Compatibility of Polymer Blends. I. Copolymers with Organic Solvents

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ABSTRACT: In this work, we present a theoretical discussion regarding the Flory–Huggins χ interaction parameter for 11 random copolymer-solvent systems along with their corresponding polymer pairs. Copolymers studied are poly(acrylonitrile-*co*-butadiene) in acetonitrile, poly(styrene-*co*-acrylonitrile) in 1,2-dichloroethane, poly(acrylonitrile-*co*-butadiene) in hexane, and poly(acrylonitrile-*co*-butadiene) in pentane. For ternary systems, the results are expressed in terms of $\chi_{1,23}$, which is reduced to the classical Flory–Huggins χ_{12} interaction parameter in case of binary mixtures. The data on $\chi_{1,23}$ may be used for an approximate estimation of the χ'_{23} interaction parameter for the limiting case of zero solvent concentration. For this purpose, at the end of each subsection of tables, the limiting value of $\chi^{\infty}_{1,23}$ is given. The limiting values of φ^{∞}_2, φ^{∞}_3, and χ'_{23} also appear at the end of each table. It should be noted that these values are obtained by the graphical extrapolation of data to zero concentration of solvent. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 492–498, 2006

Key words: compatibility; miscibility; polymer blends; copolymers; Flory-Higgins theory

INTRODUCTION

The continuing demand for polymer blends with desired properties has been propelling extensive research on liquid–liquid equilibria of polymer blends.[1–5] One motivation behind these studies is the search for miscible pairs of polymers, including copolymers, because such blends can exhibit a variety of mechanical, electrical, thermal, optical, and other properties. In addition to their potential for new materials, random copolymers are also used as compatibilizers for blends of homopolymers that are immiscible without compatibilizers.

Miscibility of polymer blends has been often defined as the capability of a mixture to form a single phase over certain ranges of temperature, pressure, and composition. Whether or not a single phase exists depends on the chemical structure, molar mass distribution, and molecular architecture of the components present. An immiscible polymer blend that exhibits macroscopically uniform physical properties is called compatible. Compatibility means the capability of individual component substances in either an immiscible polymer blend or a polymer composite to show interfacial adhesion in which interfaces between phases or components are maintained by intermolecular forces, chain entanglements, or both, across the interfaces. In the case of block copolymers, if their parent's homopolymers A and B are incompatible, the copolymer may show *segregation*, i.e., the A-segments and the B-segments are then located in separate *domains*.[6] The term domain may be used for an entity of a material system that is uniform in chemical composition and physical state.

Compatibility of polymer blends is often achieved through favorable specific interaction such as hydrogen bonding. Although a fundamental understanding of the pertinent thermodynamics plays a crucial role in the preparation of blends, there are few useful molecular thermodynamic models for polymer blends with specific interactions; a major exception is the classical incompressible model developed by Flory and Huggins.[7,8] This work applies the formalism for ternary polymer solutions developed by Panayiotou and Vera[9] to vapor–liquid equilibria (VLE) experimental data of Gupta and Prausnitz[10] to extract useful information for the compatibility of homopolymer and copolymer pairs.

Unfortunately, it is often difficult to pull a polymer off the shell that will have all the required material properties. Thermodynamic analysis of the interfaces presented here in conjunction with compatibilization of polymer blends with blocky polymer yields further useful information by which materials can be efficiently created from polymer mixtures with optimized and tunable properties. The objective of this work is to develop a simple and theoretically based molecular model, with abundant information for predicting com-

TABLE I
Summary of Polymers with Their Relevant Solvents

Polymer	V_{sp} (cm^3 g^{-1})	Solvent	T (°C)	P_s (KPa)	V_{sp} (cm^3 g^{-1})
Poly(acrylonitrile)	0.845[a]	Acetonitrile	60	50.73[b]	1.374[b]
Poly(cis-1,4-butadiene)	1.099[a]	Acetonitrile	60	50.73	1.374
Poly(acrylonitrile)	0.845	1,2-Dichloroethane	70	66.65[c]	0.849[d]
Polystyrene	0.810[a]	1,2-Dichloroethane	70	66.65	0.849
Poly(acrylonitrile)	0.845	1,2-Dichloroethane	80	93.31[c]	0.861[d]
Polystyrene	0.810	1,2-Dichloroethane	80	93.31	0.861
Poly(acrylonitrile)	0.845	Hexane	60	76.36[e]	1.608[e]
Poly(cis-1,4-butadiene)	1.099	Hexane	60	76.36	1.608
Poly(acrylonitrile)	0.845	Pentane	60	214.5[e]	1.709[e]
Poly(cis-1,4-butadiene)	1.099	Pentane	60	214.5	1.709

