Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil

Vol. 21, No. 04, pp. 611 - 619, October - December 2004

MUTUAL DIFFUSION COEFFICIENT MODELS FOR POLYMER-SOLVENT SYSTEMS BASED ON THE CHAPMAN-ENSKOG THEORY

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(Received: February 13, 2003 ; Accepted: May 24, 2004)

Abstract - There are numerous examples of the importance of small molecule migration in polymeric materials, such as in drying polymeric packing, controlled drug delivery, formation of films, and membrane separation, etc. The Chapman-Enskog kinetic theory of hard-sphere fluids with the Weeks-Chandler-Andersen effective hard-sphere diameter (Enskog-WCA) has been the most fruitful in diffusion studies of simple fluids and mixtures. In this work, the ability of the Enskog-WCA model to describe the temperature and concentration dependence of the mutual diffusion coefficient, D, for a polystyrene-toluene system was evaluated. Using experimental diffusion data, two polymer model approaches and three mixing rules for the effective hard-sphere diameter were tested. Some procedures tested resulted in models that are capable of correlating the experimental data with the refereed system well for a solvent mass fraction greater than 0.3.

Keywords: Polymer-solvent systems; mutual diffusion coefficients; Chapman-Enskog kinetic theory.

INTRODUCTION

There are numerous examples of the importance of small molecule migration in polymeric materials, such as in drying polymeric packing, controlled drug delivery, film formation, and membrane separation, etc. In general, mass transfer in these processes is strictly regarded as a diffusion-limited mechanism. Therefore, it would be useful if the diffusion coefficient of a molecule at a specific concentration and temperature could be easily determined without the necessity of experimental data measurements.

Currently, the most frequently used approach for describing diffusion in polymer-solvent systems is the Vrentas/Duda model (Vrentas and Duda, 1977a,b), which is based on the free-volume theory. One can observe from the literature that, in the predictive version, the model is capable of qualitatively representing the experimental data, but significant quantitative deviations are verified, mainly at low polymer concentrations (Reis et al., 2001). However, it is possible to improve the results significantly when parameters are obtained from regression of experimental data (Reis et al., 2001). These deviations are associated with implicit shortcomings of the model as well as with the difficulties in obtaining accurate model parameters. Though the diffusion free-volume theory has been pointed to in the literature as a reference to estimate mutual diffusion coefficients as a function of

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temperature and concentration for polymer systems, its theoretical formalism has reached such an advanced stage that improvements in its prediction capability seem to be possible only on a purely empirical basis. In this context, interest in developing models by using new approaches to improve the diffusion prediction as well as to interpret the diffusion mechanism better has grown rapidly.

In terms of practical applications and theoretical studies, the Enskog kinetic theory of hard-sphere fluids has been the most fruitful (Dariva et al., 1999a,b). In this theory, the transport properties are calculated by very simple equations relating particle mass, temperature, fluid density, particle size, and radial distribution function at contact. Based on smooth- or rough-hard-sphere theory, several empirical methods have been developed (Rocha et al., 1997). Diffusion coefficients for monatomic gases at low densities can be calculated at any temperature by using the kinetic theory (Reed and Gubbins, 1973). However, no rigorous model is available to evaluate diffusion coefficients for monatomic or polyatomic fluids at high densities in terms of a realistic description of molecular interactions (Yu and Gao, 1999). Simple semi-theoretical methods based on statistical mechanics appear to be the most promising for engineering purposes. Liu et al. (1998) provided an extensive review of diffusion coefficient prediction and correlation methods, in which several diffusion models for simple fluids are compared.

The effective hard-sphere diameter (EHSD) method has been widely used to calculate both equilibrium and transport properties. Various EHSD explicit equations have been proposed in the literature according to different criteria (Silva et al., 1998). For example, Rocha et al. (1997) and Dariva et al. (1999a,b) successfully estimated diffusivities in dense real fluids and real fluid mixtures with the Weeks-Chandler-Andersen (WCA, Weeks et al., 1971) effective hard-sphere diameter under sub and supercritical conditions.

