Poly(styrene-co-butadiene)
Acetone/Poly(styrene 5%-co-butadiene)

P(Torr) W_1 T = 50 °C

103	0.003
199	0.023
272	0.040
311	0.056
340	0.067
343	0.101
349	0.072
354	0.067
355	0.066
383	0.078
392	0.079
400	0.080
414	0.091
447	0.115
448	0.110
460	0.120

Acetone/Poly(styrene 23%-co-butadiene)

P(Torr) W_1 T = 50 °C

103	0.030
199	0.024
272	0.049
311	0.061
340	0.071
343	0.109
349	0.075
355	0.058
383	0.085
392	0.088
400	0.091
414	0.100
447	0.125
448	0.120
460	0.130

P(Torr) W_1 T = 60 °C

95	0.009
198	0.021
305	0.037
411	0.062
514	0.092
610	0.128

636	0.147
686	0.183
734	0.231

Acetone/Poly(styrene 45%-co-butadiene)

P(Torr) W_1 T = 50 °C

103	0.004
199	0.022
272	0.046
311	0.061
340	0.074
343	0.117
349	0.078
354	0.074
355	0.071
383	0.088
392	0.092
400	0.095
414	0.105
447	0.137
448	0.130
460	0.141

P(Torr) W_1 T = 60 °C

95	0.009
198	0.023
305	0.044
411	0.069
514	0.101
610	0.140
636	0.163
686	0.197
734	0.258

Acetone/Poly(styrene 50%-co-butyl methacrylate)

P(Torr) W_1 T = 60 °C

67	0.005
126	0.013
176	0.022
260	0.027
325	0.044
387	0.053
452	0.071
507	0.090
613	0.133
640	0.144
678	0.164
719	0.201
740	0.224
753	0.254

Acetonitrile/Polyacrylonitrile

P(Torr)	W_1	T = 60 °C
50	0.011	
100	0.022	
137	0.032	
174	0.041	
244	0.061	
284	0.076	

Acetonitrile/Poly(acrylonitrile-co-butadiene)

Acetonitrile/Poly(acrylonitrile 21%-co-butadiene)

P(Torr)	W_1	T = 60 °C
51	0.011	
103	0.026	
196	0.065	
226	0.085	
256	0.112	
295	0.187	

Acetonitrile/Poly(acrylonitrile 33%-co-butadiene)

P(Torr)	W_1	T = 60 °C
50	0.023	
100	0.043	
137	0.065	
174	0.091	
244	0.148	
284	0.206	

Acetonitrile/Poly(acrylonitrile 51%-co-butadiene)

P(Torr)	W_1	T = 60 °C
51	0.021	
103	0.047	
196	0.111	
226	0.144	
256	0.182	
295	0.293	

Acetonitrile/cis 1,4-Polybutadiene

P(Torr)	W_1	T = 60 °C
50	0.010	
100	0.913	
137	0.017	
174	0.024	
244	0.030	
284	0.039	

Butanol/Poly(vinyl acetate)

P(Torr)	W_1	T = 80 °C
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20	0.005
39	0.018
60	0.036
81	0.081
92	0.092
104	0.011
114	0.012

Butanol/Poly(vinyl acetate-co-ethylene)

Butanol/Poly(vinyl acetate 9%-co-ethylene)

P(Torr)	W_1	T = 80 °C
20	0.006	
39	0.012	
60	0.017	
81	0.027	
92	0.031	
104	0.034	
114	0.036	

Butanol/Poly(vinyl acetate-co-vinyl chloride)

Butanol/Poly(vinyl acetate 12%-co-vinyl chloride)

P(Torr)	W_1	T = 80 °C
20	0.007	
39	0.016	
60	0.022	
81	0.033	
92	0.040	
104	0.044	
114	0.046	

1,2 Dichloroethane/Polyacrylonitrile

P(Torr)	W_1	T = 70 °C
122	0.025	
159	0.031	
200	0.040	
231	0.043	
274	0.046	
305	0.050	
329	0.054	
345	0.058	
368	0.061	

P(Torr)	W_1	T = 80 °C
168	0.017	
205	0.020	
272	0.024	
343	0.038	
376	0.044	
432	0.053	
446	0.057	