[a] These values are taken from Ref. 11.
[b] These values are taken from Ref. 12.
[c] These values are taken from Ref. 13.
[d] These values are taken from Ref. 14.
[e] These values are taken from Ref. 15.

patibility of polymer blends within the framework of a lattice model.

In this work, compatibility parameters χ'_{23} in 11 random copolymer-solvent systems are successfully predicted by the classical Flory–Huggins model. Table I gives a summary of all copolymers with their solvents that are considered in this article. Also, the interaction parameter χ_{12} for the corresponding polymer pairs is evaluated. For ternary systems, the results are expressed in terms of $\chi_{1,23}$ parameter, which is reduced to the classical Flory–Huggins χ_{12} interaction parameter in case of binary mixtures.

Theory

We consider a mixture of two liquids 1 and 2. Molecules of type 1 (solvent) are single spheres. Molecules of type 2 (polymer) are assumed to behave like flexible chains, i.e., as if they consist of a large number of mobile segments, each having the same size as that of a solvent molecule. Further, it is assumed that each site of the quasilattice is occupied by either a solvent molecule or a polymer segment and that adjacent segments occupy adjacent sites. Let there be n_1 molecules of solvent and n_2 molecules of polymer and let there be r segments in a polymer molecule. The total number of lattice sites is $(n_1 + rn_2)$. Fractions φ_1 and φ_2 of sites occupied by the solvent and by the polymer are given by

$$\varphi_1 = \frac{n_1}{n_1 + rn_2} \qquad \varphi_2 = \frac{n_2}{n_1 + rn_2} \qquad (1)$$

Flory and Huggins[16] have shown that if the amorphous (i.e., noncrystalline) polymer and the solvent mix to form real polymer solutions, i.e., to solutions that are not athermal, the free energy of mixing is simply obtained by

$$\Delta F_M = kT(n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + \chi_{12}n_1\varphi_2) \qquad (2)$$

where χ_{12} is a dimensionless quantity, which characterizes the interaction energy per solvent molecule. The quantity $kT\chi_{12}$ represents merely the difference in energy of a solvent molecule immersed in the pure polymer ($\varphi_2 \cong 1$) compared with one surrounded by molecules of its own kind, i.e., in the pure solvent. This equation expresses the total free energy change for the formation of the solution from pure, disoriented polymer (i.e., amorphous or liquid polymer), and pure solvent.

The chemical potential μ_1 of the solvent in the solution relative to its chemical potential μ_1^0 in the pure liquid is obtained by differentiating the free energy of mixing, ΔF_M, with respect to the number n_1 of solvent molecules. Differentiation of eq. (2) with respect to n_1 (bearing in mind that φ_1 and φ_2 are functions of n_1) and multiplication of the result by Avogadro's number N to obtain the chemical potential per mole gives

$$\mu_1 - \mu_1^0 = RT\left[\ln\varphi_1 + \left(1 - \frac{1}{r}\right)\varphi_2 + \chi_{12}\varphi_2^2 \right] \qquad (3)$$

From the chemical potential, we may at once set down expressions for the activity a_1 of the solvent, using standard relation of thermodynamics.

$$(\mu_1 - \mu_1^0) = RT \ln a_1 \qquad (4)$$

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r}\right)\varphi_2 + \chi_{12}\varphi_2^2 \qquad (5)$$

Since the pure solvent has been chosen as the standard state, $a_1 = P_1/P_1^0$, to the approximation that the vapor may be regarded as an ideal gas neglecting the vapor pressure of polymer.

