

A new theory for polymer/solvent mixtures based on hard-sphere limit

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Abstract

Based on hard-sphere limit of binary mixtures with different molecular size of components a theory has been developed for calculating activities of solvents in polymer/solvent mixtures. The theory considers various chain configurations for polymer molecules, varying from extended chain to the coiled chain. According to this theory the activity of solvent can be calculated from molecular weights (MWs) and densities as the only input data. The only adjustable parameter in the calculations, is the hard-sphere diameter of polymer, which provides useful criteria for the judgement on the chain configuration of polymer.

The activity calculations have been performed for seven binary mixtures of polymer/solvent and compared with experimental data at various temperatures and for a varying range of MWs of polymers.

The solvents in the mixtures were both of polar and nonpolar natures. The activity calculations for the same systems were performed by the well-known Flory–Huggins theory. Comparing the results of calculations with those of Flory–Huggins theory indicates that, the proposed theory is able to predict the activities of the solvent with good accuracy.

The radius of gyration, excluded volume and interaction parameter for polymer chain have been calculated using the parameter obtained in the new theory. The calculated interaction parameter in the new theory, is interpreted in terms of attraction, repulsion and interchange energy of polymer and solvent in the mixture.

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1. Introduction

Phase equilibrium plays an important role in the processing and application of polymer [1]. Recently the widespread use of polymers and the need for their synthesis has increased the interest and thereby research in the field of polymer solutions [2]. The field of polymer solution thermodynamics has been proliferated with the

polymer activity models [3–6]. The activity models based on the Flory–Huggins theory [7,8] and its many modifications [9] have been quite popular for correlation and prediction of phase equilibrium of polymer solutions [10]. Although these models provide convenient ways to estimate the equilibrium behavior of polymer solutions they suffer from the inherent empiricism in their deviations from the original Flory–Huggins theory [1].

Equations of state have been proposed for predicting thermodynamic properties of polymer solutions [11], but due to complications inherent in the chain configurations, it is still a new subject for research.

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In general, thermodynamic models proposed for polymer solutions can be divided into four categories; cell models [12], lattice-fluid models [13], hole models [14] and tangent sphere models [15,16]. The cell and lattice fluid models provide different adaptations of the incompressible-lattice model of polymer mixtures [17]. Also a modified fluid-lattice theory of fluid considering a finite quasi-lattice coordination number and a constant lattice site volume for all r -mers has been developed [18].

Recent advances in statistical thermodynamics have brought to the forefront tangent-sphere models of chain like fluids. These models consider polymers as freely jointed tangent-spheres [19]. The statistical associated fluid theory [20] and the perturbed hard-sphere theory [21] have been formulated which are applicable to the mixtures with large differences in molecular size and shape. Development on sphere-chain models has become a very active field in the polymer thermodynamics [22,23].

The perturbed hard-sphere chain (PHSC) theory [24] is originated from Percus–Yevick approximation [25] and the development of molecular simulation [26–28]. It is applicable to mixtures with large differences in molecular size and shape. Relative to other theories, the PHSC theory has a possible important advantage that spherical segment diameter of one component needs not be the same as that of another component [19].

A generalized form of equation of state for hard-chain, hard-monomer mixtures has been derived, where the monomer diameter is different from the chain-segment diameter [29–32].

Based on the integral equation theory, a reference-interaction-site model has been developed for polymer mixtures. This model has been used for small, rigid molecular fluids but it requires considerable numerical computation [33].

The first-order thermodynamic perturbation theory [34] has been extended to sticky chain [35], square-well chain [36], and Lennard–Jones chains [37,38]. Improved formulation for hard-sphere chains under the Percus–Yevick approximation, has been considered and the same results as for linear hard-sphere chains have been obtained [39].

In this work the lattice origins of the previous models is totally abandoned and based on the properties derived from statistical thermodynamics for binary mixtures of hard-spheres with different size, a new activity model is developed.

The activity calculations by the new theory for several polymer/solvent mixtures are compared with the results of Flory–Huggins theory and it is shown that the new theory is able to predict the activity of solvent with good accuracy.

In what follows the essence of the theory which leads to the new model for polymer solvent mixture is presented.

2. Theory

For a binary mixture of solvent (1) and polymer (2) it is a commonly accepted assumption that polymer chain can be divided into r segments. Each segment has spherical shape and is in the same size as a solvent molecule. Due to the thermal motion [40], polymer chain can take different configurations [41] varying from a coiled chain (see Fig. 1) to a semi-extended chain (see Fig. 2) and fully extended chain (see Fig. 3).

It is seen from Figs. 1–3 that, the binary mixture of polymer/solvent consists of species with different size. These species can be considered as hard-spheres. In Fig. 1 hypothetical hard-spheres (shown by the dotted line) bound each coiled polymer chain. The diameters of the hard-sphere are represented by σ_{22} for polymer chain

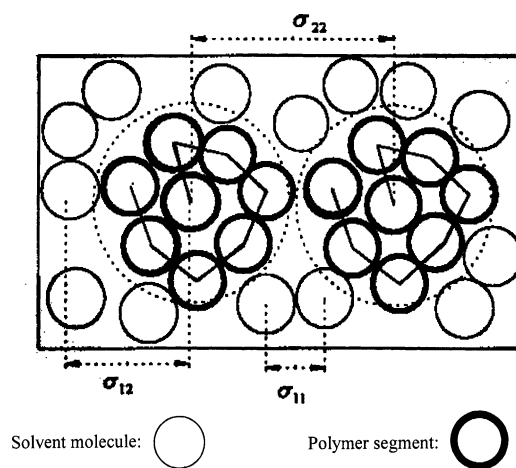


Fig. 1. The hard-sphere model for a coiled chain in a polymer/solvent mixture.

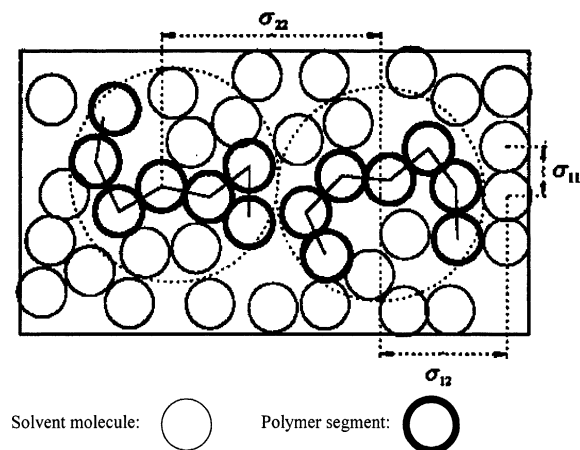


Fig. 2. The hard-sphere model for a semi-extended chain in a polymer/solvent mixture.

