**Correlation of sorption-induced swelling in polymeric films with reference to attenuated total reflectance Fourier-transform infrared spectroscopy data**

Abstract

The state of the art experimental method for measurement of polymeric film swelling is the Attenuated Total Reflectance Fourier-Transform Infrared spectroscopy (FTIR-ATR). However, the costs associated to the experimental data and set-up preparation still show the need of model development to reduce such costs. Therefore, here a model is developed for prediction of swelling behavior and data of three polymeric films and the model predictions are compared and correlated to the experimental data. For evaluation of model performance and calculations, the experimental data of dilation of polycarbonate, poly (vinyl acetate), and poly (ether urethane) induced by acetonitrile vapor sorption at 40 °C were collected. Desirable agreement was found between model calculated data and the experimental data with an averaged *R2* value of 0.95. The developed model provides a simple, straightforward, computationally feasible and easy to use method for accurate estimation of swelling data.

Keywords: Sorption; Swelling; Polymers; FTIR-ATR; Modeling; Correlation

# Introduction

Attenuated Total Reflectance Fourier-Transform Infrared (FTIR-ATR) is the state of the art method that is been used in measurement of polymeric film swelling. As a result of polymer swelling during penetrant penetration, a reduction in the local concentration of polymer chains would be observed that itself results in a decrease in the number of local polymer functional groups that can absorb IR radiation [[1](#_ENREF_1)].

A linear relationship can be assumed between the dilution of the IR absorbance of a polymer peak and the polymer dilation as given in Eq. 1 [[2](#_ENREF_2), [3](#_ENREF_3)].

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|  | 1 |

Here,  and denotes the changes in IR absorbance and sample volume, respectively.  and denotes IR absorbance and volume of pure polymer.

Eq. 1 requires that the changes in the polymer functional group are relatively minor and sample is taken as nonconstrained and may swell in any orientation. A more realistic case which has much more adherence to the physical procedure applied in FTIR-ATR spectroscopy, however, must be developed noting that the polymeric films in FTIR-ATR analysis are constrained from swelling in-plane (as attached to the ATR crystal) and only out-of-plane swelling occurs. Therefore, Eq. 1 would be modified as given in Eq. 2 [[2](#_ENREF_2), [3](#_ENREF_3)]

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Here,  denotes the Poisson ratio of polymer which can be calculated from the relationship between bulk modulus (*B*) and Young’s modulus (*E*) as given by Eq. 3.

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The bulk modulus can be estimated using some group contribution methods [[4](#_ENREF_4)] given as in Eq. 4.

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Here, *U* is the Rao function or molar sound velocity function that can be calculated using group contribution methods [[4](#_ENREF_4)], and *V* is the molar volume per structural unit of polymer given as *V*=*Mw*/*ρp* where *Mw* is molecular weight and *ρp* is the density of repeating unit of polymer.

The Attenuated Total Reflectance Fourier-Transform Infrared spectroscopy data provide accurate estimates for the correlation of sorption-induced swelling in polymeric films. However, the cost associated to the experimental data and set-up preparation still show the need of model development to reduce such costs. Therefore, here a model is developed for prediction of swelling data of three polymeric films and the model predictions are compared and correlated to the experimental data measured by FTIR-ATR method as follows.

# Model of polymer swelling

Here, attempts were made to develop a reliable model for interpretation of volume changes upon contacting an arbitrary polymeric film to an arbitrary penetrant as the FTIR-ATR data are related and correlated with these changes. For this purpose, fundamental chemical thermodynamic theories were used. Specifically, the concept of fractional changes in volume upon mixing () was used [[5](#_ENREF_5)] which is given as in Eq. 5, where *V0* is the total volume of initially used polymeric film at *T* and *P*.

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As seen in Eq. 5, the fractional change in volume upon mixing requires the application of a free energy expression (Gibbs free energy ()) [[6](#_ENREF_6)]. Thus, a reliable and consistence chemical thermodynamic theory must be utilized. In this work, a compressible regular solution free energy model developed by Ruzette and Mayes [[5](#_ENREF_5), [7](#_ENREF_7)] was used as given by Eq. 6.