The same principles can also be applied to mixtures of two amorphous polymers 1 and 2 or to a ternary polymer–polymer–solvent system. The presence of polymer 1 reduces the possible arrangements of monomeric units of polymer 2: the molar entropy of mixing can never become as positive as in polymer–solvent systems. The resulting entropy term is only slightly negative and can no longer compensate the positive enthalpy term $\Delta H_M = kT\chi_{12}n_1\varphi_2$ if the interaction parameter, χ_{12}, is positive.[17] The molar Gibbs energy of mixing becomes positive; the polymer–polymer system cannot exist as one phase and demixes. For a ternary system, the solvent activity is given by[9]

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_2}\right)\varphi_2 + \left(1 - \frac{1}{r_3}\right)\varphi_3$$
$$+ (\chi_{12}\varphi_2 + \chi_{13}\varphi_3)(1 - \varphi_1) - \chi'_{23}\varphi_2\varphi_3 \quad (6)$$

However, in the general case, χ_{12} and χ_{13} vary with composition and without a knowledge of this composition dependence, eq. (6) cannot be used for the evaluation of χ'_{23} parameter. It is important to observe that eq. (6) may be used in the limiting case of $\varphi_1 \rightarrow 0$. If X_{2P} indicates mole fraction of component 2 in the polymer mixture (zero solvent concentration) and similarly, X_{3P} for component 3, we may define r_{23} and φ_{23} as:

$$r_{23} = X_{2P}r_2 + X_{3P}r_3 \quad (7)$$

and

$$\varphi_{23} = \varphi_2 + \varphi_3 = 1 - \varphi_1 \quad (8)$$

In addition, $\chi_{1,23}$ is defined as

$$\chi_{1,23} = ((\chi_{12}\varphi_2 + \chi_{13}\varphi_3)(1 - \varphi_1) - \chi'_{23}\varphi_2\varphi_3) / \varphi_{23}^2$$

With these definitions, the solvent activity in the ternary system may be written as[9]

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{1}{r_{23}}\right)\varphi_{23} + \chi_{1,23}\varphi_{23}^2 \quad (9)$$

in direct analogy with eq. (5). Equation (9) reduces to eq. (5) for the binary case. The use of eq. (9) has the advantage of allowing to reporting data on ternary systems regardless of the dependence of χ_{12} and χ_{13} on composition.

The data on $\chi_{1,23}$ may now be used for an approximate estimation of the χ'_{23} interaction parameter for the limiting case of zero solvent concentration. For this purpose, at the end of each subsection of the tables, the limiting value of $\chi_{1,23}^{\infty}$ is shown. These values were obtained by graphical extrapolation of the data on lower solvent concentration. It should be stressed that

there is an uncertainty in this extrapolation, especially when the data do not show any clear trend.

In terms of these limiting quantities, χ'_{23} is given by[9]

$$\chi'_{23} = \frac{\chi_{12}^{\infty}\varphi_2^{\infty} + \chi_{13}^{\infty}\varphi_3^{\infty} - \chi_{1,23}^{\infty}}{\varphi_2^{\infty}\varphi_3^{\infty}}(\varphi_1^{\infty} \rightarrow 0) \quad (10)$$

In eq. (10), φ_2^{∞} and φ_3^{∞} are the segment fractions of components 2 and 3, respectively, in the polymeric mixture. From the limiting values of $\chi_{1,23}$ at zero solvent concentration and eq. (10), the χ'_{23} parameter is approximately estimated.

Application to Experimental Data

Acetonitrile(CH₃CN)(1)-polyacrylonitrile(PAN)(2)-poly(*cis*-1,4-butadiene)(*cis*-Bu)(3) (60°C)

This system was studied to see the influence of the solvent on the χ'_{23} interaction parameter. Experimental VLE data for poly(acrylonitrile-*co*-butadiene) and its parent homopolymers that are reported in Table II have been taken from Gupta and Prausnitz work.[10] As it is shown, at a given activity, solvent absorption in polyacrylonitrile is higher than in polybutadiene because polar acetonitrile molecules prefer polar segments of polyacrylonitrile to hydrocarbon segments of polybutadiene. Intuitively, one might expect that the copolymer curve should lie between the two homopolymer curves, but Table II shows that the copolymer curve lies beyond the bound of the two homopolymer curves.

