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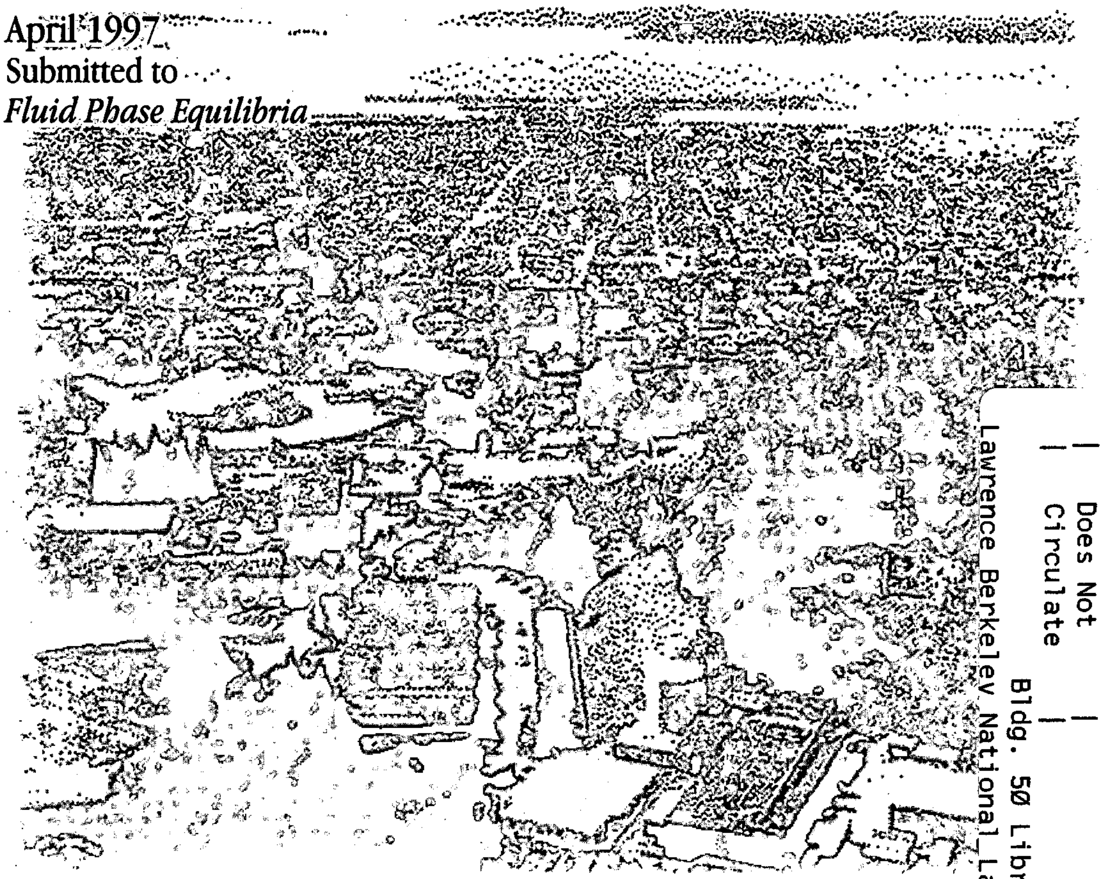

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Abstract

Vapor-liquid equilibria have been measured for comb and linear polymers using a gravimetric-sorption method in the temperature range 50 to 70 °C. Polymers were poly(styrene-co-maleic anhydride) with alkyl side chains of different length (C5, C12, C22) and poly(styrene-co-maleic anhydride) and poly(maleic anhydride). Solvents were acetone, methanol, and cyclohexane.

Due to different chemical structures, the phase behavior of the comb-polymer solutions strongly depends on the ratio backbone/side chains. Freed's lattice-cluster theory gives a good representation of the data.

Keywords: Vapor-Liquid Equilibria, Comb Polymer, Lattice-Cluster Theory.

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INTRODUCTION

Vapor-liquid equilibrium (VLE) data for polymer-solvent solutions are useful for a variety of applications e. g. surface acoustic-wave sensors, polymeric membrane-separation processes, polymer devolatilization, and vapor-phase photografting (Baker et al. (1987), Ballantine and Wohltjen (1989), High and Danner (1990), Kubota et al. (1990), Maeda et al. (1991), Matsumoto et al. (1991)).

In recent publications (Gupta and Prausnitz, 1995, 1996), we reported VLE data for some solutions of copolymers. In this work we report experimental VLE data for some solutions of comb polymers, that is, macromolecules where several side chains (teeth) are attached to a backbone. A few applications of comb polymers have been reported in the literature: Cowie and Sadaghianizadeh (1990) and Takebe et al. (1993) used comb poly(ethylene oxide) and comb polyesters as media for solid polyelectrolytes; Li et al. (1992) studied stability of colloidal alumina suspensions using a hydrophobically modified comb-like polymer; and Radke et al. (1996) suggest the use of comb polymers, instead of linear block polymers, as thermoplastic elastomers. Graft copolymers are easier to synthesize than linear block copolymers; their branched structure leads to decreased melt viscosities, thereby facilitating polymer processing. Comb polymers are also added to blends of immiscibile polymers as compatibilizers to improve mechanical properties and structural integrity of a composite material (Israel et al. (1995), Gersappe et al. (1994)).

We studied three combs with the same backbone (styrene-maleic anhydride copolymer); the teeth were alkyl chains of different length (pentyl (C5), dodecyl (C12), behenyl (C22) chains). The comb polymers were mixed with acetone at 50 and 70 °C, or with cyclohexane or methanol at 60 °C. For comparison, we also studied VLE for two linear polymers, poly(styrene-co-maleic anhydride) (PSMA) and homopolymer poly(maleic anhydride) (PMA) in acetone at 50 and methanol at 60 °C.

EXPERIMENTAL APPARATUS AND PROCEDURE

We measured VLE for several binary polymer-solvent systems using a gravimetric-sorption method described by Panayiotou and Vera (1984) and by Gupta and Prausnitz (1995).

Figure 1 shows a schematic drawing of the apparatus. It is kept in an air bath maintained at constant temperature within 0.3 °C.

Each of the three cells in the glass chamber contains one fused-quartz spring attached to an aluminum pan with the polymer sample. Because the gravimetric technique is a classical static method that requires a long time to reach equilibrium, data acquisition is accelerated by obtaining data simultaneously for three different polymers with the same solvent at the same temperature.

The springs (Ruska Instruments Corp., Houston, TX) have a sensitivity of 1 mg/mm and a maximum load limit of 250 mg. In this range, the elongation of the spring is linear with respect to weight. The springs were calibrated to obtain the relation between length and mass. The length of each spring is measured with a cathetometer with a precision of 0.05 mm; therefore, the precision in the mass measurement, 0.05 mg, gives an uncertainty of about 2% in the liquid-phase composition in the composition range 1 to 50 weight percent solvent. As the weight percent solvent rises, this uncertainty declines.

At the beginning of the experiment, a small quantity of the polymer (15 to 25 mg) is loaded into each aluminum pan. After drying the polymer under vacuum to remove moisture, oligomers or solvents, the length of the spring is measured and the dry polymer mass is calculated.

Solvent vapors are introduced by opening and closing the valve that connects the evacuated chamber to the liquid-solvent flask.

The system is allowed to attain equilibrium for several (usually 6 to 12) hours. Equilibrium is attained when the length of the spring remains constant. The total mass of the system polymer+solvent is calculated from the elongation of the spring; the weight fraction of the solvent in the liquid phase is then obtained. The pressure of the system is read from the mercury manometer with a precision of 1 torr. At the low pressures (below 1 bar, or slightly above) used here, no polymer is in the vapor phase. All readings were taken with increasing pressure.

Reliability of the apparatus and procedure was established by reproducing published experimental VLE data for polystyrene-chloroform and polystyrene-acetone (Bawn and Wajid (1956)) at 50 °C.

