

Extension of Flory-Huggins Theory to Satisfy the Hard Sphere Limit

Ali Eliassi¹, Hamid Modarres,^{2,*} and G. Ali Mansoori³

(1) Chemical Industries Research Department, Iranian Research Organization for Science and Technology (IROST), Tehran, I.R. Iran

(2) Chemical Engineering Faculty, Amir Kabir University of Technology, Tehran-15875, I.R.Iran

(3) Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607-7000, USA

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ABSTRACT

In this work Flory-Huggins theory has been extended to satisfy the hard sphere limit. The resulting equations are used to correlate the solvent activity and to calculate the polymer size parameter. Based on the extended model new equations have been derived to predict the enthalpy and entropy of dilution of various polymer solutions with diverse molecular weights in different solvents. The results obtained from the extended Flory-Huggins theory are compared with those of the original theory and with the experimental data. The comparisons indicate that the proposed extension improves the predictability of the theory for thermodynamic properties of polymer solutions.

Key Words:

polymer solutions;
Flory-Huggins theory;
hard sphere;
phase equilibria;
activity.

INTRODUCTION

Various statistical mechanical theories of polymer solutions have been developed during the last half a century [1-5]. The original and one of the best known of these theories is Flory-Huggins theory [6,7]. Several attempts have been made to improve

the predictive capability of Flory-Huggins theory which most of them have been in the direction of modifying Flory-Huggins interaction parameter (χ) by assuming that it is dependent on concentration, molecular weights of polymer and tempera-

(*)To whom correspondence should be addressed.
E-mail: hmodares@cic.aku.ac.ir

ture [8]. However, in the original work of Flory-Huggins the interaction parameter was assumed to be a function of temperature only.

The works done on Flory-Huggins theory can be classified as:

(i) those in the direction of improving the shortcomings of the theory such as correcting it for contributions of enthalpic part, non-combinatorial and combinatorial entropic parts [9-11];

(ii) presenting new methods for determining the interaction parameter (χ) [12] and increasing predictability of theory in phase separation calculations [13-22];

(iii) attempts in presenting superior theories to Flory-Huggins theory based on lattice model to predict the thermodynamic properties of polymer mixtures [23-25].

On the other hand the properties of polymers depend on size and shape of polymer chain. It has been reported that for a large size difference between polymer and solvent, Flory-Huggins theory gives rise to larger combinatorial entropy. The dependence of combinatorial entropy to size and shape of molecules has been discussed by Hildebrand [26]. It has been shown that in calculating entropy change for mixtures of molecules differing in shape as well as size, modifications in the theory are required since Flory-Huggins expression for combinatorial entropy does not distinguish the shape and the size of molecules [27, 28]. Also, the activity coefficient is a strong function of size difference between polymer and solvent for solutions of polymers in common solvents. The large deviation from ideal solution behaviour is observed merely as a consequence of differences in molecular sizes even in the absence of any energetic effects (enthalpy of mixing) [29,30]. The effect of size difference on the extra entropy in Flory-Huggins theory has been discussed by Chan and Dill [9]. Meroni et al. [31] have shown that Flory-Huggins theory for the entropy of mixing is a poor approximation and becomes worse for increasing values of the molecular diameter ratio of polymer to solvent.

Flory-Huggins theory and analytical integral equation theory have been used for studying hard sphere mixtures [32, 33]. The combination of the two theories have been extended to athermal mixtures of hard spheres and polymers [34]. The approach was applied

to all sphere/polymer size ratios, and polymer-polymer segmental attractive interactions. Bjorling et al. [35] used Flory-Huggins theory and integral equation theories to describe the equation of state and the relevant mixing properties of hard sphere binary mixtures in the limit of high size-asymmetry. They found that by choosing a physical recipe for the volume fractions of the two species in the mixture Flory-Huggins theory is a good approximation to the entropy and the Gibbs free energy of mixing at high size asymmetry [35]. Shimizu et al. [36] have generalized Flory-Huggins theory of solvation using fused hard sphere system as a reference system in their perturbation approach.

Therefore, it is completely clear that the application of Flory-Huggins theory to study polymer systems is still a source of debate [37-41] and further research should be done to clarify various aspects of this theory.

