**Binary Mutual Diffusion Coefficients of Polymer/Solvent Systems using Compressible Regular Solutions Theory and Free Volume Theory**

**Abstract**

The free volume theory has found practical application for prediction of diffusional behavior of polymer/solvent systems. In this paper, reviewing free volume theory, binary mutual diffusion coefficients in some polymer/solvent systems have been systematically presented through chemical thermodynamic modeling in terms of both activity coefficients and fugacity coefficients models. Here chemical thermodynamic model of compressible regular solution (CRS) was used for evaluation of diffusion coefficients calculations as the pure components properties would be required only. Four binary polymeric solutions of Cyclohexane/Poly isobutylene, n-Pentane/Poly isobutylene, Toluene/Poly isobutylene and Chloroform/Poly isobutylene were considered. The agreement between calculated data and the experimentally collected data was desirable and no considerable error propagation in approximating of mutual diffusion coefficients has been observed.

Keywords: polymeric membrane; thermodynamic model, free volume; mutual diffusion coefficients; polymeric solutions

1. Introduction

Phase inversion process is of the most common methods of fabrication of commercial polymeric membranes in which, frequently, a binary polymer/solvent solution cast as a thin film on a support layer and then immersed in a coagulation bath (wet casting) or exposed to air/vapor (dry casting) [[1-6](#_ENREF_1)]. During this process, polymeric materials are required to be dissolved in the solvents to obtain a polymeric solution with desirable viscosity (fluidity) for casting purposes, then these solvents must be removed either through the application of a coagulation bath or by the exposure to the ambient air or vapor [[3](#_ENREF_3),[7](#_ENREF_7)]. The solvent diffusion - or more precisely the mutual binary diffusion - in polymer at the dissolution step and solvent/nonsolvent diffusions through polymeric solution plays a key role in these polymer-processing processes [[8](#_ENREF_8),[9](#_ENREF_9)].

The experimental studies approved that the diffusion coefficients of polymer/solvent systems are depended on a wide variety of variables such as temperature, concentration, molecular weight and polymer morphology like crystallinity, crosslink density and orientation [[10](#_ENREF_10)]. For description of diffusion in polymeric solution theoretically, the appropriate procedure must be employed based on the relative concentration of polymer in the solution [[10](#_ENREF_10)]. In the concentrated regions, as of the common dope solution in the membrane forming processes, the approximate molecular theories and the free volume theory might be used [[11-15](#_ENREF_11)]. As the concentration coverage range of approximate molecular theories is limited, the later (free volume theory) has found practical application for prediction of diffusional behavior of such systems.

Although that, in literatures, the application thermodynamic models such as Flory-Huggins, entropic-FV model, and UNIQUAC can be found [[16-21](#_ENREF_16)], however, there is no systematic presentation of various available chemical thermodynamic models for the prediction of mutual diffusion coefficients using this theory for further investigation. The necessity of such systematic presentation and investigation comes to attention as one notes to the importance of these mutual diffusion coefficients for analysis of actual mass transfer phenomena. Therefore, in this paper, binary mutual diffusion coefficients in polymer/solvent systems have been focused to be presented using chemical thermodynamic models for implementation of both activity coefficients and fugacity coefficients models.

1. Free volume theory

The concept of free volume theory first was proposed by Cohen and Turnbull for molecular diffusion in liquid systems [[22](#_ENREF_22)], which then received many modification by researchers [[23-25](#_ENREF_23)] and finally compiled as a generalized theory by Vrentas and Duda [[26](#_ENREF_26),[27](#_ENREF_27)]. In this theory, the self-diffusion coefficients of polymer and solvent can be predicted through the free volume concept [[10](#_ENREF_10)] and upon coupling with the thermodynamic data of the solution, the mutual binary diffusion coefficients would be obtained [[26](#_ENREF_26)]. Later on [[28-32](#_ENREF_28)], Duda et al., proposed that the relationship between the mutual binary diffusion coefficient,, and the self-diffusion coefficient (of solvent), , can be determined [[21](#_ENREF_21)] as presented by Eqs. 1-4,

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where  is the pre-exponential factor,  the energy required to overcome to the attractive forces of a molecule,  the overlap factor to adjust the sharing of a same free volume for more than one molecule,  the specific hole free volume of component , the weight fraction of component ,  the ratio of molar volumes of the jumping unit of solvent and polymer,  free volume parameters of solvent and polymer, glass transition temperature of component ,  solvent chemical potential.

The derivative of solvent chemical potential,, demonstrates the effect of thermodynamic variation on the diffusion coefficients, as a side, it shows the potential requirement of a systematic presentation of various available chemical thermodynamic models for the prediction/calculation of mutual diffusion coefficients using this theory for further investigation. Some of the authors have attempted, for example, to examine the application of thermodynamic models such as Flory-Huggins, entropic-FV model, and UNIQUAC [[16-21](#_ENREF_16)], however their methodology cannot be extended or used for further research. The importance of these mutual diffusion coefficients for analysis of actual mass transfer phenomena indicates the necessity of such systematic investigation [[2](#_ENREF_2),[33-36](#_ENREF_33),[1](#_ENREF_1)].