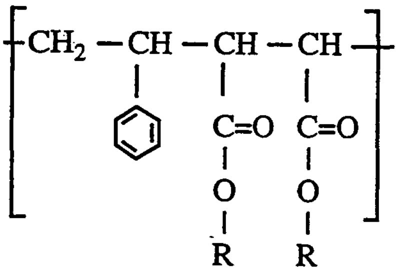
To minimize the temperature effect on VLE data, we plot the solvent activity, that is, the ratio of the system pressure to the saturation pressure of the pure solvent (P/P_1^S), as a function of liquid-phase composition. Solvent saturation pressures were obtained from the Property Data Bank, Appendix A of Reid et al. (1987).

MATERIALS

Solvents characteristics are given in Table 1. Solvents were degassed by a freeze/thaw procedure described by Panayiotou and Vera (1984).

The polymers had polydisperse molecular weights (polydispersity ca. 1.2). They were used without further fractionation because the influence of polymer molecular weight on VLE is negligible if the degree of polymerization is high.

The structure of the comb-polymer repeat unit is:



R=alkyl chain

The molecular weight of the backbone polymer is 116,000. The backbone is the copolymer poly(styrene-co-maleic anhydride) (PSMA). The alkyl side chains were attached by esterification of the anhydride group with alcohols (1-pentanol, 1-dodecanol, 1-docosanol). The yield of the reaction was approximately 50%; therefore, the molecular weights of the combs C5, C12, C22 are approximately 156,000, 213,000 and 293,400, respectively.

To compare VLE data for solutions of combs with those for solutions of the copolymer backbone (PSMA) and with those for solutions of the homopolymer poly(maleic anhydride) (PMA), we obtained PMA (MW=10,000) from Polysciences, Inc. Warrington, PA (catalog number=02348). Table 2 shows the binary systems studied.

RESULTS AND DISCUSSION

Table 3 gives experimental results.

The polymers studied are different from each other in both geometric structure and chemical composition. Therefore, it is not possible to understand separately how either of these differences affects the VLE behavior of the polymer solutions. However, because the degree of branching is light, we expect that the experimental results are primarily determined by the chemical compositions of the copolymers.

Because the backbone of every comb contains oxygen atoms of the anhydride groups, it is likely that polar solvents, like acetone or methanol, are good solvents. However, if the solvent is non-polar, e.g. cyclohexane, it is a good solvent for the alkyl side chains.

Figures 2, 3 and 4 show the affinity of cyclohexane for the teeth, and of methanol or acetone for the backbone. In each figure we plot data for the same solvent with different polymers. The amount of acetone and methanol absorbed by the polymer increases with decreasing side chain length, while the opposite holds for non-polar cyclohexane. The lines are calculated using Flory-Huggins theory or lattice-cluster theory.

In Figures 5, 6 and 7, the same results are shown, but this time, in each plot there is one single type of comb polymer with three solvents. These figures show that all the polymers absorb more acetone than methanol. The length of the side chain has no effect because the behavior of these two polar solvents is mostly influenced by the carboxyl group rather than by the alkyl chain.

By contrast, as the length of the side chain rises, the curve for cyclohexane data shifts from left to right with respect to the data for acetone and methanol.

Most of our data are reasonably well represented by classical Flory-Huggins theory which does not take into account the geometric architecture of the polymer. In addition to Flory interaction parameter χ, only the ratio r of the molar volume of the polymer to that of the solvent is required in the relation:

$$RT\ln\frac{P}{P_1^s} = RT\ln a_1 = RT\left(\ln\phi_1 + \left(1-\frac{1}{r}\right)\cdot\phi_2 + \chi\phi_2^2\right) \tag{1}$$

where R is the gas constant, T is the temperature, P is the system pressure, $P_1{}^S$ is the pure-solvent saturation pressure, a_1 is the solvent activity, ϕ_1 is the solvent volume fraction and ϕ_2 is the polymer volume fraction.

Because we do not know the densities of the polymers, we set the density of the combs equal to 1 g/cm^3 to transform the measured weight fractions to volume fractions. This approximation does not bring appreciable error. Flory's interaction parameter χ was fitted to our VLE data. The results are shown in Figures 2, 3, and 4 where lines are calculated, symbols are experimental. We do not show the results for comb C5-cyclohexane because the experimental data scatter and because the solvent absorbed was less than 15%.

Flory χ values are reported in Table 3 where y is the alkyl side-chain weight fraction in the comb. Figure 8 shows χ as a function of comb chemical composition. The dependence of χ on the weight fraction of alkyl groups in the copolymer is clear; the trend for polar solvents is opposite to that for the non-polar solvent.

Ten Brinke (1983) suggested the relation:

$$\chi = y\cdot\chi_{AC} + (1-y)\cdot\chi_{AB} - y(1-y)\cdot\chi_{BC} \tag{2}$$

for a system containing solvent A and copolymer ($C_y\ B_{1-y}$) where y denotes the copolymer composition expressed in volume fraction; we used y as weight fraction. We let B stand for the backbone repeat unit and C for the alkyl side chain. Figure 8 shows that χ is a nearly linear function of y indicating that the quadratic term in Equation (2) is negligible. We expect the interactions between the polar backbone and nonpolar teeth to be highly unfavorable, i. e. $\chi_{BC} > 0$. However, due to steric hindrance, the effective χ_{BC} is close to zero. Because of the geometry of the comb polymers, B and C units are too far to "feel" each other's presence.

Recently, Lue and Prausnitz (1997) applied Freed's lattice-cluster theory (LCT) to describe concentrated dendritic-polymer solutions. This theory, developed by Freed and coworkers (1989, 1992, and references therein), provides a systematic expansion of the partition function for polymers on a lattice. Unlike the original Flory theory, Freed's theory does not use a mean-field approximation. Lue and Prausnitz showed that according to LCT, the geometric structure of polymer molecules does not significantly affect the activity of the solvent in solution if the polymer molecules can interpenetrate. Therefore, we fitted our data with LCT for linear polymers. The equations are reported in the Appendix. The only adjustable parameter is the interaction parameter χ. Figures 2, 3 and 4 show that by removing Flory's mean-field approximation, LCT gives a better representation of the data. Table 4 gives the χ values from the fit. As with the Flory-Huggins equation, χ is a linear function of the weight fraction of the comb's teeth.

The χ values from LCT are lower than those from Flory-Huggins theory. Flory's χ is often interpreted as the sum of two contributions, the enthalpy and the entropy contribution:

$$\chi = \chi_H + \chi_S \tag{3}$$

The entropic contribution to χ follows, in part, from inadequacies of the Flory-Huggins entropy of mixing. Flory-Huggins theory gives only a first approximation of the configurational entropy of mixing; this approximate entropy gives rise to the first two terms of the sum on the right-hand side of Equation (1). However, LCT provides an improved configurational entropic contribution to the solvent chemical potential [Equation (A2) in the Appendix]. LCT gives for χ_s:

$$\chi_s = a^{(0)} - a^{(1)}(1-2\phi_2) - a^{(2)}\phi_2(2-3\phi_2) \tag{4}$$

(See Appendix for explanations of the symbols). For the systems studied here, for the investigated concentration range, χ_s is between 0.198 and 0.230.

Figure 9 shows results for PSMA and PMA with methanol. (We did not obtain data for polystyrene (PS), the other homopolymer of PSMA, because we expect that PS does not absorb a polar solvent like methanol.) Copolymer PSMA absorbs more than each of the two homopolymers PS and PMA. Similar behavior was reported previously (Gupta and Prausnitz (1996)) where it was attributed to "intramolecular repulsion" between unlike copolymer segments. Ten Brinke et al. (1983) and Paul and Barlow (1984) studied this "intramolecular repulsion" effect in polymer blends. They observed that in a homopolymer+random copolymer (A+BC) blend, miscibility may occur even if the parent homopolymers B and C are not miscible with A, i. e. if binary interactions A-B and A-C are not exothermic (positive χ_{AB} and χ_{AC} in Equation (2)). This conclusion is supported by the observation that addition of homopolymer A to copolymer BC dilutes the unfavorable interactions between the two copolymer units (i.e. positive χ_{Bc}), leading to net exothermic mixing (negative χ). In our case, B and C are styrene and maleic anhydride and the role of the homopolymer (A) is taken by the solvent.