At a given pressure, acetonitrile solubility in a copolymer is much higher than that in the corresponding homopolymers. This nonintuitive behavior is attributed to intramolecular repulsion between unlike segments of the copolymer. This repulsive interaction is weakend when acetonitrile molecules are in the vicinity of unlike copolymer segments, favoring copolymer/solvent miscibility.

Also, we can see that in spite of insolubility of parent homopolymers in acetonitrile ($\chi > 1$), copolymers are soluble in this solvent and their solubility increases with enhancement of acrylonitrile weight fraction because of interaction between polar groups. From the limiting values of $\chi_{1,23}$ at zero solvent concentration and eq. (10), the pair interaction parameter χ'_{23} is obtained. It is evident from the result of χ'_{23} quantity that the two polymers are incompatible in all concentration ranges.

1,2-dichloroethane(ClC₂H₄Cl)(1)-polystyrene(PS)(2)-poly(acrylonitrile)(PAN)(3) (70 and 80°C)

Tables III and IV display the experimental VLE data for poly(styrene-*co*-acrylonitrile) and its parent homopolymers that are taken from Gupta and Prausnitz

work.[10] At a given activity, the solubility of 1,2-dichloroethane decreases dramatically with replacement of polystyrene (PS) with polyacrylonitrile (PAN). 1,2-Dichloroethane has negligible solubility in PAN due to strong repulsion between nonpolar 1,2-dichloroethane molecules and highly polar acrylonitrile segments. 1,2-Dichloroethane also has some repulsive interaction with styrene segments, but these are not as strong as those with acrylonitrile segments. The solubility of 1,2-dichloroethane rises in the presence of PS or poly(styrene-*co*-acrylonitrile).

Flory interaction parameter, χ_{13}, indicates that 1,2-dichloroethane is a nonsolvent for PAN($\chi_{13} > 1$), when styrene segments add to PAN to build a copol-

TABLE II
Vapor-Pressure Lowering Data for the System:
Acetonitrile(1)-Polyacrylonitrile(2)-Poly(*cis*-1,4-Butadiene)(3) (60°C)

m_s/m_p	$P/P°$	φ_{23} (φ_3)	φ_2	$\chi_{1,23}$ (χ_{13})
$W_{2p} = 0.0$; $\chi_{1,23}^{\infty}$ (χ_{13}^{∞}) = 1.7119				
0.0101	0.1321	0.9875		1.4070
0.0101	0.2622	0.9875		2.1101
0.0173	0.3607	0.9788		1.9379
0.0246	0.4573	0.9702		1.8694
0.0309	0.6406	0.9628		2.0308
0.0406	0.7471	0.9517		1.9730
$W_{2p} = 0.21$; $\chi_{1,23}^{\infty}$ = 1.2720				
0.0111	0.1340	0.9854	0.1695	1.2678
0.0267	0.2700	0.9656	0.1661	1.1754
0.0695	0.5145	0.9152	0.1575	1.0597
0.0929	0.5933	0.8899	0.1531	1.0025
0.1261	0.6722	0.8561	0.1473	0.9349
0.2300	0.7747	0.7653	0.1317	0.7324
$W_{2p} = 0.33$; $\chi_{1,23}^{\infty}$ = 0.5958				
0.0235	0.1321	0.9693	0.2647	0.5203
0.0449	0.2622	0.9429	0.2576	0.6545
0.0695	0.3607	0.9144	0.2498	0.6266
0.1001	0.4573	0.8812	0.2407	0.6010
0.1738	0.6406	0.8104	0.2214	0.6110
0.2594	0.7471	0.7411	0.2024	0.5800
$W_{2p} = 0.51$; $\chi_{1,23}^{\infty}$ = 0.6600				
0.0214	0.1340	0.9714	0.4184	0.6064
0.0493	0.2701	0.9365	0.4034	0.5831
0.1249	0.5145	0.8535	0.3677	0.5530
0.1628	0.5933	0.8172	0.3520	0.5392
0.2225	0.6722	0.7658	0.3299	0.4922
0.4144	0.7747	0.6371	0.2744	0.2988
$W_{2p} = 1.0$; $\chi_{1,23}^{\infty}$ (χ_{12}^{∞}) = 1.0397				
0.0111	0.1321	0.9822		1.0606
0.0225	0.2622	0.9647		1.1176
0.0331	0.3610	0.9489		1.1177
0.0427	0.4573	0.9349		1.1617
0.0650	0.6406	0.9044		1.2200
0.0822	0.7471	0.8819		1.2384

