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Chemical Sciences Division

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Vapor-Sorption Equilibria for 4-Vinylpyridine-based Copolymer and Crosslinked Polymer /Alcohol Systems. Effect of Intramolecular Repulsion

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Abstract

Solvent activity data were obtained for three alcohols (methanol, i-propanol, t-butanol) in 4-vinylpyridine (4VP)-based polymers using a classical isothermal gravimetric-sorption method. The polymers were linear poly(4-vinylpyridine) (M_w = 160000), crosslinked poly(4-vinylpyridine) with 2% and 25% weight percent divinylbenzene as crosslinking agent, random copolymers poly(4-vinylpyridine-co-styrene) P4VP-co-S (10% and 50% styrene weight percent) and block copolymer P4VP-b-S (50% styrene weight percent). The temperature range was 55 to 70 °C.

Sorption in P4VP-co-10%S copolymer is significantly higher than that in the respective homopolymers. Sorption in P4VP-co-50%S is close to that in linear P4VP, while the sorption curve (solvent activity vs. solvent weight fraction) for P4VP-b-50%S lies inbetween those for the two parent homopolymers.

For crosslinked P4VP, the amount of solvent absorbed by the polymers strongly depends on the weight fraction of the crosslinking agent. When solvent activity is plotted as a function of solvent weight fraction for various degrees of crosslinking, there is an unexpected crossover among the curves. At low solvent activity, the largest sorption was for the 25% crosslinked polymer and the lowest for the linear polymer; however, at high solvent activity the curves switch position and the linear poly(4-vinylpyridine) absorbs more than the crosslinked poly(4-vinylpyridine).

This unusual behavior may be explained by intramolecular repulsion between bonded unlike segments (4-vinylpyridine and styrene/divinylbenzene in uncrosslinked/ crosslinked copolymers, respectively) and by elastic contributions to the solvent chemical

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potential in crosslinked P4VP. In block copolymers, segregated sequence of the unlike monomers minimizes the effect of intramolecular repulsion.

Introduction

Polymer-solvent equilibria are needed for a variety of applications in polymer production and purification processes, including, for example, recovery of organic compounds from waste air streams using a polymeric membrane;[1,2] pervaporation[3] and other membrane separation processes; surface acoustic-wave vapor sensor,[4,5] vapor-phase photografting;[6] polymer devolatilization;[7,8] and for optimum formulation of paints and coatings.[9] Moreover, experimental equilibrium data are required to develop or test molecular-thermodynamics models for polymer solutions.

Reliable experimental vapor-liquid equilibrium (VLE) data for polymer solutions are not plentiful and many literature data are frequently available for only a limited concentration range of sorbed solvent. Experimental VLE data are particularly rare for copolymers,[10-19] for crosslinked polymers,[20-28] and for polymers with unusual or well defined architecture, as brush[29] and comb polymers,[30] arborescent,[31] star-like polymer,[32] and dendrimers.[33,34] However, copolymers and polymers with unusual structure are currently of increasing commercial interest because of their particular chemico-physical properties for potential applications.

The purpose of this work is to extend our knowledge of vapor-sorption behavior of copolymers and crosslinked polymers. For copolymer-solvent systems, we examine the effect of copolymer intramolecular repulsion by comparison with the properties of the parent homopolymers; for crosslinked polymer-solvent systems, we examine the effect of elastic forces by comparison with the solution properties of corresponding linear polymers.

To our best knowledge, no previous studies have been reported on the effect of intramolecular repulsion on VLE of crosslinked polymers, and only a few papers have been published concerning intramolecular repulsion in copolymer/solvent systems.[12,30] However, much attention has been given to the influence of intramolecular repulsion on miscibility in polymer blends.[35-40] Miscibility studies have shown that, when at least one component is a statistical copolymer, miscibility in copolymer-homopolymer blends can occur for a defined copolymer composition window even if none of the parent homopolymers are mutually miscibile. The condition necessary to reach miscibility is that intramolecular repulsion between bonded unlike segments in the copolymer is sufficiently large to produce an exothermal enthalpy of mixing when polymers are blended. The mixing process causes a dilution of the unfavorable interaction between the two copolymer units; the contribution of this dilution to the total enthalpy of mixing reduces the conventional endothermic enthalpy of solution that prevents miscibility. Moreover, it has been shown that the extent of the intramolecular-repulsion effect is closely related to repeat-unit sequence: miscibility improves with alternating sequence distribution, and decreases with polymer blockiness.[41,42]

To study the intramolecular repulsion effect and the effect of elastic forces on VLE for binary polymer/solvent mixtures, we chose some 4-vinylpyridine (4VP)-based polymers, and alcohol solvents (methanol, i-propanol and t-butanol). The polymers were P4VP and PS, random copolymers P4VP-*co*-10%S and P4VP-*co*-50%S, block copolymer P4VP-*b*-50%S and crosslinked poly(4-vinylpyridine) with 2% (c-P4VP/2%DVB) and 25% (c-P4VP/25%DVB) divinylbenzene as crosslinking agent.

P4VP and its crosslinked form with divinylbenzene are useful as ion-exchange resins,[43-46] for gas-separation membranes,[47,48] for waste-water-treatment membranes[43,49] and for recovery of organic compounds like aliphatic alcohols,[50] phenols,[51,52] carboxylic acids[53,54] and inorganic acids.[55] Copolymers P4VP-co-S are useful for enzyme immobilization and for biosensors,[56-58] while block copolymers P4VP-b-S serve as compatibilizers for polymer blends.[59,60]

Experimental

Materials

All polymers were supplied by Aldrich, except copolymers P4VP-co-50%S and P4VP-b-S, that were obtained, respectively, from Scientific Polymer Products and from Polymer Source. Table 1 gives weight-average molecular weights of linear P4VP and polystyrene PS and copolymers P4VP-co-S; crosslinking-agent weight percents for crosslinked P4VP; styrene content for P4VP-co-S; and glass-transition temperatures for each polymer. With the exception of PS and P4VP-b-S, both copolymers and linear P4VP are polydisperse; provided that the polymer is not glassy or crystalline, and provided that M_w>10000,[61,62] polymer molecular weight has little effect on VLE. For random copolymers, polydispersity of chemical composition also has little effect on VLE.[61] All the polymers are in powdered form.

Table 2 gives solvent characteristics: supplier, purity, and vapor pressures at the experimental temperatures. The solvents, degassed with a standard freeze-thaw procedure described by Panayiotou and Vera,[16] were used without further purification.