455 0.060

1,2 Dichloroethane/Polystyrene

P(Torr) W_1 T = 70 °C

122 0.064
159 0.092
200 0.127
231 0.152
274 0.209
305 0.244
329 0.289
345 0.306
368 0.352

P(Torr) W_1 T = 80 °C

168 0.070
205 0.090
272 0.125
343 0.221
376 0.257
432 0.331
446 0.360
455 0.377

1,2 Dichloroethane/Poly(styrene 70%-co-acrylonitrile)

P(Torr) W_1 T = 70 °C

122 0.009
159 0.026
200 0.048
231 0.139
274 0.196
305 0.243
329 0.281
345 0.296
368 0.339

P(Torr) W_1 T = 80 °C

168 0.009
205 0.039
272 0.090
343 0.251
376 0.279
432 0.348
446 0.376
455 0.389

Chloroform/Poly(acrylonitrile 33%-co-butadiene)

P(Torr) W_1 T = 60 °C

102 0.080

201 0.170

202 0.172

297 0.262

396 0.372

449 0.424

497 0.485

550 0.563

Chloroform/cis 1,4-Polybutadiene

P(Torr) W_1 T = 60 °C

102 0.114

201 0.224

202 0.228

297 0.336

396 0.444

449 0.494

497 0.548

550 0.615

Chloroform/Poly(butyl methacrylate)

P(Torr) W_1 T = 70 °C

100 0.093

198 0.176

301 0.268

402 0.347

491 0.434

591 0.520

645 0.566

Chloroform/Poly(ethylene oxide)

P(Torr) W_1 T = 60 °C

105 0.082

211 0.276

301 0.379

399 0.459

438 0.497

496 0.540

542 0.567

594 0.585

653 0.609

Chloroform/Poly(styrene 50%-co-butyl methacrylate)

P(Torr) W_1 T = 70 °C

100 0.078

198 0.148

301 0.222

402 0.292

491 0.369

591 0.455

645 0.512

Chloroform/Poly(styrene-co-butadiene)Chloroform/Poly(styrene 5%-co-butadiene)P(Torr) W_1 T = 50 °C

64	0.040
122	0.106
191	0.204
237	0.272
287	0.341
341	0.457
357	0.489
375	0.537
403	0.580
423	0.638

Chloroform/Poly(styrene 23%-co-butadiene)P(Torr) W_1 T = 50 °C

64	0.046
122	0.111
191	0.206
237	0.270
287	0.338
341	0.449
357	0.482
375	0.514
403	0.566
423	0.621

Chloroform/Poly(styrene 45%-co-butadiene)P(Torr) W_1 T = 50 °C

64	0.043
122	0.107
191	0.205
237	0.272
287	0.343
341	0.463
357	0.500
375	0.534
403	0.592
423	0.650

Chloroform/Poly(vinyl acetate)P(Torr) W_1 T = 60 °C

105	0.088
211	0.150
301	0.245
399	0.334
438	0.371
496	0.416
542	0.444
594	0.466

653

0.490

Chloroform/Poly(vinyl acetate-co-ethylene)Chloroform/Poly(vinyl acetate 9%-co-ethylene)P(Torr) W_1 T = 60 °C

105	0.031
211	0.067
301	0.104
399	0.147
438	0.168
496	0.196
542	0.216
594	0.235
653	0.253

Chloroform/Poly(vinyl acetate 25%-co-ethylene)P(Torr) W_1 T = 60 °C

104	0.062
200	0.140
299	0.228
399	0.320
449	0.358
499	0.401
548	0.441
595	0.481

Chloroform/Poly(vinyl acetate 50%-co-ethylene)P(Torr) W_1 T = 60 °C

104	0.098
200	0.202
299	0.303
399	0.398
449	0.439
499	0.477
548	0.512
595	0.552

Chloroform/Poly(vinyl acetate 70%-co-ethylene)P(Torr) W_1 T = 60 °C

104	0.059
200	0.161
299	0.287
399	0.403
449	0.450
499	0.489
548	0.526
595	0.573

Cyclohexane/Poly(acrylonitrile-co-butadiene)Cyclohexane/poly(acrylonitrile 21%-butadiene)P(Torr) W_1 T = 60 °C