1. Theory

For a solution of interest, the chemical potential can be related to the fugacity of pure species () and fugacity of species in solution () [[37](#_ENREF_37),[38](#_ENREF_38)] as presented by Eq. 5;

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Practically, the polymeric solution would be considered as a liquid by thermodynamic models. Therefore, considering the polymer/solvent solution *as liquid*, and assuming the pure species as the standard state [[37](#_ENREF_37),[38](#_ENREF_38)], one might rewrite Eq. 5 as presented by Eq. 6 and Eq. 7,

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Where indicates the component composition. is the fugacity of component at some fixed condition known as the standard state [[37](#_ENREF_37)]. The pure species () in Eq. 7 can be calculated noting that , where,  is the saturation pressure of component, which can be calculated using Ambrose-Walton corresponding state method [[39](#_ENREF_39),[40](#_ENREF_40)]. The Poynting factor () can be neglected for this study. Setting temperature and pressure to the phase temperature and corresponding from Ambrose-Walton corresponding state method [[39](#_ENREF_39),[40](#_ENREF_40)], the fugacity coefficient for pure component () *as liquid* can be calculated employing an equation of state [[37](#_ENREF_37)]. Equations of state come to attention as they can be put into a generalized form which express as a function of and  [[37](#_ENREF_37)]. A substantial number of equations of state can be found in literatures [[41-47](#_ENREF_41)].

The simplest form of equations of state are the cubic ones that can be formulated in a generic form [[37](#_ENREF_37)] as presented by Eq. 8, where and;

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Cubic equations of state can be linked to the fugacity coefficient [[37](#_ENREF_37)] as presented by Eq. 9;

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Where,, and . ,,  and  are parameters specific to equations of state (EOS).

Here,  *as liquid* can be calculated from Eq. 10 using an iterative root seeking method [[37](#_ENREF_37)].

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For calculation of, one might use Eq. 11. However, prior to the application of Eq. 11,  *as liquid* must be calculated from Eq. 10 by substitution of the mixture parameters.

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Using van der Waals two parameters mixing rules (vdW2) [[37](#_ENREF_37)], we have Eqs. 12-14;

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The application of equations of state require the knowledge of physicochemical properties of components such as critical pressure and temperature, acentric factor, etc. [[37](#_ENREF_37)], however, as frequently, there are insufficient data for critical properties of polymers [[48-50](#_ENREF_48)], one should estimate these data using some appropriate group contribution methods (GCM) such as Constantinou and Gani group contribution method [[39](#_ENREF_39)].

As shown in Eq. 6, for calculation of chemical potential (and then mutual binary diffusion coefficient), it’s also possible to use the activity coefficient models such as Nonrandom Two Liquids model (NRTL) [[38](#_ENREF_38)], Universal Quasi-Chemical theory (UNIQUAC) [[38](#_ENREF_38)], Flory-Huggins [[51](#_ENREF_51)], and Compressible Regular Solution theory (CRS) [[52](#_ENREF_52)]. Models such as Nonrandom Two Liquids model (NRTL) and Universal Quasi-Chemical theory (UNIQUAC) [[37](#_ENREF_37),[38](#_ENREF_38)] are empirical models that require the adjustment (fitting) of some interaction parameters to available data [[53](#_ENREF_53),[38](#_ENREF_38),[54-56](#_ENREF_54)]. While these chemical thermodynamic models provide a correlative approach (as they need some data to be trained to prior to the prediction), a predictive model would result in a straightforward calculation and is of most interest.

The Compressible Regular Solution theory (CRS) [[52](#_ENREF_52),[57](#_ENREF_57),[58](#_ENREF_58)] (presented by Eqs. 15-17) requires no interaction parameter determination and only the pure component properties are needed which can be obtained by group contribution methods.

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This model provides a straightforward calculation toward activity coefficients and thermodynamic properties with desirable accuracy (errors lower than 0.1% found in literatures) [[49](#_ENREF_49),[52](#_ENREF_52),[59](#_ENREF_59),[58](#_ENREF_58),[60](#_ENREF_60),[61](#_ENREF_61)]. In this model, the solubility parameter values at temperature  requires the estimation of the solubility parameter at 298 K through group contribution methods such as widely used group contribution method of Hoftyzer and van Krevelen [[40](#_ENREF_40)]. The reduced density (hard-core density) can be calculated from the modified Sanchez-Lacombe Lattice Fluid model (SL-LF) [[62](#_ENREF_62),[53](#_ENREF_53)] using an iterative root seeking technique and the Constantinou and Gani group contribution method modified by Boudouris et al. [[63](#_ENREF_63)]. In addition, the coefficient of thermal expansion for each component can be calculated through the modified Sanchez-Lacombe Lattice Fluid model (SL-LF) [[63](#_ENREF_63)] and the relationship . For calculation of, one might useequality [[63](#_ENREF_63)], where  is the molecular weight of components (for polymer the repeating unit).