In the present work, by taking into account the size ratio of polymer to solvent, attempt is made to clarify the limitation of Flory-Huggins theory in application to polymer-solvent mixtures. In this approach the size ratio of polymer to solvent is represented as the ratio of hard sphere diameters. Then by introducing the hard sphere limit for the mixtures of hard spheres with infinite size ratio as a necessary condition, Flory-Huggins theory is improved to satisfy this limit. In what follows, the main points of the approach used in this paper are described.

The Extension of G^E in Flory-Huggins Theory

Tukur et al. [42] for a binary hard-sphere mixture of infinite size ratio have presented the following limit for excess Helmholtz free energy of the mixture:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial A_{hs}^E / RT}{\partial \sigma_i} \right)_{T, \rho, x_i, \sigma_{j \neq i}} = \frac{\frac{\pi}{2} N_A \rho x_i x_j \sigma_j^2}{1 - \frac{\pi}{6} N_A \rho x_j \sigma_j^3} \quad (1)$$

where, ρ , N_A , T , x_i and σ_i are the mixture density, Avogadro's number, absolute temperature, mole fraction and molecular diameter of component i , respectively. It has been shown that [42] the above expression is rigorously valid when there exists an infinite size ratio of molecules in the binary mixtures. At low pressure the Helmholtz free energy and Gibbs free energy can be

approximated, $(A^E)_{T,p} \approx (G^E)_{T,p}$ [43], and eqn (1) can be written for the excess Gibbs free energy, G^E as:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial G_{hs}^E / RT}{\partial \sigma_i} \right)_{T,P,x,\sigma_{j \neq i}} = \frac{\frac{\pi}{2} N_A \rho x_i x_j \sigma_j^2}{1 - \frac{\pi}{6} N_A \rho x_j \sigma_j^3} \quad (2)$$

The excess Gibbs free energy in Flory-Huggins theory, G_{FH}^E , is in the following form [44]:

$$\frac{G_{FH}^E}{RT} = x_1 \left[\ln \phi_1 + \left(1 - \frac{1}{r}\right) \phi_2 + \chi_{12} \phi_2^2 - \ln x_1 \right] + x_2 \left[\ln \phi_2 - (r-1) \phi_1 + \chi_{12} r \phi_1^2 - \ln x_2 \right] \quad (3)$$

where, ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, and χ_{12} is the interaction parameter and r is the segment number. The segment number can be approximated as the ratio of molar volume of polymer (v_2) to molar volume of solvent (v_1) and can be represented as: $r = \frac{v_2}{v_1}$. Also, the following relation represents r as the ratio of molecular diameter of polymer (σ_2) to that of solvent (σ_1):

$$r = \frac{v_2}{v_1} = \frac{\frac{4}{3} \pi \left(\frac{\sigma_2}{2}\right)^3 N_0}{\frac{4}{3} \pi \left(\frac{\sigma_1}{2}\right)^3 N_0} = \left(\frac{\sigma_2}{\sigma_1}\right)^3 \quad (4)$$

where, N_0 is the Avogadro's number.

It can be shown that Flory-Huggins excess Gibbs function, as expressed by eqn (3), cannot satisfy the hard sphere limit required by eqn (2):

$$\lim_{\sigma_1 \rightarrow 0} \left(\frac{\partial G_{FH}^E / RT}{\partial \sigma_1} \right)_{T,P,x,\sigma_2} = 0 \quad (5)$$

It is obvious that the hard sphere limit of G_{FH}^E is in contrast with the non-zero limit predicted by eqn (2) and it needs an extension to satisfy this limit.

In the extension of Flory-Huggins excess Gibbs function for satisfying the hard sphere limit we take the advantage of perturbation theory approach and consider G_{FH}^E as a reference state and then add a ΔG^E as a perturbation term for the hard-sphere limit:

$$G^E = G_{FH}^E + \Delta G^E \quad (6)$$

where, G_{FH}^E is given by eqn (3) and the perturbation term ΔG^E will be obtained in the following manner:

For a binary mixture of solvent (1) and polymer (2) the hard-sphere limit of eqn (2) can be expressed in terms of packing fraction η_i as:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial G^E / RT}{\partial \sigma_i} \right)_{T,P,x,\sigma_j} = \frac{3}{1-\eta_j} \left(\frac{\eta_j x_i}{\sigma_j} \right) \quad (7)$$

$i, j=1,2$ and $i \neq j$

where,

$$\eta_i \equiv \frac{\pi}{6} N_A \rho x_i \sigma_i^3 \quad (8)$$

is the packing fraction of component i and ρ is the density of the mixture.