103	0.030
147	0.062
198	0.084
240	0.114
267	0.177
268	0.176
286	0.210
298	0.216
323	0.283

Cyclohexane/Poly(acrylonitrile 51%-co-butadiene)P(Torr) W_1 T = 60 °C

103	0.007
143	0.011
147	0.015
196	0.024
198	0.024
240	0.032
267	0.047
298	0.060
323	0.091

Cyclohexane/cis 1,4-PolybutadieneP(Torr) W_1 T = 60 °C

101	0.082
152	0.134
202	0.189
252	0.272
286	0.338

Cyclohexane/Poly(styrene-co-butadiene)Cyclohexane/Poly(styrene 5%-co-butadiene)P(Torr) W_1 T = 60 °C

36	0.027
79	0.057
127	0.103
149	0.120
186	0.152
221	0.189
253	0.233
282	0.276
305	0.323

Cyclohexane/Poly(styrene 23%-co-butadiene)P(Torr) W_1 T = 23.5 °C

14.8	0.015
22.4	0.035
34.0	0.074
51.2	0.141
57.3	0.197
67.7	0.276
75.2	0.328

P(Torr) W_1 T = 60 °C

36	0.018
79	0.052
127	0.088
186	0.136
221	0.168
253	0.208
282	0.244
305	0.287

Cyclohexane/Poly(styrene 45%-co-butadiene)P(Torr) W_1 T = 23.5 °C

14.8	0.011
22.4	0.028
34.0	0.063
51.2	0.127
57.3	0.176
67.7	0.253
75.2	0.301

P(Torr) W_1 T = 60 °C

36	0.021
79	0.050
127	0.087
149	0.103
186	0.130
221	0.163
253	0.200
282	0.240
305	0.282

Cyclohexane/Poly(vinyl acetate-co-ethylene)Cyclohexane/Poly(vinyl acetate 25%-co-ethylene)P(Torr) W_1 T = 80 °C

56	0.011
108	0.037
199	0.074
298	0.140
412	0.228
416	0.238

455	0.277
481	0.300
528	0.369

Cyclohexane/Poly(vinyl acetate 50%-co-ethylene)

P(Torr)	W_1	T = 80 °C
56	0.005	
108	0.025	
199	0.046	
298	0.104	
412	0.159	
416	0.170	
455	0.205	
481	0.225	
528	0.287	

Cyclohexane/Poly(vinyl acetate 70%-co-ethylene)

P(Torr)	W_1	T = 80 °C
56	0.004	
108	0.026	
199	0.042	
298	0.081	
412	0.123	
416	0.133	
455	0.156	
481	0.191	
528	0.242	

Hexane/Polyacrylonitrile

P(Torr)	W_1	T = 60 °C
93	0.001	
188	0.007	
270	0.007	
325	0.009	

Hexane/Poly(acrylonitrile-co-butadiene)

Hexane/Poly(acrylonitrile 21%-co-butadiene)

P(Torr)	W_1	T = 60 °C
97	0.025	
192	0.044	
291	0.082	
334	0.104	
381	0.134	
431	0.170	
478	0.236	
487	0.251	

Hexane/Poly(acrylonitrile 33%-co-butadiene)

P(Torr)	W_1	T = 60 °C
93	0.002	

188	0.017
270	0.026
325	0.037

Hexane/Poly(acrylonitrile 51%-co-butadiene)

P(Torr)	W_1	T = 60 °C
97	0.018	
192	0.020	
291	0.029	
334	0.033	
381	0.041	
431	0.044	
478	0.062	
487	0.062	

Hexane/cis 1,4-Polybutadiene

P(Torr)	W_1	T = 60 °C
93	0.036	
188	0.078	
270	0.115	
325	0.146	

Hexane/Poly(styrene-co-butadiene)

Hexane/Poly(styrene 23%-co-butadiene)

P(Torr)	W_1	T = 70 °C
104	0.014	
205	0.043	
289	0.063	
366	0.110	
461	0.162	
564	0.262	

Hexane/Poly(styrene 45%-co-butadiene)