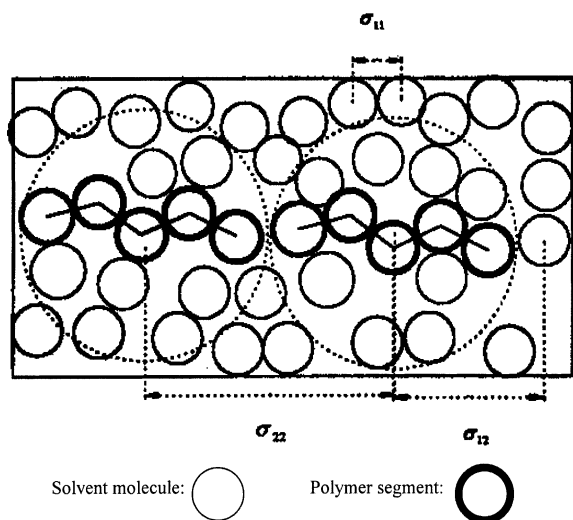


Fig. 3. The hard-sphere model for a fully extended chain in a polymer/solvent mixture.

and σ_{11} for the solvent molecule. Fig. 2 shows a semi-extended chain and that, the polymer chains, due to the thermal motion is bounded in a larger hard-sphere. Fig. 3 shows a fully extended chain and polymer is bounded in a larger sphere and then σ_{22} is at the maximum value. Therefore the hard-sphere diameter of polymer, is varying between a minimum value in the coiled chain to a maximum value in the fully extended chain.

The minimum value of σ_{22} can be approximated by the following equation (see Fig. 1):

$$\frac{4}{3}\pi\left(\frac{\sigma_{22}}{2}\right)^3 \cong \frac{4}{3}\pi\left(\frac{\sigma_{11}}{2}\right)^3 r \quad (1)$$

Thus

$$\sigma_{22} = \sqrt[3]{r}\sigma_{11} \quad (2)$$

The maximum value of σ_{22} from Fig. 3 is

$$\sigma_{22} = r\sigma_{11} \quad (3)$$

Therefore the range of variation of σ_{22} can be represented as:

$$\sqrt[3]{r}\sigma_{11} < \sigma_{22} < r\sigma_{11} \quad (4)$$

The number of segment r is defined as:

$$r \cong \frac{v_2}{v_1} \quad (5)$$

where v_2 and v_1 are the molar volumes of polymer and solvent respectively. The molar volume can be expressed in terms of molecular weight (MW), M and density ρ :

$$v_2 = \frac{M_2}{\rho_2} \quad \text{and} \quad v_1 = \frac{M_1}{\rho_1} \quad (6)$$

then from Eq. (5) we have:

$$r \cong \frac{M_2 \rho_2}{M_1 \rho_1} \quad (7)$$

In solvent (1) polymer (2) mixture, $\sigma_{22} \gg \sigma_{11}$ since the MW of polymer is much higher than that of solvent ($M_2 \gg M_1$).

Therefore the number of segments r is large and from inequality represented by Eq. (4) a polymer–solvent mixture can be considered as a mixture of hard-spheres with infinite size difference or very small size ratio ($\sigma_{11}/\sigma_{22} \cong 0$). Properties of hard-sphere mixtures with various size differences between the components have been investigated by several researchers [42–45]. It is worth to mention that all of the equation of state for hard-spheres reported in literature suffer from a major deficiency as they fail to meet the correct limit as closest-packing, where the compressibility factor must tend to infinity [46]. The solutions of the Percus–Yevick equation for hard-sphere mixture resulted in an analytic equation of state for hard-spheres [43,47]. It is also shown that in dense binary mixtures of hard-spheres phase separation occurs when the size ratio, σ_{11}/σ_{22} is less than 0.2 and the partial packing fractions, $(\pi/6)\rho\sigma_{ii}^3$, of the two species are comparable [44].

From statistical mechanics it is demonstrated that the following expression exists for the partial derivative of Helmholtz function (A) with respect to σ_{11} , the molecular size diameter of component one, [48,49]:

$$\left(\frac{\partial A/RT}{\partial \sigma_{11}}\right)_{T,n,x,\sigma_{22}} = 2\pi n(x_1^2\sigma_{11}^2g_{11} + x_1x_2\sigma_{12}^2g_{12}) \quad (8)$$

where x is mole fraction, n is number density and $\sigma_{12} = (\sigma_{11} + \sigma_{22}/2)$.

In Eq. (8) g_{11} and g_{12} are the pair correlation function [50,51], and by taking its asymptotic limit as ($\sigma_{11} \rightarrow 0$) we get:

$$\lim_{\sigma_{11} \rightarrow 0} \left(\frac{\partial A/RT}{\partial \sigma_{11}}\right)_{T,n,x,\sigma_{22}} = 2\pi n x_1 x_2 \left(\frac{\sigma_{22}}{2}\right)^2 \lim_{\sigma_{11} \rightarrow 0} g_{12} \quad (9)$$

For a hard-sphere mixture the limiting value ($\sigma_{11} \rightarrow 0$) of the pair correlation function is already available and it is given as [52]:

$$\lim_{\sigma_{11} \rightarrow 0} g_{12}^{\text{hs}} = \frac{1}{1 - (\pi/6)nx_2\sigma_{22}^3} \quad (10)$$

The excess Helmholtz function is defined as the difference between the Helmholtz function change upon mixing in the real state (ΔA) and that of ideal state (ΔA_i^{id})

$$A^E = \Delta A - \Delta A_i^{\text{id}} \quad (11)$$

For a binary hard-sphere mixture, differentiating Eq. (11) with respect to σ_{11} at constant T , n , σ_{22} and

composition, and by taking the limit of the partial derivative of A^E with respect to σ_{11} , as $\sigma_{11} \rightarrow 0$, we get

$$\lim_{\sigma_{11} \rightarrow 0} \left(\frac{\partial A^E}{\partial \sigma_{11}} \right)_{T,n,x,\sigma_{22}} = \lim_{\sigma_{11} \rightarrow 0} \left(\frac{\partial \Delta A}{\partial \sigma_{11}} \right)_{T,n,x,\sigma_{22}} \quad (12)$$

where $[\partial \Delta A^{\text{id}} / \partial \sigma_{11}]_{T,n,x,\sigma_{22}} = 0$.

