Vapor–Liquid Equilibria of Copolymer + Solvent and Homopolymer + Solvent Binaries: New Experimental Data and Their Correlation

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Sixty-four isothermal data sets for vapor–liquid equilibria (VLE) for polymer + solvent binaries have been obtained using a gravimetric sorption technique, in the range 23.5–80 °C. Solvents studied were acetone, acetonitrile, 1-butanol, 1,2-dichloroethane, chloroform, cyclohexane, 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). The 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 nonideal 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 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 20 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 copolymer + 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 Section

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 (25–50 mg) of polymer is loaded onto 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 allowed to equilibrate 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 mg. These springs are equipped with reference pointers on the top and bottom of the spring. Quartz spring calibration (length versus mass, a linear correlation) is independent of temperature in the range of interest (23–80 °C). The buoyancy effect on the calibration was also negligible. Spring length was measured using a cathetometer with a precision of 0.05 mm. Hence, mass was measured with a precision of 0.05 mg. The typical error in the measurements of mass fraction solvent in the solvent + polymer mixture, w_1, was about 2%.

Pressure was measured using a mercury manometer kept at the same temperature as that of the polymer

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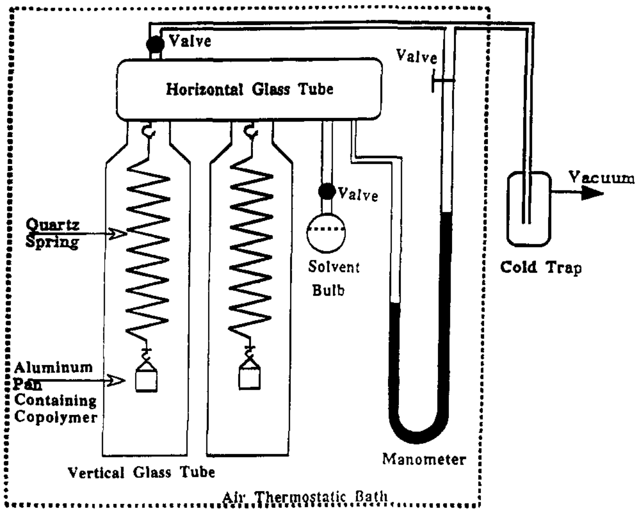

Figure 1. Experimental apparatus for VLE measurement of polymer + solvent binary solutions. (Here VLE of two polymers with a common solvent can be measured simultaneously.)

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 0.1 kPa, except in the cases of cyclohexane (23.5 °C), octane (60 °C), and toluene (23.5 °C) where the precision was 0.01 kPa. The temperature of the air bath was controlled within 0.5 °C of the set point.

The reproducibility of the experimental procedure was checked by comparing our VLE data with literature values (Bawn et al., 1950; Kun et al., 1993) for the toluene + polystyrene system at 35 °C. Good agreement was observed.

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 1 along with their molecular weight (M_w), polydispersity (M_w/M_n), and glass-transition temperature (t_g). For copolymers, the mass percent compositions of the two constituent polymer segments are specified. All copolymers used here were random copolymers. Glass-transition temperatures for copolymers were calculated from the Fox–Flory equation

$$1/(t_g + 273.15) = F_1/(t_{g1} + 273.15) + F_2/(t_{g2} + 273.15) \qquad (1)$$

where t_g = glass-transition temperature of the copolymer, t_{g1} and t_{g2} = glass-transition temperatures of parent homopolymers, and F_1 and F_2 = mass fractions of monomers 1 and 2, respectively. All temperatures are in degrees Celsius.

Both copolymers and homopolymers had polydisperse molecular weights. These were used without further fractionation because the 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) and Bonner and Prausnitz (1974)).