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Experimental apparatus and procedure

Solvent activities were measured using a classic gravimetric sorption technique. Figure 1 shows a schematic diagram of the apparatus. The apparatus and the experimental procedure have been described in detail by Panayiotou and Vera[16] and by Gupta and Prausnitz.[14]

The amount of solvent absorbed by a polymer is measured at increasing solvent pressure, typically through steps of 1/10 of solvent vapor pressure (P_1^{sat}). To avoid solvent condensation in the system, all experimental data are below 0.90-0.95 P_1^{sat}. The solvent pressure is read from a mercury manometer with an uncertainty of 1 torr. The solvent weight fraction is calculated by measuring the elongation of calibrated quartz springs with sensitivity of about 1 mm/mg using a cathetometer (model KM274, Heerbrugg, Switzerland) with a precision of 0.1 mm. Uncertainty in the solvent weight-fraction w_1 is 2-5% above w_1=0.1 and increases to 5-10% below w_1=0.1. The temperature is controlled with an air bath within 0.3 °C.

A small amount of polymer (15-25 mg) is loaded in each Teflon pan that hangs from the calibrated spring. Before solvent is admitted, the glass chambers containing the polymer samples are evacuated to remove volatile low-molecular-weight impurities including air. The capacity of the apparatus to keep the desired vacuum is tested before each experiment: the apparatus is acceptable if the pressure reading does not change within the experimental error in 24h.

Table 3 lists the binary systems studied and the Appendix gives experimental results.

Glass-transition temperature

The glass-transition temperature T_g for each polymer was measured with a differential scanning calorimeter Seiko DSC6200 using a heating rate of 10 °C/min. No glass transition was detected in the 25% crosslinked P4VP in the range 25-350 °C; the latter temperature is close to the thermal degradation temperature (T_{deg}=330-380 °C) of P4VP.[62-64] For random copolymers P4VP-*co*-S, T_g was also calculated using the Flory-Fox equation:

$$\frac{1}{T_g} = \frac{w_{p1}}{T_{g,p1}} + \frac{w_{p2}}{T_{g,p2}} \tag{1}$$

where T_g is the glass-transition temperature of the copolymer, $T_{g,p1}$ and $T_{g,p2}$ are the glass-transition temperatures of the parent homopolymers, and w_{p1} and w_{p2} are the mass faction of the parent monomers. Table 1 shows measured glass-transition temperatures. Measured T_g and those calculated by Equation (1) are in very good agreement.

Results and discussion

To present our data, we plot solvent activity a_1 as a function of the solvent weight fraction in the polymer phase w_1. Because the experimental pressure is always lower than 1.5 bar, we consider the vapor phase as ideal gas. The solvent activity in the vapor phase is the ratio of solvent pressure (P) to the pure-solvent vapor pressure at the experimental temperature. Pure-solvent vapor pressures P_1^{sat} are calculated using the equation suggested by Daubert and Danner.[65]

Copolymers P4VP-co-S and P4VP-b-S

Figure 2 shows VLE for five P4VP-*co*-S random copolymers + methanol; the polymers have different percent styrene content %S. The two limiting cases %S=0 and %S=100 correspond to homopolymers P4VP and PS, respectively. As discussed later, the good affinity of the polar segments of P4VP for methanol determines the high solvent sorption in this polymer. Because methanol is not a solvent for PS, the PS solvent sorption curve is close to the vertical axis. Intuitively, one might expect that the solvent sorption in P4VP-*co*-S copolymers is the average of P4VP and PS sorption, weighted by the comonomer unit content, as reported for some other copolymer + solvent systems.[14] However, P4VP-*co*-10%S absorbs more methanol than either of the two homopolymers.

Figure 3 shows similar behavior for four P4VP-*co*-S polymers with i-propanol. Again, the P4VP-*co*-10%S sorption curve lies to the right of the P4VP curve, while P4VP-*co*-50%S shows almost the same sorption as P4VP homopolymer. Analogous results were obtained by Gupta and Prausnitz[12] for poly(butadiene-co-acrylonitrile) + acetonitrile and poly(butadiene-co-acrylonitrile) + methyl ethyl ketone.

This non-intuitive behavior may be explained by intramolecular repulsion between unlike segments in a random copolymer. The addition of styrene units in P4VP changes the chemical affinity of the polymer for alcohol. Two competitive factors affect the VLE:

1. the poor affinity of styrene for methanol and i-propanol;

2. the solvent-screening effect of unfavorable intramolecular interaction (repulsion) between 4VP and styrene units in the copolymer.

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For the binary system P4VP-*co*-S/alcohol, a measure of affinity is provided by the Flory-Huggins interaction parameter $\chi_{(AB)C}$, where AB stands for copolymer and C fro solvent (or homopolymer):

$$\chi_{(AB)C} = \chi_{AC}\phi_A + \chi_{BC}\phi_B - \chi_{AB}\phi_A\phi_B \tag{2}$$

where χ_{AC}, χ_{BC} and χ_{AB} are Flory interaction parameter for A-C, B-C and A-B, respectively (A = 4VP, B = S, C = alcohol); ϕ_A and ϕ_B represent the volume faction of monomer A and B, respectively.

Parameter $\chi_{(AB)C}$ provides an inverse measure of affinity: the lower the parameter, the higher the affinity.

The contribution of styrene affinity to the total copolymer affinity for methanol or i-propanol is represented by the second term in Equation (2), while the contribution of intramolecular repulsion is given by the third term. Equation (2) shows that even if the added comonomer units lower the average segmental affinity ($\chi_{AC}\phi_A + \chi_{BC}\phi_B > \chi_{AC}$) for the solvent, a sufficiently large χ_{AB} can overcome this effect and globally produce an enhanced favorable solvent/copolymer interaction (small or negative $\chi_{(AB)C}$) for some copolymer compositions.

This enhanced favorable interaction is observed for P4VP-*co*-S random copolymer + alcohol systems. The interaction parameter P4VP-PS χ_{AB} has been measured by Clarke *et al.*[66] by three different methods. Even if Clarke *et al.* were not able to give a well-defined value of χ_{AB} but only a range, they pointed out that the lower limit is an order of magnitude greater than the largest value of χ_{AB} reported for other nonionic systems. The strong repulsion between 4VP-and-S-bonded segments determines the VLE behavior in P4VP-*co*-10%S, while the poor affinity of PS for alcohol balances

the intramolecular repulsion effect in P4VP-*co*-50%S + i-propanol ($\chi_{(AB)C} \approx \chi_{AC}$) and determines the VLE in P4VP-*co*-50%S + methanol. From our data, we expect a maximum in alcohol affinity for P4VP-*co*-S, for %S<50%.