To include the deviation of polymer chain from hard-sphere shape and adjust the limit represented by eqn (7) to a real chain, the perturbation term is $\frac{f\varepsilon_i}{RT} \left(\frac{\eta_j x_i}{\sigma_j} \right)$ introduced to the hard sphere limit and then

the final result will be:

$$\lim_{\sigma_i \rightarrow 0} \left(\frac{\partial G^E / RT}{\partial \sigma_i} \right)_{T,P,x,\sigma_j} = \frac{3}{1-\eta_j} \left(\frac{\eta_j x_i}{\sigma_j} \right) + \frac{f\varepsilon_i}{RT} \left(\frac{\eta_j x_i}{\sigma_j} \right) \quad (9)$$

where, ε_1 is the energy parameter, which is a measure of molecular interactions and f/RT has been included to consider both any deviation from the hard-sphere shape for molecules and also the effect of temperature on the molecular interactions. This factor satisfies the requirement that, as $T \rightarrow \infty$ the hard-sphere limit will be approached. It is worth noting that the factor $\eta_i x_i / \sigma_j$ has been introduced to take into account the effect of packing fraction as a measure of the molecular separations.

Integrating eqn (9) for the cases where $i=1$ and $j=2$:

$$\Delta(G^E / RT)_{T,P,x,\sigma_1} = \frac{3}{1-\eta_1} (\eta_1 x_2 s) + \frac{f\varepsilon_1}{RT} (\eta_1 x_2 s) + G(\eta_2, x_1) \quad (10)$$

and for the case $i = 2$ and $j = 1$:

$$\Delta(G^E / RT)_{T,P,x,\sigma_2} = \frac{3}{1-\eta_2} (\eta_2 x_1 / s) + \tag{11}$$

$$\frac{f\varepsilon_2}{RT} (\eta_2 x_1 / s) + G(\eta_1, x_2)$$

where, $S \equiv \sigma_2 / \sigma_1$ and $G(\eta_2, x_1)$ and $G(\eta_1, x_2)$ are the integration constants.

By adding eqn (10) to eqn (11) we have:

$$\Delta(G^E / RT)_{T,P,x,\sigma} = \frac{3}{1-\eta_1} (\eta_1 x_2 s) + \frac{3}{1-\eta_2} (\eta_2 x_1 / s) + \frac{f\varepsilon_2}{RT} \left(\frac{\eta_2 x_1}{s} \right) + G(\eta_2) x_1 + G(\eta_1) x_2 \tag{12}$$

In the above equation, the integration constants $G(\eta_i, x_j)$ have been represented as $G(\eta_i) x_j$ since the variables η_i and x_j must be separable to satisfy the requirement that, as $x_j \rightarrow 0$ the function $G(\eta_i, x_j)$ vanishes. To proceed further it is convenient to assume that:

$$G(\eta_i) = C \eta_i \tag{13}$$

where, the constant C can be evaluated by ideal mixture limit, namely for $\varepsilon_1 = \varepsilon_2$ and $\sigma_1 = \sigma_2$, $G^E = 0$ and then $G^E = 0$. Then from eqn (12), C can be obtained in the following form:

$$C = -\frac{f\varepsilon_2}{RT} - \frac{3}{\eta_1 / x_1 + \eta_2 / x_2} \left(\frac{\eta_1 / x_1}{1-\eta_1} + \frac{\eta_2 / x_2}{1-\eta_2} \right) \tag{14}$$

From eqns (6) and (12) to (14) the final equation for G^E will be obtained as:

$$G^E = G_{FH}^E + \left\{ 3RT \left[(\eta_1 / (1-\eta_1)) (s-1) / x_1 + (\eta_2 / (1-\eta_2)) (s^{-1}-1) / x_2 \right] + \alpha \cdot (\eta_1 (Es-1) / x_1 + \eta_2 (s^{-1}-1) / x_2) \right\} x_1 x_2 \tag{15}$$

where, $\alpha = f\varepsilon_2$ and $E = \frac{\varepsilon_2}{\varepsilon_1}$.