Dividing Eq. (12) by RT and then combining it with the limit of the partial derivatives represented by Eqs. (9) and (10) gives, the following limiting value for the partial derivative of the excess Helmholtz free energy of a hard-sphere mixture:

$$\begin{aligned} \lim_{\sigma_{11} \rightarrow 0} \left(\frac{\partial A_{\text{hs}}^E / RT}{\partial \sigma_{11}} \right)_{T,n,x,\sigma_{22}} &= \frac{(\pi/2)nx_1x_2\sigma_{22}^2}{(1 - (\pi/6)nx_2\sigma_{22}^3)} \\ &= \frac{3x_1\eta_2}{\sigma_{22}(1 - \eta_2)} \end{aligned} \quad (13)$$

where η_2 is the packing fraction of component 2 and is defined as:

$$\eta_2 = \frac{\pi}{6}nx_2\sigma_{22}^3 \quad (14)$$

Eq. (13) is exact and it is applicable for calculation of the limiting excess Helmholtz free energy when the size difference between the components of the hard-sphere mixture goes to infinity.

It is generally accepted that for liquids the following assumption is valid [42].

$$\begin{aligned} G^E & \text{ (at constant } T \text{ and } P) \\ &= A^E \text{ (at constant } T \text{ and } V) \end{aligned} \quad (15)$$

From Eq. (13) the partial derivative of the excess Gibbs free energy with respect to σ_{11} in the limit $\sigma_{11} \rightarrow 0$ can be expressed as:

$$\begin{aligned} \lim_{\sigma_{11} \rightarrow 0} \left(\frac{\partial G_{\text{hs}}^E / RT}{\partial \sigma_{11}} \right)_{T,\rho^*,x,\sigma_{22}} &= (\pi/2)N\rho^*x_1x_2\sigma_{22}^2 \\ & / (1 - (\pi/6)N\rho^*x_2\sigma_{22}^3) \end{aligned} \quad (16)$$

where N is the Avogadro's number and ρ^* is the molar density of the mixture. Eq. (16) predicts a non-zero limit for partial derivative of G_{hs}^E/RT with respect to σ_{11} as $\sigma_{11} \rightarrow 0$.

In what follows we examine the excess Gibbs function of Flory–Huggins theory (G_{FH}^E) to see if the hard-sphere limit predicted by Eq. (16) is satisfied. The G_{FH}^E is expressed as [53].

$$\begin{aligned} \frac{G_{\text{FH}}^E}{RT} &= x_1 \left[\ln \frac{\phi_1}{x_1} + \left(1 - \frac{1}{r}\right) \phi_2 + \chi \phi_2^2 \right] \\ &+ x_2 \left[\ln \frac{\phi_2}{x_2} - (r-1)\phi_1 + \chi r \phi_1^2 \right] \end{aligned} \quad (17)$$

where ϕ 's represent the volume fractions of solvent (1) and polymer (2)

$$\phi_1 = \frac{x_1v_1}{x_1v_1 + x_2v_2}, \quad \phi_2 = \frac{x_2v_2}{x_1v_1 + x_2v_2} \quad (18)$$

and the other symbols in Eq. (17) have been defined earlier. As

$$\lim_{\sigma_{11} \rightarrow 0} \frac{\partial v_1}{\partial \sigma_{11}} = 0, \quad \lim_{\sigma_{11} \rightarrow 0} \frac{\partial v_2}{\partial \sigma_{11}} = 0 \quad (19)$$

then

$$\lim_{\sigma_{11} \rightarrow 0} \frac{\partial \phi_2}{\partial \sigma_{11}} = - \lim_{\sigma_{11} \rightarrow 0} \frac{\partial \phi_1}{\partial \sigma_{11}} \quad (20)$$

Therefore considering Eqs. (19) and (20) and differentiating Eq. (17) with respect to σ_{11} and taking the limit as $\sigma_{11} \rightarrow 0$ we get:

$$\lim_{\sigma_{11} \rightarrow 0} \left(\frac{\partial G_{\text{FH}}^E / RT}{\partial \sigma_{11}} \right)_{T,\rho^*,x,\sigma_{22}} = 0 \quad (21)$$

As it is seen from Eq. (21), Flory–Huggins theory can not satisfy the hard-sphere limit predicted by Eq. (16). In a subsequent paper we intend to correct this theory for the hard-sphere limit.

To apply the hard-sphere limit predicted for polymer solvent mixture Eq. (16) might be integrated immediately to give:

$$\frac{G_{\text{hs}}^E}{RT} = \frac{(\pi/2)N\rho^*x_1x_2\sigma_{22}^2\sigma_{11}}{1 - (\pi/6)N\rho^*x_2\sigma_{22}^3} + C \quad (22)$$

where C is constant of integration. For an ideal mixture of equal molecular size ($\sigma_{11} = \sigma_{22}$), it is required that $(G_{\text{hs}}^E/RT) = 0$. Hence, C may be evaluated as:

$$C = - \frac{(\pi/2)N\rho^*x_1x_2\sigma_{11}^3}{1 - (\pi/6)N\rho^*x_2\sigma_{11}^3} \quad (23)$$

This result may be substituted into Eq. (22) and the following equation for G_{hs}^E/RT will be obtained:

$$\frac{G_{\text{hs}}^E}{RT} = \frac{(\pi/2)N\rho^*x_1x_2\sigma_{22}^2\sigma_{11}}{1 - (\pi/6)N\rho^*x_2\sigma_{22}^3} - \frac{(\pi/2)N\rho^*x_1x_2\sigma_{11}^3}{1 - (\pi/6)N\rho^*x_2\sigma_{11}^3} \quad (24)$$