CONCLUSIONS

VLE data have been obtained for PMA, PSMA and three comb-like polymers in acetone, cyclohexane and methanol. The combs have PSMA as backbone and alkyl side chains of different length (C5, C12, C22). The amount of solvent absorbed by the comb is mainly affected by the comb's ratio of non-polar teeth/polar backbone. This observation is confirmed by the linear dependence of the Flory's interaction parameter χ on the chemical compositions of the combs. Methanol is more soluble in copolymer PSMA than in either of the parent homopolymers, consistent with previous observations for some other copolymer/solvent systems.

ACKOWLEDGMENTS

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APPENDIX

In lattice-cluster theory, polymer architecture is characterized by a set of seven parameters, known as counting indecies: M, $N^{(1)}$, $N^{(2)}$, $N^{(3)}$, $N^{(\perp)}$, $N^{(1,1)}$, and $N^{(1,2)}$. M is the number of segments in each molecule (analogous to r in the Flory-Huggins equation). $N^{(1)}$ is the number of bonds in each molecule. $N^{(2)}$ is the number of consecutive bonds. Two consecutive bonds are bonds with a site in common. $N^{(3)}$ is the number of ways three consecutive bonds can be chosen. $N^{(\perp)}$ is the number of ways three bonds intersect. $N^{(1,1)}$ is the number of nonconsecutive bonds. $N^{(1,2)}$ is the number of ways in which a consecutive pair of bonds and a single bonds, with no sites in common with the two consecutive bonds, can be chosen. For example, for 2,2-dimethyl pentane (each site is a methyl or methylene group): M=7, $N^{(1)}=6$, $N^{(2)}=8$, $N^{(3)}=4$, $N^{(\perp)}=4$, $N^{(1,1)}=14$, and $N^{(1,2)}=12$. For a linear polymer, $N^{(1)}$ is (M-1), $N^{(2)}$ is (M-2), $N^{(3)}$ is (M-3), $N^{(\perp)}$ is zero, $N^{(1,1)}$ is (M-2)(M-3)/2, and $N^{(1,2)}$ is (M-3)(M-4).

In the following equations, β is equal to $(k_BT)^{-1}$, where k_B is the Boltzmann constant.

Upon mixing, the change in chemical potential of the solvent, $\Delta\mu_1$, is:

$$\Delta\mu_1 = \Delta\mu_1^{ath} + \Delta\mu_1^{int} \tag{A1}$$

where $\Delta\mu_1^{ath}$, the change in chemical potential for an athermal solution, is:

$$\beta\Delta\mu_1^{ath} = \ln(1-\phi_2) + \left(1-\frac{1}{M}\right)\phi_2 + a^{(0)}\phi_2^{\,2} - a^{(1)}\phi_2^{\,2}(1-2\phi_2) - a^{(2)}\phi_2^{\,3}(2-3\phi_2) \tag{A2}$$

and $\Delta\mu_1^{int}$, the contribution of attractive interactions, is:

$$\begin{aligned}\beta\Delta\mu_1^{int} = {} & A^{(1)}\phi_2^{\,2} - \left(A^{(2)}+B^{(3)}\right)\phi_2^{\,2}(1-\phi_2)(1-3\phi_2) - A^{(3)}\phi_2^{\,2}(1-\phi_2)(1-2\phi_2)\left(1-9\phi_2+10\phi_2^{\,2}\right)\\ & - A^{(4)}\phi_2^{\,2}(1-\phi_2)\left(1-27\phi_2+138\phi_2^{\,2}-294\phi_2^{\,3}+306\phi_2^{\,4}-126\phi_2^{\,5}\right)\\ & + \left(B^{(1)}+B^{(2)}\right)2\phi_2^{\,2}(1-\phi_2) - B^{(4)}2\phi_2^{\,3}(1-\phi_2)(1-2\phi_2)\\ & - C^{(1)}2\phi_2^{\,2}(1-\phi_2)(1-2\phi_2)(3-4\phi_2) + C^{(2)}3\phi_2^{\,2}(1-\phi_2)^2\\ & - C^{(3)}\phi_2^{\,2}(1-\phi_2)^2\left(1-10\phi_2+15\phi_2^{\,2}\right) + C^{(4)}4\phi_2^{\,2}(1-\phi_2)^3\end{aligned} \tag{A3}$$

The $a^{(i)}$ parameters depend only on the architecture of the polymer molecule:

$$a^{(0)} = \frac{1}{z}[K^{(1)}]^2 + \frac{1}{z^2}\Big\{-4K^{(1)}K^{(2)} + \frac{8}{3}[K^{(1)}]^3 - 2K^{(1)}K^{(3)} + [K^{(2)}]^2 - 2K^{(1)}\left(K^{(1,2)} - K^{(1)}K^{(2)}M\right)$$

$$+2[K^{(1)}]^4 + 2[K^{(1)}]^2\left(K^{(1,1)} - [K^{(1)}]^2M\right) - 6K^{(1)}K^{(\perp)}\Big\};$$

$$a^{(1)} = \frac{1}{z^2}\left\{\frac{8}{3}[K^{(1)}]^3 + 2[K^{(1)}]^4 + 2[K^{(1)}]^2\left(K^{(1,1)} - [K^{(1)}]^2M\right)\right\};$$

$$a^{(2)} = \frac{1}{z^2}2[K^{(1)}]^4 \tag{A4}$$

and

$$A^{(1)} = \frac{\beta\varepsilon z}{2};\ A^{(2)} = -\frac{(\beta\varepsilon)^2 z}{4};\ A^{(3)} = -\frac{(\beta\varepsilon)^3 z}{12};\ A^{(4)} = -\frac{(\beta\varepsilon)^4 z}{48};$$

$$B^{(1)} = -\beta\varepsilon K^{(1)};\ B^{(2)} = \frac{\varepsilon}{z}\left(2K^{(2)} + K^{(3)} + 3K^{(\perp)} + K^{(1,2)} - K^{(1)}K^{(2)}M\right);$$

$$B^{(3)} = -\frac{2\beta\varepsilon}{z}K^{(1)}\left(2K^{(1)} + K^{(1,1)} - [K^{(1)}]^2M\right);\ B^{(4)} = -\frac{4\beta\varepsilon}{z}[K^{(1)}]^3;$$

$$C^{(1)} = -\frac{(\beta\varepsilon)^2}{2}K^{(1)};\ C^{(2)} = -(\beta\varepsilon)^2K^{(2)};\ C^{(3)} = -(\beta\varepsilon)^2[K^{(1)}]^2;$$

$$C^{(4)} = -\frac{(\beta\varepsilon)^2}{2}\left(K^{(1,1)} - [K^{(1)}]^2M\right) \tag{A5}$$

where $K^{(i)} = N^{(i)} / M$ (i=1, 2, 3, or $\perp$) and $K^{(i,j)} = N^{(i,j)} / M$ (i=1, or 2), ϕ_1 and ϕ_2 are volume fraction of solvent and polymer respectively, z is the lattice coordination number, here set equal to 6, and ε, the parameter that characterizes the attractive interactions in the system, is related to Flory-Huggins χ by $\chi = \frac{\beta\varepsilon z}{2}$.

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Table 1. Characteristics of solvents

Solvent	Supplier	Lot number	Purity
Acetone	Fisher Scientific, Pittsburgh, PA	952818	99.6%
Methanol	Fisher Scientific, Pittsburgh, PA	952430	99.9%
Cyclohexane	Fisher Scientific, Pittsburgh, PA	902968	99.9%

Table 2. Systems studied

Polymer	Solvent	T (°C)
Combs (C5, C12, C22) PSMA, PMA	Acetone	50
Combs (C5, C12, C22)	Acetone	70
Combs (C5, C12, C22) PSMA, PMA	Methanol	60
Combs (C5, C12, C22)	Cyclohexane	60

Table 3.