The derivative of chemical potential (), as presented in Eq. 1, has been calculated analytically by many researchers [[16-21](#_ENREF_16)]. However, we calculated this derivation numerically (See appendix A) as the relationship for chemical potential has been readily provided through Eqs. 6-7 in an explicit form, so investigation of the effect of different chemical thermodynamic models in a systematic way can be possible.

1. Polymeric solutions studied

The collected binary polymeric systems from literatures are Cyclohexane/Poly isobutylene, n-Pentane/Poly isobutylene, Toluene/Poly isobutylene and Chloroform/Poly isobutylene [[64](#_ENREF_64)], for which the free volume parameters defined in Eqs. 1-4 are already available. The details of selected systems are summarized in **Table 1**. In order to evaluate the mutual diffusion coefficients, the activity coefficients model of CRS has been considered together with the free volume theory here as discussed above. For future researches, the implementation of other chemical thermodynamic models would simply be carried out.

**Table 1.** Details of free volume parameters for selected systems [[64](#_ENREF_64)]

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| components | () | () | () | () | () | () | () |  | () |
| Cyclohexane  +  Poly isobutylene | 1.04×10-3 | 3.02×10-3 | 3.16×10-4 | -157.81 | -117.93 | 1.008 | 1.005 | 0.44 | 2630 |
| n-Pentane  +  Poly isobutylene | 7.32 | 2.41×10-3 | 3.16×10-4 | -38.39 | -117.93 | 1.158 | 1.005 | 0.43 | 9950 |
| Toluene  +  Poly isobutylene | 1.42×10-3 | 2.20×10-4 | 3.16×10-4 | -102.72 | -117.93 | 0.917 | 1.005 | 0.53 | 1070 |
| Chloroform  +  Poly isobutylene | 9.02×10-3 | 7.12×10-4 | 3.16×10-4 | -29.43 | -117.93 | 0.510 | 1.005 | 0.35 | 3780 |

1. Result and discussion

The required properties of the pure component of considered systems in CRS model, i.e. solubility parameter, coefficient of thermal expansion and hard-core density were determined using the Hoftyzer and van Krevelen group contribution method modified Sanchez-Lacombe Lattice Fluid model and Constantinou and Gani group contribution method modified by Boudouris et al. respectively. The mutual binary diffusion coefficients of considered polymer/solvent simply were calculated noting that in Appendix A,  and correspond to the chemical potential of solvent () and mass fraction of solvent () respectively. The correlation results of CRS implementation for mutual diffusion coefficients of considered systems compared with Experimental data are illustrated in **Figure 1**-**Figure 4**.

The predication capability of CRS theory for mutual coefficients of considered binary solutions is demonstrated and the agreement between calculated data and the experimentally collected data is desirable. The application of CRS theory together with the proposed algorithm provides a predictive method of mutual diffusion coefficients calculation. The algorithm presnted here is sufficiently reliable as no considerable error propagation in approximating of mutual diffusion coefficients (or more precisely, in chemical potential derivative) has been observed. It is essential to note that it’s possible to evaluate any chemical thermodynamic model of interest such as activity coefficients models and/or fugacity coefficients, for each, the methods of implementation have been provided.

**Figure 1.** The Experimental data and CRS implementation in new computational algorithm correlations for Cyclohexane/Poly isobutylene mutual diffusion coefficients

**Figure 2.** The Experimental data and CRS implementation in new computational algorithm correlations for Toluene/Poly isobutylene mutual diffusion coefficients

**Figure 3.** The Experimental data and CRS implementation in new computational algorithm correlations for n-Pentane/Poly isobutylene mutual diffusion coefficients

**Figure 4.** The Experimental data and CRS implementation in new computational algorithm correlations for Chloroform/Poly isobutylene mutual diffusion coefficients

1. Conclusion

In this paper, reviewing free volume theory, binary mutual diffusion coefficients in four polymer/solvent systems have been focused to be studied where first straightforward algorithm was presented for implementation of both activity coefficients and fugacity coefficients models. It’s possible to evaluate any chemical thermodynamic model of interest for diffusion coefficient calculations. The activity coefficients model of CRS has been considered here as a predictive model for binary polymeric solutions of Cyclohexane/Poly isobutylene, n-Pentane/Poly isobutylene, Toluene/Poly isobutylene and Chloroform/Poly isobutylene. The agreement between calculated data and the experimentally collected data was desirable and no considerable error propagation in approximating of mutual diffusion coefficients has been observed.

**Appendix A**

The first derivative () of a given function () can be calculated at each point of interest () using the central difference approximation [[65](#_ENREF_65)]. However, to improve calculations accuracy and compensate the error of truncations, it is more precise to use a coupled central difference approximation formula of high and low accuracy as presented in Eq. 18 [[65](#_ENREF_65)], where and are two-step sizes around the point of interest i.e.. It has been believed that this type of formulation approaches us as close as possible to the real value of derivative at the point of interest () [[65](#_ENREF_65)]. Therefore, using the explicit relationships of chemical potential and all aforementioned details of studied models (and any model of interest) and Eq. 18, one could readily calculate the property of interest and establish a standalone computer routine for any future investigation.

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