Starting with eqn (15) the expressions for the other thermodynamic properties of polymer solution can be derived.

The expressions for the activity of solvent, $\alpha_1 = x_1 \gamma_1$, and activity of polymer, $\alpha_2 = x_2 \gamma_2$, can be derived from eqn (15) using the well known thermodynamic

equation; $\ln \gamma_i = \frac{\partial}{\partial n_i} \left(\frac{nG^E}{RT} \right)_{T,P,n_{j \neq i}}$, the final equations are:

$$\ln a_1 = \ln a_1^{FH} + \left\{ 3 \left(\frac{\eta_1 / x_1 (s-1)}{(1-\eta_1)^2} + \frac{\eta_2 / x_2 (s^{-1}-1)(1-\eta_2/x_2)}{(1-\eta_2)^2} \right) + \frac{\alpha}{RT} \left(\eta_1 / x_1 (Es-1) + (s^{-1}-1) \eta_2 / x_2 \right) \right\} x_2^2 \tag{16}$$

and

$$\ln a_2 = \ln a_2^{FH} + \left\{ 3 \left(\frac{\eta_1 / x_1 (1-\eta_1/x_1)(s-1)}{(1-\eta_1)^2} + \frac{\eta_2 / x_2 (s^{-1}-1)}{(1-\eta_2)^2} \right) + \frac{\alpha}{RT} \left(\eta_1 (Es-1) / x_1 + \eta_2 (s^{-1}-1) / x_2 \right) \right\} x_1^2 \tag{17}$$

In the above equations α_1^{FH} and α_2^{FH} are Flory-Huggins solvent and polymer activities, respectively. Using eqns (16) and (17) in the following equation for the entropy of dilution:

$$\Delta S_i = -R \left[\partial (\ln a_i) / \partial T \right]_{P,\varphi_2} \tag{18}$$

for solvent (1) and polymer (2) the results will be:

$$\Delta \bar{S}_1 = \Delta \bar{S}_1^{FH} - 3R \left(\frac{\eta_1 / x_1 (s-1)}{(1-\eta_1)^2} + \frac{\eta_2 / x_2 (1/s-1)(1-\eta_2/x_2)}{(1-\eta_2)^2} \right) x_2^2 \tag{19}$$

$$\Delta \bar{S}_2 = \Delta \bar{S}_2^{FH} - 3R \left(\frac{\eta_1 / x_1 (1-\eta_1/x_1)(s-1)}{(1-\eta_1)^2} + \frac{\eta_2 / x_2 (1/s-1)}{(1-\eta_2)^2} \right) x_2^2 \tag{20}$$

where, $\Delta\bar{S}_1^{FH}$ and $\Delta\bar{S}_2^{FH}$ are Flory-Huggins solvent and polymer entropy of dilutions. In a similar manner, and using:

$$\Delta\bar{H}_i = -RT^2 \left(\partial \ln a_i / \partial T \right)_{P, \varphi_2} \quad (21)$$

the following expressions for the heat of dilution will be obtained:

$$\Delta\bar{H}_1 = \Delta\bar{H}_1^{FH} + \alpha \left[(1/s - 1) \eta_2 / x_2 + (Es - 1) \eta_1 / x_1 \right] x_2^2 \quad (22)$$

$$\Delta\bar{H}_2 = \Delta\bar{H}_2^{FH} + \alpha \left[(1/s - 1) \eta_2 / x_2 + (Es - 1) \eta_1 / x_1 \right] x_1^2 \quad (23)$$

where, $\Delta\bar{H}_1^{FH}$ and $\Delta\bar{H}_2^{FH}$ are, Flory-Huggins solvent and polymer enthalpy of dilutions, respectively.

In the next section the above equations are used to calculate properties of various polymer solutions and the results are compared with the calculations based on the original Flory-Huggins relations.

CALCULATION PROCEDURE

For utilizing the proposed extension of Flory-Huggins theory, initially we have to determine the parameters appearing in the theory. Parameters E and σ_1 are calculated using group contribution methods [45,46]. Then, from the experimental data of activities we are able to determine the parameters χ_{12} , σ_2 and α .

In order to test the extended model, the experimental data for polymer/solvent solutions with various size differences are needed. For the present study, the application of the extended Flory-Huggins equation is investigated for seven different polymer/solvent solution systems, for which the experimental data are already available and also used in the calculations of thermodynamic properties when the original Flory-Huggins theory was originally proposed [44]. These systems are polymers with different molecular weights in various solvents.