P(Torr)	W_1	T = 70 °C
104	0.016	
205	0.038	
289	0.061	
366	0.103	
461	0.155	
564	0.249	

Methanol/Poly(vinyl acetate)

P(Torr)	W_1	T = 80 °C
102	0.021	
213	0.030	
299	0.041	
394	0.053	
493	0.062	
593	0.08	

Methanol/Poly(vinyl acetate 10%-co-vinyl chloride)P(Torr) W_1 T = 80 °C

102	0.021
213	0.030
299	0.041
394	0.053
493	0.062
593	0.08

Octane/Poly(acrylonitrile-co-butadiene)**Octane/Poly(acrylonitrile 21%-co-butadiene)**P(Torr) W_1 T = 60 °C

21.4	0.036
31.4	0.052
38.1	0.064
44.3	0.079
51.8	0.111
63.1	0.158

Octane/Poly(acrylonitrile 51%-co-butadiene)P(Torr) W_1 T = 60 °C

21.4	0.007
31.4	0.010
38.1	0.013
44.3	0.015
51.8	0.021
63.1	0.026

Pentane/PolyacrylonitrileP(Torr) W_1 T = 60 °C

100	0.005
202	0.007
401	0.011
485	0.010
581	0.010
673	0.010
763	0.010
868	0.011
976	0.011

Pentane/Poly(acrylonitrile-co-butadiene)**Pentane/Poly(acrylonitrile 21%-co-butadiene)**P(Torr) W_1 T = 60 °C

171	0.008
270	0.016
351	0.021
491	0.033
630	0.046
730	0.055
850	0.070
936	0.078

1032 0.089

Pentane/Poly(acrylonitrile 33%-co-butadiene)P(Torr) W_1 T = 60 °C

100	0.009
202	0.014
401	0.025
485	0.027
581	0.032
673	0.036
763	0.044
868	0.050
976	0.055

Pentane/Poly(acrylonitrile 51%-co-butadiene)P(Torr) W_1 T = 60 °C

171	0.010
270	0.009
351	0.013
491	0.019
630	0.022
730	0.022
850	0.026
936	0.027
1032	0.034

Pentane/cis 1,4-PolybutadieneP(Torr) W_1 T = 60 °C

100	0.012
202	0.024
401	0.046
485	0.061
581	0.082
673	0.095
763	0.117
868	0.134
976	0.155

Pentane/Poly(styrene-co-butadiene)**Pentane/Poly(styrene 23%-co-butadiene)**P(Torr) W_1 T = 60 °C

171	0.008
270	0.016
351	0.021
491	0.033
630	0.046
730	0.055
850	0.070
936	0.078
1032	0.089

Pentane/Poly(styrene 45%-co-butadiene)P(Torr) W_1 T = 60 °C

171	0.010
270	0.009
351	0.013
491	0.019
630	0.022
730	0.022
850	0.026
936	0.027
1032	0.034

Toluene/Poly(styrene-co-butadiene)Toluene/Poly(styrene 23%-co-butadiene)P (Torr) W_1 T = 35 °C

7.0	0.029
15.6	0.031
22.8	0.032
32.7	0.037
36.2	0.037
41.1	0.038

Toluene/Poly(styrene 5%-co-butadiene)P(Torr) W_1 T = 35 °C

7.0	0.043
15.6	0.099
22.8	0.184
32.7	0.319
36.2	0.416
41.1	0.513

List of Figures

Figure 1. Experimental apparatus for vapor-liquid equilibria (VLE) measurement of polymer/solvent binary solutions. (Here VLE of two polymers with a common solvent can be measured simultaneously).

Figure 2. VLE for cyclohexane/poly(ethylene-co-vinyl acetate) solutions.

Figure 3. VLE for chloroform/polystyrene, poly(styrene-co-butyl methacrylate), and poly(butyl methacrylate) solutions.

Figure 4. VLE for cyclohexane/cis-1,4-polybutadiene, and poly(butadiene-co-acrylonitrile) solutions.

Figure 5. VLE for n-hexane/cis-1,4-polybutadiene, and poly(butadiene-co-acrylonitrile) solutions.

Figure 6. VLE for n-pentane/poly(butadiene-co-acrylonitrile) solutions.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720