W_{2p}	φ_2^{∞}	φ_2^{∞}	χ'_{23}
0.21	0.1720	0.8280	2.2770
0.33	0.2731	0.7269	4.6975
0.51	0.4307	0.5693	3.1093

TABLE III
Vapor-Pressure Lowering Data for the System:
1,2-Dichloroethane(1)-Polystyrene(2)-Polyacrylonitrile(3) (70°C)

m_s/m_p	$P/P°$	φ_{23} (φ_3)	φ_2	$\chi_{1,23}$ (χ_{13})
$W_{2p} = 0.0$; $\chi_{1,23}^{\infty}$(χ_{13}^{∞}) = 1.0657				
0.0256	0.2446	0.9749		1.3687
0.0320	0.3181	0.9688		1.4431
0.0417	0.4006	0.9598		1.4539
0.0449	0.4621	0.9568		1.5435
0.0482	0.5476	0.9538		1.6691
0.0526	0.6106	0.9498		1.7160
0.0571	0.6587	0.9457		1.7337
0.0616	0.6902	0.9417		1.7252
0.0650	0.7367	0.9388		1.7565
$W_{2p} = 0.70$; $\chi_{1,23}^{\infty}$ = 2.2490				
0.0091	0.2446	0.9918	0.7094	2.4430
0.0267	0.3181	0.9763	0.6983	1.6988
0.0504	0.4006	0.9561	0.6838	1.3728
0.1614	0.4621	0.8718	0.6236	0.5401
0.2438	0.5476	0.8183	0.5853	0.4256
0.3210	0.6106	0.7738	0.5534	0.3662
0.3908	0.6587	0.7375	0.5275	0.3355
0.4205	0.6902	0.7231	0.5172	0.3637
0.5129	0.7367	0.6816	0.4875	0.3386
$W_{2p} = 1.0$; $\chi_{1,23}^{\infty}$ (χ_{12}^{∞}) = 0.6610				
0.0684	0.2446	0.9426		0.5696
0.1013	0.3181	0.9172		0.5092
0.1455	0.4006	0.8852		0.4654
0.1792	0.4621	0.8622		0.4682
0.2642	0.5476	0.8094		0.3754
0.3227	0.6106	0.7766		0.3796
0.4065	0.6587	0.7340		0.3208
0.4409	0.6902	0.7179		0.3429
0.5432	0.7367	0.6738		0.3102

W_{2p}	φ_2^{∞}	φ_3^{∞}	χ'_{23}
0.70	0.7152	0.2848	−7.23034

ymer. χ decreases such that 1,2-dichloroethane can slightly dissolve PS and poly(styrene(0.70)–acrylonitrile) especially at high activities. As it is shown by the values of χ_{12} and χ_{13} parameters, the nature of interaction between solvent and two polymers is different, but because of attraction between polar styrene and acrylonitrile segments, χ'_{23} is negative and two polymers show compatibility in all ranges of concentration and in both temperatures.

