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Solvent Diffusion Modeling in Silicone

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ABSTRACT: The diffusion of solvents into a polymer matrix is critical in various applications, such as medicine and electronic coatings. Previously, one-dimensional modeling of solvent diffusion in a highly cross-linked epoxy resin was successfully established by using the PC-SAFT approach. This study extends the approach to consider all spatial dimensions for silicone to validate the applicability of the model to different polymers. As a result, it is now possible to take all geometric aspects into account when modeling solvent uptake using an equation of state. The extended model shows improved correlations between experimental data and swelling curves compared to those of the established one-dimensional model. In addition, the Maxwell-Stefan diffusion coefficient was found to be highly susceptible to overestimation when only one dimension is considered. The temperature dependence of the diffusion coefficient was taken into account, and for the first time, the drying of a polymer sample was modeled from the swelling results using the developed model.



1. INTRODUCTION

The diffusion of solvents in polymers plays a crucial role in everyday life. On the one hand, the polymers should absorb the solvent to capture it, such as water in hydrogels,¹ or for drug delivery formulations. On the other hand, the polymer should act as a barrier to the diffusion of solvents, as in the case of polymers used as coatings.² In recent years, the focus of polymer diffusion research has been on the analysis of solvent uptake in strongly swelling polymer networks.^{3,4} However, the diffusion of solvents through the polymer barriers also plays a key role, e.g., in the case of coatings for electronics, where the diffusion through the coating material significantly impacts the lifecycle of electronic devices.⁵ As coating materials for electronics, two key features must be fulfilled, namely environmental protection and electrical isolation.⁶ The most commonly used polymers for encapsulation of electronics are epoxy resins, polyurethane, phenolic resins, and silicon. Multiple properties of the polymer play a role here such as filler, polymer type, cross-linking, microscopic damage, and the type of solvent.' In principle there are two methods of measuring the solvent uptake in the polymer networks, the gravimetric method and spectroscopic methods.⁸ Gravimetric methods provide solvent uptake of the entire sample, whereas spectrometric methods can resolve the uptake within the sample. While experimental data on the diffusion of polymers in coatings are scarce, there are many modeling-based works. The starting point for most modeling works on diffusion of solvents in polymer networks is Fickian diffusion or Langmuirlike approaches.⁹ However, these models require knowledge of the equilibrium sorption from either experimental data or

thermodynamic models. The challenge in the thermodynamic description of polymer-solvent systems lies in the size differences of the molecules. The first approach to the thermodynamic description of these systems was developed independently by Flory and Huggins.^{10'} Holes still need to be introduced into this approach to account for compressible fluids, such as in the Sanchez–Lacombe equation of state.¹¹ However, it is not possible to consider associating substances such as water in the classical Flory-Huggins theory. A way to take this into account is offered by the Statistical Association Fluid-Theory (SAFT) equations of state (EOS).¹² A representative of the SAFT-EOS is the Perturbed Chain (PC)-SAFT EOS, which was developed by Gross and Sadowski.¹³ All the above approaches consider the polymers as free chains, but in polymer networks, they are cross-linked. Due to the cross-linking of the chains, elastic forces arise during solvent absorption, which counteract the absorption. One approach to take this into account is the affine network theory developed by Flory and Rehner¹⁴, which considers the Gaussian stretching of the network and assumes fixed crosslinking points in the polymer network. This forms the basis for further developments such as by Miao et al.¹⁵ who considered a non-Gaussian behavior of the network. In addition, the

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phantom network approach was developed by James and Guth,¹⁶ which assumes that the cross-links in the network are fluctuating. Both approaches, the affine network and the phantom network, have been used in combination with Gibbs excess energy models¹⁷⁻²⁰ or EOS^{21,22} to model hydrogel swelling. These approaches also formed the basis for a thermodynamic model to describe the solvent uptake of epoxy resins in liquid solvent environments as well as from saturated water steam. For this purpose, the equilibrium model developed by Arndt and Sadowski²¹ was used to calculate swelling of the highly cross-linked epoxy resins used for electronic encapsulation in pure solvents and solvent mixtures.²³ In this way, the prediction of swelling could also be verified. In addition, the swelling in salt solutions of epoxy resins was investigated in ref 24. The developed thermodynamic model forms the basis for the investigation of mass transfer and also offers the possibility of taking into account the various interactions between the polymer and the solvent. This can be achieved by a Maxwell-Stefan approach.²⁵ Here, the gradient of the chemical potential is considered as the driving force for the mass transfer. However, the influence of the polymer chains must also be considered in describing diffusion. Thereby, the viscoelasticity of the polymer chains below the glass transition temperature plays an important role, since the polymer chains are less mobile in the glassy state.²⁶ This viscoelasticity leads to different non-Fickian solvent uptake behaviors of the polymer resins. For this reason, the mass transfer model developed by Krenn et al.²⁷ was combined with a Kelvin Voigt model.²⁸ This approach describes the elastic behavior during slow deformations but also includes resistances due to fast deformation. It can be represented by the parallel connection of a spring and a viscous damper. By the combination with a thermal diffusion model describing the temperature dependence of the driving force, it can also determine the influence of electrical components acting as heat source and describe the potential of energy harvesting in electrical components.²⁹ Additionally, Borrmann et al.³⁰ described the water sorption in polymer networks, particularly for drug delivery systems using this approach.