Figure 2 shows also VLE data for P4VP-*b*-50%S block copolymer + methanol. The sorption curve lies to the left of the P4VP-*co*-50%S sorption curve and between the two homopolymer curves. In a block copolymer the intramolecular repulsion between unlike bonded segments is much reduced because of the segregated distribution sequence $[A]_n[B]_m$ (n, m large). Block copolymers minimize the unfavorable A-B interaction by microphase separation and micelle formation.[41] The microstructure (lamellae, cylindrical or spherical shape) is governed by the relative block lengths.[66]

Crosslinked P4VP

Previously reported VLE for solutions of crosslinked polymers has shown that the introduction of crosslinks in polymeric linear chains lowers the amount of sorption at fixed solvent activity. Experimental data for crosslinked poly(dimethylsiloxane) PDMS[21,24] and styrene-butadiene rubber SBR with various solvents[26,27] showed this decrease in sorption. Moreover, as shown by gel-swelling data, increasing the degree of crosslinking reduces solvent sorption and swelling.[67,68] This reduction follows because, during vapor sorption, the solvent mixes with the polymer chains in an entropically driven process; as the polymer imbibes more solvent, the volume increases. In a polymer network, this sorption-swelling process forces the polymer molecules to assume an extended, less-probable configurations. The entropic gain due to mixing is accompanied by a decrease in entropy of the elongated polymer strands in the network that retains the solvent. Equilibrium is reached when the effect of elastic expansion of the polymer

chains balances that of mixing. For linear polymers, there is no elastic effect because the polymer chains are not connected by crosslinks, and volume increase due to addition of solvent is not accompanied by a significant deformation of the polymer chains. Introduction of crosslinks in polymeric linear chains reduces solvent sorption because of the elastic contribution; the magnitude of this effect is proportional to the number of polymer-chain links.

Our experimental data show unexpected VLE for crosslinked P4VP compared with that for linear P4VP. At low solvent activity, the trend in the amount of sorption with degree of crosslinking is exactly the opposite of that predicted by the discussion above. The expected behavior is recovered only at high solvent activity.

Figure 4(a) compares VLE for linear P4VP, c-P4VP/2%DVB and c-P4VP/25%DVB with methanol at T=70°C. At low methanol activity ($a_1 < 0.7$), solvent sorption increases with degree of crosslinking, while for $a_1 > 0.7$, sorption is a decreasing function of crosslinking concentration. At low activity, the difference in sorption between c-P4VP/2%DVB and c-P4VP/25%DVB is only slightly greater than the experimental error, but data for the same systems at 55°C confirms the observed trend at 70°C, as shown in Figure 4(b). The experimental measurements were repeated twice; the indicated results for the respective polymer/solvent couples were reliably reproducible.

Additional evidence for this unexpected behavior is shown in Figure 5(a) where data are shown for i-propanol sorption in the same polymers at 70°C. When i-propanol is the solvent, the dependence of solvent sorption on the degree of crosslinking is much stronger, erasing any doubt about the sorption curve cross-over. Again, at $a_1 < 0.8$, c-P4VP/25%DVB exhibits the highest sorption and linear P4VP the lowest. However,

when the solvent activity is raised above 0.8, the curves switch relative position; the greatest solvent affinity is then observed for the linear polymer.

Figure 5(b) shows sorption of t-butanol in linear and crosslinked P4VP. Comparing the sorption curves for linear P4VP and P4VP/25%DVB, we reach similar conclusions concerning the crosslinking effect. At low solvent activity, the sorption curves for linear P4VP and P4VP/2%DVB overlap. Because of the very small sorption of t-butanol due to the low affinity of P4VP for this solvent and because of the high experimental error at very low amount of sorbed solvent, cross-over of these two sorption curves cannot be detected.

The apparent disagreement between our results and those reported by others at low solvent activity may be resolved upon considering the results presented in the previous section where it was shown that the sorption of methanol (or i-propanol) for random P4VP-*co*-10%S is much higher than that for P4VP homopolymer, in spite of the poor affinity of styrene for a low-molecular-weight alcohol. The increase in the amount of sorbed solvent follows from the solvent-screening effect of intramolecular repulsion between unlike segments that constitute the copolymer.

The crosslinked P4VP polymers used in this work are copolymers of 4-vinylpyridine (4VP) and divinylbenzene (DVB). These repeating units are the same constitutive units as those for P4VP-*co*-S, except for the double vinyl functional group in DVB monomer (that allows crosslinking) instead of the single bond in styrene. The unfavorable interaction between 4VP and DVB is the same as that between 4VP and styrene. Moreover, because the same DVB monomeric unit links together two P4VP chains, the number of 4VP units covalently bonded with a single DVB unit is twice that

in the non-linked copolymer. As a result, we expect that intramolecular repulsion in the crosslinked copolymers is stronger than that in the non-linked copolymers at fixed copolymer composition.

This expectation is confirmed upon comparing the data for P4VP-co-10%S + i-propanol and for c-P4VP/2%DVB + i-propanol at low solvent activity (Figure 6). Lower comonomer concentration in the crosslinked copolymer is able to produce the same increase in vapor sorption. Hence, intramolecular repulsion can explain why, at low solvent activity, the sorption rises with degree of crosslinking. However, at high solvent activity, recovery of the usual trend (higher sorption in linear homopolymer P4VP) follows from the contribution of elastic forces that are small at low solvent concentration but become increasingly important as more solvent enters the polymer.

Sorption dependence on solvent quality

Figure 7(a)-(e) shows results similar to those presented above. However, in each part of Figure 7 there is only one polymer with three different solvents. Linear P4VP absorbs more methanol than i-propanol; the sorption of t-butanol is low compared to those of the other two alcohols, especially for a_1<0.65. These results are in agreement with data for osmotic second virial coefficient B and for viscosity η for P4VP in methanol and i-propanol:[69] B and η increase in the direction i-propanol<methanol, showing that P4VP has the greatest affinity for the smallest alcohol.

The affinity of P4VP for alcohol probably follows from the formation of a specific interaction (hydrogen bond, acid–base interaction) between the –OH group in the alcohol and the basic nitrogen in the pyridine ring. Indeed, it has been shown

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experimentally that the absorption capacity of carboxylic acids and substituted phenols in P4VP increases with solvent acidity.[53,54] Moreover, Boyes and Strauss[69] recognized the existence of an H-bond in P4VP t-butanol system because of the negative temperature coefficient of the solubility of this polymer in a t-butanol/benzene mixture.