Hexane(C₆H₁₄)(1)-poly(acrylonitrile)(PAN)(2)-poly(*cis*-butadiene)(*cis*-Bu)(3) (60°C)

Experimental VLE data[10] for poly(acrylonitrile-*co*-butadiene) and its parent homopolymers are shown in Table V. At a given activity, progressing from PAN to poly(acrylonitrile-*co*-butadiene) to poly(*cis*-Bu), the solubility of hexane increases with the butadiene content in the copolymer. Hexane has negligible solubility in PAN due to strong repulsion between nonpolar cyclohexane segments and highly polar acrylonitrile

TABLE IV
Vapor-Pressure Lowering Data for the System: 1,2-Dichloroethane(1)-Polystyrene(2)-Polyacrylonitrile(3) (80°C)

m_s/m_p	$P/P°$	φ_{23} (φ_3)	φ_2	$\chi_{1,23}$ (χ_{13})
$W_{2p} = 0.0$; $\chi_{1,23}^\infty$ $(\chi_{13}^\infty) = 1.8455$				
0.0173	0.2401	0.9827		1.7051
0.0204	0.2926	0.9796		1.7558
0.0246	0.3890	0.9756		1.8826
0.0395	0.4898	0.9613		1.7065
0.0460	0.5369	0.9552		1.6753
0.0560	0.6173	0.9460		1.6662
0.0604	0.6377	0.9420		1.6398
0.0638	0.6505	0.9389		1.6185
$W_{2p} = 0.70$; $\chi_{1,23}^\infty = 2.1261$				
0.0091	0.2400	0.9917	0.7093	2.4110
0.0406	0.2926	0.9639	0.6894	1.2142
0.0989	0.3890	0.9163	0.6554	0.7389
0.3351	0.4898	0.7637	0.5462	−0.0598
0.3870	0.5369	0.7368	0.5270	−0.0441
0.5337	0.6173	0.6699	0.4791	−0.0980
0.6026	0.6377	0.6425	0.4596	−0.1545
0.6367	0.6505	0.6298	0.4504	−0.1666
$W_{2p} = 1.0$; $\chi_{1,23}^\infty(\chi_{12}^\infty) = 0.5816$				
0.0753	0.2400	0.9363		0.4456
0.0989	0.2926	0.9180		0.4196
0.1429	0.3890	0.8857		0.4320
0.2837	0.4898	0.7959		0.1257
0.3459	0.5369	0.7619		0.0882
0.4948	0.6173	0.6910		0.0023
0.5625	0.6377	0.6630		−0.0575
0.6051	0.6505	0.6465		−0.0876

W_{2p}	φ_2^∞	φ_3^∞	χ'_{23}	
0.70	0.7152	0.2848	−5.81544	

segments. Flory interaction parameter, χ_{13}, indicates that hexane is a fairly good solvent for poly(*cis*-Bu) with χ_{13} close to zero, but when acrylonitrile segments are added to poly(*cis*-Bu) to build a copolymer, χ increases with rising percentage of acrylonitrile in copolymer composition. Therefore, hexane is a moderate solvent for poly(acrylonitrile(0.21)–butadiene) with $\chi_{1,23} < 1$ and is a nonsolvent for poly(acrylonitrile(0.33)–butadiene), poly(acrylonitrile(0.51)–butadiene), and PAN. Poly(acrylonitrile(0.33)–butadiene) shows the largest value of $\chi_{1,23}$ at zero solvent concentration between three copolymers, which is an indication of the least interaction of this copolymer with solvent and therefore the largest compatibility. Results obtained using hexane as a solvent show that poly(acrylonitrile-*co*-butadiene) is more compatible than results obtained when acetonitrile is used as a solvent.

Pentane(C₅H₁₂)(1)-poly(acrylonitrile)(PAN)(2)-poly(*cis*-butadiene)(*cis*-Bu)(3) (60°C)

Experimental VLE data[10] for poly(acrylonitrile-*co*-butadiene) and its parent homopolymers are shown in

Table VI. Solvent absorption in the copolymer increases as its butadiene content rises. This rise is expected because the hydrocarbon segments of pentane are better liked by hydrocarbon segments of butadiene, whereas polar segments of acrylonitrile repulse nonpolar pentane molecules. Once again, Flory interaction parameter, χ, implies that with rising acrylonitrile concentration in copolymer composition, polymer/solvent interaction weakens such that pentane can highly dissolve poly(*cis*-Bu) with χ_{13} close to zero and be a border solvent for poly(acrylonitrile(0.21)–butadiene) and dissolves poly(acrylonitrile(0.33)–butediene) at low activities.