Taking into account the discussion above, the aim of this work is to study the potential of the Chapman-Enskog theory together with the WCA effective hard-sphere diameter formalism to represent the temperature and concentration dependence of the mutual diffusion coefficient in polymeric systems. The results of different calculation procedures are reported, testing the mono- and polyatomic formalisms, different combining rules, and some parameter estimation strategies. Then the resulting models are used, either to predict mutual diffusion coefficients of the polystyrene-toluene system at 110°C over almost the entire composition range (Liu, 1980) or to predict mutual diffusion coefficients at infinite dilution of polystyrene in toluene as a function of temperature (Zielinski, 1996). The results obtained for each approach employed in this work are compared with experimental data.

THEORY

As discussed previously, large number of diffusion models has been advanced lately in order to improve the prediction capability of diffusivities in dense fluids as well as to provide a better interpretation of the diffusion mechanism. Accordingly, interest in the Chapman-Enskog transport theory has markedly increased due mainly to its well-based formalism, making it the backbone of transport treatment. In previous works (Dymond, 1985; Speedy, 1987; Heyes, 1988; Erkey et al., 1990; Erpenbeck and Wood, 1991, Harris, 1992; Amoros, 1994; Ruckenstein and Liu, 1997; Liu et al., 1998; Yu and Gao, 1999), some theoretical details and shortcomings, implicit in the original Enskog models for dense fluids (Chapman and Cowling, 1970) have been discussed and some changes have been proposed with the aim of making it possible to calculate diffusion coefficients for more complex fluids in wider ranges of temperatures and compositions. Nevertheless, to date the diffusion studies involving macromolecules show that applicability of the original Enskog model is still limited.

Self-diffusion in hard-sphere fluids at low densities, $D(\rho \to 0)$ or simply D_0, can be described by the following equation (Reed and Gubbins, 1973):

$$D_0 = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{1}$$

where k is the Boltzmann constant, T the absolute temperature, σ the molecular diameter, ρ the number density, and m the particle mass.

For dense fluid, however, rigorous treatment is much more complicated. To overcome the inherent arising difficulties, Chapman and Enskog kept the binary collisions assumption and relaxed the molecular chaos consideration for velocities (but not for positions) to derive the following simple equation for a system formed of hard spheres (Reed and Gubbins, 1973):

$$D_E = \frac{D_0}{g(\sigma)} \qquad (2)$$

where g(σ) is the radial distribution function at contact.

Inspection of Eq. (2) shows that as density increases, diffusion approaches zero, whereas when $\rho \to 0$, $g(\sigma) \to 1$ and $D_E \to D_0$.

Recently, much attention has been dedicated to the study of properties of simple fluids, using models such as the hard-sphere (HD), square-well (SW), and Lennard-Jones (LJ) fluid models. In terms of transport properties, molecular dynamic simulations (MDS) have been carried out for these fluids as the technique makes use of a well-defined hypothesis and is rigorous within the physical limits established in the simulations. Thus MDS data obtained for simple fluids are used in the development of empirical correlations (high densities - Ruckenstein and Liu, 1997 and chain connectivity - Yu and Gao, 1999) to correct the Enskog model for more complex fluids at wider density intervals.

The radial distribution function at the interface used in this paper was proposed by Carnahan and Starling (1969):

$$g(\sigma) = \frac{1 - 0.5\eta}{(1-\eta)^3} \qquad (3)$$

where

$$\eta = \frac{1}{6}\pi\rho^* = \frac{1}{6}\pi\rho\sigma^3 \qquad (4)$$

Concerning the effective hard-sphere diameter, the present approach is based on an idea of Schrodt and Davis (1974), whereby the requirement that the pair-potential function has a hard-sphere core cut-off is eliminated. Their results for excess pressure are essentially the same as those of the Weeks-Chandler-Andersen (Andersen et al., 1971) perturbation theory of liquids, and hence they postulated that the properties of a real system obey the kinetic equation of a hard-sphere system of diameter d. The WCA theory predicts very well the equilibrium structure as given by the radial distribution function, especially for liquids and dense fluids. Thus, all the σ in the diffusion coefficient equations are replaced by the WCA hard-sphere diameter, d. In this work, the accurate proposal of Souza and Ben-Amotz is chosen (1993),

$$d(\rho,t) = 2^{1/6}\sigma\left\{1+\left[\frac{\left(T^* + a_2T^{*2} + a_3T^{*4}\right)}{a_1\left(1+a_4\rho^* + a_5\rho^{*2} + a_6\rho^{*3}\right)}\right]^{1/2}\right\}^{-1/6} \qquad (5)$$