Steric hindrance in the formation of specific interaction may have some influence on the affinity of alcohol/P4VP: moving from methanol to i-propanol and t-butanol, the specific interaction of –OH with pyridine N become less probable because of the more restrictive orientation requirement. The role of steric hindrance is indicated by observed insolubility of t-butanol in poly(2-vinylpyridine) where the interacting site in the polymer is in a position more hidden than that in P4VP.[70]

For the three alcohols studied here, similar affinity has been observed for c-P4VP/2%DVB: again, the highest sorption is observed with methanol and the lowest with t-butanol. For c-P4VP/25%DVB, the sorption curves for the three alcohols do not show any significant difference. Similar behavior has been observed for P4VP-*co*-S: increasing %S from 10% to 50% cancels any difference in sorption between methanol and i-propanol. At high comonomer concentration, the reduction of solvent affinity for P4VP in the direction methanol>i-propanol>t-butanol is probably balanced by the increased solvent affinity of styrene segments for higher aliphatic alcohols.

As expected, sorption at 70°C is less than that at 55°C when compared at the same solvent activity.

Conclusion

New VLE sorption data for alcohols have been obtained for crosslinked 4VP/DVB and for linear 4VP/S copolymers at 55-70°C. Solvent sorption depends

strongly on the comonomer (S or DVB) content. Intramolecular repulsion between unlike bonded segments enhances solvent sorption for some copolymer compositions. The effect of intramolecular repulsion appears to be larger in the crosslinked copolymers where a single DVB unit is covalently bonded to a higher number of 4VP segments. In block copolymers, the segregated sequence (blockiness) of unlike monomers minimizes repulsive interactions.

Surprisingly, at low solvent activity, the amount of sorbed solvent in crosslinked copolymers increases with crosslinker concentration (DVB) because of the intramolecular repulsion effect. However, at high solvent activity, where elastic forces hinder solvent sorption, sorption decreases with crosslinker concentration.

Comparing the sorption of methanol, i-propanol and t-butanol in the same copolymer, the difference in the amount of sorbed alcohol decreases significantly upon increasing the percent S or DVB content in a 4VP-based copolymer: the reduction of solvent affinity for P4VP in the direction methanol>i-propanol>t-butanol seems to be balanced by the increased solvent affinity of S or DVB segments for aliphatic alcohols with longer hydrocarbon content.

Acknowledgment

References

(1) Baker, R.W.; Yoshioka, N.; Mohr, J.M; Kahn, A.J. *J. Membr. Sci.*, **1987**, *31*, 259.

(2) Matsumoto, K.; Ishii, K.; Kuroda, T.; Inoue, K.; Iwama A. *Polym. J.*, **1991**, *23*, 491.

(3) Maeda, Y.; Tsuyumoto, M.; Karakane, H.; Tsugaya, H. *Polym. J.*, **1991**, *23*, 501.

(4) Ballantine, D.S.; Wohltjen, H. *Anal. Chem.*, **1989**, *61*, 704A .

(5) Grate, J.W.; Klusty, M.; McGill, R.A.; Abraham, M.H.; Whithing, G.; Andonian-Haftvan, J. *Anal. Chem.*, **1992**, *64*, 610.

(6) Kubota, H.W., *Acta Polym.*, **1986**, *37*, 1.

(7) High, M.S.; Danner, R.P. *Fluid Phase Equilibria*, **1990**, *55*, 1.

(8) Albalak R.J. *Polymer Devolatilization*; Marcel Dekker, NY, 1996.

(9) Napper, D.H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press, Inc.: London, 1983.

(10) Tanbonliong, J.O.; Prausnitz, J.M. *Polymer*, **1997**, *38*, 23, 5775.

(11) Wohlfarth, C. *Macromol. Chem. Phys.*, **1997**, *198*, 2689.

(12) Gupta, R.B.; Prausnitz, J.M. *Fluid Phase Equilibria*, **1996**, *117*, 77.

(13) Cornejo-Bravo, J.M.; Siegel, R.A. *Biomaterials*, **1996**, *17*, 1187.

(14) Gupta, R.B.; Prausnitz, J.M. *J. Chemical Engineering and Data*, **1995**, *40*, 784.

(15) Iwai Y.; Myiamoto, S.; Ikeda, H.; Arai, Y. *Fluid Phase Equilibria*, **1991**, *68*, 197.

(16) Panayioutou C.P.; Vera, J.H. *Polym. J.*, **1984**, *16*, 89.

(17) Bonner D.C.; Prausnitz, J.M. *J. Polym. Sci.* **1974**, *21*, 51.

(18) Cornelliusson R.; Rice, S.A.; Yamakawa, H. *J. Chem. Phys.* **1963**, *38*, 1768.

(19) Moore, W.R.; Shuttleworth, R. *J. Polym. Sci., Part A-1*, **1963**, 733.

(20) Mantovani, F.; Grassi, M.; Colombo, I.; Lapasin, R. *Fluid Phase Equilibria* **2000**, *167*, 63.

(21) Zhao, Y; Eichinger, B.E. *Macromolecules* **1992**, *25*, 6988.

(22) Neuburger, N.A.; Eichinger, B.E. *Macromolecules* **1988**, *21*, 3060.

(23) Brotzman, R.W.Jr.; Eichinger, B.E. *Macromolecules* **1983**, *16*, 1131.

(24) Brotzman, R.W.Jr.; Eichinger, B.E. *Macromolecules* **1982**, *15*, 53.

(25) Brotzman, R.W.Jr.; Eichinger, B.E. *Macromolecules* **1981**, *14*, 1445.

(26) Yen L.Y.; Eichinger, B.E. *J.Polym. Sci.* **1978**, *16*, 121.

(27) Yen L.Y.; Eichinger, B.E., *J.Polym. Sci.* **1978**, *16*, 117.

(28) Gee, G.; Herbert, J.B.M.; Roberts, R.C. *Polymer* **1965**, *6*, 541.

(29) Jayachandran, K.N.; Chatterji, P.R.; Prausnitz, J.M. *Macromolecules* **1998**, *31*, 7, 2375.

(30) Mio, C.; Jayachandran, K.N.; Prausnitz, J.M. *Fluid Phase Equil.* **1997**, *141*, 165.

(31) Lieu, J.G; Prausnitz, J.M.; Gauthier, M. *Polymer* **2000**, *41*, 219.

(32) Mio, C.; Prausnitz, J.M. *Polymer* **1998**, *39*, 25,6401.

(33) Lieu, J.G.; Liu, M.J.; Frechet, J.M.J.; Prausnitz, J.M. *J. Chem. Eng. Data* **1999**, *44*, 3, 613.

(34) Mio, C.; Kiritsov, S.; Thio, Y.; Brafman, R.; Prausnitz, J.M.; Hawker, C.; Malmstrom E.E. *J. Chem Eng. Data* **1998**, *43*, 4, 541.