Vapor-liquid equilibrium data for comb (C5, C12, C22) and linear (PMA, PSMA) polymers

P= pressure; P_1^s= saturated vapor pressure

w_1 =solvent weight fraction in the liquid phase

Solvent: Acetone; T=50°C; P_1^s = 612 torr

w_1 (C5)	w_1 (C12)	w_1 (C22)	P (torr)
0.043	0.035	0.026	106.0
0.058	0.050	0.035	156.0
0.068	0.059	0.043	196.0
0.086	0.079	0.055	243.0
0.112	0.107	0.073	295.5
0.152	0.139	0.096	346.5
0.194	0.174	0.126	406.0
0.241	0.214	0.154	448.0
0.325	0.288	0.201	492.0
0.369	0.335	0.231	513.0

Solvent: Acetone; T=50°C; P_1^s = 612 torr

w_1 (PMA)	w_1 (PSMA)	P (torr)
0.058	0.098	215.5
0.107	0.144	278.0
0.184	0.181	336.5
0.259	0.217	389.0
0.278	0.229	400.0
0.361	0.286	454.0
0.500	0.379	489.0

Solvent: Acetone; T=70°C; P_1^s = 1196 torr

w_1 (C5)	w_1 (C12)	w_1 (C22)	P (torr)
0.015	0.022	0.024	230.0
0.032	0.039	0.036	317.5
0.050	0.053	0.050	408.5
0.076	0.073	0.063	494.5
0.109	0.102	0.085	587.0
0.151	0.137	0.110	679.5
0.206	0.183	0.142	786.0
0.255	0.222	0.173	857.5
0.294	0.254	0.194	896.0

Solvent: Cyclohexane; T=60°C; P_1^s= 390 torr

w_1 (C5)	w_1 (C12)	w_1 (C22)	P (torr)
--	0.010	0.024	50.5
0.004	0.022	0.033	76.5
0.006	0.037	0.057	10.0
0.018	0.059	0.071	13.5
0.019	0.065	0.094	15.5
0.025	0.086	0.119	18.5
0.047	0.113	0.154	218.0
0.054	0.144	0.191	251.5
0.066	0.179	0.235	279.0
0.108	0.231	0.290	300.5
0.126	0.308	0.370	326.5

Solvent: Methanol; T=60°C; P_1^s = 635 torr

w_1 (C5)	w_1 (C12)	w_1 (C22)	P (torr)
0.030	0.024	0.018	128.0
0.044	0.034	0.025	190.0
0.060	0.050	0.035	247.5
0.085	0.069	0.046	296.0
0.118	0.093	0.060	354.5
0.153	--	0.080	400.5
0.217	0.165	0.105	457.5
0.266	0.192	0.121	489.5

Solvent: Methanol; T=60°C; P_1^s = 635 torr

w_1 (PMA)	w_1 (PSMA)	P (torr)
0.024	0.068	127.5
0.044	0.094	175.5
0.078	0.122	229.5
0.118	0.170	286.5
0.147	0.206	339.0
0.179	0.239	393.0
0.203	0.263	434.5
0.248	0.300	484.5
0.306	0.343	505.0

Table 4. Flory's interaction parameter using Flory-Huggins (FH) and Lattice-Cluster Theory (LCT)

	y	Acetone at 50 °C FH/LCT	Methanol at 60 °C FH/LCT	Cyclohexane at 60 °C FH/LCT
C5	0.253	0.405/0.240	0.601/0.423	1.370/1.274
C12	0.446	0.506/0.366	0.780/0.685	0.660/0.529
C22	0.595	0.812/0.721	1.155/1.064	0.385/0.225
PSMA	0	0.158/-0.013	0.052/-0.132	--

y = alkyl side-chain weight fraction in the comb.

List of Figures

Figure 1. Experimental apparatus for vapor-liquid equilibra for polymer/solvent systems.

Figure 2. Activity of acetone in comb C5, comb C12, comb C22 and linear PSMA polymers at 50 °C; symbols, experimental; lines, calculations using Flory-Huggins equation (—) and Lattice-Cluster theory (----).

Figure 3. Activity of methanol in comb C5, comb C12, comb C22 and linear PSMA polymers at 60 °C; symbols, experimental; lines, calculations using Flory-Huggins equation (—) and Lattice-Cluster theory (----).

Figure 4. Activity of cyclohexane in comb C5, comb C12, comb C22 and linear PSMA polymers at 60 °C; symbols, experimental; lines, calculations using Flory-Huggins equation (—) and Lattice-Cluster theory (----).

Figure 5. Activity of acetone at 50 °C, cyclohexane at 60 °C, methanol at 60 °C in comb C5.

Figure 6. Activity of acetone at 50 °C, cyclohexane at 60 °C, methanol at 60 °C in comb C12.

Figure 7. Activity of acetone at 50 °C, cyclohexane at 60 °C, methanol at 60 °C in comb C22.

Figure 8. Flory's interaction parameter (χ) versus weight fraction of alkyl side-chains in comb polymers (y).

Figure 9. Activity of methanol in PMA and PSMA at 60 °C.

