

Sorption Mechanism in Organic Solutions of Uncharged Polymers

Fatemeh Sabzi,¹ Fatemeh Ayatollahi,² Ali Boushehri³

¹Department of Chemical Engineering, Shiraz University of Technology, Shiraz 71555-313, Iran

²Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

³Department of Chemical Engineering, University of California, Berkeley, California 94720

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ABSTRACT: In this work, we use the vapor-sorption equilibrium data to show the degree of solvent upturn in each solvent-polymer system. For this purpose, 20 isothermal data sets for five polymer + solvent binaries have been used in the temperature range of 298–413 K. Solvents studied are benzene, pentane, hexane, toluene, and chlorobenzene. Homopolymers studied are: polystyrene, poly(vinyl acetate), polyisobutylene, and polyethylene. According to these data sets, solvent weight fraction in the polymer is plotted against solvent vapor activity that is

calculated assuming an ideal gas phase of pure solvent vapor neglecting the vapor pressure of the polymer. We use the Flory-Huggins theory to obtain dimensionless interaction parameter, χ . Also the Zimm-Lundberg clustering theory and non-ideality thermodynamic factor, Γ are used to interpret the equilibrium data. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1867–1875, 2010

Key words: sorption phenomena; VLE data; Flory-Huggins interaction parameter

INTRODUCTION

The peculiarities of polymer solutions have attracted much attention because of the widespread (biological, pharmaceutical and many other) applications of dissolved macromolecular substances, e.g., for improvement of the wettability, biocompatibility or adhesion of surfaces, regulation of interfacial processes, etc. The effects observed in a variety of systems are due to the adsorption of the dissolved macromolecules, but in certain cases, the presence of free polymer in the solution plays a role.^{1–4} The thermodynamic characteristics of macromolecular solutions are closely related to the magnitude of relevant (segment-solvent and segment-segment) interaction energies. The thermodynamic quality of solvent is, therefore, a key factor that substantially affects the chain dimensions in solution and also, how a dissolved polymer acts in an application.

The classical mean-field theory derived by Flory and Huggins⁵ is still widely used to represent the thermodynamic features of polymer solutions. The theory assumes that the distribution of segments throughout the solution is homogeneous as if the coils could interpenetrate without any hindrance. The quality of solvent is characterized through the

interaction parameter (χ). For a binary solution, χ_{12} measures the Solvent (1)-Segment (2) interaction and theoretically ranges from below zero for a very good solvent, to 0.5 (in an ideally poor solvent) or greater. Nevertheless, the experimental values of χ are less discriminative than would be expected on the basis of the wide structural and compositional variety of the polymers in the various solvents.

Sorption data are pertinent to a variety of applications including packaging and coating technology, membrane separation of gases and vapors, drug-delivery systems, biocompatible materials for biomedical applications, and contact lens industry.^{6–9} The sorption of solvent vapor by polymers often portrays large vapor uptakes and according to the BET classification,¹⁰ almost all the polymers exhibit a Type III isotherm.^{11,12} Two possible explanations for a large degree upturn at high activity are clustering of solvent molecules or plasticization of the polymer matrix induced by solvent sorption. In clustering the proportion of clustered molecules increases with increasing sorbet concentration, then it would be expected that the diffusion coefficient of the polymer-penetrant system would decrease with increasing concentration and contrasts with the behavior of sorbet solvents or swelling agents when diffusion increases with concentration that is in agreement with the concept of plasticization. Zimm and Lundberg theory¹³ provides a method to determine the extent of clustering of the solvent molecule inside the polymer matrix. The advantage of this integral is

Correspondence to: F. Sabzi (f.sabzi@sutech.ac.ir).

TABLE I
Summary of Polymers with Their Relevant Solvents

Polymer	M_n	V_{sp}^a (cm ³ g ⁻¹)	Solvent	T (K)	P_s^b (KPa)	V_{sp}^b (cm ³ g ⁻¹)
Polystyrene	3600	0.95	Benzene	303	16.18	1.14
Polystyrene	3600	0.95	Benzene	323	36.55	1.17
Polystyrene	3600	0.95	Benzene	343	73.85	1.20
Poly(vinyl acetate)	158,000	0.84	Toluene	313	7.890	1.18
Poly(vinyl acetate)	158,000	0.84	Toluene	333	18.52	1.21
polyisobutylene	1170	1.08	Pentane	308	98.70	1.64
polyisobutylene	1170	1.08	Pentane	318	158.0	1.66
polyisobutylene	1170	1.08	Pentane	328	187.0	1.69
polyisobutylene	2,250,000	1.09	Pentane	308	98.70	1.64
polyisobutylene	2,250,000	1.09	Pentane	318	158.0	1.66
polyisobutylene	2,250,000	1.09	Pentane	328	187.0	1.69
polyisobutylene	50,000	1.07	Hexane	298	20.16	1.53
polyisobutylene	50,000	1.07	Hexane	313	37.26	1.56
polyisobutylene	50,000	1.07	Hexane	338	90.87	1.62
polyethylene	3280	1.04	Chlorobenzene	393	72.37	1.00
polyethylene	3280	1.04	Chlorobenzene	403	95.86	1.02
polyethylene	3280	1.04	Chlorobenzene	413	125.2	1.03
polyethylene	6220	1.08	Chlorobenzene	393	72.37	1.00
polyethylene	6220	1.08	Chlorobenzene	403	95.86	1.02
polyethylene	6220	1.08	Chlorobenzene	413	125.2	1.03