Until now, this model has only been tested for epoxy resins, and diffusion has only been considered in one dimension. The modeling in three dimensions is important to describe the diffusion behavior properly.³¹ Therefore, we will analyze the applicability of the developed model to silicone and determine the influence of the considered spatial dimensions on the diffusion behavior. Furthermore, we want to shed some light on the drying of the polymer resin. Predicting the drying behavior in addition to the solvent uptake is imperative for analyzing the lifecycle for coating and encapsulation applications in the medical or automotive sector. In these applications, sensitive electronic and mechanical components are expected to undergo multiple swelling and drying cycles. For instance, steam-pressure sterilization of surgical equipment, such as medical drills, necessitates such cycles. Therefore, these components could greatly benefit from accurate predictions for drying procedures between uses.

2. THEORY

2.1. Phase Equilibrium. The thermodynamic basis of the mass transfer investigations is the PC-SAFT EOS.¹³ PC-SAFT delivers an expression for the Helmholtz energy of a system with different components:

$$a_{\rm res} = a_{\rm hc} + a_{\rm disp} + a_{\rm assoc} + a_{\rm elastic} \tag{1}$$

where $a_{\rm hc}$ considers the formation of a chain of hard spheres, $a_{\rm disp}$ is the disperse van der Waals contribution, and $a_{\rm assoc}$ considers the formation of hydrogen bonding in the system. The Helmholtz energy (1) without the elastic term ($a_{\rm elastic}$) considers the polymer chains as free chains without any cross-linking.

For nonassociating and non-cross-linked compounds, the residual Helmholtz free energy consists only of $a_{\rm hc}$ and $a_{\rm disp}$, utilizing a modified square-well potential. Here, $a_{\rm hc}$ accounts for repulsive forces between molecules in relation to the molecular volume, while $a_{\rm disp}$ represents attractive forces between molecules. Both terms are well described by Gross and Sadowski in their initial introduction of the PC-SAFT theory:³³

$$a_{\rm hc} = \bar{m}a_{\rm hs} - \sum_{i} x_i(m_i - 1) \ln g_{ii}^{\rm hs}(\sigma_{ii})$$

$$a_{\rm disp} = -2\pi\rho I_1(\eta, \bar{m}) \overline{m^2 \epsilon \sigma^3} - \pi\rho \bar{m} C_1 I_2(\eta, \bar{m}) \overline{m^2 \epsilon^2 \sigma^3}$$
(3)

In these equations, m_i denotes the segment number, and x_i represents the mole fraction of component *i*. Additionally, \overline{m} is the mean segment number in the system, ρ indicates the total number density of molecules in the mixture, ϵ signifies the depth of the pair potential, and ρ is the segment diameter. The free energy of the hard sphere $a_{\rm hs}$ and the radial pair distribution function of the hard sphere segments $g_{ii}^{\rm hs}(\sigma_{ii})$ are calculated using the approach as suggested by Boublik³² and Monsoori et al.³³ $I_1(\eta, \overline{m})$, $I_2(\eta, \overline{m})$ and C_1 are correlations provided by Gross and Sadowski,¹³ where η represents the packing fraction and σ_{ii} is the segment diameter of component *i*.

Attractive forces between molecules induced by functional groups are considered by the association contribution term a_{assoc} . This enables the proper modeling of attractive forces between specific association sites. In this work, a_{assoc} is described by Wertheim's theory,³⁴ as suggested by Gross and Sadowski:³⁶

$$a_{\text{assoc}} = \sum_{i} x_{i} \sum_{A_{i}} \ln(X^{A_{i}}) - \frac{X^{A_{i}}}{2} + \frac{1}{2}$$
(4)

$$X^{A_i} = \left(1 + \rho \sum_j x_j \sum_{B_j} X^{B_j} \Delta^{A_i B_j}\right)^{-1}$$
(5)

Here, X^{A_i} represents the fraction of nonbonded association sites of type A on component i, and $\Delta^{A_i B_j}$ is the bonding strength between association sites of type A and type B. In this context, the association scheme defines both the numbers of association sites of each molecule and the utilization of each $\Delta^{A_i B_i}$. Here, only the 2B scheme was used, which considers two equivalent association sides per molecule containing one electron acceptor and one electron donor site.³⁵ This scheme has already been well-established for the used solvents water and isopropanol and had also been employed in similar works,^{24,27,29} considering the swelling of polymers with these solvents. Additionally, silicone possesses no association sites; therefore, only the calculation of the self-association of the solvent was required.