where $T^*(\equiv T/(\varepsilon/k))$ is the reduced temperature, ε is the Lennard-Jones energy parameter and a_1=1.5001, a_2=-0.03367, a_3=0.0003935, a_4=-0.09835, a_5=0.04937, a_6=-0.1415 are constants. Rocha et al. (1997), Ruckenstein and Liu (1997), and Yu and Gao (1999) found that the energy parameter, ε, is insensitive to the experimental self-diffusion data; therefore it was assumed that the molecular energy is the sum of all the LJ segment energies. Analogous to the LJ fluid, the relation obtained from viscosity data (Reid et al., 1987) was employed to determine the energy parameters, as follows:

$$N(\varepsilon/k) = \frac{T_C}{1.2593} \qquad (6)$$

where T_C is the critical temperature. The chain segment critical temperature was calculated using the Joback group contribution method (Reid et al., 1987).

Binary Systems

For a binary mixture, the mutual diffusion coefficient is obtained straightforwardly by replacing d by d_{12}, the cross hard-sphere diameter; ρ by ρ_m, the mixture density, and m by m_{12} $(\equiv m_1m_2/(m_1+m_2))$, the reduced mass of solute 1 and solvent 2:

$$D_{12} = \frac{3}{8\rho_m d_{12}^2}\left(\frac{kT}{2\pi m_{12}}\right)^{1/2}\frac{1}{g(d_{12})} \qquad (7)$$

The combining rules used for d_{12} will be commented on later. The radial distribution function at contact, $g(d_{12})$, is calculated by using the Carnahan-Starling equation extended to mixtures by Mansoori et al. (1971):

$$g(d_{ij}) = \frac{1}{1-\xi_3} + \frac{3d_id_j}{d_i+d_j}\frac{\xi_2}{(1-\xi_3)^2} + 2\left(\frac{d_id_j}{d_i+d_j}\right)^2\frac{\xi_2^2}{(1-\xi_3)^3} \qquad (8)$$

where

$$\xi_s = \frac{\pi}{6}\sum_{i=1}^{N}\rho_i d_i^s, \quad s = 0, 1, 2, 3 \qquad (9)$$

Throughout this work, the reduced density of mixture, ρ^*_m, is calculated by

$$\rho^*_m = \sum_{i=1}^{N} \rho_i d_i^3 \tag{10}$$

where ρ_i is the density of component i in mixture ($x_i\rho_m$).

It is believed that, during the process of diffusion in polymeric systems, a series of phenomena not considered in the original Enskog model occurs, which makes its use prohibitive for these systems from a practical point of view. Effects caused by molecular asymmetry (highly nonspherical molecules), chain connectivity, entanglement of polymeric segments, etc. may be mentioned as examples. Recently, Reis (2001) proposed a correction term for high densities and used a chain connectivity expression in the original Enskog model. The resulting equation was applied to the polystyrene-toluene system at 110°C in a wide range of compositions. The results were compared to experimental data (Liu, 1980) and to those obtained from the models of Yu and Gao (1999) and Enskog-WCA (Rocha et al., 1997). It was verified that there is a concentration range where all the studied models have very similar performances and represent the experimental mutual diffusion coefficient data qualitatively well. The influence of chain connectivity was observed to be more significant at higher polymer concentrations where disagreement between experiment and theory is evident. Thus, according to the results shown in Figure 1, the upgrade proposed for the Enskog model did not contribute in fact towards an understanding of the diffusion mechanism in concentrated polymeric systems.

In the present work, a systematic study of the original Enskog model is presented for dense fluids by testing some combining rules for the cross EHSD, using mono and polyatomic expressions and different data fitting strategies.

CALCULATION PROCEDURES

For the cross EHSD, d_{12}, the following combining rule (Eq. (11)) and two mixing rules (Eqs. (12) and (13)) are tested:

(a) $$d_{12} = \frac{d_1 + n_2 d_2}{2}; \tag{11}$$

(b) $$d_{12} = x_1 d_1 + x_2 n_2 d_2; \tag{12}$$

(c) $$d_{12} = \phi_1 d_1 + \phi_2 n_2 d_2. \tag{13}$$

where d_i is the effective diameter of component i, n_2 the number of polymer segments, x_i the molar fraction of component i, and ϕ_i the volume fraction of component i.