^a All values are taken from Ref. 14.

^b All values are taken from Ref. 15.

that it can be obtained directly from equilibrium data.

The present study deals with the thermodynamic interactions and sorption mechanism in homogeneous solutions of 4 uncharged polymers, which may have relevance in controlling the physical properties of polymer-containing systems. We have used 20 isothermal vapor-liquid equilibrium (VLE) data sets to show the degree of solvent uptake and to analyze the solvent sorption characteristics at different temperatures ranging from 298 K to 413 K. Table I gives a summary of all polymers with their relevant solvents that are considered here.

FLORY-HUGGINS THEORY

For an exact characterization of thermodynamic properties of solution, one of the most important quantities is the chemical potential of the solvent (μ_1):

$$\Delta\mu_1 = RT \ln a_1 \quad (1)$$

It can be obtained from the relative thermodynamic activity of the solvent (a_1), e.g., by determining the osmotic pressure in a solution. According to Raoult's law, the activity a_1 of the solvent in the solution should equal its mole fraction X_1 . In a binary solution consisting of solvent and a polymer having a molecular weight a thousand times or more that of the solvent, only a very small percentage by weight of the solvent is sufficient to bring its mole fraction X_1 very close to unity. Hence, according to Raoult's law

$$a_1 = \frac{P_1}{P_1^0} \quad (2)$$

the partial pressure P_1 of the solvent in the solution should be very nearly equal to that of the pure solvent P_1^0 over the greater portion of the composition range. Experiments do not confirm this prediction. The underlying basis for the failure of the ideal solution law lies in its use of the mole fraction as the composition variable. It consequently presupposes that the effect of a large polymeric solute molecule on the activity of the solvent should be equal to that of an ordinary solute molecule, which may be no larger than one unit in the polymer chain.

As we mentioned in earlier works and according to the Flory-Huggins theory,⁵ the chemical potential of the solvent for solution of an uncharged polymer is:

$$(\mu_1 - \mu_1^0) = RT [\ln(1 - \phi_2) + (1 - (1/r)\phi_2) + \chi_{12}\phi_2^2] \quad (3)$$

Here, ϕ_1 and $\phi_2 = 1 - \phi_1$ are the volume fractions of solvent and polymer, respectively; r is of course, the ratio of the molar volumes of the solute and solvent. From the chemical potential we may at once set down expression for the activity a_1 of the solvent using standard relations of thermodynamics:

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{r}\right) \phi_2 + \chi_{12}\phi_2^2 \quad (4)$$

Since the pure solvent has been chosen as the standard state, $a_1 = P_1/P_1^0$, then the vapor may be regarded as an ideal gas. The influence of the chain length vanishes with increase in molecular weight of polymer, and then we set the ratio of $1/r$ equal to zero. The χ value provides an indication to explain the solvent power of penetrate for polymers. Say penetrate is a good solvent for ($\chi \cong 0$), a non-solvent for ($\chi > 1$) and there is a borderline for solvency strength when χ is very close to 1.

THE CLUSTERING FUNCTION

Solvent molecules have a tendency to form clusters when absorbed in a polymer.¹⁶ To provide a measure for clustering, Zimm and Lundberg^{13,17} defined the clustering function:

$$G_{11}/v_1 = -\phi_2[\partial(a_1/\phi_1)/\partial a_1] - 1 \quad (5)$$

where 1 refers to solvent molecules. The quantity $\phi_1(G_{11}/v_1)$ is the mean number of Type 1 molecules in excess of the mean concentration of Type 1 molecules in the neighborhood of a given Type 1 molecule; thus, it measure the clustering tendency of Type 1 molecules.