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

Experimental Data. Table 1 gives a summary of all the new data obtained in this study. Table 2 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-four data sets were obtained

Table 1. Summary of New Experimental Vapor–Liquid Equilibrium Results for Polymer + Solvent Systems

polymer (wt % copolymer composition)	polymer characteristics: M_w	M_w/M_n	t_g/°C	catalog no. (SPP)[a]	temperature/°C: acetone	acetonitrile	1-butanol	1,2-dichloroethane	chloroform	cyclohexane	hexane	methanol	octane	pentane	toluene
polyacrylonitrile	150 000		85	134		60		70, 80			60			60	
poly(21% acrylonitrile-*co*-butadiene)			−64	523		60				60	60		60	60	
poly(33% acrylonitrile-*co*-butadiene)			−50	528		60			60		60			60	
poly(51% acrylonitrile-*co*-butadiene)			−25	530		60				60	60		60	60	
poly(*cis*-1,4-butadiene)	250 000		−85	206		60			60	60	60			60	
poly(butyl methacrylate)			27						70						
poly(ethylene oxide)	5 000 000		−67	345					60						
polystyrene	110 000	1.1	100	580				70, 80							
poly(70% styrene-*co*-acrylonitrile)	185 000		95	495				70, 80							
poly(5% styrene-*co*-butadiene)			−80	199	50				50	60					35
poly(23% styrene-*co*-butadiene)			−60	200	50, 60				50	23.5, 60	70			60	35
poly(45% styrene-*co*-butadiene)			−30	201	50, 60				50	23.5, 60	70			60	
poly(50% styrene-*co*-butyl methacrylate)	200 000	1.9	56	595	60				70			80			
poly(vinyl acetate)	194 000	3.1	30	024C			80		60						
poly(9% vinyl acetate-*co*-ethylene)			−118	506			80		60						
poly(25% vinyl acetate-*co*-ethylene)	88 000	4.4	−103	245					60	80					
poly(50% vinyl acetate-*co*-ethylene)	250 000	4.2	−74	785					60	80					
poly(70% vinyl acetate-*co*-ethylene)	280 000	5.6	−42	786					60	80					
poly(12% vinyl acetate-*co*-vinyl chloride)	30 000	2.1	75	063			80								
poly(10% vinyl acetate-*co*-vinyl chloride)	115 000		76	068								80			

[a] SPP = Scientific Polymer Products, Ontario, NY.

Table 2. New Experimental Vapor–Liquid Equilibrium Data for Polymer + Solvent Systems (w_1 = Mass Fraction Solvent in Polymer Phase, t = Temperature, and P = Pressure)

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
Acetone + Poly(styrene-*co*-butadiene)							
Acetone + Poly(5% styrene-*co*-butadiene)							
t = 50 °C							
13.7	0.003	45.3	0.067	51.1	0.078	59.6	0.115
26.5	0.023	46.5	0.072	52.3	0.079	59.7	0.110
36.3	0.040	47.2	0.067	53.3	0.080	61.3	0.120
41.5	0.056	47.3	0.066	55.2	0.091		
Acetone + Poly(23% styrene-*co*-butadiene)							
t = 50 °C							
26.5	0.024	46.5	0.075	52.3	0.088	59.6	0.125
36.3	0.049	47.3	0.058	53.3	0.091	59.7	0.120
41.5	0.061	51.1	0.085	55.2	0.100	61.3	0.130
45.3	0.071						
t = 60 °C							
12.7	0.009	54.8	0.062	81.3	0.128	91.5	0.183
26.4	0.021	68.5	0.092	84.8	0.147	97.9	0.231
40.7	0.037						
Acetone + Poly(styrene 45%-*co*-butadiene)							
t = 50 °C							
13.7	0.004	45.3	0.074	51.1	0.088	59.6	0.137
26.5	0.022	46.5	0.078	52.3	0.092	59.7	0.130
36.3	0.046	47.2	0.074	53.3	0.095	61.3	0.141
41.5	0.061	47.3	0.071	55.2	0.105		
t = 60 °C							
12.7	0.009	54.8	0.069	81.3	0.140	91.5	0.197
26.4	0.023	68.5	0.101	84.8	0.163	97.9	0.258
40.7	0.044						
Acetone + Poly(50% styrene-*co*-butyl methacrylate)							
t = 60 °C							
8.9	0.005	43.3	0.044	81.7	0.133	95.9	0.201
16.8	0.013	51.6	0.053	85.3	0.144	98.7	0.224
23.5	0.022	60.3	0.071	90.4	0.164	100.4	0.254
34.7	0.027	67.6	0.090				
Acetonitrile + Polyacrylonitrile							
t = 60 °C							
6.7	0.011	18.3	0.032	32.5	0.061	37.9	0.076
13.3	0.022	23.2	0.041				
Acetonitrile + Poly(acrylonitrile-*co*-butadiene)							
Acetonitrile + Poly(21% acrylonitrile-*co*-butadiene)							
t = 60 °C							
6.8	0.011	26.1	0.065	34.1	0.112	39.3	0.187
13.7	0.026	30.1	0.085				
Acetonitrile + Poly(33% acrylonitrile-*co*-butadiene)							
t = 60 °C							
6.7	0.023	18.3	0.065	32.5	0.148	37.9	0.206
13.3	0.043	23.2	0.091				
Acetonitrile + Poly(51% acrylonitrile-*co*-butadiene)							
t = 60 °C							
6.8	0.021	26.1	0.111	34.1	0.182	39.3	0.293
13.7	0.047	30.1	0.144				
Acetonitrile + Poly(*cis*-1,4-butadiene)							
t = 60 °C							
6.7	0.010	18.3	0.017	32.5	0.030	37.9	0.039
13.3	0.010	23.2	0.024				