In the first stage, from Bondi's method of group contribution [46] the van der Waals volume of solvent molecules were calculated and then by considering spherical shape for solvent molecule the parameter σ_1 was calculated. The values of σ_1 for various solvents are reported in Table 1. While Bondi's method provides a reasonable approximation by considering spherical shape for small solvent molecules, it is not a reasonable method for calculating σ_2 for large polymer molecules. Therefore, the parameters χ_{12} , σ_2 and α are calculated by eqn (16) from experimental activity data using a least square method. The values of these parameters are reported in Table 1.

The parameter E, the ratio of energy parameters of solvent to polymer can be expressed in terms of σ_1 , σ_2 and the molecular weights M_1 and M_2 by the following equation [47]:

$$E = \frac{\varepsilon_1}{\varepsilon_2} = \left(\frac{\sigma_1}{\sigma_2} \right)^3 \frac{M_1 (0.34 + \sum \Delta P_1)^{-2}}{M_2 (0.34 + \sum \Delta P_2)^{-2}} \quad (24)$$

where, ΔP_1 and ΔP_2 are obtained from structural group

Table 1. Parameters used for the present study.

System	Group-cont method		Flory-Huggins			Modified theory	
	σ_1 (nm)	E(-)	σ_2 (nm)	χ_1 (-)	σ_2 (nm)	χ_1 (-)	α (J/mol) $\times 10^{-3}$
Benzene + PDMS 3,850	0.535	1.620	1.895	0.809	1.500	0.426	-36.271
Benzene + PDMS 15,700	0.535	1.250	3.027	0.756	1.720	0.536	-78.789
Toluene + PS 290,000	0.574	1.602	7.797	0.343	6.300	0.114	806.077
MEK + PS 290,000	0.539	1.480	7.732	0.725	6.800	0.149	693.142
Acetone + PS 15,700	0.499	1.384	2.870	0.915	2.570	0.220	-18.426
Propylacetate+PS 290,000	0.585	2.624	7.748	0.649	6.200	0.397	493.637
Benzene + PIB 45,000	0.535	2.227	4.735	0.673	3.370	0.399	-63.756

parameters of solvent and polymer, respectively. The values of σ_1 and E for seven binary mixtures of polymer/solvent are reported in Table 1.

Using the experimental activity data for seven binary mixtures of polymer/solvent in eqn (3), χ_{12} and σ_2 have been calculated for the original Flory-Huggins theory. The same experimental data were used in eqn (16) to calculate χ_{12} , σ_2 and α for the modified Flory-Huggins theory. The numerical values of all the parameters are reported in Table 1.

In the next stage, by using the same calculated parameters as mentioned above, the enthalpy of dilution of the solvents for seven different polymer/solvent solution systems and the entropy of dilutions for four

binary polymer-solvent mixtures have been calculated by eqns (22) and (19), respectively.

DISCUSSIONS

The results of calculations of activity for two different systems are shown in Figure 1. Figures 2 and 3, respectively, represent the results of calculations of enthalpy of dilutions $\Delta\bar{H}_1$ (by eqn (22)) and entropy of dilutions $\Delta\bar{S}_1/\phi_1^2$ (by eqn (19)) for two binary polymer/solvent mixtures for both the original and the modified Flory-Huggins theory. In the same figures the experimental data have been presented. According to Figures 2 and