From the limiting values of $\chi_{1,23}$ at zero solvent concentration, the pair interaction parameter χ'_{23} is estimated. Incidentally, the system poly(acrylonitrile-

TABLE V
Vapor-Pressure Lowering Data for the System: Hexane(1)-Polyacrylonitrile(2)-Poly(*cis*-1,4-Butadiene)(3) (60°C)

m_s/m_p	$P/P°$	φ_{23} (φ_3)	φ_2	$\chi_{1,23}$ (χ_{13})
$W_{2p} = 0.0$; $\chi_{1,23}^\infty$ $(\chi_{13}^\infty) = 0.1481$				
0.0373	0.1624	0.9482		0.2158
0.0846	0.3287	0.8898		0.2568
0.1299	0.4714	0.8402		0.3425
0.1710	0.5670	0.7998		0.3776
$W_{2p} = 0.21$; $\chi_{1,23}^\infty = 0.7063$				
0.0256	0.1689	0.9615	0.1654	0.5606
0.0460	0.3352	0.9330	0.1605	0.7781
0.0893	0.5081	0.8777	0.1510	0.7094
0.1161	0.5828	0.8467	0.1457	0.6816
0.1547	0.6653	0.8055	0.1386	0.6541
0.2048	0.7530	0.7578	0.1304	0.6559
0.3089	0.8342	0.6748	0.1161	0.5869
0.3351	0.8499	0.6567	0.1130	0.5793
$W_{2p} = 0.33$; $\chi_{1,23}^\infty = 2.7696$				
0.0020	0.1624	0.9968	0.2723	2.9648
0.0173	0.3287	0.9735	0.2659	1.6286
0.0267	0.4714	0.9596	0.2621	1.6267
0.0384	0.5670	0.9429	0.2575	1.5216
$W_{2p} = 0.51$; $\chi_{1,23}^\infty = 1.1846$				
0.0183	0.1689	0.9714	0.4184	0.8516
0.0204	0.3352	0.9682	0.4170	1.4805
0.0299	0.5081	0.9542	0.4110	1.5944
0.0341	0.5828	0.9480	0.4083	1.6337
0.0427	0.6653	0.9357	0.4030	1.5996
0.0460	0.7530	0.9311	0.4011	1.6842
0.0661	0.8342	0.9039	0.3893	1.5388
0.0661	0.8499	0.9039	0.3893	1.5617
$W_{2p} = 1.0$; $\chi_{1,23}^\infty$ $(\chi_{12}^\infty) = 3.5108$				
0.0010	0.1624	0.9981		3.4619
0.0070	0.3287	0.9867		2.2849
0.0070	0.4714	0.9867		2.6553
0.0091	0.5670	0.9830		2.6123

W_{2p}	φ_2^∞	φ_3^∞	χ'_{23}	
0.21	0.1720	0.8280	0.1417	
0.33	0.2731	0.7269	−8.5794	
0.51	0.4307	0.5693	1.6795	

TABLE VI
Vapor-Pressure Lowering Data for the System:
Pentane(1)-Polyacrylonitrile(2)-Poly(*cis*-1,4-Butadiene)(3)
(60°C)