Regarding the structure of the components, the solvent is always treated as a single hard sphere, whereas, for polymer molecules, two possibilities are tested, resulting in the following systems:

- System (1): the solvent and polymer molecules are single hard spheres (n_2=1);
- System (2): the solvent molecule is a hard sphere and the polymer is treated as a group of hard spheres without any connectivity restriction.

For the following are the experimental data fitting used:

- Data source (i): mutual diffusion coefficient data at infinite dilution of polystyrene in toluene as a function of temperature (Zielinski, 1996);
- Data source (ii): mutual diffusion coefficient data for polystyrene-toluene, as a function of composition, obtained at 110°C by Liu (1980).

In addition, for the procedures involving System (2), different parameter estimation strategies were adopted. In strategy 1, the polymer segment diameter, σ_2, is adjusted while the number of segments (n_2) is taken as the ratio of polymer molecular weight to its monomeric unit molecular weight (for polystyrene, n_2 = 2875 segments). In strategy 2, the number of segments is adjusted and the segment (monomer) diameter is calculated by the following equation (Dariva et al., 1999b):

$$\sigma_{segment} = \left(\frac{V_{C,segment}}{V_{C,solvent}}\right)^{1/3} \sigma_{solvent} \tag{14}$$

where $V_{c,i}$ is the molar critical volume of component i. The chain segment critical volume was calculated using the Joback group contribution method (Reid et al., 1987). In strategy 3, both parameters are adjusted.

The adjusted parameter values, from a given data source, were employed in model extrapolations for comparison with the other data source. The least-squares method was used for all parameter estimations.

A summary of the adopted strategies is presented in Table 1. It should be emphasized that, for all procedures listed in this table, the radial distribution function of the monomer-monomer type was used; therefore restrictions of chain connectivity were not introduced.

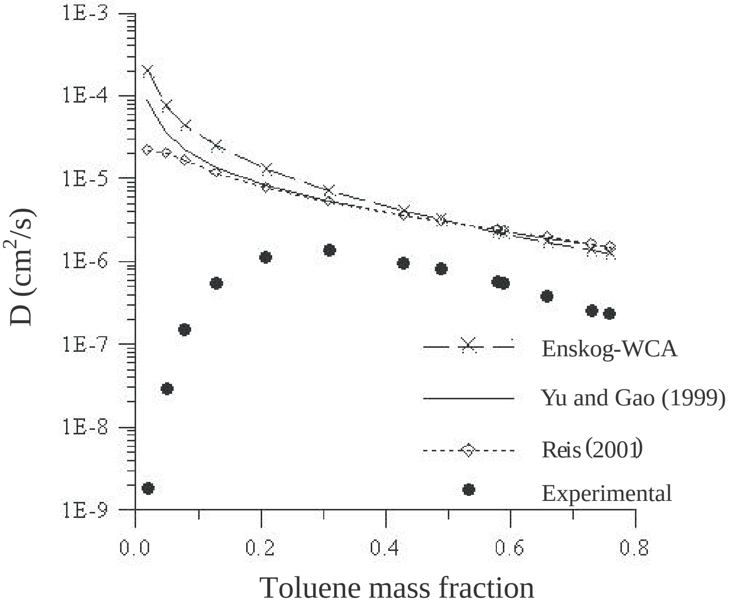

Figure 1: Comparison of calculated and experimental (Liu, 1980) mutual diffusion coefficients for the polystyrene-toluene system at 110°C as a function of toluene mass fraction.

Table 1: Summary of calculation procedures employed in this work.