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The parameters and terms in Eq. 6 are as follows. indicates the volume fraction of component “”, is the reduced density (hard-core density) that can be obtained using the Sanchez-Lacombe equation of state (SL-EOS) [[4](#_ENREF_4), [8-12](#_ENREF_8)] given by . In SL-EOS, the parameters ,,  and  are reduced pressure, temperature, density and volume defined as ,  and . Here, ,  and  are characteristic pressure, temperature and density developed for modified (SL-EOS) [[9](#_ENREF_9)] that can be obtained using the group contribution method of Constantinou and Gani [[10](#_ENREF_10), [13](#_ENREF_13)].is number of segments present in hard-core volume of  that can be obtained using equality [[8](#_ENREF_8)].  is the hard-core solubility parameter at reference temperature of 298 K that can be obtained using the Hoftyzer and van Krevelen group contribution method [[14](#_ENREF_14)] and the method of Ref. [[15](#_ENREF_15)], *k* is the Boltzmann constant. Subscript *s* and *p* indicates the sorped penetrant and polymer respectively.

The fractional change in volume, then, can be determined by doing differentiation as given by Eq. 7 [[5](#_ENREF_5), [6](#_ENREF_6)].

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here, is the isothermal compressibility factor which can be obtained by using in which  can be obtained from the modified Sanchez-Lacombe equation of state (SL-EOS) [[4](#_ENREF_4), [8-12](#_ENREF_8)]. Also, .

Eq. 7 relates the temporal volume fraction of penetrant within the polymeric film to the changes in film volume. Therefore, Eq. 7 needs that values of  be calculated which itself is a function of penetrant penetration depths. For ease of calculations, with regards to the small thickness of polymeric films, one might assume that the volume fraction is equal to its equilibrium volume fraction at the interface of polymeric film and feed stream (), therefore, values of  can be calculated using a suitable solubility model.

The solubility model used in this work was obtained from Ref. [[16](#_ENREF_16)] as given in Eq. 8.

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Here  and are given as follows [[16](#_ENREF_16)] in which *p* denotes pressure.

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Therefore, calculation of swelling can be made easily using model equations. The calculated data should be compared to relevant experimental data for validation of results. A detailed step-by-step application of developed method follows.

1. Select the penetrant of interest (acetonitrile vapor here) and the polymeric material considered,
2. Determine the chemical structure of penetrant and polymer repeating unit selected in # ‎1,
3. Calculate lattice fluid parameters using group contribution method of Constantinou and Gani [[13](#_ENREF_13)] utilizing the chemical structure of # ‎2,
4. Calculate solubility parameters at reference temperature (298 K) using van Krevelen group contribution method [[4](#_ENREF_4)] utilizing the chemical structure of # ‎2,
5. Calculate reduced hard core densities of penetrant and polymer by inserting lattice fluid parameters of # ‎3 in the SL-EOS [[11](#_ENREF_11), [17](#_ENREF_17)] and solving it using an iterative root seeking method,
6. Calculate solubility parameters at operating temperatures using data of # ‎5,
7. Calculate as ,
8. Calculate the penetrant content () within the polymer film at the given condition using solubility model,

# Data for model validation

For evaluation of model performance and calculations, the experimental data of dilation of polycarbonate (PC), poly (vinyl acetate) (PVAc), and poly (ether urethane) (PEUT), induced by acetonitrile vapor sorption at 40 °C were collected from Ref. [[2](#_ENREF_2)]. The chemical structures of considered compounds are illustrated in Fig. 1.

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| Fig. 1. Chemical structure of considered polymers [[2](#_ENREF_2)] |

The characteristic parameters of considered systems are listed in Table 1.

Table 1. Characteristic parameters of considered systems [[2](#_ENREF_2), [18](#_ENREF_18)]

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| --- | --- | --- | --- |
| Compounds | (K) | (MPa) | (g/cm3) |
| PC  [[2](#_ENREF_2)] | 534 | 755 | 1.275 |
| PVAc  [[2](#_ENREF_2)] | 510 | 592 | 1.284 |
| PEUT  [[2](#_ENREF_2)] | 450 | 550 | 1.132 |
| CH3CN [[2](#_ENREF_2)] | 910 | 505 | 0.855 |

As the data of Ref. [[2](#_ENREF_2)] are illustrated in terms of ratio of applied pressures and vapor pressure, for calculation of vapor pressure of acetonitrile, the Antoine equation was used as given in Eq. 11 where  denotes the temperature in Celsius degree and vapor pressure is in *kPa*.

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The constants *A*-*C* were retrieved from Ref. [[19](#_ENREF_19)] as listed in Table 2.