(35) Cowie J.M.G., *Makromol. Chem., Macromol. Symp.* **1992**, *58*, 63.

(36) Krause S., *Macromolecules* **1991**, *24*, 2108.

(37) Kambour, R.P.; J.T. Bendler and R.C. Bopp, *Macromolecules* **1983**, *16*, 753.

(38) Paul, D.R.; Barlow, J.W. *Polymer* **1984**, *25*, 487.

(39) ten Brinke, G.; Rubinstein, E.; Karasz, F.E.; MacKnight, W.J.; Vukovic, R. *J. Appl. Phys.* **1984**, *56*, 9, 2440.

(40) ten Brinke, G.; Karasz, F.E.; MacKnight, W.J. *Macromolecules* **1983**, *16*, 12, 1827.

(41) Angerman, H.; Hadziioannu, G.; ten Brinke, G. *Phys. Rew. E.* **1994**, *50*, 5, 3808.

(42) Jacobson, H.S.; Gordon, D.J.; Nelson, G.V.; Balazs, A. *Adv. Mat.* **1992**, *4*, 3, 198.

(43) Marsh, S.F.; Jarvinen, G.D.; Jong, S.K.; Jaewook, N.; Bartsch, R.A. *Reactive and Functional Polymers* **1997**, *35*, 1-2, 75.

(44) Mika,A.M.; Childs, R.F.; West, M.; Lott, J.N.A. *J. Membr. Sci.* **1997**, *136*, 1-2, 221.

(45) Mika, A.M.; Childs, R.F.; Dickson, J.M.; McCarry, B.E.; Gagnon, R. *J. Membr. Sci.* **1997**, *135*, 1, 81.

(46) Mika, A.M.; Childs, R.F.; Dickson, J.M. *J. Membr. Sci.* **1998**, *153*, 1, 45.

(47) Chung T.-S.; Shieh, J.-J.; Lau, W.W.Y.; Srinivasan, M.P.; Paul, D.R. *J. Membr. Sci.* **1999**, *152*, 2, 211.

(48) Shieh, J.J.; Chung, T.-S.; Paul, D.R. *Chem. Eng. Sci.* **1999**, *54*, 675.

(49) Lebrun, C.; Deniau, G.; Viel, P.; Lecayon, G. *Surf. Coat. Tech.* **1998**, *100-101*, 474.

(50) Uramoto H.; Kawabata, N. *J. Applied Polymer Science* **1993**, *50*, 115.

(51) Uramoto H.; Kawabata, N. *J. Applied Polymer Science* **1993**, *49*, 799.

(52) Kawabata N.; Higuchi I.; Yoshida, J. *Environm. Sci. Tech.* **1979**, *13*, 11, 1396.

(53) Kawabata N.; Higuchi, I.; Yoshida, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3253.

(54) Kawabata N.; Higuchi, I.; Yoshida, *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 386.

(55) Stachera D.M.; Childs, R.F.; Mika, A.M.; Dickson, J.M. *J. Membr. Sci.* **1998**, *148*, 119.

(56) Volotovsky, V.; Kim, N. *Biosensor and Bioelectronics* **1998**, *13*, 9, 1029.

(57) Soldatkin A.P.; Martelet, C.; Jaffrezic-Renault, N.; Gorchkov, D.V. *Mat. Sci Eng. C* **1995**, *5*, 1, 35.

(58) Jdanova, A.S.; Poyard, S.; Soldatkin, A.P.; Jaffrezic-Renault, N.; Martelet, C. *Anal. Chim. Acta* **1996**, *321*, 35.

(59) Xu, S.; Tang, T.; Chen, B.; Huang, B. *Polymer* **1999**, *40*, 2239.

(60) Xu, S.; Tang, T.; Chen, B.; Huang, B. *Polymer* **1999**, *40*, 3399.

(61) Bogdanic, G.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1995**, *34*, 324.

(62) Li, X.-L. *React. Funct. Polym.* **1999**, *42*, 53.

(63) Azhari S.J.; Diab, M.A. *Polym. Degr. Stab.* **1998**, *60*, 253.

(64) Khairou K.S.; Diab, M.A. *Polym. Degr. Stab.* **1994**, *44*, 17.

(65) Daubert, T.E.; Danner, R.P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation.;* Hemisphere Publishing Corp., New York, 1989.

(66) Clarke, C.J.; Eisenberg, A.; La Scala, J.; Rafailovich, M.H.; Sokolov, J.; Li, Z.; Qu, S.; Nguyen, D.; Schwraz, S.A.; Strzhenechny, Y; Sauer, B.B. *Macromolecules* **1997**, *30*, 4184.

(67) Horkay, F.; Hecht A.M.; Geissler, E. *J.Chem. Phys.* **1989**, *91*, 4, 2706.

(68) McKenna, G.B.; Flynn, K.M.; Chen, Y. *Polym. Comm.* **1988**, *29*, 272.

(69) Boyes, A.G.; Strauss, U.P. *J. Polym. Sci.* **1956**, *22*, 463.

(70) Arichi, S.; Matsuura, H.; Tanimoto, Y.; Murata, H. *Bull. Chem. Soc. Jap.* **1966**, *39*, 434.

Table 1. Polymer Properties

Homopolymer	M_w		T_g (°C)	Lot #	Supplier
P4VP	160000	-	154.0	12338MS	Aldrich
PS	382100	-	107.5	11538MS	Aldrich
Copolymer	M_w	%w Styrene	T_g (°C)	Lot #	Supplier
P4VP-*co*-10% S	1200000-1500000	10	149.4 (148.8)[1]	03001HN	Aldrich
P4VP-*co*-50% S	60000	50	128.2 (129.4)[1]	03	Sp^2
P4VP-*b*-50% S	47600[2]	50	107.0; 151.0[3]	-	Polymer Source
Crosslinked		%w DVB	T_g (°C)	Lot #	Supplier
c-P4VP/2% DVB	-	2	156.6	16312LR	Aldrich
c-P4VP/25% DVB	-	25		03505AQ	Aldrich

[1] Glas-transition temperature in brackets calculated by Equation (1).

[2] M_n: PS(21400); P4VP(20700), M_w/M_n=1.13

[3] Two glass-transition temperatures: $T_{g,p1}$=107.0 °C for PS block, $T_{g,p2}$=151.0 °C for P4VP block.