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
1-Butanol + Poly(vinyl acetate)							
t = 80 °C							
2.7	0.005	8.0	0.036	12.3	0.092	15.2	0.012
5.2	0.018	10.8	0.081	13.9	0.011		
1-Butanol + Poly(vinyl acetate-*co*-ethylene)							
1-Butanol + Poly(9% vinyl acetate-*co*-ethylene)							
t = 80 °C							
2.7	0.006	8.0	0.017	12.3	0.031	15.2	0.036
5.2	0.012	10.8	0.027	13.9	0.034		
1-Butanol + Poly(vinyl acetate-*co*-vinyl chloride)							
1-Butanol + Poly(12% vinyl acetate-*co*-vinyl chloride)							
t = 80 °C							
2.7	0.007	8.0	0.022	12.3	0.040	15.2	0.046
5.2	0.016	10.8	0.033	13.9	0.044		
1,2-Dichloroethane + Polyacrylonitrile							
t = 70 °C							
16.3	0.025	30.8	0.043	40.7	0.050	46.0	0.058
21.2	0.031	36.5	0.046	43.9	0.054	49.1	0.061
26.7	0.040						
t = 80 °C							
22.4	0.017	36.3	0.024	50.1	0.044	59.5	0.057
27.3	0.020	45.7	0.038	57.6	0.053	60.7	0.060
1,2-Dichloroethane + Polystyrene							
t = 70 °C							
16.3	0.064	30.8	0.152	40.7	0.244	46.0	0.306
21.2	0.092	36.5	0.209	43.9	0.289	49.1	0.352
26.7	0.127						
t = 80 °C							
22.4	0.070	36.3	0.125	50.1	0.257	59.5	0.360
27.3	0.090	45.7	0.221	57.6	0.331	60.7	0.377
1,2-Dichloroethane + Poly(70% styrene-*co*-acrylonitrile)							
t = 70 °C							
16.3	0.009	30.8	0.139	40.7	0.243	46.0	0.296
21.2	0.026	36.5	0.196	43.9	0.281	49.1	0.339
26.7	0.048						
t = 80 °C							
22.4	0.009	36.3	0.090	50.1	0.279	59.5	0.376
27.3	0.039	45.7	0.251	57.6	0.348	60.7	0.389
Chloroform + Poly(33% acrylonitrile-*co*-butadiene)							
t = 60 °C							
13.6	0.080	26.9	0.172	52.8	0.372	66.3	0.485
26.8	0.170	39.6	0.262	59.9	0.424	73.3	0.563
Chloroform + Poly(*cis*-1,4-butadiene)							
t = 60 °C							
13.6	0.114	26.9	0.228	52.8	0.444	66.3	0.548
26.8	0.224	39.6	0.336	59.9	0.494	73.3	0.615
Chloroform + Poly(butyl methacrylate)							
t = 70 °C							
13.3	0.093	40.1	0.268	65.5	0.434	86.0	0.566
26.4	0.176	53.6	0.347	78.8	0.520		

Table 2. (Continued)

Chloroform + Poly(ethylene oxide)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
14.0	0.082	53.2	0.459	66.1	0.540	79.2	0.585
28.1	0.276	58.4	0.497	72.3	0.567	87.1	0.609
40.1	0.379						

Chloroform + Poly(50% styrene-*co*-butyl methacrylate)

t = 70 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.3	0.078	40.1	0.222	65.5	0.369	86.0	0.512
26.4	0.148	53.6	0.292	78.8	0.455		