m_s/m_p	$P/P°$	φ_{23} (φ_3)	φ_2	$\chi_{1,23}$ (χ_{13})
$W_{2P} = 0.0; \chi_{1,23}^\infty(\chi_{13}^\infty) = 0.2762$				
0.0121	0.0620	0.9815		0.2343
0.0246	0.1254	0.9632		0.2822
0.0482	0.2494	0.9302		0.3971
0.0650	0.3016	0.9082		0.3414
0.0893	0.3613	0.8780		0.2694
0.1050	0.4182	0.8596		0.3140
0.1325	0.4741	0.8291		0.2783
0.1547	0.5394	0.8060		0.3334
0.1834	0.6065	0.7780		0.3752
$W_{2P} = 0.21; \chi_{1,23}^\infty = 1.0092$				
0.0081	0.1063	0.9868	0.1698	1.1291
0.0163	0.1678	0.9737	0.1675	0.9296
0.0214	0.2182	0.9656	0.1661	0.9471
0.0341	0.3054	0.9464	0.1628	0.8868
0.0482	0.3916	0.9260	0.1593	0.8628
0.0582	0.4536	0.9120	0.1569	0.8750
0.0753	0.5282	0.8890	0.1529	0.8493
0.0846	0.5818	0.8770	0.1509	0.8800
0.0977	0.6415	0.8606	0.1481	0.8990
$W_{2P} = 0.33; \chi_{1,23}^\infty = 0.5184$				
0.0091	0.0620	0.9850	0.2690	0.4484
0.0142	0.1254	0.9768	0.2668	0.7434
0.0256	0.2494	0.9588	0.2619	0.9161
0.0277	0.3016	0.9556	0.2610	1.0512
0.0331	0.3613	0.9475	0.2588	1.0937
0.0373	0.4182	0.9411	0.2570	1.1509
0.0460	0.4741	0.9284	0.2536	1.1163
0.0526	0.5394	0.9190	0.2510	1.1565
0.0582	0.6066	0.9112	0.2489	1.2163
$W_{2P} = 0.51; \chi_{1,23}^\infty = 0.9992$				
0.0101	0.1063	0.9830	0.4234	0.8812
0.0091	0.1678	0.9847	0.4242	1.4554
0.0132	0.2182	0.9780	0.4213	1.3753
0.0194	0.3054	0.9679	0.4169	1.3729
0.0225	0.3916	0.9630	0.4148	1.5050
0.0225	0.4536	0.9630	0.4148	1.6635
0.0267	0.5282	0.9564	0.4119	1.6806
0.0277	0.5818	0.9547	0.4112	1.7537
0.0352	0.6415	0.9432	0.4063	1.6656
$W_{2P} = 1.0; \chi_{1,23}^\infty (\chi_{12}^\infty) = -0.2578$				
0.0050	0.0620	0.9899		0.8448
0.0070	0.1254	0.9859		1.2364
0.0111	0.2494	0.9780		1.5154
0.0101	0.3016	0.9799		1.8033
0.0101	0.3613	0.9799		1.9913
0.0101	0.4182	0.9799		2.1435
0.0101	0.4741	0.9799		2.2743
0.0111	0.5394	0.9779		2.3218
0.0111	0.6065	0.9779		2.4444

W_{2p}	φ_2^∞	φ_3^∞	χ'_{23}
0.21	0.1720	0.8280	-5.7918
0.33	0.2731	0.7269	-1.9547
0.51	0.4307	0.5693	-3.8866

co-butadiene) is predicted to form a compatible blend. Results obtained using pentane as a solvent show that poly(acrylonitrile-*co*-butadiene) is more compatible than results obtained when hexane is used as solvent; but between three copolymers, poly(acrylonitrile(0.33)–butadiene) shows the most compatibility in hexane and the least compatibility in the presence of pentane.

CONCLUSIONS

This work applies the formalism for ternary polymer solutions developed by Panayiotou and Vera to VLE experimental data of Gupta and Prausnitz to extract useful information for the compatibility of homopolymer and copolymer pairs. Twenty-one isothermal data sets for VLE have been used for 8 polymer/solvent binaries and for 10 copolymer/solvent binaries to study compatibility of polymer blends. The equilibrium solubility of a penetrant in a polymer depends on its mutual compatibility. Equations based on theories of polymer solution tend to be more successful when there is some kind of similarity between the penetrant and the monomer repeat unit in the polymer, e.g., for nonpolar penetrants in polymers that do not contain appreciable polar groups. Expected nonideal behavior has been observed for systems containing hydrocarbons and poly(acrylonitrile-*co*-butadiene). The role of intramolecular interaction in vapor–liquid equilibria of copolymer/solvent systems is well documented for poly(acrylonitrile-*co*-butadiene), which have higher affinity for acetonitrile than do polyacrylonitrile or polybutadiene.

Although χ'_{23} data reported in this work yield useful information concerning compatibility of polymer blends, nevertheless the value of χ'_{23} should be taken with caution. Extrapolation of the $\chi_{1,23}$ values for the limiting case of zero solvent concentration is probably the main cause of uncertainty. In addition, as discussed in the text, the solvent used for the study may also affect the value of χ'_{23}.

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