P4VP = poly(4-vinylpyridine)

PS = polystyrene

S = styrene

DVB = divinylbenzene

Table 2. Solvent Properties

Solvent	T^{exp} (°C)	P^{sat} (torr)	Supplier	Lot #	Purity
Methanol	55	515	Fisher	992326	99.9%
Methanol	70	938	Fisher	992326	99.9%
i-propanol	70	455	Fisher	992487	99.9%
t-butanol	70	458	J. T. Baker	8210519	99.9%

Table 3. Systems Studied

Polymer	Solvent	T (°C)
Homopolymer		
P4VP	methanol	55
P4VP	methanol, i-propanol, t-butanol	70
PS	methanol, i-propanol	70
Copolymer		
P4VP-co-10%S	methanol, i-propanol	70
P4VP-co-50% S	methanol, i-propanol	70
P4VP-b-50% S	methanol, i-propanol	70
Crosslinked polymer		
C-P4VP/ 2% DVB	methanol	55
C-P4VP/ 2% DVB	methanol, i-propanol, t-butanol	70
C-P4VP/ 25% DVB	methanol	55
C-P4VP/ 25% DVB	methanol, i-propanol, t-butanol	70

Figure captions

Figure 1. Schematic diagram of the experimental apparatus for VLE measurements.

Figure 2. Solvent activities for binary solutions of linear poly(4VP-co-S) copolymers in methanol at 70 °C. Effect of intramolecular repulsion.

Figure 3. Solvent activities for binary solutions of poly(4VP-co-S) copolymers in i-propanol at 70 °C. Effect of intramolecular repulsion.

Figure 4. Solvent activities for binary solutions of crosslinked poly(4-vinylpyridine) in methanol (a) at 70 °C and (b) at 55 °C. Effect of crosslinking concentration.

Figure 5. Solvent activities for binary solutions of crosslinked poly(4-vinylpyridine) (a) in i-propanol and (b) in t-butanol at 70 °C. Effect of crosslinking concentration.

Figure 6. Comparison of i-propanol sorption in crosslinked and nonlinked 4-vinylpyridine copolymers. Comonomers: divinylbenzene (2% weight percent) for the crosslinked polymer; styrene (10% weight percent) for the non-linked polymer.

Figure 7. Activities of methanol, i-propanol and t-butanol at 70 °C in (a) linear poly(4-vinylpyridine); (b) 2% crosslinked poly(4-vinylpyridine) and (c) 25% crosslinked poly(4-vinylpyridine). Activities of methanol and i-propanol at 70 °C in (d) poly(4VP-co-10%S) and (e) poly(4VP-co-50%S).
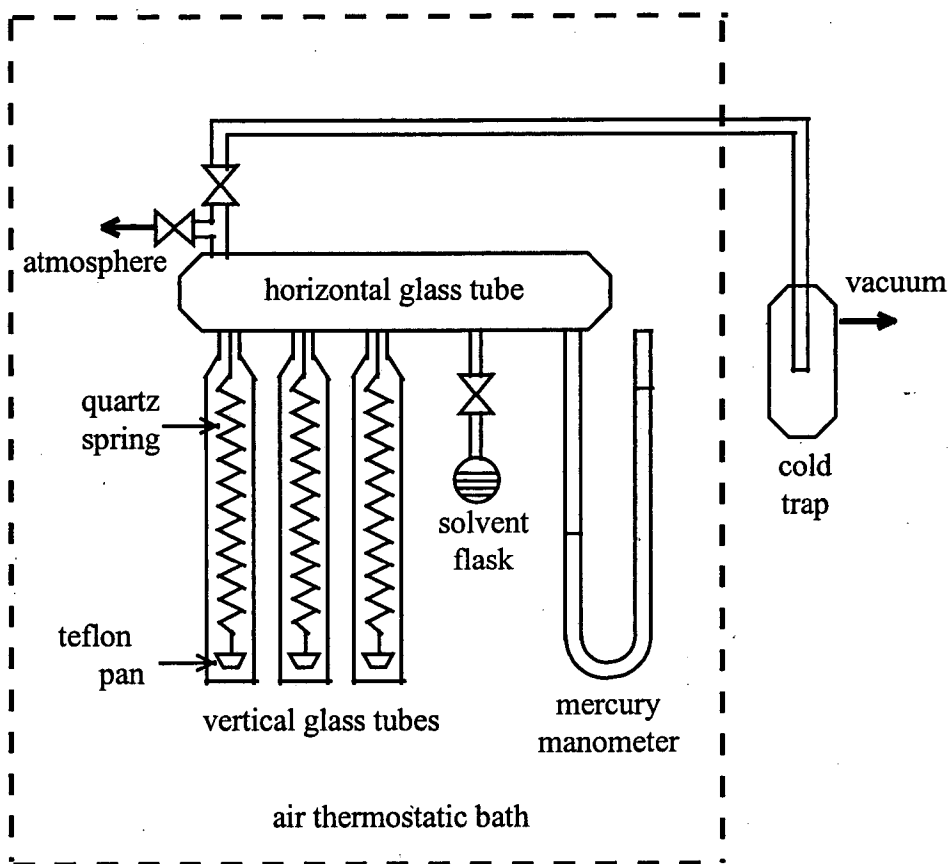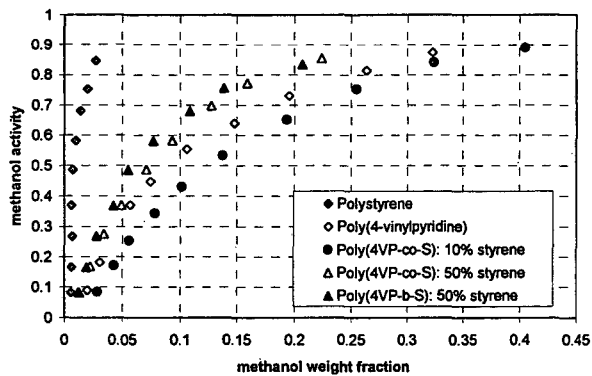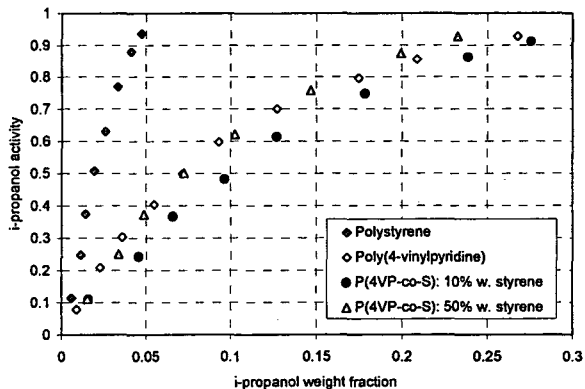
Figure 1.

Figure 2.