This relation is generally valid for systems of negligible compressibility. When the activity coefficient does not vary with concentration, as for example in the case of an ideal solution, G_{11} is minus one molecular volume. This means that a particular Type 1 molecule in such a system excludes its own volume to the other molecules but otherwise does not affect their distribution. This is what would be expected for an ideal solution, of course. For athermal polymer solutions, however, γ_1 decreases with increasing ϕ_1 so that G_{11}/v_1 is greater than -1 and may actually become positive. In $G_{11}/v_1 = 0$ clustering is just sufficient to overcome the excluding effect of the central solvent molecule, such that when $G_{11}/v_1 > 0$ ¹⁸ (sorption isotherm convex towards the pressure axis) there is an overall tendency for molecular pair association or clustering of Type1 molecules to occur. This can only mean that the first solvent molecules enter the polymer structure and loosen the structure and make it easier for subsequent molecules to enter in the neighborhood of the first than to go elsewhere. Conversely, when $G_{11}/v_1 < -1$ (isotherm concave towards the pressure axis) there is an overall tendency for polymer-solvent pairs to be preferred and tendency of solvent molecules to remain isolated and increasingly so as G_{11}/v_1 becomes more negative.

To calculate G_{11}/v_1 or G_{ss}/v_s ¹⁹ we first fit experimental equilibrium data²⁰ (ϕ_1 versus a_1) with eq. (5), where we assume $\chi = C_1\phi_1 + C_2$ with C_1 and C_2

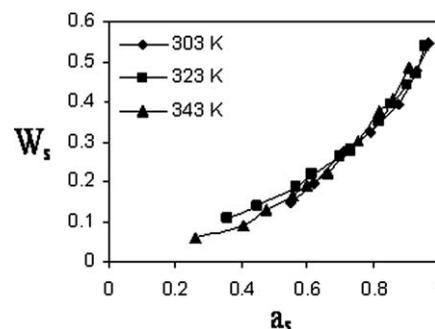


Figure 1 Sorption isotherm for benzene in PS ($M_n = 3600$) at 303, 323, and 343 K.

constants. We then differentiate the resulting smooth function. Although the calculated values may vary somewhat with differing smoothing procedures,¹⁹ the following conclusions remain valid. Also, in this work, we have calculated thermodynamic non-ideality factor, Γ ,¹⁹ defined by:

$$\Gamma = \frac{\partial \ln a_s}{\partial \ln \phi_s} \quad (6)$$

that can be calculated from the clustering function²⁰:

$$\Gamma = \frac{1 - \phi_s}{1 + \phi_s G_{ss}/v_s} \quad (7)$$

In the event of an ideal system, the clustering function is equal to -1 ; and Γ is equal to 1. When G_{ss}/v_s is greater than -1 and solvent molecules tend to cluster, the non-ideality factor decreases with rising solvent content in system with a tendency to cluster. Conversely, Γ is an increasing function of composition when G_{ss}/v_s is less than -1 , i.e., for systems where solvent molecules tend to remain isolated.

APPLICATION TO EXPERIMENTAL DATA

System: polystyrene (PS) with $M_n = 3600$ in benzene at 303, 323, and 343 K

In Figure 1 solvent weight fraction in the polymer has been plotted against solvent-vapor activity by using VLE data sets of Orbey et al.²¹ work. According to the BET classification,¹⁰ all systems obey a Type III isotherm. As it has been shown, there is no difference between various temperatures in sorption of solvent and their sorption strength goes high with increasing solvent-vapor activity. In Figure 2 Flory-Huggins interaction parameter, $\chi < 1$, which is calculated from eq. (4) indicates that benzene can moderately solve PS at all above-mentioned temperatures, but with a little difference in

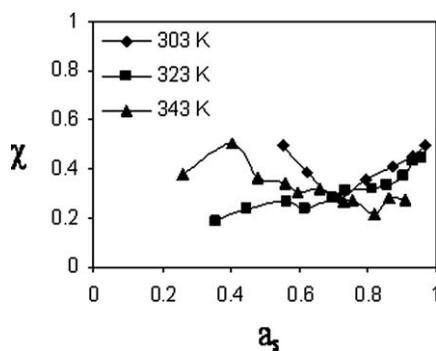


Figure 2 Flory interaction parameter χ versus benzene-vapor activity for PS ($M_n = 3600$) at 303, 323, and 343 K.

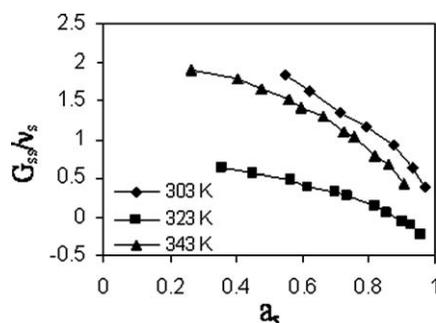


Figure 3 Clustering function G_{ss}/v_s at various benzene-vapor activities for PS ($M_n = 3600$) at 303, 323, and 343 K.