Chloroform + Poly(styrene-*co*-butadiene)

Chloroform + Poly(5% styrene-*co*-butadiene)

t = 50 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
8.5	0.040	31.6	0.272	47.6	0.489	53.7	0.580
16.3	0.106	38.3	0.341	50.0	0.537	56.4	0.638
25.5	0.204	45.5	0.457				

Chloroform + Poly(23% styrene-*co*-butadiene)

t = 50 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
8.5	0.046	31.6	0.270	47.6	0.482	53.7	0.566
16.3	0.111	38.3	0.338	50.0	0.514	56.4	0.621
25.5	0.206	45.5	0.449				

Chloroform + Poly(45% styrene-*co*-butadiene)

t = 50 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
8.5	0.043	31.6	0.272	47.6	0.500	53.7	0.592
16.3	0.107	38.3	0.343	50.0	0.534	56.4	0.650
25.5	0.205	45.5	0.463				

Chloroform + Poly(vinyl acetate)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
14.0	0.088	53.2	0.334	66.1	0.416	79.2	0.466
28.1	0.150	58.4	0.371	72.3	0.444	87.1	0.490
40.1	0.245						

Chloroform + Poly(vinyl acetate-*co*-ethylene)

Chloroform + Poly(9% vinyl acetate-*co*-ethylene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
14.0	0.031	53.2	0.147	66.1	0.196	79.2	0.235
28.1	0.067	58.4	0.168	72.3	0.216	87.1	0.253
40.1	0.104						

Chloroform + Poly(25% vinyl acetate-*co*-ethylene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.9	0.062	39.9	0.228	59.9	0.358	73.1	0.441
26.7	0.140	53.2	0.320	66.5	0.401	79.3	0.481

Chloroform + Poly(50% vinyl acetate-*co*-ethylene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.9	0.098	39.9	0.303	59.9	0.439	73.1	0.512
26.7	0.202	53.2	0.398	66.5	0.477	79.3	0.552

Chloroform + Poly(70% vinyl acetate-*co*-ethylene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.9	0.059	39.9	0.287	59.9	0.450	73.1	0.526
26.7	0.161	53.2	0.403	66.5	0.489	79.3	0.573

Cyclohexane + Poly(acrylonitrile-*co*-butadiene)

Cyclohexane + Poly(21% acrylonitrile-*co*-butadiene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.7	0.030	32.0	0.114	35.7	0.176	39.7	0.216
19.6	0.062	35.6	0.177	38.1	0.210	43.1	0.283
26.4	0.084						

Cyclohexane + Poly(51% acrylonitrile-*co*-butadiene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.7	0.007	26.1	0.024	32.0	0.032	39.7	0.060
19.1	0.011	26.4	0.024	35.6	0.047	43.1	0.091
19.6	0.015						

Cyclohexane + Poly(*cis*-1,4-butadiene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
13.5	0.082	26.9	0.189	33.6	0.272	38.1	0.338
20.3	0.134						

Cyclohexane + Poly(styrene-*co*-butadiene)

Cyclohexane + Poly(5% styrene-*co*-butadiene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
4.8	0.027	19.9	0.120	29.5	0.189	37.6	0.276
10.5	0.057	24.8	0.152	33.7	0.233	40.7	0.323
16.9	0.103						

Cyclohexane + Poly(23% styrene-*co*-butadiene)

t = 23.5 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
2.00	0.015	4.53	0.074	7.64	0.197	10.03	0.328
2.99	0.035	6.83	0.141	9.03	0.276		

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
4.8	0.018	16.9	0.088	29.5	0.168	37.6	0.244
10.5	0.052	24.8	0.136	33.7	0.208	40.7	0.287

Cyclohexane + Poly(45% styrene-*co*-butadiene)

t = 23.5 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
2.00	0.011	4.53	0.063	7.64	0.176	10.03	0.301
2.99	0.028	6.83	0.127	9.03	0.253		

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
4.8	0.021	19.9	0.103	29.5	0.163	37.6	0.240
10.5	0.050	24.8	0.130	33.7	0.200	40.7	0.282
16.9	0.087						

Cyclohexane + Poly(vinyl acetate-*co*-ethylene)