In a binary mixtures the excess Gibbs free energy is expressed by the following well-known equation [54]

$$\frac{G_{\text{hs}}^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (25)$$

where γ represents the activity coefficient. The activity coefficient of solvent γ_1 is [11]:

$$\ln \gamma_1 = \frac{G_{\text{hs}}^E}{RT} + (1 - x_1) \left(\frac{\partial G_{\text{hs}}^E / RT}{\partial x_1} \right)_{T,P} \quad (26)$$

Therefore on combining Eqs. (24) and (25) and after rearrangement we get

$$\ln \gamma_1 = \frac{(\pi/2)N\rho^*x_1x_2\sigma_{22}^2\sigma_{11}}{[1 - (\pi/6)N\rho^*x_2\sigma_{22}^3]} - \frac{(\pi/2)N\rho^*x_1x_2\sigma_{11}^3}{[1 - (\pi/6)N\rho^*x_2\sigma_{11}^3]} + \left[\frac{(\pi/2)N\rho^*\sigma_{22}^2\sigma_{11}(1 - 2x_1)x_2(1 - (\pi/6)N\rho^*x_2\sigma_{22}^3) - \pi^2/12N^2\rho^{*2}\sigma_{22}^5\sigma_{11}x_1x_2^2}{[1 - (\pi/6)N\rho^*x_2\sigma_{22}^3]^2} \right] - \left[\frac{(\pi/2)N\rho^*\sigma_{11}^3(1 - 2x_1)x_2(1 - (\pi/6)N\rho^*x_2\sigma_{11}^3) - \pi^2/12N^2\rho^{*2}\sigma_{11}^6x_1x_2^2}{[1 - (\pi/6)N\rho^*x_2\sigma_{11}^3]^2} \right] \quad (27)$$

And therefore the activity of solvent can be obtained from Eq. (26) and the definition; $a_1 = \gamma_1x_1$.

3. Calculations

The activity model represented by Eq. (27) was applied to seven binary polymer mixtures. The activities of solvents for these solutions have been obtained by osmometric measurements at different temperatures [55–57]. To calculate activity coefficient of solvent by Eq. (27) the value of σ_{11} was calculated by $\sigma_{11} = 2(3M_1/4\pi N\rho_1)^{1/3}$, the density of solvent ρ_1 was obtained from reference [58], the molar density ρ^* at various temperatures was calculated from the molar densities of

pure polymer and pure solvent using the following mixing rule.

$$\frac{1}{\rho^*} = \sum_{i=1}^2 x_i \frac{1}{\rho_i^*} \quad (28)$$

Fortunately the application of this simple mixing rule was very successful since it resulted in very small root mean square differences (r.m.s.d) in the activity calculations. The molar densities ρ_i^* were calculated by $\rho_i^* = \rho_i/M_i$ ($i = 1, 2$) and the value of ρ_2 the density of polymer was obtained from reference [59].

To proceed with the activity calculations an objective function (r.m.s.d) was defined in the following form:

Table 1

Comparison between the results obtained from new theory and Flory–Huggins theory at various temperatures for binary polymer/solvent mixtures

Mixture, polymer MW + solvent	Temperature (°C)	σ_{22} (Å)	r.m.s.d.		No. of experimental data point	Ref.
			New theory	Flory–Huggins theory		
PS 90000 + chloroform	25	58.6	0.009	0.016	4	[55,60]
PS 290000 + chloroform	25	88.7	0.018	0.022	11	[55,60]
	50	88.9	0.009	0.010	12	
PS 290000 + propylacetate	25	85.9	0.025	0.023	11	[55,60]
	70	86.7	0.021	0.080	10	
PS 290000 + MEK	25	85.9	0.039	0.019	11	[57,60]
	70	85.9	0.025	0.024	6	
PS 290000 + toluene	25	88.5	0.024	0.053	12	[57,60]
	60	88.0	0.011	0.017	6	
PIB 45000 + benzene	25	44.5	0.020	0.016	8	[56,60]
	40	46.4	0.029	0.020	10	
	65	47.2	0.027	0.022	11	
PIB 100000 + cyclohexane	25	62.4	0.002	0.009	10	[56,60]
	40	61.5	0.031	0.037	10	
	65	63.0	0.016	0.017	10	

MW: molecular weight, PS: polystyrene, PIB: polyisobutylene.

Objective function = OF

$$= \frac{1}{N_p} \sqrt{\sum_{i=1}^{N_p} \left(\frac{a_{\text{exp}} - a_{\text{cal}}}{a_{\text{exp}}} \right)^2} \quad (29)$$

where N_p is the number of experimental data point, a_{exp} and a_{cal} are respectively the experimental and calculated activities. The a_{cal} , was calculated by numerical method (nonlinear regression) and optimization (minimization). The polymer diameter value σ_{22} was calculated by considering the range of variation represented by Eq. (4). The optimum value of σ_{22} for each polymer solution is reported in Table 1.

4. Results and discussion

In Table 1 the reported r.m.s.d for the activity of solvent in each system shows that the new theory properly fits the experimental data and it can be concluded that this theory which has only one adjustable parameter, that is σ_{22} , can express the behavior of polymer–solvent mixtures. Also the optimized values of σ_{22} reported in Table 1 indicate that for the same polymer in different solvents, very close values of σ_{22} are obtained, e.g. at 25 °C, for the mixtures: polystyrene (PS) (290000) + chloroform $\sigma_{22} = 88.7 \text{ \AA}$, PS (290000) + MEK $\sigma_{22} = 85.9 \text{ \AA}$ and PS (290000) + toluene $\sigma_{22} = 88.5 \text{ \AA}$.

Also in Table 1 the r.m.s.d values for the activities of solvents in the mixtures calculated by the Flory–Huggins theory have been reported. The activity of solvent in the Flory–Huggins theory can be calculated by the following equation:

$$\ln a_1 = \ln(1 - \varphi_2) + \varphi_2 \left(1 - \frac{1}{r} \right) + \chi_1 \varphi_2^2 \quad (30)$$

where φ_2 is the volume fraction of polymer, r is the number of segments in polymer chain and χ_1 is the interaction parameter. The volume fraction φ_2 can be calculated from MWs and densities via the following equations.

$$\varphi_2 = \frac{x_2 v_2}{x_1 v_1 + x_2 v_2} = \frac{x_2 (M_2 / \rho_2)}{x_1 (M_1 / \rho_1) + x_2 (M_2 / \rho_2)} \quad (31)$$

The number of segment r is calculated using $r = (M_2 \rho_1 / M_1 \rho_2)$. The interaction parameter χ_1 for each polymer–solvent mixture was obtained from reference [60].