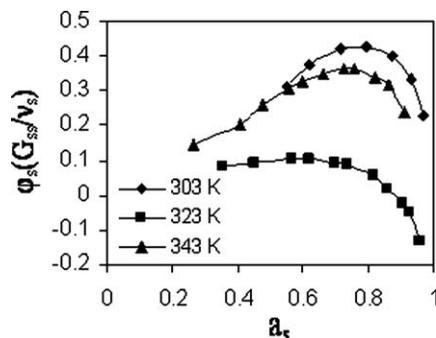


Figure 4 Mean cluster size $\phi_s(G_{ss}/v_s)$ at various benzene-vapor activities for PS ($M_n = 3600$) at 303, 323, and 343 K.

its power when different temperature has been applied.

Positive values of clustering function G_{ss}/v_s and mean cluster size $\phi_s(G_{ss}/v_s)$ in Figures 3 and 4 which are calculated from eq. (5) confirm that benzene makes cluster in this system. Our results obtained for χ also indicate that when polymer-solvent interaction is weak, solvent molecule attach to each other more and make cluster in the polymer matrix. Non-ideality factor, Γ , in Figure 5 calculated from eq. (7) is a decreasing function of solvent-vapor activity and confirms the tendency of solvent molecules to cluster that was mentioned previously.

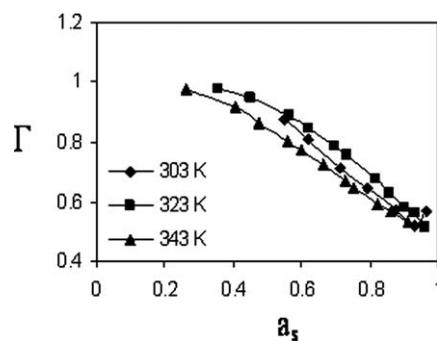


Figure 5 Thermodynamic factor Γ versus benzene-vapor activity for PS ($M_n = 3600$) at 303, 323, and 343 K.

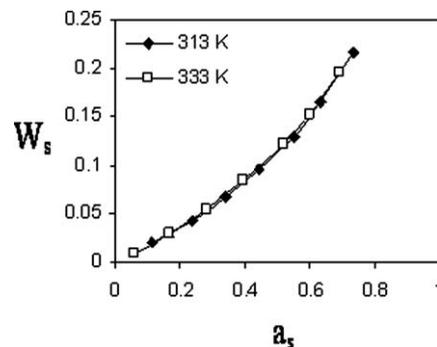


Figure 6 Sorption isotherm for toluene in PVA ($M_n = 158,000$) at 313 and 333 K.

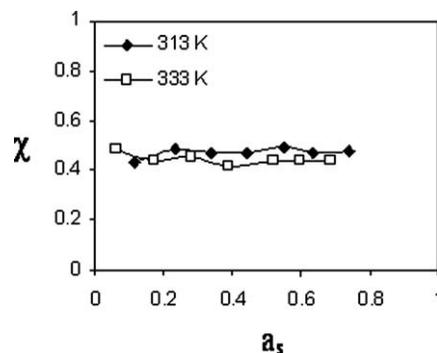


Figure 7 Flory interaction parameter χ versus toluene-vapor activity for PVA ($M_n = 158,000$) at 313 and 333 K.

System: poly vinyl acetate (PVA) with $M_n = 158,000$ at 313 and 333 K

Figure 6 displays VLE data sets²¹ for a system containing PVA with toluene as a solvent. The solubility of toluene rises in proportion of solvent content in this system. It is evident from Figure 6 that sorption of solvent in the polymer has the same behavior when examined for both temperatures 313 and 333 K. In Figure 7 Flory-Huggins interaction parameter, $\chi < 1$, indicates that toluene is a fairly good solvent for PVA. The increasing amount of solvent activity does not affect the interaction between polymer and

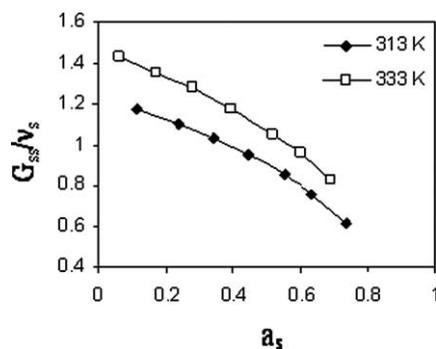


Figure 8 Clustering function G_{ss}/v_s at various toluene-vapor activities for PVA ($M_n = 158,000$) at 313 and 333 K.