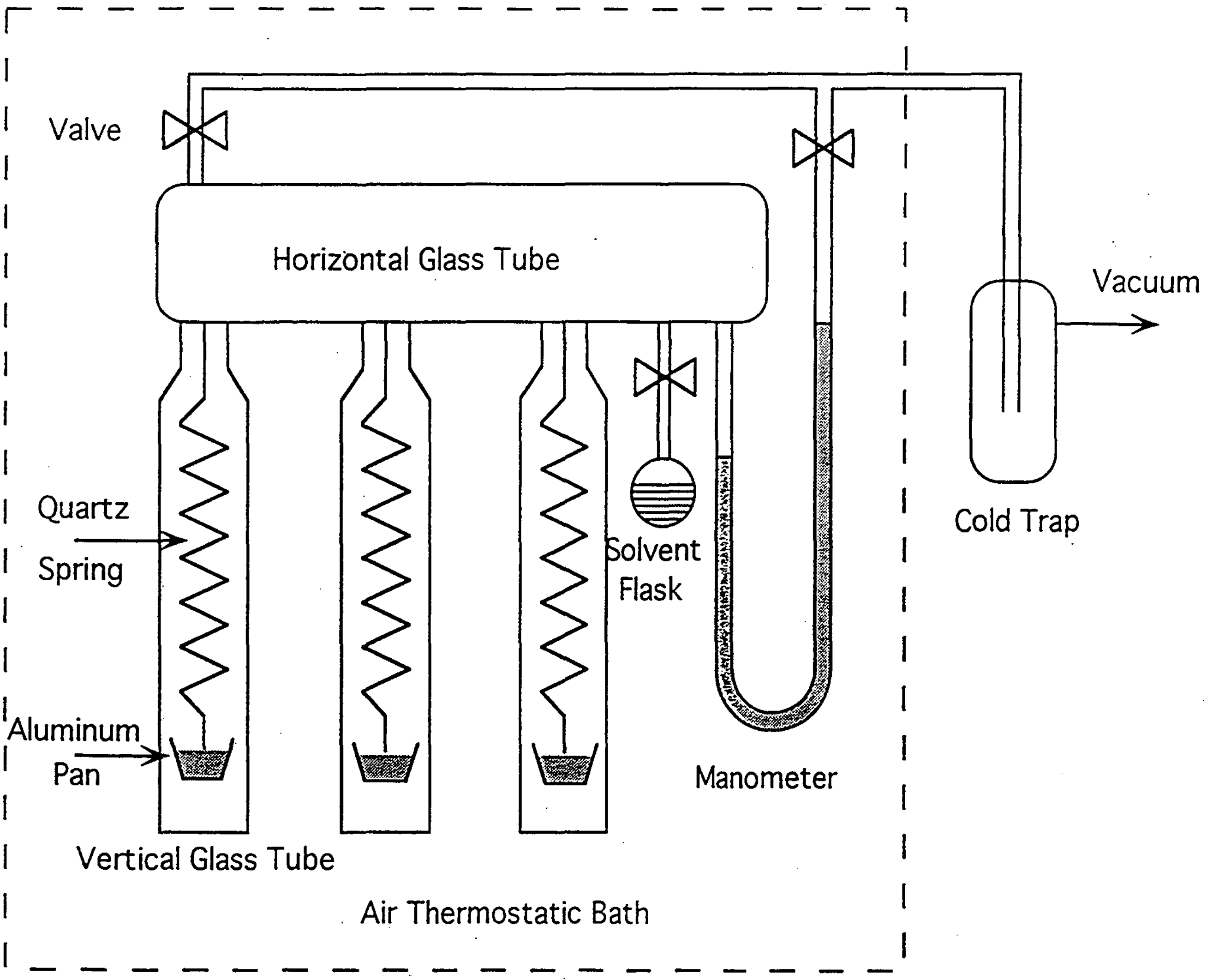

Valve
Horizontal Glass Tube
Vacuum
Quartz
Spring
Solvent
Flask
Cold Trap
Aluminum
Pan
Manometer
Vertical Glass Tube
Air Thermostatic Bath

Figure 1

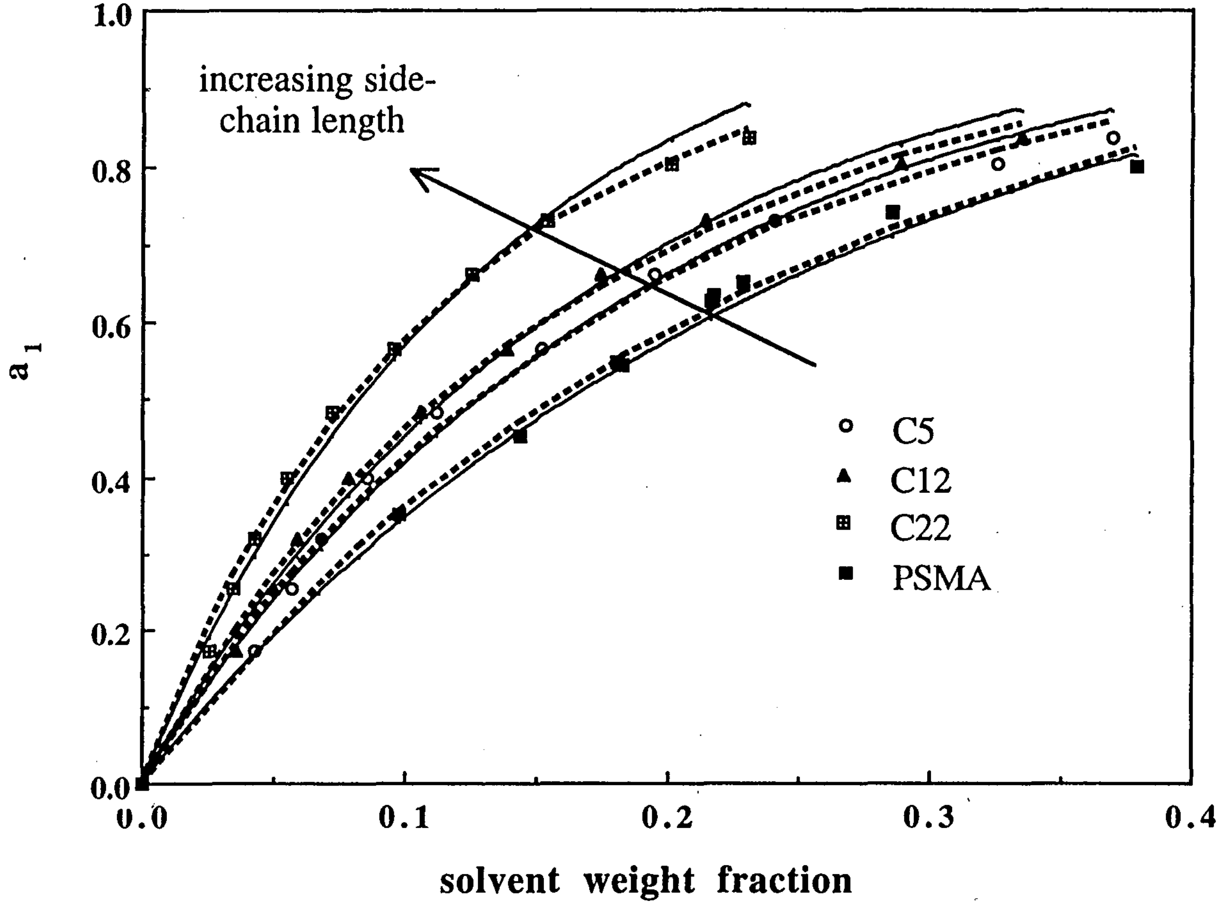

increasing side-chain length
1.0
0.8
0.6
0.4
0.2
0.0
a_1
0.0
0.1
0.2
0.3
0.4
solvent weight fraction
○ C5
▲ C12
⊞ C22
■ PSMA

Figure 2

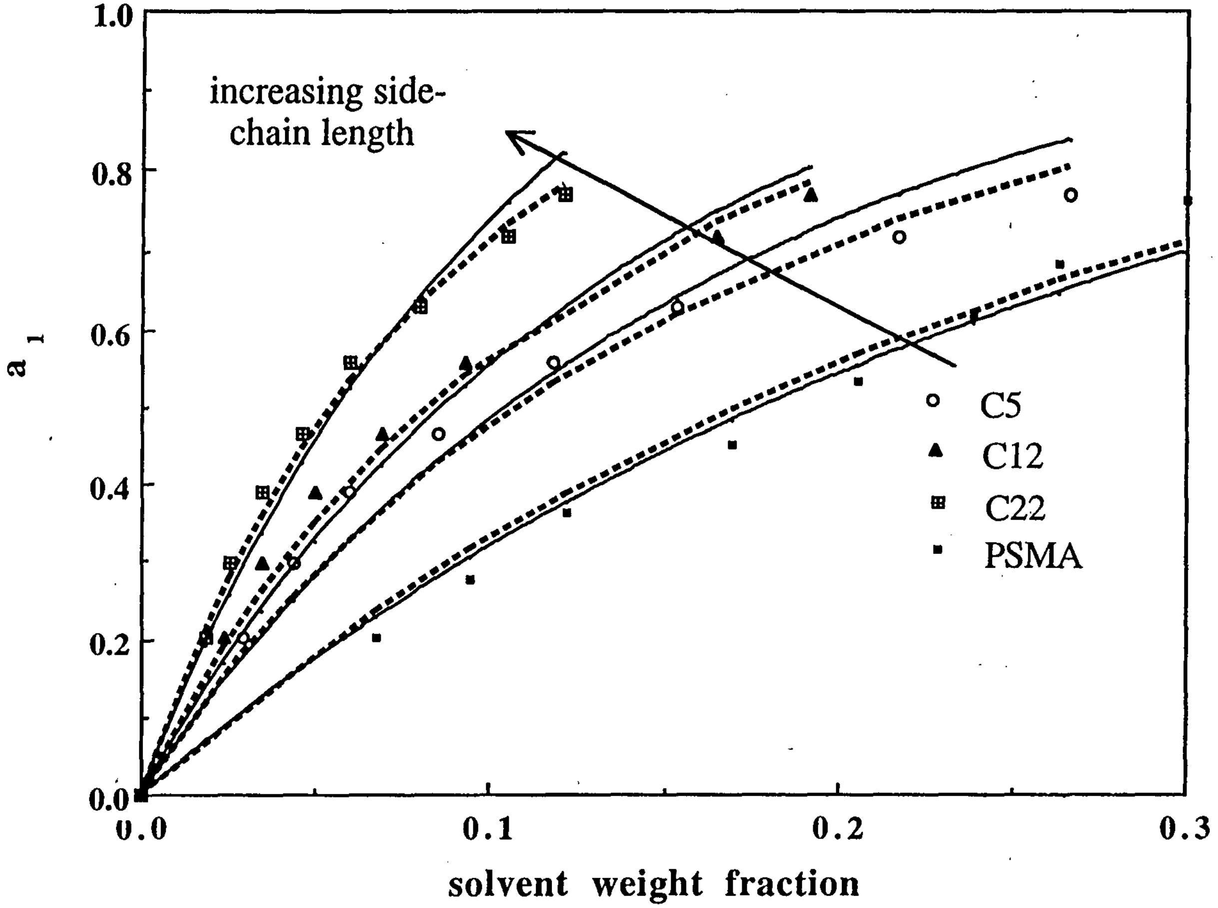

1.0
0.8
0.6
0.4
0.2
0.0
a 1
0.0
0.1
0.2
0.3
solvent weight fraction
increasing side-chain length
C5
C12
C22
PSMA