Figure 3.
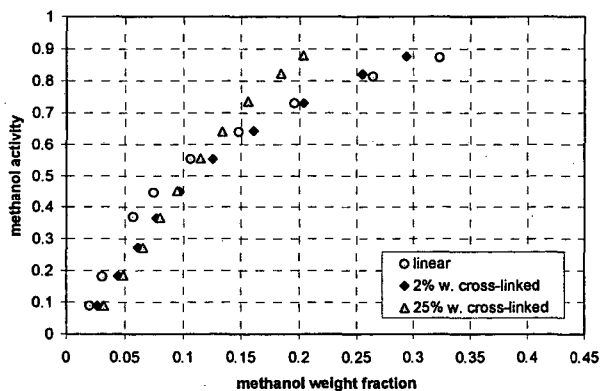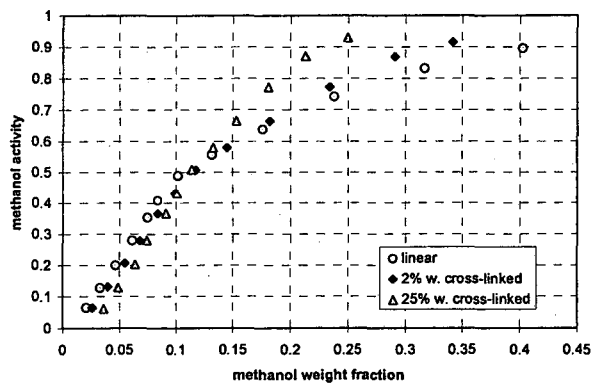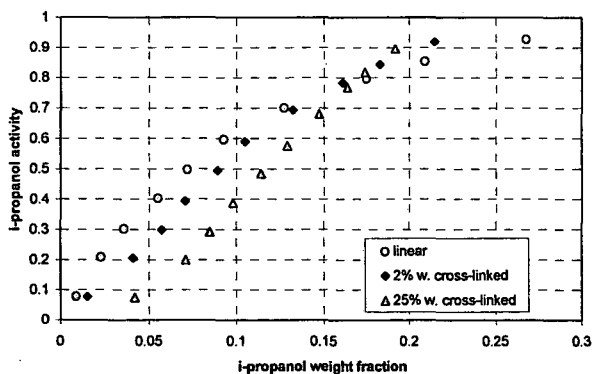

Figure 4(a).

Figure 4(b).

Figure 5(a).
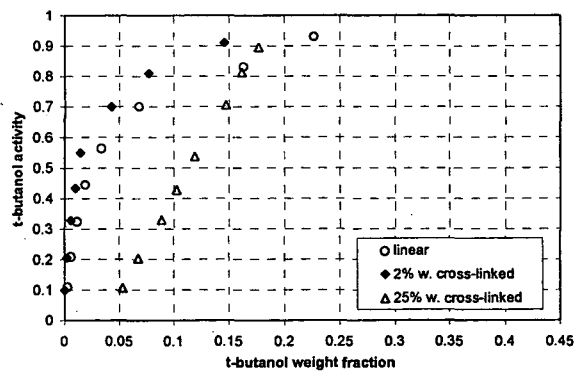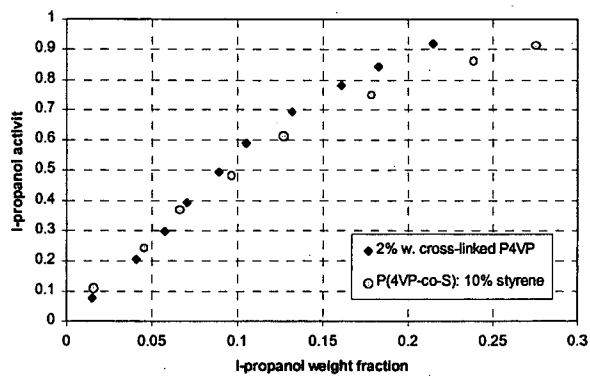

Figure 5(b).

Figure 6.
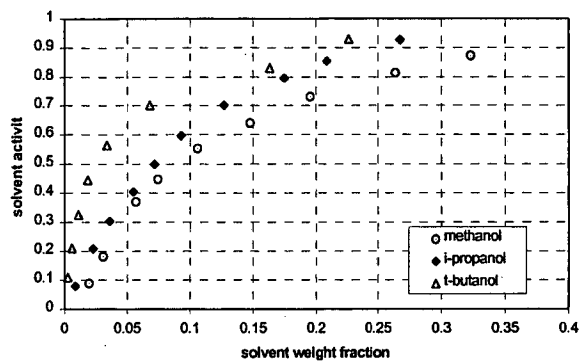

Figure 7(a)
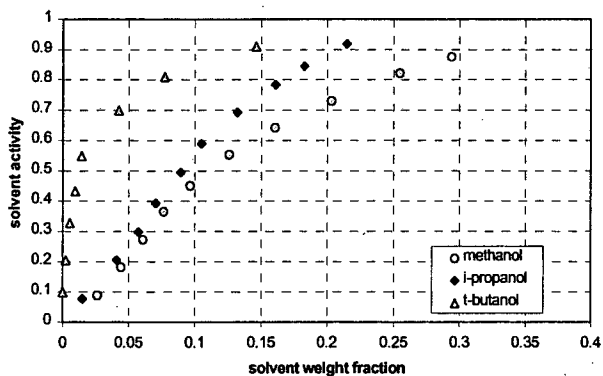
Figure 7(b)
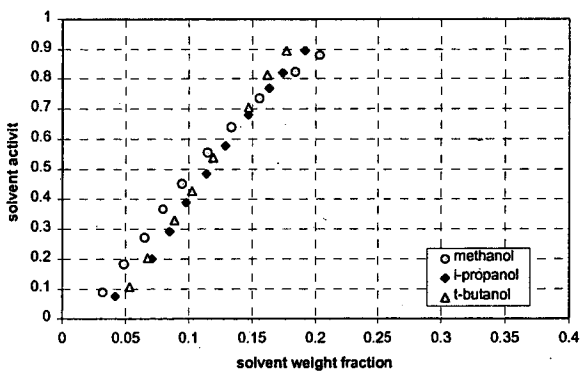
Figure 7(c)
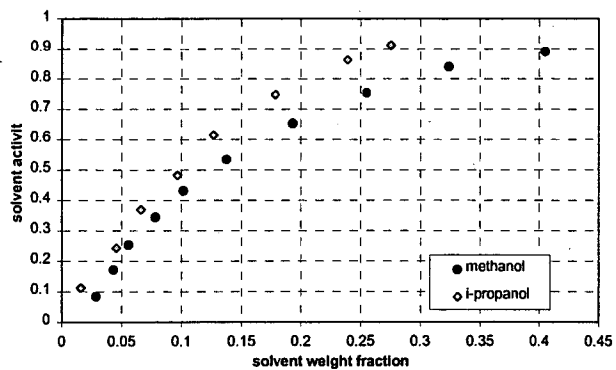
Figure 7(d)
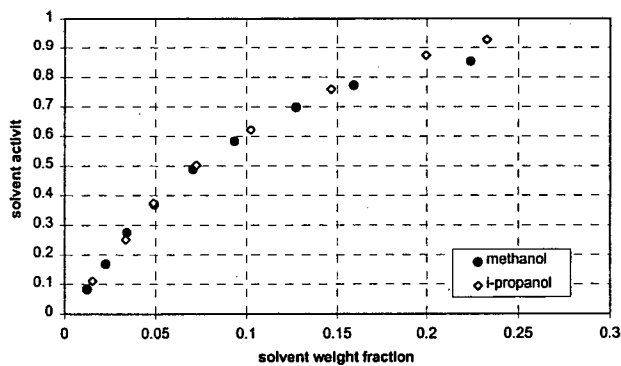
Figure 7(e)