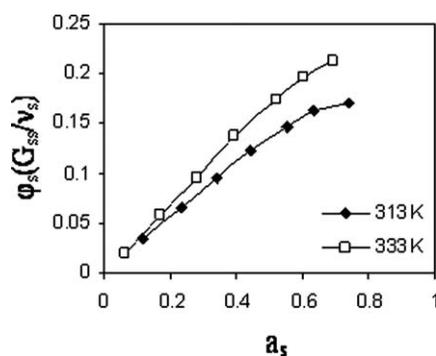


Figure 9 Mean cluster size $\phi_s(G_{ss}/v_s)$ at various toluene-vapor activities for PVA ($M_n = 158,000$) at 313 and 333 K.

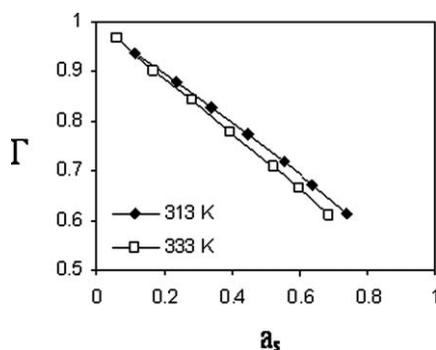


Figure 10 Thermodynamic factor Γ versus toluene-vapor activity for PVA ($M_n = 158,000$) at 313 and 333 K.

solvent. A better interaction between solvent and polymer can be seen when temperature increases.

Figures 8 and 9 show values of the clustering function G_{ss}/v_s and mean cluster size $\phi_s(G_{ss}/v_s)$ versus solvent-vapor activity. Positive values of these parameters accompanied with convexity of sorption isotherm indicate that toluene molecules tend to make cluster in PVA. Decreasing trend of non-ideality factor, Γ , in Figure 10 also is a confirmation on exiting of solvent clusters in this polymer.

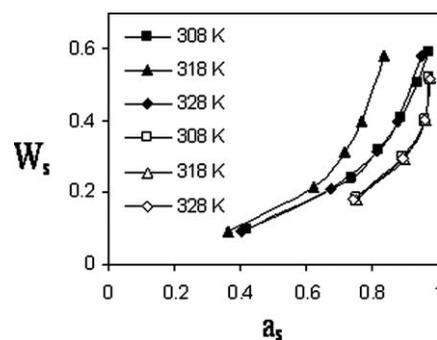


Figure 11 Sorption isotherm for pentane in PIB with $M_n = 1170$ (filled symbols) and $M_n = 2,250,000$ (open symbols) at 308, 318, and 328 K.

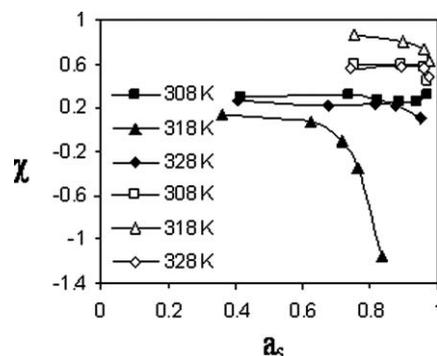


Figure 12 Flory interaction parameter χ versus pentane-vapor activity for PIB with $M_n = 1170$ (filled symbols) and $M_n = 2,250,000$ (open symbols) at 308, 318, and 328 K.

System: polyisobutylene (PIB) with $M_n = 1170$ and $M_n = 2,250,000$ in pentane at 308, 318, and 328 K

In Figure 11 solvent weight fraction in PIB with $M_n = 1170$ and $M_n = 2,250,000$ given by Orbey et al.²¹ and Haghtalab et al.²² has been plotted against solvent-vapor activity. According to the BET classification,¹⁰ all systems obey a Type III isotherm. Almost all isotherms are convex toward the activity axis and display a large degree of solvent uptake at relatively high activities. As it has been shown, in the case of PIB with $M_n = 2,250,000$, there is no difference between various temperatures in sorption of solvent and their sorption strength goes high with increasing solvent-vapor activity. It is also evident that at the same activity PIB with $M_n = 1170$ absorbs more solvent than PIB with $M_n = 2,250,000$.

Figure 12 gives Flory-Huggins interaction parameter, χ , which is calculated from eq. (4) as a function of solvent vapor activity. Both PIB show a moderate interaction with pentane at all above-mentioned temperatures except PIB with $M_n = 1170$ at 318 K where it has a negative χ and strong interaction in activities greater than 0.7. As a result of more positive interaction between PIB with $M_n = 2,250,000$ and solvent,

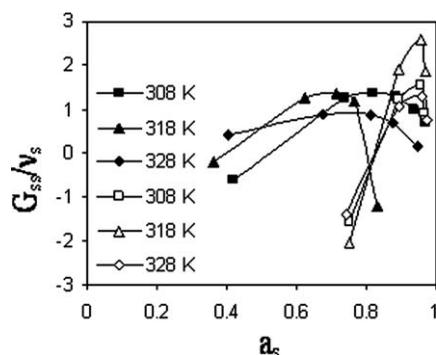


Figure 13 Clustering function G_{ss}/v_s at various pentane-vapor activities for PIB with $M_n = 1170$ (filled symbols) and $M_n = 2,250,000$ (open symbols) at 308, 318, and 328 K.

