Vapor−Liquid Equilibria of Several Copolymer + Solvent Systems

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Vapor−liquid-equilibrium (VLE) data for several copolymer + solvent systems at 298.15 K and 308.15 K have been obtained using the classical gravimetric-sorption method. The solvents studied were benzene and toluene. The copolymers studied were poly(styrene-*co*-methyl methacrylate), poly(styrene-*co*-butadiene), and poly(*n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate). The molecular thermodynamic model based on a close-packed lattice model developed by Hu et al. was used to correlate the experimental data.

Introduction

Vapor−liquid-equilibrium (VLE) data for polymer solutions including copolymer solutions are necessary for process and product design in coating industries[1,2] as well as in metallurgy,[3,4] vapor-phase photografting,[5] and pervaporation,[6] recovery of organic vapors using polymeric membranes,[7,8] and manufacturing membranes for separation processes.

Copolymers are gaining an increasing amount of commercial interest because of their unique and designable physical properties. However, VLE data for copolymer solutions in the literature are rare, compared to those of homopolymer solutions; experimental VLE data of the latter case are available for about 1000 systems today.[9] In this work, binary VLE data were measured for systems of three copolymers, poly(styrene-*co*-methyl methacrylate), poly(styrene-*co*-butadiene), and poly(*n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate), and two solvents, benzene and toluene, at 298.15 K and 308.15 K and were correlated by a molecular thermodynamic model for polymer solutions based on lattice theory.[10]

Experimental Section

Materials. All copolymers were supplied by the Department of Polymer Engineering of East China University of Science and Technology in Shanghai, China. They are listed in Table 1 along with their molecular weights M_w and polydispersity indexes M_w/M_n. Benzene and toluene were distilled twice and then degassed with a standard freeze−thaw procedure[11] described previously. The purity of the solvents is greater than 99.9%.

Apparatus and Procedure. There are several experimental methods that can be used to measure VLE data of binary polymer solutions. These include piezoelectric sorption, light scattering, and gravimetric sorption. In this work, the classical gravimetric-sorption technique[11−13] was used. Figure 1 shows the schematic diagram of the apparatus. A copolymer sample of known mass was loaded into aluminum pans and was suspended on a precalibrated quartz spring inside an evacuated glass chamber after it was dried under vacuum for 12 to 24 h to remove moisture or solvents. Solvent vapor was introduced into the evacuated system by quickly opening and closing the solvent valve that connects the evacuated chamber to the solvent flask. Equilibrium was assumed when the extension of springs did not change over 12 h. The pressure of the system was read with a mercury manometer. The total mass of the aluminum pan was calculated from the

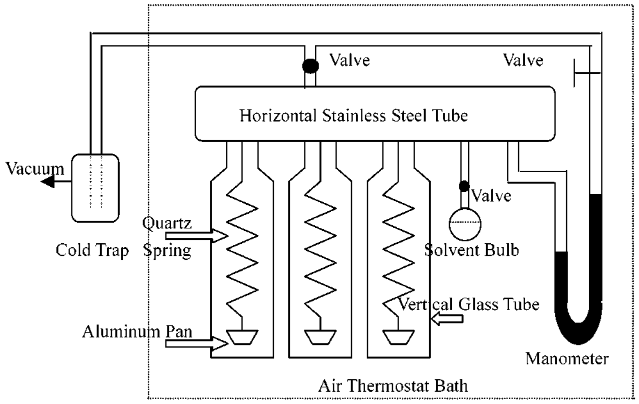

Figure 1. Experimental apparatus for vapor−liquid-equilibrium measurements.