Figs. 4 and 5 show the variation of activity calculated by the new theory and by Flory–Huggins theory versus volume fraction of solvent (φ_1) for PS (290000) + chloroform and polyisobutylene (PIB) (100000) + cyclohexane mixtures. Comparison of these figures shows that the trend of variation of activity is the same

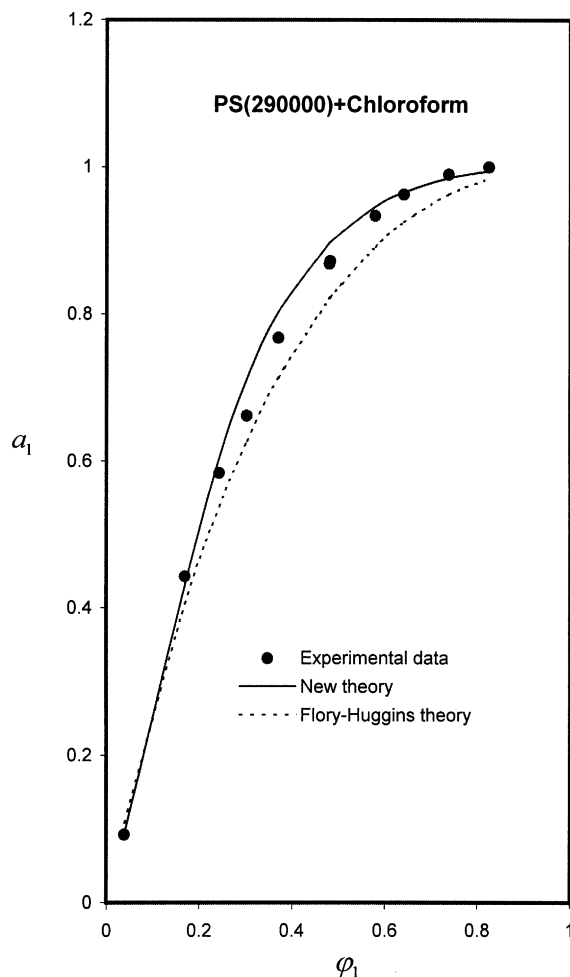


Fig. 4. Activity of chloroform (a_1) versus volume fraction (φ_1) of chloroform for PS (290000)/chloroform mixture, at 25 °C, experimental data (●), calculated by the Flory–Huggins theory (---) and by the new theory (—).

in both theories, which lends support to the ideas used in presenting the new theory.

The consistency of the new theory for predicting the activity of polymer a_2 can be examined by application of the Gibbs–Duhem equation. This equation for a binary mixture can be written as:

$$\varphi_1 \ln a_1 + \varphi_2 \ln a_2 = 0 \quad (32)$$

The activity of polymer a_2 can be obtained by integrating the above equation:

$$\ln a_2 = - \int_{\infty}^{\ln a_1} \frac{\varphi_1}{\varphi_2} \ln a_1 \quad (33)$$

The usual procedure to evaluate this integral is to calculate the area under the curve obtained by plotting the variation of (φ_1/φ_2) versus $\ln a_1$. However, the lower

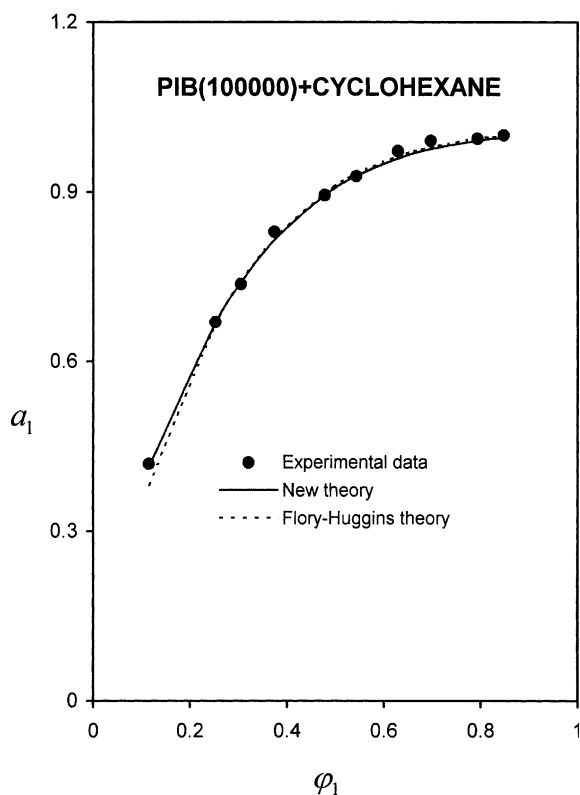


Fig. 5. Activity of cyclohexane (a_1) versus volume fraction (ϕ_1) of cyclohexane for PIB (100 000)/chloroform mixture, at 25 °C, experimental data (●), calculated by the Flory–Huggins theory (···) and by the new theory (—).

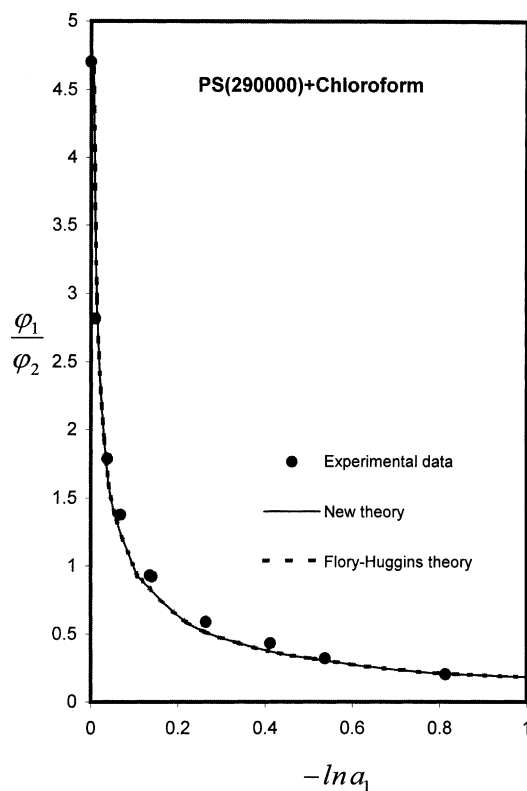


Fig. 6. Variations of volume fraction ratio (ϕ_1/ϕ_2) versus ($-\ln a_1$) for PS (290 000)/chloroform mixture, at 25 °C, experimental data (●), calculated by the Flory–Huggins theory (···) and by the new theory (—).