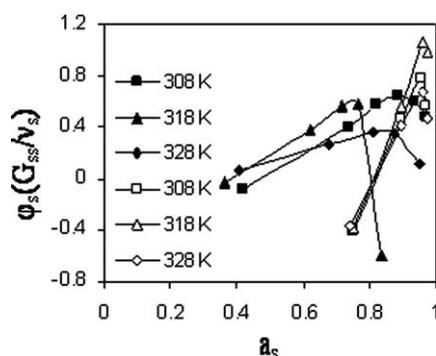


Figure 14 Mean cluster size $\phi_s(G_{ss}/v_s)$ at various pentane-vapor activities for PIB with $M_n = 1170$ (filled symbols) and $M_n = 2,250,000$ (open symbols) at 308, 318, and 328 K.

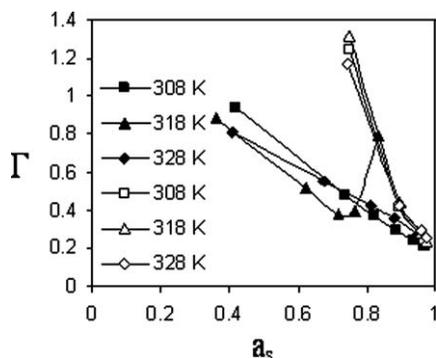


Figure 15 Thermodynamic factor Γ versus pentane-vapor activity for PIB with $M_n = 1170$ (filled symbols) and $M_n = 2,250,000$ (open symbols) at 308, 318, and 328 K.

we observe a less degree of uptake for this polymer in Figure 11.

Positive values of clustering function G_{ss}/v_s and mean cluster size $\phi_s(G_{ss}/v_s)$ displayed in Figures 13 and 14 represent the tendency of pentane molecules to make cluster especially in activities greater than 0.8 for all above-mentioned temperatures. Decreasing trend of non-ideality factor in Figure 15 is also

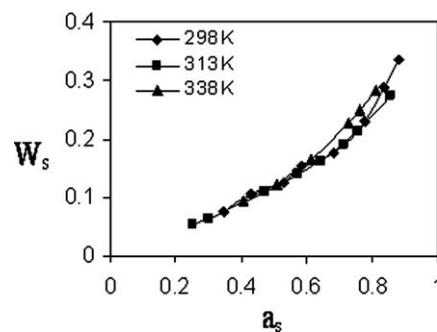


Figure 16 Sorption isotherm for hexane in PIB ($M_n = 50,000$) at 298, 313, and 338 K.

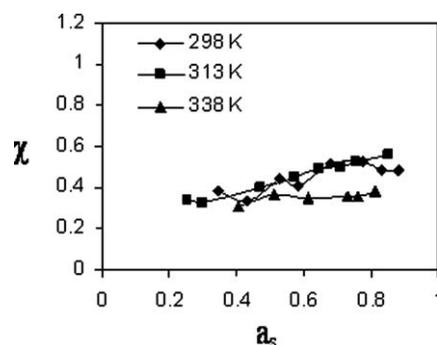


Figure 17 Flory interaction parameter χ versus hexane-vapor activity for PIB ($M_n = 50,000$) at 298, 313, and 338 K.

an indication of clustering to occur. In the case of PIB with $M_n = 2,250,000$ clustering happens more at higher activities. Negative values of clustering function and mean cluster size at activities smaller than 0.8, indicates that plasticization dominates at this region.

An unusual behavior is seen for PIB with $M_n = 1170$ at temperature 318 K where there is a large uptake of solvent in PIB but strong solvent-polymer interaction, negative values of mean cluster size and increasing trend of thermodynamic factor at activities greater than 0.8 suggest that solvent-solvent interaction is smaller than solvent-polymer interaction, then solvent molecules are liable to remain isolated when absorbed in the polymer.