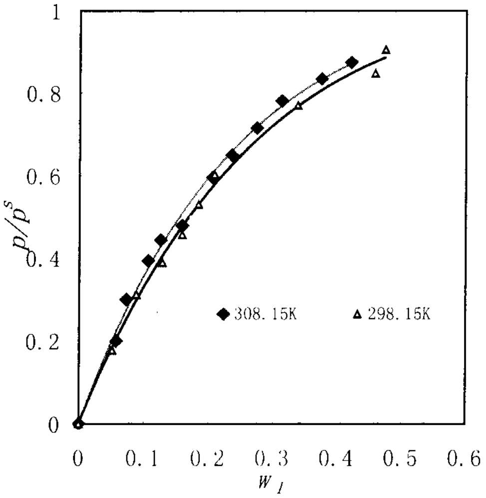

Figure 2. VLE data for benzene + poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate) at 298.15 K and 308.15 K: solid diamonds and upper triangles, experimental results; lines, calculated results with the model of Hu et al.[10]

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10.1021/je010238i CCC: $22.00

Table 1. Molecular Weights and Polydispersity Indexes of Copolymers

copolymer (mass % copolymer composition)	M_w/g·mol^{-1}	M_w/M_n
poly(41.45% styrene-*co*-methyl methacrylate)	12 060	
poly(4.1% styrene-*co*-butadiene)	100 000	
poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	26 382	1.17
poly(93.94% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	90 015	1.12
poly(89.54% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	87 820	1.17
poly(59.43% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	95 732	1.14

Table 2. Experimental VLE Data for Copolymer + Solvent Systems

p/p^s	w_1	p/p^s	w_1
Benzene + Poly(41.45% styrene-*co*-methyl methacrylate)			
T = 308.15 K			
0.1997	0.0138	0.6496	0.1844
0.3003	0.0224	0.7154	0.2197
0.3938	0.0565	0.7815	0.2614
0.4438	0.0827	0.8347	0.3214
0.4787	0.111	0.8752	0.3747
0.596	0.158		
T = 298.15 K			
0.1771	0.0197	0.6024	0.1559
0.3120	0.0293	0.7700	0.2542
0.3894	0.0401	0.8483	0.3296
0.4572	0.0576	0.9056	0.3946
0.5305	0.1137		
Benzene + Poly(4.1% styrene-*co*-butadiene)			
T = 308.15 K			
0.1997	0.0471	0.6496	0.2289
0.3003	0.0756	0.7154	0.2637
0.3938	0.1044	0.7815	0.3098
0.4438	0.125	0.8347	0.3742
0.4787	0.1442	0.8752	0.4297
0.596	0.1959		
T = 298.15 K			
0.1771	0.0459	0.6024	0.1864
0.3120	0.08	0.7700	0.3014
0.3894	0.1117	0.8483	0.37
0.4572	0.1364	0.9056	0.4275
0.5305	0.1656		
Benzene+ Poly(95.13%*n*-butylhacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)			
T = 308.15 K			
0.1997	0.0578	0.6496	0.2355
0.3003	0.073	0.7154	0.2741
0.3938	0.1069	0.7815	0.3125
0.4438	0.1259	0.8347	0.3748
0.4787	0.1591	0.8752	0.4209
0.596	0.2055		
T = 298.15 K			
0.1771	0.0516	0.6024	0.2087
0.3120	0.0884	0.7700	0.3376
0.3894	0.1283	0.8483	0.458
0.4572	0.1589	0.9056	0.474
0.5305	0.184		

p/p^s	w_1	p/p^s	w_1
Toluene + Poly(4.1% styrene-*co*-butadiene)			
T = 308.15 K			
0.1697	0.0386	0.4540	0.1238
0.2975	0.0633	0.5655	0.1863
0.3693	0.0913	0.7310	0.2417
0.3967	0.1097	0.9832	0.3378
Toluene + Poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)			
T = 308.15 K			
0.1697	0.0044	0.4540	0.0941
0.2975	0.0298	0.5655	0.172
0.3693	0.0605	0.7310	0.2193
0.3967	0.0917	0.9832	0.3243
Toluene + Poly(93.94% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)			
T = 308.15 K			
0.271	0.0264	0.7673	0.0524
0.38	0.031	0.8771	0.0703
0.4728	0.0355	0.9541	0.0892
0.5783	0.0373		
Toluene + Poly(89.54% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)			
T = 308.15 K			
0.271	0.0205	0.7673	0.0545
0.38	0.0275	0.8771	0.0747
0.4728	0.0402	0.9541	0.0966
0.5783	0.047		
Toluene + Poly(59.43% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)			
T = 308.15 K			
0.271	0.0135	0.7673	0.0448
0.38	0.0158	0.8771	0.0712
0.4728	0.0226	0.9541	0.0813
0.5783	0.0255		

elongation of the spring, and thusly the weight fraction of solvent in the liquid phase was obtained. A new pressure and solubility of the solvent were obtained by adding more solvent vapor into the chambers until the vapor pressure of the solvent was close to the saturated vapor pressure of the solvent.