Table 2. Constants of Antoine equation for acetonitrile

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| --- | --- | --- | --- |
| **Constant** | ***A*** | ***B*** | ***C*** |
| **Value** | 14.8950 | 3413.10 | 250.523 |

The calculations were done by using the developed model and the results are compared to the experimental data in the following section.

# Results and discussion

The calculations were done by using the developed model and the results are compared to the experimental data. In Fig. 2, the correlation results of model calculation (solid lines) and experimental data collected from Ref. [[2](#_ENREF_2)] for the sorption of acetonitrile in polycarbonate (PC) at 40 °C are shown. Based on the results, significant accuracy and agreement between calculated and experimental data was achieved demonstrating the reliability of developed model.

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| ***a*** |
| ***b*** |
| Fig. 2. The correlation results of model calculation (solid lines) and experimental data collected from Ref. [[2](#_ENREF_2)] (open circles): (*a*) sorption isotherm of acetonitrile in polycarbonate (PC) at 40 °C; (*b*) swelling data induced by sorption of acetonitrile in polycarbonate (PC) at 40 °C |

In Fig. 3, the correlation results of model calculation (solid lines) and experimental data collected from Ref. [[2](#_ENREF_2)] for the sorption of acetonitrile in poly (vinyl acetate) (PVAc) at 40 °C are shown. Based on the results, significant accuracy and agreement between calculated and experimental data was achieved demonstrating the reliability of developed model.

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| ***a*** |
| ***b*** |
| Fig. 3. The correlation results of model calculation (solid lines) and experimental data collected from Ref. [[2](#_ENREF_2)] (open circles): (*a*) sorption isotherm of acetonitrile in poly (vinyl acetate) (PVAc) at 40 °C; (*b*) swelling data induced by sorption of acetonitrile in poly (vinyl acetate) (PVAc) at 40 °C |

In Fig. 4, the correlation results of model calculation (solid lines) and experimental data collected from Ref. [[2](#_ENREF_2)] for the sorption of acetonitrile in poly (ether urethane) (PEUT) at 40 °C are shown. Based on the results, significant accuracy and agreement between calculated and experimental data was achieved demonstrating the reliability of developed model.

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| ***a*** |
| ***b*** |
| Fig. 4. The correlation results of model calculation (solid lines) and experimental data collected from Ref. [[2](#_ENREF_2)] (open circles): (*a*) sorption isotherm of acetonitrile in poly (ether urethane) (PEUT) at 40 °C; (*b*) swelling data induced by sorption of acetonitrile in poly (ether urethane) (PEUT) at 40 °C |

The correlation performance of developed model for all three benchmark systems was desirable and significant agreement was revealed. The base Gibbs free energy thermodynamic model has shown great accuracy and reliability in description of polymeric solutions and mixtures thermodynamic behavior in various reports [[20](#_ENREF_20), [21](#_ENREF_21)], thus using this model in the development of our model was a good and consistent choice.

The physical chemical basis of model originates in the fractional change in volume, the modified Sanchez-Lacombe equation of state and the compressible regular solution free energy model of Ruzette and Mayes which are shown to be consistent and reliable in description of polymeric mixtures and solutions behavior in various works [[6](#_ENREF_6), [8](#_ENREF_8), [20](#_ENREF_20), [22-26](#_ENREF_22)].

The approved theoretical basis, simplicity of equations application and use, straightforward and predictive procedure, desirable agreement and accurate calculations, all demonstrate the suitability of developed model for further applications. Its accuracy shows the potential of model for prior estimation of swelling data right before the experimental measurement for possible cost reduction.

# Conclusion

For estimation of swelling behavior of sorbent induced swelling in polymeric films, here, a theoretical model was developed and examine using a number of experimental data of dilation of polycarbonate, poly (vinyl acetate), and poly (ether urethane) induced by acetonitrile vapor sorption at 40 °C. The collected data measured by using the state of the art experimental method of polymeric film swelling measurements i.e. the Attenuated Total Reflectance Fourier-Transform Infrared spectroscopy were used. Desirable agreement was found between model calculated data and the experimental data. The developed model provides a simple and straightforward method for accurate estimation of swelling data which is computationally feasible and easy to use. The approved theoretical basis, simplicity of equations application and use, straightforward and predictive procedure, desirable agreement and accurate calculations, all demonstrate the suitability of developed model for further applications.

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