System: polyisobutylene (PIB) with $M_n = 50,000$ in hexane at 298, 313, and 338 K

Figure 16 displays VLE data sets²² for a system containing PIB with hexane as a solvent. The solubility of hexane rises in proportion of solvent content in this system. It is evident from Figure 16 that sorption of solvent in the polymer has the same behavior when examined for temperatures 298, 313, and 338 K. In Figure 17 Flory-Huggins interaction parameter, $\chi < 1$, indicates that hexane is a fairly good

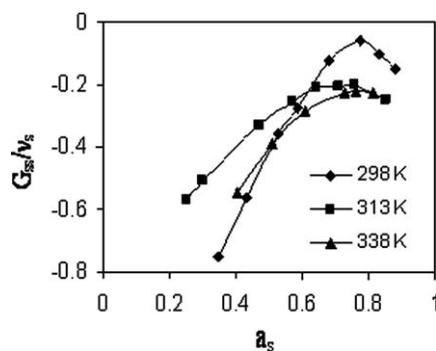


Figure 18 Clustering function G_{ss}/v_s at various hexane-vapor activities for PIB ($M_n = 50,000$) at 298, 313, and 338 K.

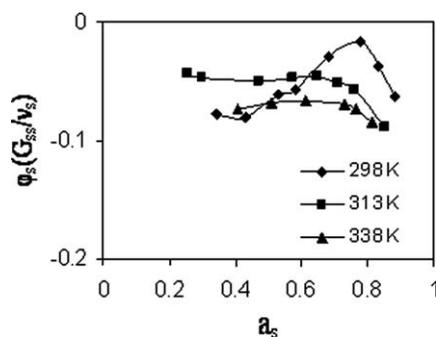


Figure 19 Mean cluster size $\phi_s(G_{ss}/v_s)$ at various hexane-vapor activities for PIB ($M_n = 50,000$) at 298, 313, and 338 K.

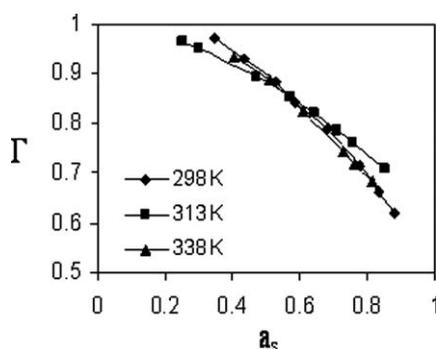


Figure 20 Thermodynamic factor Γ versus hexane-vapor activity for PIB ($M_n = 50,000$) at 298, 313, and 338 K.

solvent for PIB. The increasing amount of solvent does not affect the interaction between polymer and solvent.

Figures 18 and 19 show values of the clustering function G_{ss}/v_s and mean cluster size $\phi_s(G_{ss}/v_s)$ versus solvent-vapor activity. Negative values of these parameters accompanied with convexity of sorption isotherm and decreasing trend of non-ideality factor in Figure 20 suggest that the polymer matrix is plasticized by the solvent.

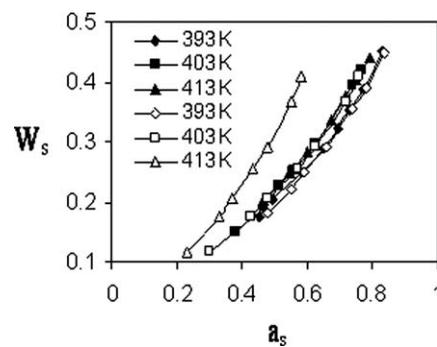


Figure 21 Sorption isotherm for chlorobenzene in PE with $M_n = 3280$ (filled symbols) and $M_n = 6220$ (open symbols) at 393, 403, and 413 K.

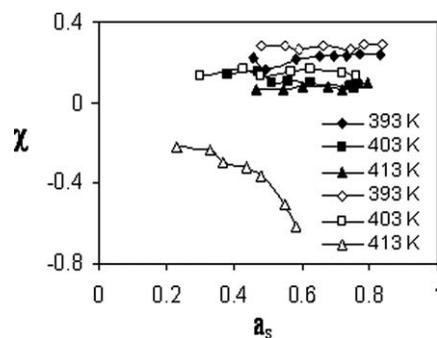


Figure 22 Flory interaction parameter χ versus chlorobenzene-vapor activity for PE with $M_n = 3280$ (filled symbols) and $M_n = 6220$ (open symbols) at 393, 403, and 413 K.

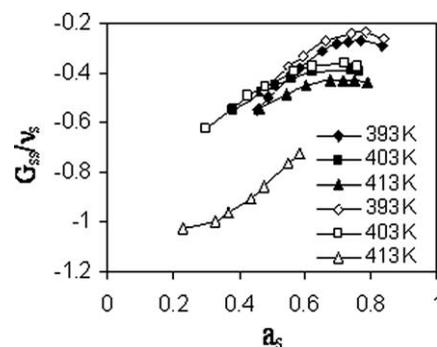


Figure 23 Clustering function G_{ss}/v_s at various chlorobenzene-vapor activities for PE with $M_n = 3280$ (filled symbols) and $M_n = 6220$ (open symbols) at 393, 403, and 413 K.