The experimental error in solvent activity is estimated to be 1 to 2%.

Results and Discussion

Table 2 lists 11 sets of experimental VLE data for 8 binary copolymer + solvent systems. Figures 2−4 show the reduced pressures versus the concentration of benzene in liquid solution of poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate), poly(4.1% styrene-*co*-butadiene), and poly(41.45% styrene-*co*-methyl methacrylate), at 298.15 K and 308.15 K. The results show that the temperature effect on the absorption is not obvious in a small temperature range. Figures 5 and 6 show the VLE data of both benzene and toluene solutions of poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate) and poly(4.1% styrene-*co*-butadiene) at 308.15 K, respectively. It is shown that the absorption of benzene in the first copolymer is higher than that of toluene. However, the absorptions of benzene and toluene in the second copolymer are almost equal. These behaviors are expected because toluene has a nonpolar methyl group which is repulsive toward the polar segment N in poly(95.13%

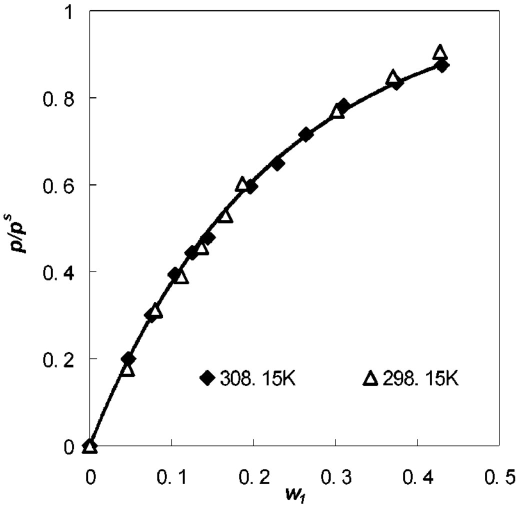

Figure 3. VLE data for benzene + poly(4.1% styrene-*co*-butadiene) at 298.15 K and 308.15 K: solid diamonds and upper triangles, experimental results; lines, calculated results with the model of Hu et al.[10]

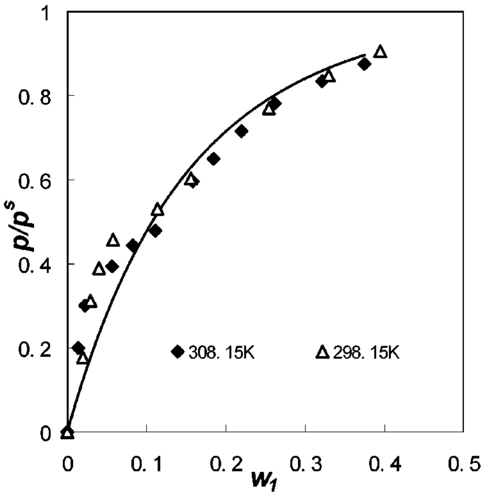

Figure 4. VLE data for benzene + poly(41.45% styrene-*co*-methyl methacrylate) at 298.15 K and 308.15 K: solid diamonds and upper triangles, experimental results; lines, calculated results with the model of Hu et al.[10]

n-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate); however, there is no polar segment in poly(41.45% styrene-*co*-methyl methacrylate).

Figure 7 illustrates the effect of the molecular weight and the composition on the VLE data of toluene + poly(*n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate) at 308.15 K. Obviously, the behavior of the VLE data for this copolymer with 95.13% *n*-butyl methacrylate and $M_w = 26\,832$ is notably different from those of the other samples. It seems that the compositions of diblock copolymers have only a minor effect; on the contrary, the molecular weight plays a more important role in the VLE behavior.