Procedure	System[1]	Combining rule[2]	Data Source[3]	Remarks[4]
1	(1)	(a)	(i)	strategy 1
2	(1)	(b)	(i)	strategy 1
3	(1)	(c)	(i)	strategy 1
4	(1)	(a)	(ii)	strategy 1
5	(1)	(b)	(ii)	strategy 1
6	(1)	(c)	(ii)	strategy 1
7	(2)	(a)	(i)	strategy 1
8	(2)	(a)	(i)	strategy 2
9	(2)	(a)	(i)	strategy 3
10	(2)	(b)	(i)	strategy 1
11	(2)	(b)	(i)	strategy 2
12	(2)	(b)	(i)	strategy 3
13	(2)	(c)	(i)	strategy 1
14	(2)	(c)	(i)	strategy 2
15	(2)	(c)	(i)	strategy 3
16	(2)	(a)	(ii)	strategy 1
17	(2)	(a)	(ii)	strategy 2
18	(2)	(a)	(ii)	strategy 3
19	(2)	(b)	(ii)	strategy 1
20	(2)	(b)	(ii)	strategy 2
21	(2)	(b)	(ii)	strategy 3
22	(2)	(c)	(ii)	strategy 1
23	(2)	(c)	(ii)	strategy 2
24	(2)	(c)	(ii)	strategy 3

[1]Systems: (1) - the solvent and polymer molecules are single hard spheres (n_2=1); (2) - the solvent molecule is a hard sphere and the polymer is treated as a group of hard spheres without any connectivity restriction; [2](a) combining rule: Eq. (11); (b) mixing rule: Eq. (12); (c) mixing rule: Eq (13); [3]Data source (i): Zielinski (1996); (ii): Liu (1980); [4]strategy 1: σ_2 is adjusted using only the data source indicated on the same line in Table 1 (n_2=2875); strategy 2: n_2 is adjusted using only the data source indicated on the same line in Table 1 (σ_2=5.7774Å); strategy 3: both parameters are adjusted using only the data source indicated on the same line in Table 1.

RESULTS AND DISCUSSION

The results for the mutual diffusion coefficient for polystyrene at infinite dilution in toluene as a function of temperature are shown in Figure 2 while, a comparison between the experimental and the calculated mutual diffusion coefficient of the polystyrene-toluene system at 110°C as a function of composition is depicted in Figure 3.

In these figures, results for the other procedures are not presented, since they do not aggregate important new information and would just make graph analysis very confusing. The results obtained with procedures 7 and 8 for both illustrations are similar to the ones obtained with procedure 1. Procedures 15, 17 and 14 give results very similar to those of 12, 16 and 23, respectively. Also, procedures 1, 12, 16, 18, and 23 provide results similar to those of procedures 8, 15, 17, 7, and 22, respectively. Results for the diffusion coefficient at infinite dilution obtained with procedure 13 are similar to those obtained with procedure 1, while for mutual diffusion, procedure 13 provided values smaller than 10^{-10} cm^2/s in the whole concentration range. Other procedures not mentioned or not shown in Figures 2 and 3 resulted in numerical problems and as a consequence they are not included in the analysis.

It can be observed from Figure 2 that, of the proposed procedures, only procedures 1 and 18 acceptably represent the experimental data. In Figure 3, one can see that procedures 1 and 18 can describe the experimental data for solvent mass fractions greater than 0.3 qualitatively well, since both models show deviations that are smaller than one order of magnitude, a result considered satisfactory in diffusion studies involving polymeric systems. Not only is poor agreement observed for all models at higher polymer concentrations but in addition an opposite trend in the experimental data is found.