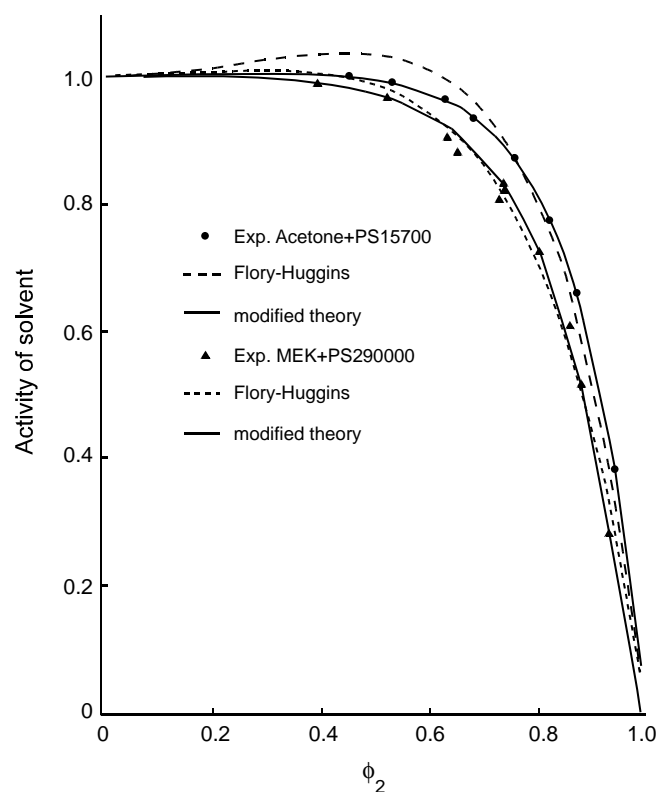


Figure 1. Solvent (1) activity a_1 versus volume fraction of polymer (2) ϕ_2 for two solutions systems of [acetone (1)/PS15,700(2)] and solution of [MEK(1)/PS290,000] at 25°C. For the first system, the solid circles are the experimental data [50], the dashed thick lines are the calculations based on the Flory-Huggins theory and the solid thick lines are the calculations based on the modified theory. For the second system, the solid triangles are the experimental data [49], the dashed thin lines are the calculations based on the Flory-Huggins theory and the solid thin lines are the calculations based on the modified theory.

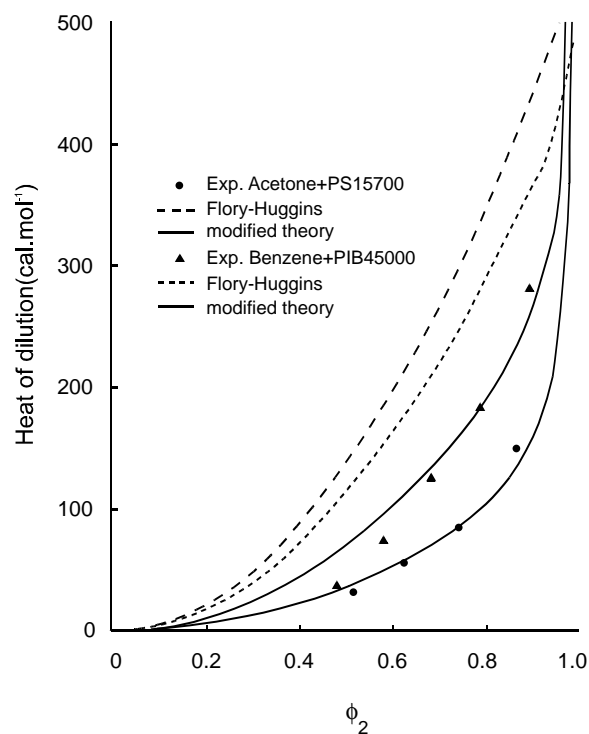


Figure 2. Solvent (1) $\Delta\bar{H}_1$ heat of dilution versus ϕ_2 volume fraction of polymer (2) for two solution systems of [acetone(1)/PS15,700] at 25°C and [benzene(1)/PIB45,000(2)] at 65°C. For the first system, the solid circles are the experimental data [50], the dashed thick lines are the calculations based on the Flory-Huggins theory and the solid thick lines are the calculations based on the modified theory. For the second system, the solid triangles are the experimental data [51], the dashed thin lines are the calculations based on the Flory-Huggins theory and the solid thin lines are the calculations based on the modified theory.

3, the enthalpy of dilution and entropy of dilution predicted, respectively, from the original Flory-Huggins theory are not in agreement with the experimental data especially for high molecular weight polymers. But, for the extended theory the calculations of enthalpy of dilution and entropy of dilution respectively by eqns (22) and (19) are in very good agreement with the experimental data for both low and high molecular weight polymers. Also, as it is seen from Figure 3, the entropy of dilutions predicted by the original Flory-Huggins theory, are nearly constant and independent of the kind of polymer under consideration.

The mean absolute errors in calculation of activity of solvent (a_1), enthalpy of dilution ($\Delta\bar{H}_1$) and entropy of dilution ($\Delta\bar{S}_1/\phi_1^2$) for various binary mixtures of polymer/solvent are reported in Table 2.