The molecular thermodynamic model for polymer solutions based on lattice theory, developed by Hu et al.,[10] was used to correlate the experimental VLE data. The model is composed of two terms, the entropy contribution and the energy contribution. By using an effective chain-insertion probability for the entropy, one may derive the former term. A series expansion for the energy is adopted to account for

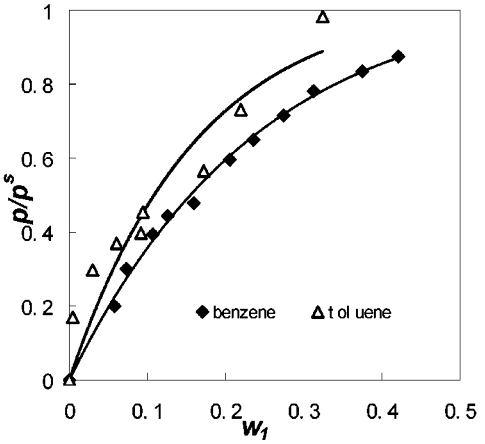

Figure 5. VLE data for benzene + poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate) and toluene + poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate) at 308.15 K: solid diamonds and upper triangles, experimental results; lines, calculated results with the model of Hu et al.[10]

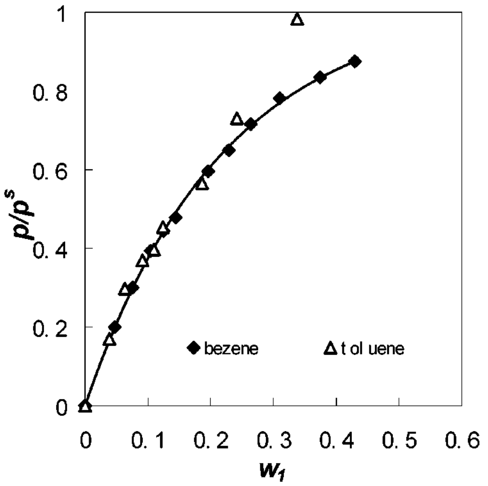

Figure 6. VLE data for benzene + poly(4.1% styrene-*co*-butadiene) and toluene + poly(4.1% styrene-*co*-butadiene) at 308.15 K: solid diamonds and upper triangles, experimental results; lines, calculated results with the model of Hu et al.[10]

interactions between segments for the latter term. The activity of the solvent is given by

$$\begin{aligned}\ln \alpha_i = {} & \frac{\ln \varphi_i}{r_i} + \sum_j [({r_i}^{-1} - {r_j}^{-1}) + 2b_2({r_i}^{-1} - {r_j}^{-1})^2 + \\ & (2 + {r_i}^{-1} + {r_j}^{-1} - \nu_{-1})\tilde{\epsilon}_{ij}{}^{(e)}]\varphi_j - \sum_j\sum_k [b_2({r_j}^{-1} - {r_k}^{-1})^2 + \\ & (1 + 0.5{r_k}^{-1} + {r_j}^{-1} - \nu_{-1})\tilde{\epsilon}_{jk}{}^{(e)}]\varphi_j\varphi_k + \\ & 1.5c_2(\sum_j\sum_k \varphi_j\varphi_k\tilde{\epsilon}_{jk}{}^{(e)})(\sum_j \varphi_j\tilde{\epsilon}_{ij}{}^{(e)} - 0.75\sum_j\sum_k \varphi_j\varphi_k\tilde{\epsilon}_{ij}{}^{(e)})\end{aligned} \quad (1)$$

with

$$b_2 = 2C_s/9, \quad C_s = 0.3 \quad (2)$$

$$c_2 = -1.074 \quad (3)$$

$$\nu_{-1} = r^{-1} = \sum_i \varphi_i {r_i}^{-1} \quad (4)$$

$$\varphi_i = x_i r_i / \sum_j x_j r_j \quad (5)$$

Table 3. Model Parameters[a]