Figure 3

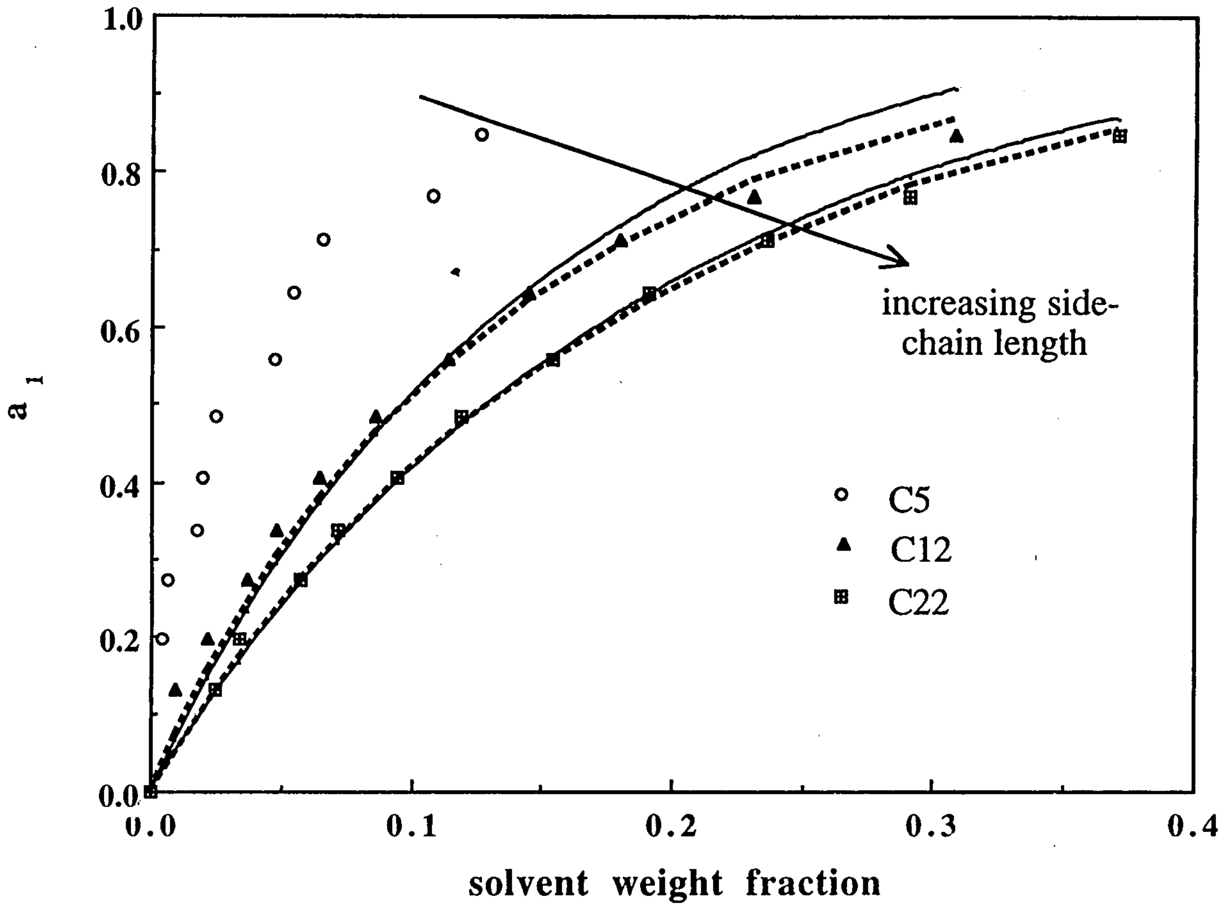
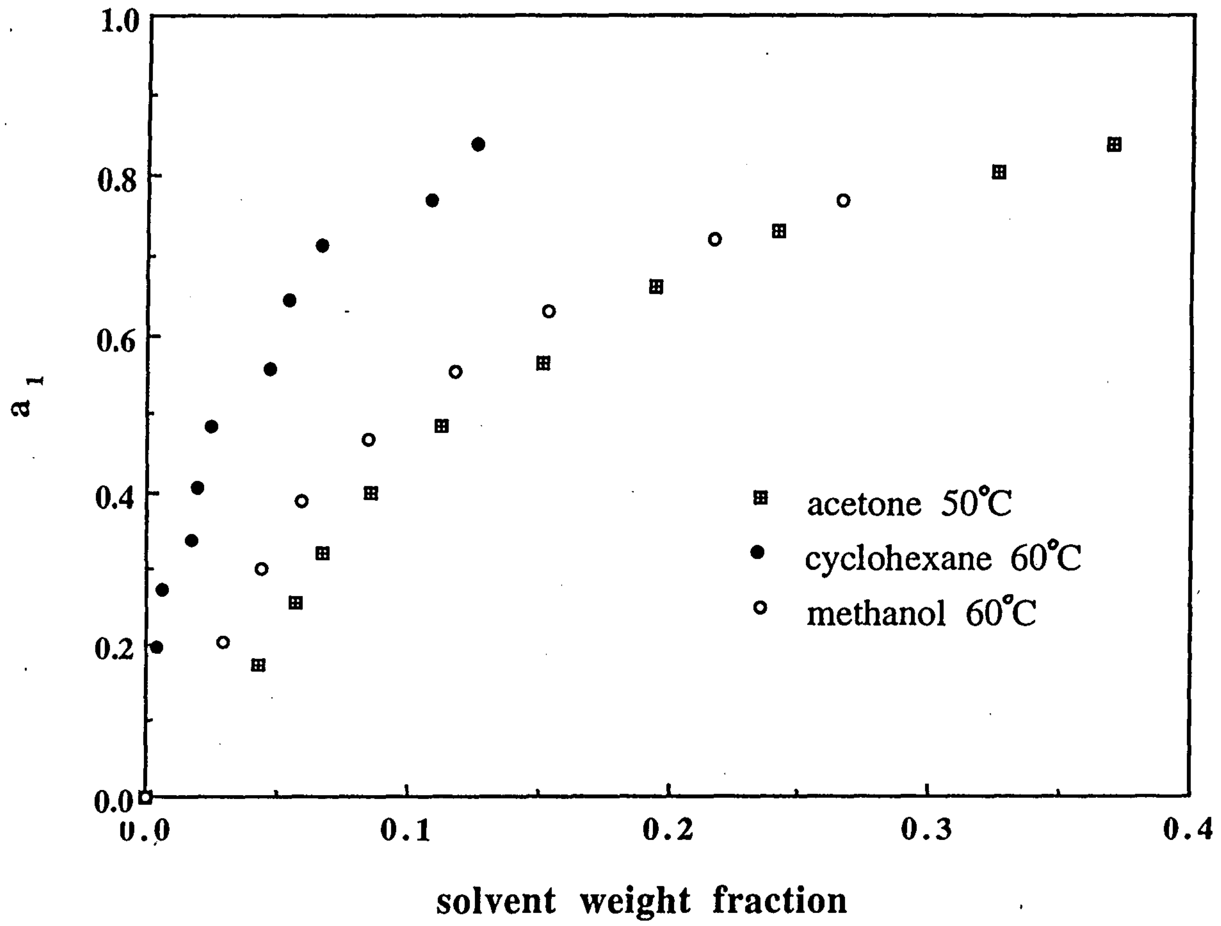