It is worth mentioning that the parameter χ_{12} reported in Table 1, for (toluene + PS290,000) and (MEK + PS290,000) calculated by the modified model are much less than those of other systems. This can be justified by the related equation derived from original Flory-Huggins theory where, for $\Delta\bar{H}_1 \approx 0$ predicts: $\chi_{12} \approx 0$. The reported values of size parameter σ_2 in Table 1, for the three PS 290,000 solution systems show small differences. This may be attributed to the differences in the experimental activity data arise from nature of solvents interactions in these solution systems.

According to Table 1, as it is expected, the values

of α parameter are different for different polymer/solvent systems. The variation of α versus the size ratio (σ_2/σ_1) of the polymer/solvent systems is shown in Figure 4. As mentioned before, parameter was introduced in eqn (15) to include the deviation of polymer/solvent systems from hard sphere behaviour. As Figure 4 shows, for the polymer/solvent mixtures where the molecular weight of polymer is high the large values of size ratio parameter α indicate more pronounced deviation from hard sphere behaviour for these mixtures.

Overall consideration of the results reported in this paper demonstrates the ability of the extended Flory-Huggins theory for calculation of thermodynamic properties of polymer solution systems with appreciable size ratio of polymer to solvent.

It worth mentioning again that, most modifications in Flory-Huggins theory, so far, have been focused on improving the interaction parameter χ . In this work a different aspect of Flory-Huggins theory was explored and the theory was extended to satisfy the necessary hard sphere limit. It is unfortunate that this aspect of theory has not been investigated by other researchers and a rigorous comparison with similar results is not possible. However, the results of calculations in this paper indicated that the extension of the theory, to satisfy the hard sphere limit, promotes its accuracy, in predicting thermodynamic properties to an appreciative extent.

Table 2. Mean absolute errors (MAE)* in calculation of activity of solvent (a_1), enthalpy of dilution ($\Delta\bar{H}_1$) and entropy of dilution ($\Delta\bar{S}_1/\phi_1^2$) for various binary mixtures of polymer/solvent.

System	a_1^{FH}	a_1^M	$\Delta\bar{H}_1^{FH}$	$\Delta\bar{H}_1^M$	$\frac{\Delta\bar{S}_1^{FH}}{R\phi_2^2}$	$\frac{\Delta\bar{S}_1^M}{R\phi_2^2}$	No. of exp. data	Ref. of exp. data
Benzene + PDMS 3,850	0.03	0.03	33	21.3	0.11	0.04	10	48
Benzene + PDMS 15,700	0.03	0.03	25.9	14.8	0.10	0.08	8	48
Toluene + PS 290,000	0.01	0.00	85.06	43.72	0.38	0.15	12	49
MEK + PS 290,000	0.02	0.01	230.23	30.06	0.70	0.07	11	49
Acetone + PS 15,700	0.03	0.03	0.00	184.01	6.64	n.a.	8(1), 4(2)	50
Propylacetate + PS 290,000	0.00	0.00	114.08	17.91	n.a.	n.a.	11(1), 5(2)	50
Benzene + PIB 45,000	0.01	0.00	n.a.	n.a.	n.a.	n.a.	9(1), 5(2)	51

n. a. = experimental data are not available. (1) number of experimental data for activity; (2) number of experimental data for enthalpy.

* $MEA = \frac{1}{n} \sum |E^{\text{exp}} - E^{\text{cal}}|$, where, $E^{\text{exp}} - E^{\text{cal}}$ are, respectively, the experimental data and the calculated values [using the Flory-Huggins theory (FH) or the modified theory (M)]. n is number of experimental data.