Cyclohexane + Poly(25% vinyl acetate-*co*-ethylene)

t = 80 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
7.5	0.011	39.7	0.140	55.5	0.238	64.1	0.300
14.4	0.037	54.9	0.228	60.7	0.277	70.4	0.369
26.5	0.074						

Cyclohexane + Poly(50% vinyl acetate-*co*-ethylene)

t = 80 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
7.5	0.005	39.7	0.104	55.5	0.170	64.1	0.225
14.4	0.025	54.9	0.159	60.7	0.205	70.4	0.287
26.5	0.046						

Cyclohexane + Poly(70% vinyl acetate-*co*-ethylene)

t = 80 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
7.5	0.004	39.7	0.081	55.5	0.133	64.1	0.191
14.4	0.026	54.9	0.123	60.7	0.156	70.4	0.242
26.5	0.042						

Hexane + Polyacrylonitrile

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
12.4	0.001	25.1	0.007	36.0	0.007	43.3	0.009

Hexane + Poly(acrylonitrile-*co*-butadiene)

Hexane + Poly(21% acrylonitrile-*co*-butadiene)

t = 60 °C

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
12.9	0.025	38.8	0.082	50.8	0.134	63.7	0.236
25.6	0.044	44.5	0.104	57.5	0.170	64.9	0.251

Table 2. (Continued)

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
Hexane + Poly(33% acrylonitrile-*co*-butadiene)							
t = 60 °C							
12.4	0.002	25.1	0.017	36.0	0.026	43.3	0.037
Hexane + Poly(51% acrylonitrile-*co*-butadiene)							
t = 60 °C							
12.9	0.018	38.8	0.029	50.8	0.041	63.7	0.062
25.6	0.020	44.5	0.033	57.5	0.044	64.9	0.062
Hexane + Poly(*cis*-1,4-butadiene)							
t = 60 °C							
12.4	0.036	25.1	0.078	36.0	0.115	43.3	0.146
Hexane + Poly(styrene-*co*-butadiene)							
Hexane + Poly(23% styrene-*co*-butadiene)							
t = 70 °C							
13.9	0.014	38.5	0.063	61.5	0.162	75.2	0.262
27.3	0.043	48.8	0.110				
Hexane + Poly(45% styrene-*co*-butadiene)							
t = 70 °C							
13.9	0.016	38.5	0.061	61.5	0.155	75.2	0.249
27.3	0.038	48.8	0.103				
Methanol + Poly(vinyl acetate)							
t = 80 °C							
13.6	0.021	39.9	0.041	65.7	0.062	79.1	0.080
28.4	0.030	52.5	0.053				
Methanol + Poly(10% vinyl acetate-*co*-vinyl chloride)							
t = 80 °C							
13.6	0.029	39.9	0.032	65.7	0.037	79.1	0.038
28.4	0.030	52.5	0.037				
Octane + Poly(acrylonitrile-*co*-butadiene)							
Octane + Poly(21% acrylonitrile-*co*-butadiene)							
t = 60 °C							
2.90	0.036	5.08	0.064	6.91	0.111	8.41	0.158
4.19	0.052	5.91	0.079				
Octane + Poly(51% acrylonitrile-*co*-butadiene)							
t = 60 °C							
2.85	0.007	5.08	0.013	6.91	0.021	8.41	0.026
4.19	0.010	5.91	0.015				
Pentane + Polyacrylonitrile							
t = 60 °C							
13.3	0.005	64.7	0.010	89.7	0.010	115.7	0.011
26.9	0.007	77.5	0.010	101.7	0.010	130.1	0.011
53.5	0.011						