limit of this integral may cause inaccuracies in its evaluation. Therefore, to confirm the consistency in the activity calculations of polymer and solvent, it is sufficient to show that the calculated a_2 s by the new theory are close to those of the Flory–Huggins and the experimental data. In Figs. 6 and 7 the variations of (ϕ_1/ϕ_2) versus $\ln a_1$, calculated by the new theory, Flory–Huggins theory and the experimental results are shown. It is seen from these figures that the calculated curves are very close to the experimental data and hence the activities of polymer are in agreement with the experimental data and thus the consistency in the results is confirmed.

In Fig. 8 the calculated hard-sphere diameters (σ_{22}), for polymer solvent mixtures, is plotted versus MW of polymers. As it is seen from this figure, the variation of σ_{22} , shows the expected trend, that is, on increasing the MW of polymer σ_{22} increases.

Further physical explanations about the parameter σ_{22} can be given by calculating the radius of gyration for the studied polymers. The root-mean-square distance of chain elements from the center of gravity of the polymer chain, $\langle R_G^2 \rangle^{1/2}$, is used to study the chain configuration.

For flexible chain, the following equation has been suggested [61].

$$\langle R_G^2 \rangle^{1/2} = nl^2/6 \quad (34)$$

where n is the number of segments in the polymer chain and l is the segment lengths. The number of segments, n , is defined as:

$$n = (M_W^p/M_W^m)/n_m^s \quad (35)$$

where M_W^p and M_W^m are the MWs of polymer and monomer respectively and n_m^s is the number of monomers in a segment. For PS and PIB as flexible chains the values of n_m^s are respectively 7.3 and 7.9 (Å) [40].

For solid-sphere the radius of gyration is given by the following equation [62]:

$$\langle R_G^2 \rangle_{\text{solid-sphere}}^{1/2} = \sqrt{\frac{3}{5}} \left(\frac{3M}{4\pi\rho N_0} \right)^{1/3} \quad (36)$$

The radius of gyration for the hard-sphere polymer chain presented in the new theory is:

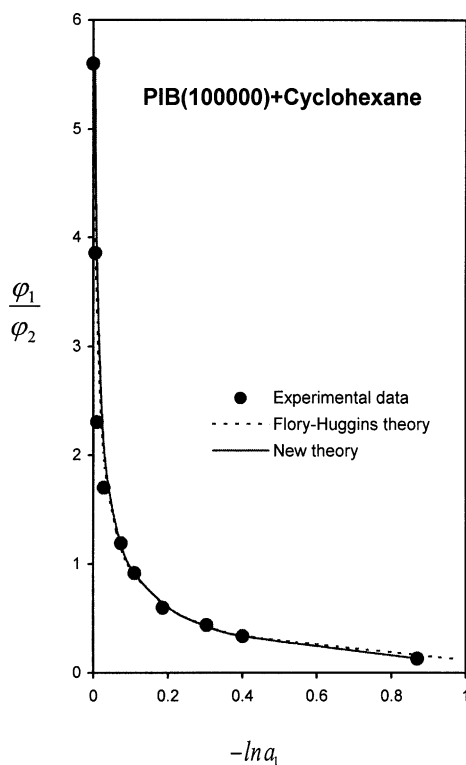


Fig. 7. Variations of volume fraction ratio (ϕ_1/ϕ_2) versus ($-\ln a_1$) for PIB (100000)/cyclohexane mixture, at 25 °C, experimental data (●), calculated by the Flory–Huggins theory (···) and by the new theory (—).

$$\langle \overline{R_G^2} \rangle_{\text{hard-sphere}}^{1/2} = \sqrt{\frac{3}{5}} \left(\frac{\sigma_{22}}{2} \right) \quad (37)$$

The radius of gyration for the studied polymer, calculated by Eqs. (34)–(37), are reported in Table 2. As it is seen from the results in Table 2 the radius of gyration for polymers calculated by Eq. (34) is in the expected range and therefore it is in agreement with the polymer configurations presented by Figs. 1–3 in the new theory.

The hard-sphere diameter σ_{22} can be used to calculate the excluded volume of polymers. In the concept of excluded volume for polymer chain the segments interact and cannot approach each other within a certain distance. In other words, the segments have a finite excluded volume [61].

Table 2

Root mean square gyration radius calculated for flexible coil, solid sphere and Eqs. (34)–(37) in the new theory at 25 °C

System	MW	Flexible coil	Solid sphere	New theory
PS + acetone	15700	9.282	13.991	11.541
PS + chloroform	90000	22.224	25.046	22.695
PS + propylacetate	290000	39.894	36.984	34.353
PIB + benzene	45000	20.587	20.867	17.234
PIB + cyclohexane	100000	30.689	27.230	24.167

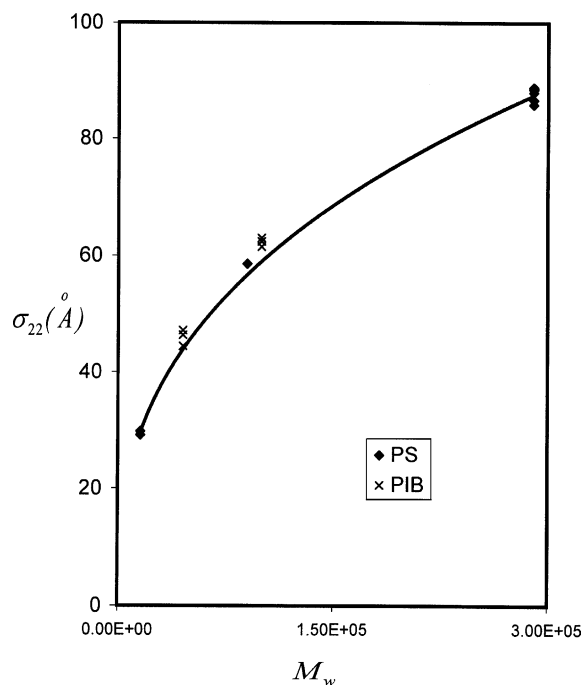


Fig. 8. The variation of σ_{22} versus MW in the polymer/solvent mixtures.