System: polyethylene (PE) with $M_n = 3280$ and $M_n = 6220$ in chlorobenzene at 393, 403, and 413 K

In Figure 21 solvent weight fraction for PE with $M_n = 3280$ and $M_n = 6220$ ²² has been plotted against solvent-vapor activity. According to the BET classification Type III, solubility of chlorobenzene rises in proportion of solvent content in these systems. It is evident from Figure 21 that sorption of solvent in PE with $M_n = 3280$ has the same behavior when

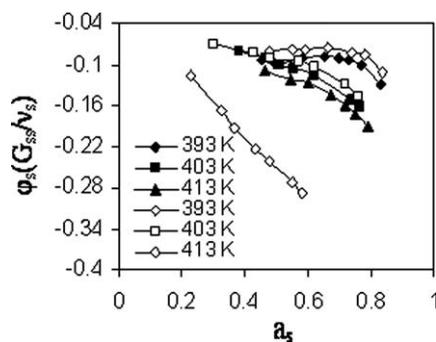


Figure 24 Mean cluster size $\phi_s(G_{ss}/v_s)$ at various chlorobenzene-vapor activities for PE with $M_n = 3280$ (filled symbols) and $M_n = 6220$ (open symbols) at 393, 403, and 413 K.

examined in all above-mentioned temperatures and has different behavior when PE with $M_n = 6220$ has been used as absorbent.

In Figure 22 Flory-Huggins interaction parameter, $\chi \geq 0$, indicates that chlorobenzene is a fairly good solvent for PE. Both PE show a moderate interaction with chlorobenzene at all above-mentioned temperatures except PE with $M_n = 6220$ at 413 K where it has a negative χ and strong interaction with solvent. Interaction parameter χ , is temperature-dependent and a good interaction between solvent and polymer can be seen when temperature increases. Large uptake of the solvent at lower activities especially for PE with $M_n = 6220$ at 413 K shown in Figure 21, is also a confirmation of this behavior.

Figures 23 and 24 show values of the clustering function G_{ss}/v_s and mean cluster size $\phi_s(G_{ss}/v_s)$ versus solvent-vapor activity. Negative values of these parameters combined with the large upturn in the equilibrium isotherm and decreasing trend of non-ideality factor in Figure 25 suggest that the polymer matrix is plasticized by the solvent. The system of PE with $M_n = 6220$ at 413 K with more negative amount of clustering function and mean cluster size has a different behavior and shows more tendency of solvent molecules to plasticize polymer matrix.

CONCLUSION

20 isothermal data sets of vapor-liquid equilibrium for five polymer-solvent binaries in the temperature range of 298–413 K have been used to study sorption of solvent vapor in the polymer. Convexity of isotherms towards activity axis means that formation of solvent-solvent pairs is preferred and solvent molecules does not tend to remain isolated. This can only mean that the first solvent molecules enter the polymer structure and loosen the structure and make it easier for subsequent molecules to enter in the neighborhood of the first than to go elsewhere. Ideal behavior is expected when there is a similarity

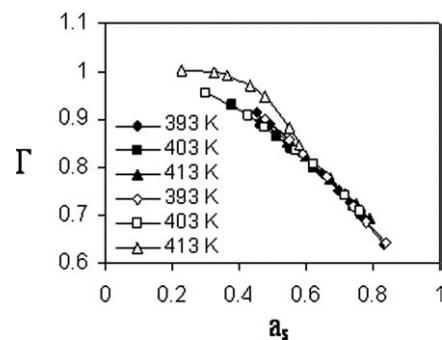


Figure 25 Thermodynamic factor Γ versus chlorobenzene-vapor activity for PE with $M_n = 3280$ (filled symbols) and $M_n = 6220$ (open symbols) at 393, 403, and 413 K.

between the solvent and the monomer repeat unit in the polymer. Flory-Huggins interaction parameter, χ for these systems was evaluated, and it was shown that χ is dependent on studied temperatures especially for sorption isotherm of pentane in polyisobutylene at 318 K and for system of chlorobenzene in polyethylene at 413 K.

Towards obtaining some information on the molecular state of dissolved solvent, we applied the clustering theory of Zimm and Lundberg. As a rule, when there exist a weak polymer-solvent interaction and decreasing function Γ , large amounts of solvent uptake can be interpreted by clustering, and if clustering of solvent molecules does not occur, plasticization is responsible for large upturn of the penetrate. In contrast, observing of a strong polymer-solvent interaction and increasing function Γ means that solvent molecules are liable to remain isolated.

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