1.0
0.8
0.6
0.4
0.2
0.0
a 1
0.0
0.1
0.2
0.3
0.4
solvent weight fraction
increasing side-chain length
C5
C12
C22

Figure 4



1.0
0.8
0.6
0.4
0.2
0.0
a 1
0.0
0.1
0.2
0.3
0.4
solvent weight fraction
acetone 50°C
cyclohexane 60°C
methanol 60°C

Figure 5

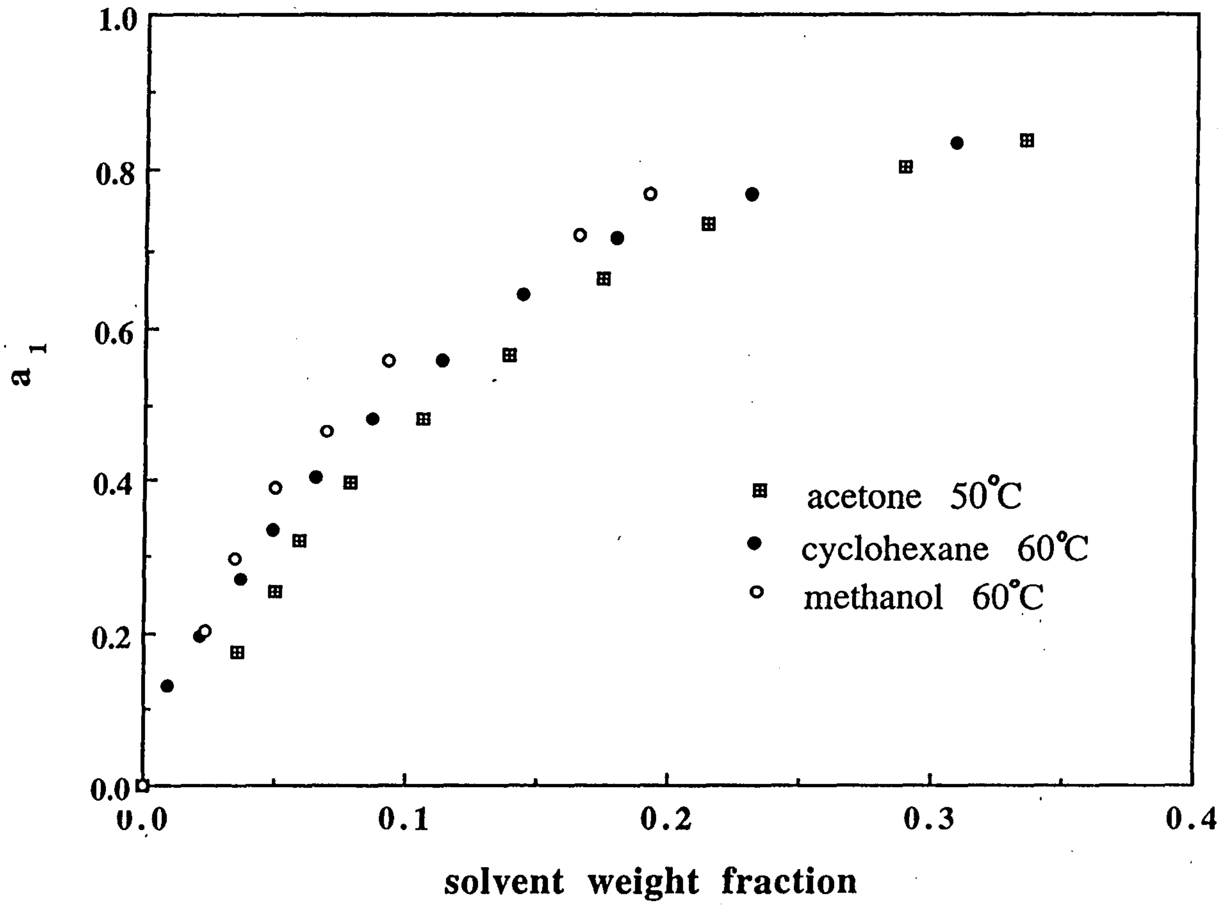

1.0
0.8
0.6
0.4
0.2
0.0
a_1
0.0
0.1
0.2
0.3
0.4
solvent weight fraction
⊞ acetone 50°C
● cyclohexane 60°C
○ methanol 60°C

Figure 6

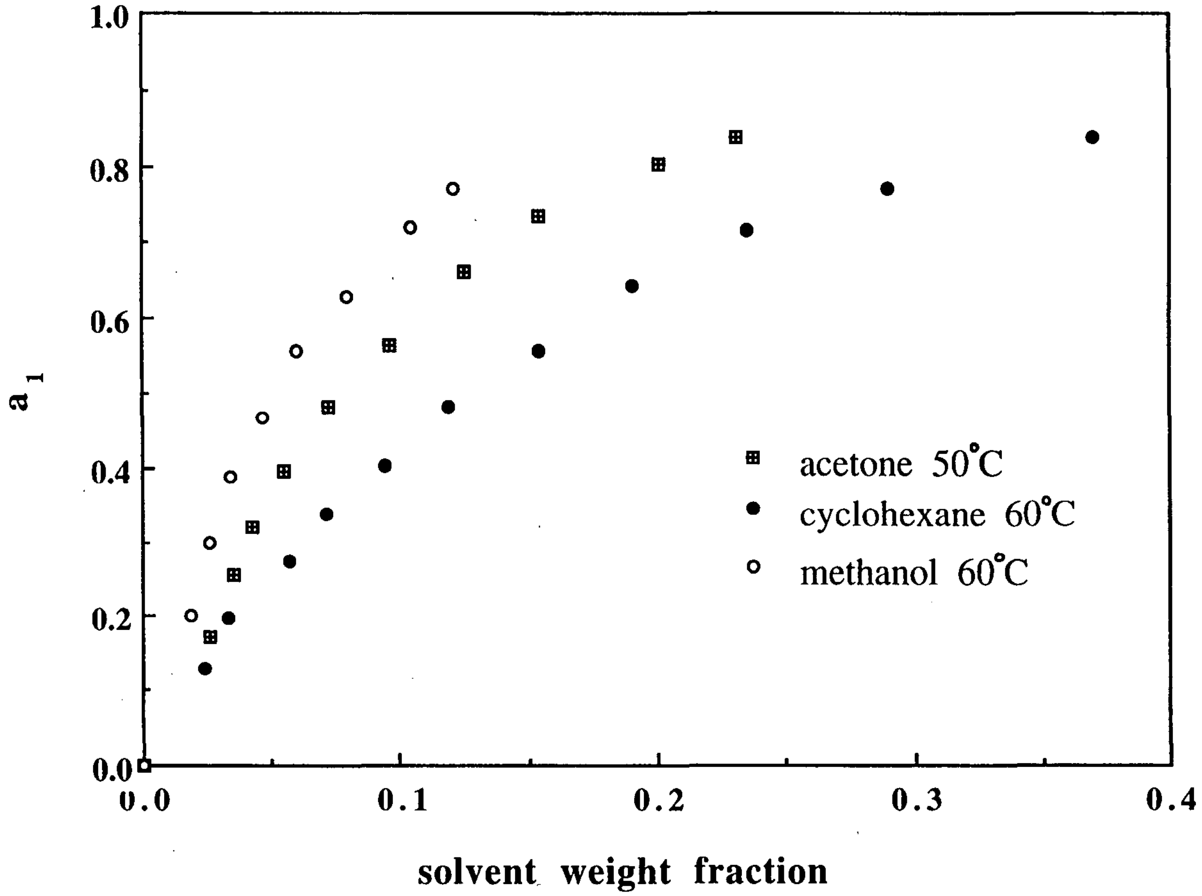

1.0
0.8
0.6
0.4
0.2
0.0
a_1
0.0
0.1
0.2
0.3
0.4
solvent weight fraction
acetone 50°C
cyclohexane 60°C
methanol 60°C