For a polymer, an excluded volume parameter, v is defined by Flory as [41]:

$$v = (1 - 2\chi)a^d \quad (38)$$

where χ is the interaction parameter and a^d is the monomer volume.

In the new theory, following the Flory's suggestion of excluded volume, we propose a similar equation for the excluded volume of polymer chain as:

$$\frac{2}{3}\pi\sigma_{22}^3 = (1 - 2\chi_{\text{total}}) \left(\frac{4}{3}\pi(\sigma_{11}/2)^3 \right) f \quad (39)$$

By considering the polymer solvent models presented by Figs. 1–3 an excluded volume for polymer chain in the form of hard-sphere in the new theory is defined as:

$$v = \frac{1}{2} \left(\frac{4}{3}\pi\sigma_{22}^3 \right) \quad (40)$$

and an interaction volume in the new theory, instead of monomer volume in Flory's theory, is defined as:

Table 3

The total interaction parameters χ_{total} calculated by Eq. (44), the Flory–Huggins interaction parameters χ_{FH} and the hard-sphere interaction parameters χ_{New} for polymer–solvent systems ($\chi_{\text{total}} = \chi_{\text{FH}} + \chi_{\text{New}}$)

System	Temperature (°C)	Polymer-MW	χ_{total}	χ_{FH}	χ_{New}
PS + chloroform	25	90 000	−17.99	0.35	−18.34
PS + chloroform	25	290 000	−27.48	0.35	−27.83
PS + chloroform	50	290 000	−27.54	0.35	−27.89
PS + propylacetate	25	290 000	−25.61	0.60	−26.21
PS + propylacetate	70	290 000	−23.75	0.60	−24.35
PS + MEK	25	290 000	−25.61	0.65	−26.26
PS + MEK	70	290 000	−25.61	0.65	−26.26
PS + toluene	25	290 000	−25.96	0.40	−26.36
PS + toluene	60	290 000	−25.81	0.40	−26.21
PS + acetone	25	15 700	−9.18	0.85	−10.03
PS + acetone	50	15 700	−8.98	0.85	−9.83
PIB + benzene	25	45 000	−13.10	0.75	−13.85
PIB + benzene	40	45 000	−13.68	0.75	−14.43
PIB + benzene	65	45 000	−13.92	0.75	−14.67
PIB + cyclohexane	25	100 000	−17.33	0.40	−17.73
PIB + cyclohexane	40	100 000	−17.07	0.40	−17.47
PIB + cyclohexane	65	100 000	−17.50	0.40	−17.90

$$a^d = \left(\frac{4}{3} \pi (\sigma_{11}/2)^3 \right) f \quad (41)$$

where f is the surface ratio of polymer to solvent and is introduced in Eq. (41) to account for the number of solvent molecules surrounding the polymer chain. Therefore:

$$f = \frac{4\pi(\sigma_{22}/2)^2}{4\pi(\sigma_{11}/2)^2} = \frac{\sigma_{22}^2}{\sigma_{11}^2} \quad (42)$$

From Eq. (39)–(42) and after simplification we obtain;

$$\chi_{\text{total}} = \frac{1}{2} - 2 \frac{\sigma_{22}}{\sigma_{11}} \quad (43)$$

where χ_{total} can be defined as

$$\chi_{\text{total}} = \chi_{\text{FH}} + \chi_{\text{New}} \quad (44)$$

χ_{total} comprises of two terms, χ_{FH} , the Flory–Huggins interaction parameter which represents the segment–solvent interaction and χ_{New} which represents the polymer–solvent interaction.

Table 3 shows the calculated values of the interaction parameters. As expected χ_{FH} and χ_{New} have apposite sign and χ_{New} has larger magnitude, which indicates the existence of both repulsive and attractive interaction between solvent and polymer chain. To explain this, consider χ which in terms of interchange energy w , is given by [11,20]:

$$\chi = \frac{w}{kT} \quad (45)$$

where $k = R/N_0$ and

$$w = \Gamma_{12} - \frac{1}{2}(\Gamma_{11} + \Gamma_{22}) \quad (46)$$

In the above equation Γ_{12} , Γ_{11} and Γ_{22} represent the interaction energies of pair molecules in the mixture, and respectively are for the interaction of solvent–solvent (11), solvent–solute (12) and solute–solute (22) molecules.

In Flory's theory χ refers not to the interchange energy of polymer chain but rather to the interchange energy of segment and solvent. In the new theory w in Eq. (46) has its usual significant, that is, it refers to the solvent and polymer, interaction.

To have a true solution; $\Gamma_{12} < 0$ and $w < 0$, which means there is attraction or affinity between solvent and polymer to form a molecular pair. The calculated results by the new theory presented in Table 3 show negative values of χ which means that; $w < 0$ and $\Gamma_{12} < 0$, and this is consistent with the true behavior of polymer–solvent solutions.

5. Conclusion

A new theory for calculating the solvent activity in polymer–solvent mixtures is developed. The theory is based on the application of hard sphere limit to a binary mixture with large difference in molecular size of the components. The activity calculations indicate good agreement with the experimental data and with the Flory–Huggins theory. The consistency in the calculation of the activities of solvent and polymer is confirmed by the application of the Gibbs–Duhem equation.

It was shown that the parameter σ_{22} in the new theory has a physical interpretation and can be related to MW, radius of gyration, excluded volume and interaction parameter (χ) of the polymer chain.

The interaction parameter (χ) of polymer–solvent mixture is calculated by the new theory and is interpreted in terms of attractive and repulsive interactions.