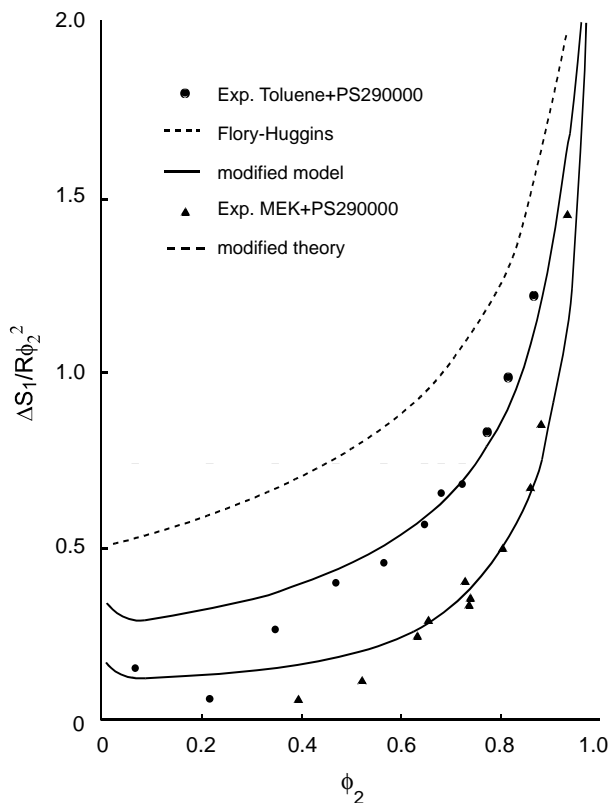


Figure 3. Solvent (1) $\Delta\bar{S}_1$ entropy of dilution versus ϕ_2 volume fraction of polymer (2) for two solution systems of [toluene(1)/PS290,000(2)] and [MEK(1)/PS290,000(2)] at 25°C . For the first system, the solid circles are the experimental data [49], the thick lines are the calculations based on the modified theory. For the second system, the solid triangles are the experimental data [49], and the solid dashed lines are the calculations based on the modified theory. For both systems, the dashed thin lines are the calculations based on the Flory-Huggins theory.

SYMBOLS

- A : Helmholtz free energy
- a : activity
- E : is equal to ϵ_2/ϵ_1
- f : a parameter for considering any deviation from the hard sphere shape
- G : Gibbs free energy
- $G(\eta_i, x_j)$: integration constant
- \bar{H} : enthalpy of dilution
- M : molecular weight
- N : number of molecules
- n : number of moles
- R : gas constant

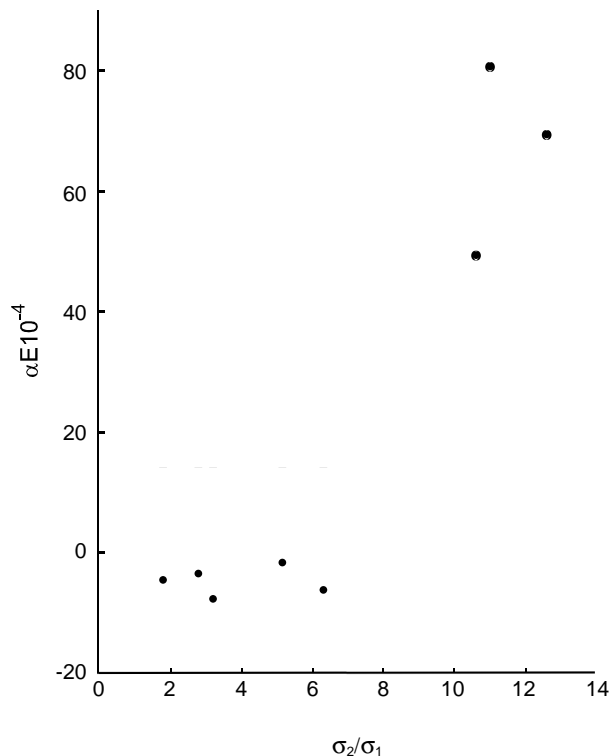


Figure 4. The variation of α values versus σ_2/σ_1 polymer/solvent mixtures studied in this work.

- r : number of segments
- \bar{S} : entropy of dilution
- s : is equal to σ_2/σ_1
- T : absolute temperature
- v : molecular volume
- x : mole fraction

Greek letters

- α : is equal to $f\epsilon_2$
- ϵ : energy parameter
- η : packing fraction
- ϕ : volume fraction
- χ : interaction parameter
- ρ : density (mole/volume)
- σ : molecular diameter

Subscripts

- A : avogadro
- hs : hard sphere
- i, j : discrete component identifiers
- M : mixing
- P : pressure
- T : absolute temperature
- x : mole fraction

σ : molecular diameter

Superscript

FH: Flory-Huggins

E: excess

M: modified

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