P/kPa	w_1	P/kPa	w_1	P/kPa	w_1	P/kPa	w_1
Pentane + Poly{acrylonitrile-*co*-butadiene)							
Pentane + Poly(21% acrylonitrile-*co*-butadiene)							
t = 60 °C							
22.8	0.008	65.5	0.033	97.3	0.055	124.8	0.078
36.0	0.016	84.0	0.046	113.3	0.070	137.6	0.089
46.8	0.021						
Pentane + Poly(33% acrylonitrile-*co*-butadiene)							
t = 60 °C							
13.3	0.009	64.7	0.027	89.7	0.036	115.7	0.050
26.9	0.014	77.5	0.032	101.7	0.044	130.1	0.055
53.5	0.025						
Pentane + Poly(51% acrylonitrile-*co*-butadiene)							
t = 60 °C							
22.8	0.010	65.5	0.019	97.3	0.022	124.8	0.027
36.0	0.009	84.0	0.022	113.3	0.026	137.6	0.034
46.8	0.013						
Pentane + Poly(*cis*-1,4-butadiene)							
t = 60 °C							
13.3	0.012	64.7	0.061	89.7	0.095	115.7	0.134
26.9	0.024	77.5	0.082	101.7	0.117	130.1	0.155
53.5	0.046						
Pentane + Poly(styrene-*co*-butadiene)							
Pentane + Poly(23% styrene-*co*-butadiene)							
t = 60 °C							
22.8	0.008	65.5	0.033	97.3	0.055	124.8	0.078
36.0	0.016	84.0	0.046	113.3	0.070	137.6	0.089
46.8	0.021						
Pentane + Poly(45% styrene-*co*-butadiene)							
t = 60 °C							
22.8	0.010	65.5	0.019	97.3	0.022	124.8	0.027
46.8	0.013	84.0	0.022	113.3	0.026	137.6	0.034
Toluene + Poly(styrene-*co*-butadiene)							
Toluene + Poly(23% styrene-*co*-butadiene)							
t = 35 °C							
0.90	0.029	3.04	0.032	4.83	0.037	5.48	0.038
2.08	0.031	4.36	0.037				
Toluene + Poly(5% styrene-*co*-butadiene)							
t = 35 °C							
0.93	0.043	3.04	0.184	4.83	0.416	5.48	0.513
2.08	0.099	4.36	0.319				

by varying the 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–c). For ordinary VLE at low pressures, it is often possible to use the 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 and VLE phase diagrams at high pressures and account for solvent compressibility. For binary polymer solutions, the PHSC theory successfully reproduces all types of observed liquid–liquid equilibrium phase diagrams, including upper or lower critical solution temperatures (UCST or LCST), or both, and 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

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

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. The subscript ij,kl denote the pair containing the kth segment of component i and the lth 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

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

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

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

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

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

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

where

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

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}(1 - \kappa_{AB}) \quad (8)$$

Parameters σ_A and ϵ_A pertain to segment A; κ_{AB} and λ_{AB} are adjustable intersegmental 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

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

and

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

In summary, each pure solvent or homopolymer is characterized by three molecular constants: r, segment number per molecule; σ, segment size; and ϵ, nonbonded 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.

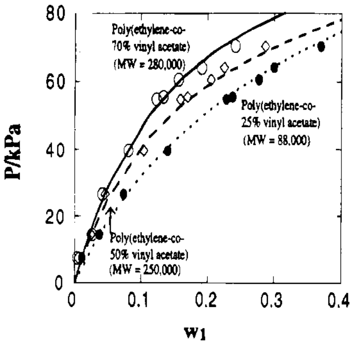

Figure 2. VLE for cyclohexane + poly(ethylene-*co*-vinyl acetate) solutions: w_1, mass fraction cyclohexane; points, new experimental data; lines, calculation using PHSC equation of state parameters [cyclohexane + polyethylene, $\kappa = 0$, $\lambda = -0.0344$; cyclohexane + poly(vinyl acetate), $\kappa = 0$, $\lambda = -0.005$; poly(vinyl acetate) + polyethylene, $\kappa = 0$, $\lambda = -0.164$].

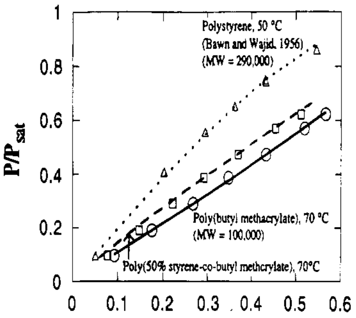

Figure 3. VLE for chloroform + polystyrene, poly(styrene-*co*-butyl methacrylate), and poly(butyl methacrylate) solutions: w_1, mass fraction chloroform; points, experimental data; lines, calculation using PHSC equation of state parameters [chloroform + polystyrene, $\kappa = 0$, $\lambda = -0.025$; chloroform + poly(butyl methacrylate), $\kappa = 0$, $\lambda = -0.05$; polystyrene + poly(butyl methacrylate), $\kappa = 0$, $\lambda = -0.04$].