References

- [1] Firouzi F, Modarress H, Mansoori GA. *Eur Polym J* 1998;34(10):1489.
- [2] Kumar AR, Gupta K. *Fundamentals of polymers*. New-York: McGraw-Hill Book Company; 1998.
- [3] Oishi F, Prausnitz JM. *Ind Eng Chem Proc Des Dev* 1978;17:333.
- [4] Holten-Andersen J, Rasmussen P, Fredensland A. *Ind Eng Chem Res* 1987;26:1382.
- [5] Chen F, Fredensland A, Rasmussen P. *Ind Eng Res* 1990;29:875.
- [6] High MS, Danner RP. *Fluid Phase Equilib* 1989;53:323.
- [7] Flory PJ. *J Chem Phys* 1942;10:51.
- [8] Flory PJ. *J Chem Phys* 1944;12:425.
- [9] Koningsveld R, Kleintjens LI. *Macromolecules* 1971;14:637.
- [10] Taimoori M, Modarress H, Mansoori GA. *J Appl Polym Sci* 2000;78:1328.
- [11] Prausnitz JM. *Molecular thermodynamics of fluid phase equilibria*. Prentice Hall PTR; 1999.
- [12] Rodgers PI. *J Appl Polym Sci* 1993;48:1061.
- [13] Costas M, Sanctuary BC. *J Phys Chem* 1981;85:3153.
- [14] Jain RK, Simha R. *Macromolecules* 1980;13:1501.
- [15] Chen SJ, Economou IG, Radosz M. *Macromolecules* 1992;25:4987.
- [16] Schafer B, Lambert SM, Song Y, Prausnitz JM. Thermodynamics properties of associated fluid including polymers comparison of three association models combined with the perturbed hard-sphere chain equation of state. In: *AICHE Annual Meeting*, San Francisco, CA, 1994.
- [17] Sanchez IC, Lacombe RH. *J Phys Chem* 1976;80:2568.
- [18] Panayiotou C, Vera JH. *Polym J* 1982;14:681.
- [19] Chapman WG, Jackson G, Gubbins KE. *Mol Phys* 1988;65:057.
- [20] Flory PJ. *Principles of polymer chemistry*. London: Cornell University Press; 1953 [Chapter 12].
- [21] Wu CS, Chen YP. *Fluid Phase Equilib* 1994;100:103.
- [22] Dickman R, Hall CK. *J Chem Phys* 1986;85:4108.
- [23] Honnell KG, Hall CK. *J Chem Phys* 1991;95:4481.
- [24] Song Y, Lambert SM, Prausnitz JM. *J Chem Eng Sci* 1994;49:2765.
- [25] Lee L. *Molecular thermodynamics of nonideal fluids*. 1990 [Chapter 6].
- [26] Chiew YC. *J Chem Phys* 1990;93:5067.
- [27] Rostami S, Walsh DJ. *Macromolecules* 1985;18:1228.
- [28] Percus JK, Yevick G. *J Phys Rev* 1958;110:1.
- [29] Wichert JM, Hall CK. *Chem Eng Sci* 1994;49:2793.
- [30] Schweizer KS, Curro JG. *J Chem Phys* 1988;89:3342.
- [31] Schweizer KS, Curro JG. *J Chem Phys* 1990;149:105.
- [32] Schweizer KS, Yethiraj A. *J Chem Phys* 1993;98:9053.
- [33] Chandler D, Andersen HC. *J Chem Phys* 1972;57:1930.
- [34] Chaw MYC, O'Lenick R, Radosz M. *J Chem Phys* 1993;100:3803.
- [35] Wertheim MS. *J Chem Phys* 1987;87:7323.
- [36] Sherwood AE, Prausnitz JM. *J Chem Phys* 1964;41:413.
- [37] Guggenheim EA, McGlashan ML. *Proc R Soc (London)* 1960;A255:456.
- [38] Banaszak MY, Chiew C, O'Lenick R, Radosz M. *Phys Rev E* 1993;48:3760.
- [39] Mitlin VS, Sanchez IC. *J Chem Phys* 1993;99:533.
- [40] Tager A. *Physical chemistry of polymers*. Moscow: Mir Publishers; 1978 [Chapter 3].
- [41] De Gennes PG. *Scaling concepts in polymer physics*. Cornell University Press; 1979 [Chapter 1].
- [42] Tukur NM, Hamad EZ. *J Chem Phys* 1999;110:7.
- [43] Lebovitz JL, Rowlinson JS. *J Chem Phys* 1964;41:133.
- [44] Biben T, Hansen JP. *Phys Rev Lett* 1991;66:2215.
- [45] Van Laar JJ. *Z Phys Chem* 1913;83:599.
- [46] Wilson GM. *J Am Chem Soc* 1964;86:127.
- [47] Mansoori GA, Carnahan NF, Starling KE, Leland TW. *J Chem Phys* 1971;54:1523.
- [48] Hamad EZ, Mansoori GA. *Fluid Phase Equilib* 1989;51:13.
- [49] Hamad EZ. *J Chem Phys* 1994;101:10195.
- [50] Lebovitz JL. *Phys Rev A* 1964;133:895.
- [51] Lee LL. *Molecular thermodynamics of nonideal fluids*. Boston: Butterworths; 1988.
- [52] Jackson G, Rowlinson J, Leng C. *J Chem Soc, Faraday Trans* 1986;1:3461.
- [53] Eliassi A. *Experimental and thermodynamical study of phase equilibria for polymer systems used in biotechnology*. PhD Thesis, Amirkabir University, 1998.
- [54] Walas SM. *Phase equilibria in chemical engineering*. Butterworths Publisher; 1985 [Chapter 4].
- [55] Bawn CEH, Wajid MA. *J Chem Soc, Faraday Trans* 1956;52:1658.
- [56] Bawn CEH, Patel RD. *J Chem Soc, Faraday Trans* 1956;52:1664.
- [57] Bawn CEH, Freeman RFJ. *J Chem Soc, Faraday Trans* 1950;46:677.
- [58] Washburn EW. *International critical tables of numerical data physics chemistry and technology*. McGraw-Hill; 1926. p. 800.
- [59] Danner RP, High MS. *Handbook of polymer solution thermodynamics*. New York: AIChE; 1993 [Chapter 3].
- [60] Allan BF. *CRC handbook of polymer–liquid interaction*. CRC Press; 1990 [Chapter 1].
- [61] Kamide K, Dobashi T. *Physical chemistry of polymer solutions*. Elsevier Science; 2000. p. 317, 340.
- [62] MacQuarrie DA. *Statistical thermodynamics*. Harper and Row Publisher; 1973. p. 273.