Figure 7

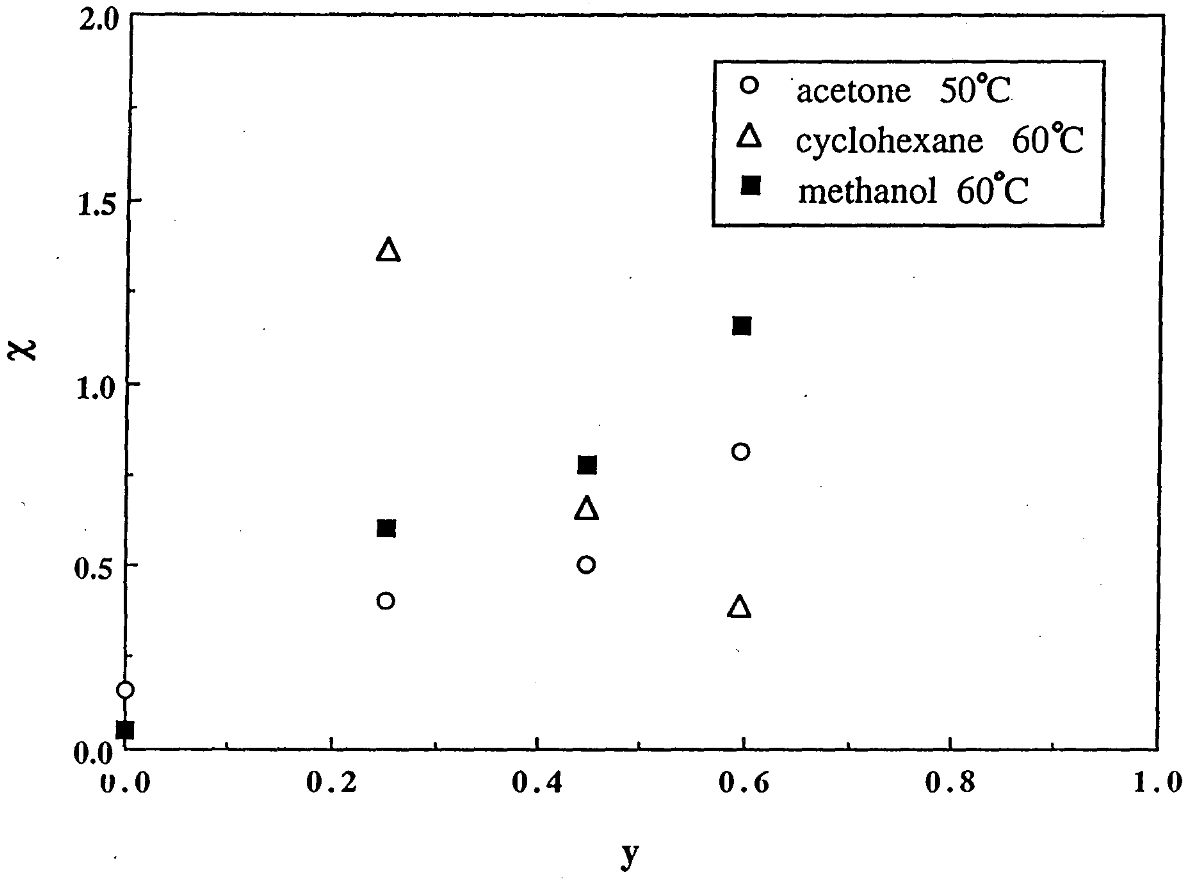

○ acetone 50℃
△ cyclohexane 60℃
■ methanol 60℃
χ
2.0
1.5
1.0
0.5
0.0
0.0
0.2
0.4
0.6
0.8
1.0
y

Figure 8

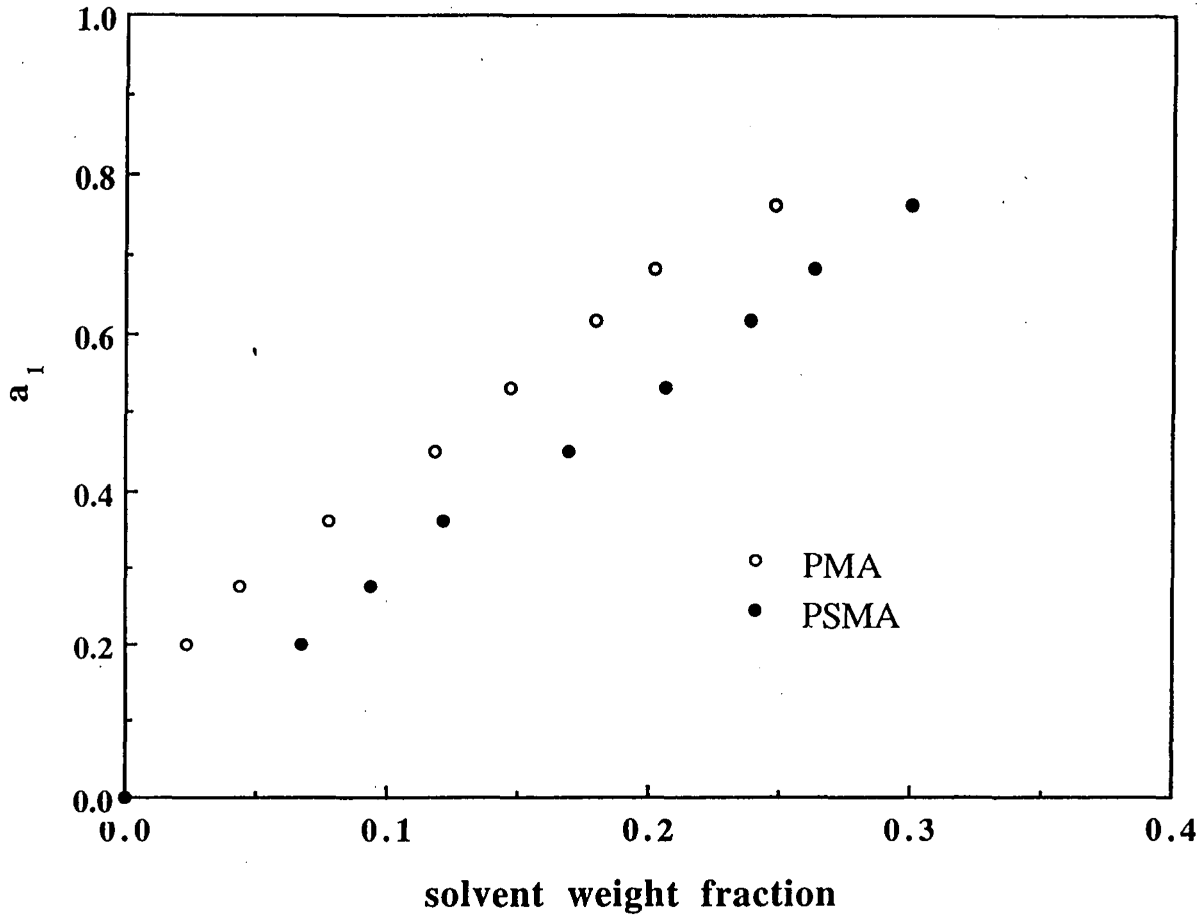

1.0
0.8
0.6
0.4
0.2
0.0
a 1
0.0
0.1
0.2
0.3
0.4
solvent weight fraction
○ PMA
● PSMA

Figure 9

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