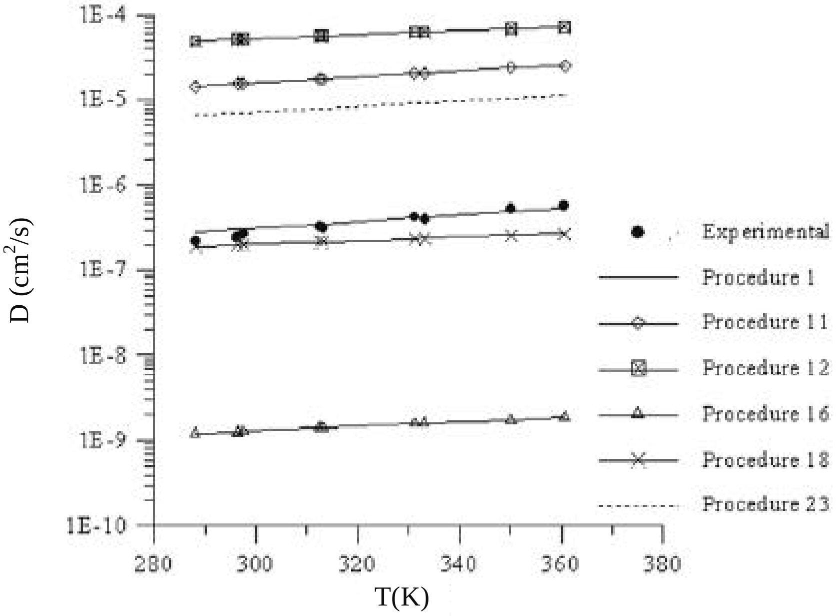

Figure 2: Diffusion coefficient of polystyrene at infinite dilution in toluene as a function of temperature. Experimental data from Zielinski (1996). Fitted parameters in Procedure 1 - ($\sigma_2 = 52.3Å \pm 0.9Å;\ n_2 = 1$); Procedure 11 - ($\sigma_2 = 5.7774Å;\ n_2 = 99.9 \pm 6x10^4$); Procedure 12 - ($\sigma_2 = 0.2Å \pm 71Å;\ n_2 = 9999.76 \pm 3x10^7$). Parameters employed in Procedure 16 - ($\sigma_2 = 0.74Å \pm 0.7Å;\ n_2 = 2875$); Procedure 18 - ($\sigma_2 = 0.033Å \pm 33Å;\ n_2 = 6406 \pm 7x10^6$); Procedure 23 - ($\sigma_2 = 5.7774Å;\ n_2 = 163 \pm 106$).

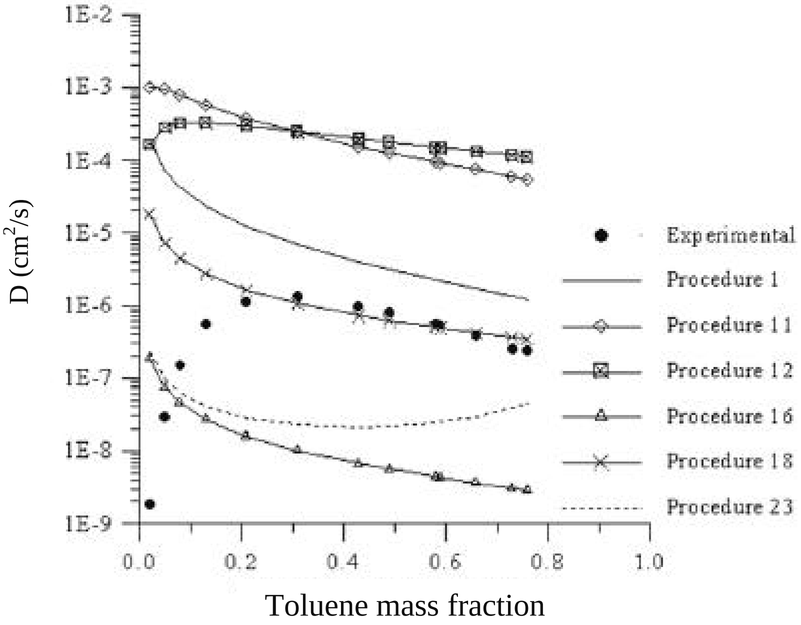

Figure 3: Mutual diffusion coefficient for polystyrene-toluene system as a function of toluene mass fraction at 110°C. Experimental data from Liu (1980). Parameters employed in Procedure 1 - ($\sigma_2 = 52.3Å \pm 0.9Å;\ n_2 = 1$); Procedure 11 - ($\sigma_2 = 5.7774Å;\ n_2 = 99.9 \pm 6x10^4$); Procedure 12 - ($\sigma_2 = 0.2Å \pm 71Å;\ n_2 = 9999.76 \pm 3x10^7$). Fitted parameters in Procedure 16 - ($\sigma_2 = 0.74Å \pm 0.7Å;\ n_2 = 2875$); Procedure 18 - ($\sigma_2 = 0.033Å \pm 33Å;\ n_2 = 6406 \pm 7x10^6$); Procedure 23 - ($\sigma_2 = 5.7774Å;\ n_2 = 163 \pm 106$).