solvent	copolymer	T/K	r	$\tilde{\epsilon}_{ij}^{(e)}$
toluene	poly(4.1% styrene-*co*-butadiene)	308.15	1467	0.1
benzene	poly(4.1% styrene-*co*-butadiene)	308.15	1467	8.975×10^{2}
benzene	poly(4.1% styrene-*co*-butadiene)	298.15	1467	9.975×10^{-2}
toluene	poly(41.45% styrene-*co*-methyl methacrylate)	308.15	1135	0.28
benzene	poly(41.45% styrene-*co*-methyl methacrylate)	308.15	1135	0.182
benzene	poly(41.45% styrene-*co*-methyl methacrylate)	298.15	1138	0.234
toluene	poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	308.15	16269	0.198
benzene	poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	308.15	16314	7.065×10^{-2}
benzene	poly(95.13% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	298.15	16477	3.075×10^{-2}
toluene	poly(93.94% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	308.15	2302.257	0.550
toluene	poly(89.54% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	308.15	2186.317	0.538
toluene	poly(59.43% *n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate)	308.15	2720.884	0.617

[a] r is the chain length of the polymer; $\tilde{\epsilon}_{ij}^{(e)}$ is the effective reduced interchange energy.

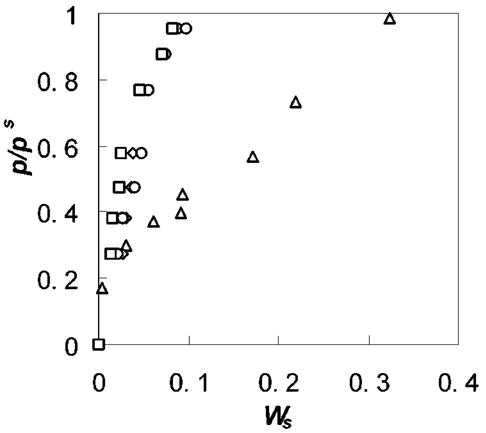

Figure 7. Comparison among the VLE data for toluene + poly(*n*-butyl methacrylate-*co*-*N*,*N*-dimethylaminoethyl methacrylate) with different compositions and molecular weights at 308.15 K: triangles, with 95.13% *n*-butyl methacrylate and M_w; diamonds, with 93.94% *n*-butyl methacrylate and M_w; circles, with 89.54% *n*-butyl methacrylate and M_w; squares, with 59.43% *n*-butyl methacrylate and M_w.

where φ is the volume fraction, x is the mole fraction, and r is the chain length of the polymer, and $\tilde{\epsilon}_{ij}^{(e)}$ is the effective reduced interchange energy calculated by

$$\tilde{\epsilon}_{ij}^{(e)} = \tilde{\epsilon}_{ij}/[1 - 0.2911(1 - r_i^{-1})(1 - r_j^{-1})(1 - 2r_i^{-1}r_j^{-1}) \exp(0.6048r_{ij} - 2.744r_{ij}^{2})] \quad (6)$$

$$r_{ij} = r_i^{-1} + r_j^{-1} - 1.25r_i^{-1}r_j^{-1} \quad (7)$$

$$\tilde{\epsilon}_{ij} = \epsilon_{ij}/kT = (\epsilon_{ii}^{*} + \epsilon_{jj}^{*} - 2\epsilon_{ij}^{*})/kT \quad (8)$$

where $\tilde{\epsilon}_{ij}$ is the reduced interchange energy and ϵ^{*} is the interaction energy between segments of polymer or solvent. In this work, the chain length of solvents is set to equal 1; then $\tilde{\epsilon}_{ij}^{(e)} = \tilde{\epsilon}_{ij}$.

The correlated results are compared with experimental data as shown in Figures 2−6; the model parameters are listed in Table 3. It is shown that all of the experimental VLE data can be satisfactorily correlated.

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Received for review August 22, 2001. Accepted March 30, 2002. This work was supported by the National Science Foundation of China (Project No. 29736170, 20025618) and the Doctoral Research Foundation sponsored by the Ministry of Education of China.

JE010238I