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 a 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; Song et al., 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 the copolymer poly(styrene-*co*-butyl methacrylate) and chloroform with the parent homopolymers polystyrene and

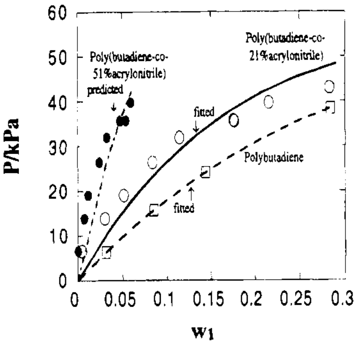

Figure 4. VLE for cyclohexane + poly(*cis*-1,4-butadiene) and poly(butadiene-*co*-acrylonitrile) solutions: w_1, mass fraction cyclohexane; points, new experimental data; lines, calculation using PHSC equation of state parameters [cyclohexane + polyacrylonitrile, $\kappa = 0.082$, $\lambda = -0.08$; cyclohexane + poly(*cis*-1,4-butadiene), $\kappa = 0$, $\lambda = -0.021$; poly(*cis*-1,4-butadiene) + polyacrylonitrile, $\kappa = 0.027$, $\lambda = 0.0$].

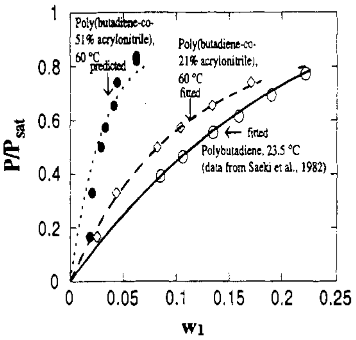

Figure 5. VLE for hexane + poly(*cis*-1,4-butadiene) poly(butadiene-*co*-acrylonitrile) solutions: w_1, mass fraction hexane; points, experimental data; lines, calculation using PHSC equation of state parameters [hexane + polyacrylonitrile, $\kappa = 0.168$, $\lambda = -0.33$; hexane + poly(*cis*-1,4-butadiene), $\kappa = -0.023$; $\lambda = -0.02$; poly(*cis*-1,4-butadiene) + polyacrylonitrile, $\kappa = 0.027$, $\lambda = 0.0$].

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(50% styrene-*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. The solubility of chloroform rises in proportion to the 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) at 60 °C. For these systems, solubility is not a simple function of copolymer composition.

Figure 4 compares VLE data for cyclohexane + poly(butadiene-*co*-acrylonitrile) 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 nonpolar 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.

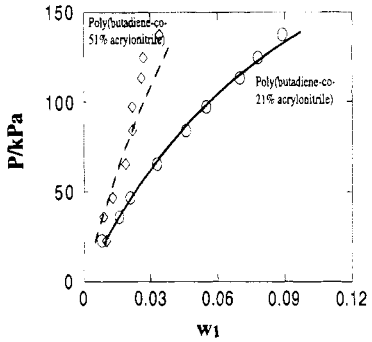

Figure 6. VLE for pentane + poly(butadiene-*co*-acrylonitrile) solutions: w_1, mass fraction pentane; points, new experimental data; lines, calculation using PHSC equation of state parameters: [pentane + polyacrylonitrile, $\kappa = 0$, $\lambda = -0.06$; pentane + poly(*cis*-1,4-butadiene), $\kappa = 0$, $\lambda = -0.085$; poly(*cis*-1,4-butadiene) + polyacrylonitrile, $\kappa = 0.027$, $\lambda = 0$].

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 43 copolymer + solvent binaries and for 14 homopolymer + solvent binaries, using a gravimetric absorption technique. "Expected" nonideal behavior has been obtained for systems such as cyclohexane + poly(ethylene-*co*-vinyl acetate) and chloroform + poly(styrene-*co*-butyl methacrylate). However, strong nonlinear nonideal 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.

Acknowledgment

For experimental assistance, the authors are grateful to Gary Yeung, Bin W. Zhao, and Kathy Yi. Helpful discussions with David Soane, Toshiaki Hino, Yuhua Song, and Stephen Lambert are much appreciated.

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Received for review February 6, 1995. Accepted March 7, 1995.[⊗] This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF0098. For additional financial support, the authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, E.I. du Pont de Nemours (Philadelphia, PA), and Koninklijke Shell (Amsterdam, The Netherlands).

JE950036K

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.