In that concentration region (mass fraction of toluene smaller than 30%), a sharp decrease in the mutual diffusion coefficient is observed, which is not foreseen by most of the models. One should note that despite the large quantitative deviation with procedure 12, it seems to be the only model that had a correct qualitative trend for higher polymer concentrations. However, as this model provided highly correlated parameters with unacceptable parametric uncertainties, application of procedure 12 did not result in a statistically significant model. According to Nyström and Roots (1991), this fast decrease at low solvent concentrations is associated with steric impediments resulting from entanglement of the polymeric chains. Polymer molecules are intertwined allowing very frequent collisions of a solvent molecule with the same polymer molecule due to the restrictions of chain connectivity, a physically significant situation not considered in the model. The Enskog model merely states that diffusion of small hard spheres among bigger ones will always be greater than the opposite situation.

Some additional comments on the strategies employed in this work should be made. First, simultaneous fitting of the two polymer parameters (σ_2, n_2) was shown to be inadequate due to the high parametric correlation observed. The mixing rule based on the molar fraction, Eq. (12), did not result in a statistically significant model. Models obtained with the procedures assuming the polymer to be a polysegmented molecule and fitting the parameters from mixing data were also found to be inadequate, since the parameter standard deviations were on the same order of magnitude as the parameters. One should also note that application of procedure 1 resulted in a polymer diameter larger by one order or more of magnitude than the diameters obtained with all other procedures. This is an expected and reasonable result, since it reflects the fact that the polymer is not being treated as a polysegmented molecule.

Certainly, a more extensive study must be conducted using a larger amount of experimental data and other polymeric systems for more reliable conclusions. Furthermore, the effect of chain entanglements on diffusion requires more detailed study to be able to incorporate it into the modified Enskog model discussed in this work. These topics, including experimental measurement and molecular dynamic simulation are in progress within our research group.

CONCLUSIONS

In this work, the performance of the Enskog model to estimate the mutual diffusion coefficient of polymer-solvent systems was studied. For this purpose, we adopted various calculation procedures involving different combining and mixing rules for the cross EHSD, two kinds of experimental data set, some parameter estimation strategies, and the use of mono and polyatomic approaches. It was shown that, in general, the behavior of the resulting models was similar and these models can provide a satisfactory representation of the mutual diffusion data only within a certain concentration range. Beyond a limiting solvent concentration value, agreement between experiment and theory deteriorates fast as the solution is enriched with polymer. The results reported here might be useful for those interested in the development of a challenging research area of great industrial appeal.

ACKNOWLEDGEMENTS

The authors thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), and PRONEX for providing a scholarship and supporting this research.

NOMENCLATURE

D	self-diffusion coefficient	(cm^2/s)
D_0	self-diffusion coefficient at low densities, $D(\rho \rightarrow 0)$,	(cm^2/s)
D_{12}	mutual diffusion coefficient	(cm^2/s)
D_E	self-diffusion coefficient at high densities	(cm^2/s)
T	temperature	(K)
T^*	reduced temperature,	$T/(\varepsilon_{LJ}/k)$
$V_{C,\ segment}$	molar critical volume of the segment	(cm^3/mol)
$V_{C,\ solvent}$	molar critical volume of the solvent	(cm^3/mol)
a_i	constants of Eq. (5)	(-)
d	effective hard-sphere diameter	(Å)
d_{12}	cross effective hard-sphere diameter	(Å)
$g(\sigma)$	radial distribution function at contact	(-)
k	Boltzmann constant	(J/(molecK))
m	particle mass	(Kg)
m_{12}	reduced mass of mixing	(-)
n_c	number of polymer segments	(-)
x_i	molar fraction of component i	(-)

Greek Letters

ε	Lennard-Jones energy parameter	(J)
ϕ_I	volume fraction of component i	(-)
η	packing factor	(-)
π	constant (3,1415...)	(-)
ρ_i	number density of component i	(molecules/cm^3)
ρ_m	mixture number density	(molecules/cm^3)
ρ^*	reduced density	(-)
σ	molecular diameter	(Å)
$\sigma_{solvent}$	solvent molecular diameter	(Å)
$\sigma_{segment}$	polymer segment molecular diameter	(Å)

Symbols

EHSD	effective hard-sphere diameter
HS	hard sphere
LJ	Lennard-Jones
MDS	molecular dynamics simulations
SW	square well
WCA	Weeks-Chandler-Andersen

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