Appendix: Experimental Solvent-Activity Data for Solvent-Polymer Systems

w_1 = weight fraction of solvent

a_1 = activity of solvent

(a) P4VP/methanol, 70°C		**(b) PS/methanol, 70°C**		**(c) P(4VP-*co*-10%S)/methanol, 70°C**	
w_1	a_1	w_1	a_1	w_1	a_1
0.020	0.088	0.006	0.081	0.029	0.084
0.031	0.181	0.006	0.165	0.043	0.171
0.057	0.369	0.007	0.266	0.056	0.255
0.075	0.447	0.006	0.370	0.078	0.344
0.106	0.553	0.008	0.485	0.102	0.431
0.148	0.640	0.010	0.581	0.138	0.533
0.196	0.729	0.014	0.680	0.194	0.652
0.264	0.813	0.020	0.752	0.255	0.753
0.323	0.873	0.027	0.845	0.324	0.840
				0.405	0.891

Appendix (continued)

(d) P(4VP-*co*-50%S)/methanol, 70°C		(e) P(4VP-*b*-50%S)/methanol, 70°C		(f) P4VP/i-propanol, 70°C	
w_1	a_1	w_1	a_1	w_1	a_1
0.013	0.083	0.013	0.081	0.0089	0.078
0.023	0.168	0.019	0.165	0.023	0.208
0.034	0.275	0.028	0.267	0.036	0.302
0.049	0.371	0.043	0.368	0.055	0.403
0.071	0.487	0.056	0.486	0.072	0.498
0.094	0.582	0.077	0.581	0.093	0.596
0.127	0.698	0.109	0.680	0.127	0.700
0.159	0.772	0.139	0.756	0.175	0.795
0.224	0.854	0.207	0.834	0.209	0.854
				0.268	0.927

Appendix (continued)

	(g) PS/i-propanol, 70°C			(h) P(4VP-*co*-10%S)/methanol, 70°C			(i) P(4VP-*co*-50%S)/methanol, 70°C	
w_1	a_1		w_1	a_1		w_1	a_1
0.006	0.113		0.016	0.111		0.015	0.111
0.011	0.247		0.046	0.243		0.034	0.250
0.014	0.374		0.066	0.368		0.049	0.374
0.019	0.507		0.097	0.482		0.073	0.501
0.026	0.629		0.127	0.614		0.103	0.621
0.034	0.768		0.179	0.747		0.147	0.758
0.041	0.879		0.239	0.862		0.200	0.874
0.047	0.936		0.275	0.911		0.233	0.928

Appendix (continued)

(j) 2% c-P4VP/methanol, 70°C	
w_1	a_1
0.027	0.088
0.045	0.182
0.061	0.272
0.077	0.365
0.096	0.451
0.126	0.553
0.161	0.642
0.203	0.729
0.255	0.820
0.294	0.876

(k) 25% c-P4VP/methanol, 70°C	
w_1	a_1
0.032	0.088
0.049	0.182
0.065	0.272
0.080	0.366
0.095	0.452
0.115	0.555
0.134	0.640
0.156	0.735
0.184	0.823
0.203	0.879

(l) 2% c-P4VP/i-propanol, 70°C	
w_1	a_1
0.015	0.077
0.041	0.205
0.057	0.298
0.071	0.393
0.089	0.494
0.105	0.589
0.132	0.692
0.161	0.782
0.183	0.843
0.215	0.918

Appendix (continued)

(m) 25% c-P4VP/ i-propanol, 70°C

w_I	a_I
0.042	0.075
0.071	0.2
0.085	0.292
0.098	0.388
0.114	0.484
0.129	0.576
0.147	0.68
0.163	0.767
0.174	0.818
0.192	0.896

(n) P4VP/t-butanol, 70°C

w_I	a_I
0.003	0.109
0.006	0.209
0.011	0.325
0.019	0.445
0.034	0.564
0.068	0.701
0.163	0.830
0.227	0.930

(o) 2% c-P4VP/ t-butanol, 70°C

w_I	a_I
0.000	0.099
0.002	0.205
0.006	0.328
0.010	0.433
0.014	0.549
0.043	0.699
0.077	0.809
0.146	0.910

Appendix (continued)

(p) 25% c-P4VP/ t-butanol, 70°C		(q) P4VP/methanol, 55°C		(r) 2% c-P4VP/methanol, 55°C	
w_1	a_1	w_1	a_1	w_1	a_1
0.053	0.107	0.021	0.065	0.026	0.064
0.067	0.203	0.033	0.128	0.040	0.131
0.089	0.329	0.047	0.200	0.055	0.206
0.103	0.427	0.061	0.280	0.068	0.278
0.119	0.538	0.075	0.354	0.084	0.365
0.147	0.705	0.084	0.408	0.099	0.430
0.162	0.812	0.102	0.489	0.118	0.506
0.177	0.895	0.132	0.556	0.145	0.578
		0.176	0.638	0.182	0.663
		0.238	0.742	0.234	0.772
		0.317	0.832	0.291	0.868
		0.403	0.896	0.342	0.916

Appendix (continued)

(s) 25% c-P4VP/methanol, 55°C

w_1	a_1
0.036	0.062
0.049	0.129
0.064	0.203
0.074	0.279
0.091	0.366
0.101	0.431
0.114	0.508
0.133	0.579
0.153	0.665
0.181	0.773
0.213	0.871
0.25	0.93