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| general parameters | | | | | |
|------------------------------|----------|---------------------|---------------------------|-----------------------|---------------------------|
| | silicone | water | isopropanol | heptane | cyclohexane |
| M [g/mol] | 600.0 | 18.015 | 60.096 | 100.203 | 84.147 |
| | | PC-SAFT parameters | and network parameters | | |
| | silicone | water ²⁷ | isopropanol ²⁷ | heptane ³⁷ | cyclohexane ³³ |
| σ [Å] | 4.83816 | 3.0007 | 3.2085 | 3.8049 | 3.8499 |
| $\varepsilon/k_{\rm B}$ [K] | 355.71 | 366.51 | 208.42 | 238.40 | 278.11 |
| m [-] | 7.5991 | 1.0656 | 3.0929 | 3.4831 | 2.5303 |
| ε^{AB}/k_{B} [K] | | 2500.7 | 2253.9 | | |
| κ ^{AB} [-] | | 0.034868 | 0.024675 | | |
| assoc.mod. [-] | | 2B | 2B | | |
| ϕ [-] | 3.7497 | | | | |
| α_{\max} [-] | 3.7579 | | | | |

Table 1. Physical Data, Network Parameters, and PC-SAFT Parameters Determined and/or Used in This Work

By the introduction of cross-linking in the polymer network, the elastic forces influence the equilibrium and, therefore, are considered as follows:

$$a_{\text{elastic}} = x_{\text{pol}} \cdot \frac{\phi - 2}{\phi} \cdot \left[\frac{3}{2} \frac{\left(\frac{\nu_{\text{polymer}}}{\nu_0}\right)^{2/3} - 1}{1 - \left(\frac{1}{\alpha_{\text{max}}} \frac{\nu_{\text{polymer}}}{\nu_0}\right)^{2/3}} - \ln\left(\frac{\nu_{\text{polymer}}}{\nu_0}\right) \right]$$
(6)

The expression for the elastic contribution (6) was suggested by Miao et al.¹⁵ Here, X_{pol} represents the mole fraction of the cross-linked polymer, ϕ signifies the network functionality, while $v_{polymer}$ and v_0 represent the volume of the polymer and solvent mixture in the actual state and in the dry state (0), respectively. Moreover, α_{max} is the maximum swollen volume in relation to the dry state.

For the application of the PC-SAFT EOS, the model parameters must be determined. For nonpolar molecules, these parameters are the chain length m, the temperatureindependent diameter of a hard sphere σ , and the disperse energy ε . By considering polar molecules, also the association term has to be included and parametrized by the association volume κ_{AB} and the association energy ε_{AB} . Furthermore, the association scheme must be determined in advance. As in this work only hydroxy groups are present, the 2B association scheme³⁶ is applied with one association site on the hydrogen and one on the oxygen. For solvents, the pure solvent parameters are fitted to the vapor pressure and liquid density. The challenge hereby is the determination of the PC-SAFT parameter for the polymers, as they have no vapor pressure. Therefore, these parameters are fitted to the experimental swelling data of the respective polymer in various solvents. To describe the binary system, an additional binary parameter k_{ii} is used describing the deviation from the geometric mixing rule for the disperse energy of unlike segments ϵ_{ii} :

$$k_{ij} = k_{ij}^{a} + k_{ij}^{b} \frac{1}{T[K]} + k_{ij}^{c} \frac{1}{(T[K])^{2}}$$
⁽⁷⁾

The temperature dependence of the binary interaction parameter is fitted to experimental data. The suggested approach was also applied by Krenn et al. in previous works.^{23,24,29} The PC-SAFT parameters for the materials used in this work can be found in Table 1 and Table 2.

2.2. Diffusion. PC-SAFT delivers an expression of the chemical potential. This chemical potential can be utilized as the driving force in a Maxwell-Stefan approach²⁷ for calculating the mass transfer within the polymer network. In previous

 Table 2. Binary Interaction Parameters Determined in This

 Work

| component i | component j | k^a_{ij} [-] | k_{ij}^{b} [K] | k_{ij}^{c} [K] |
|-------------|-------------|----------------|------------------|------------------|
| water | silicone | 0.67713 | -210.712 | 0 |
| isopropanol | silicone | -0.2569 | 207.75 | -33543 |
| heptane | silicone | 0.069580 | -48.899 | 0 |
| cyclohexane | silicone | -0.42327 | 104.74 | 0 |

works^{23,24,29} the Maxwell-Stefan approach was combined with a viscoelastic model, because the mass transfer changes below the glass transition temperature due to the elasticity of the polymer chains.³⁸ However, in the case of mass transfer in silicon, this is not necessary, as the investigated temperatures are above the glass transition temperature. Given that the polymer's molar flow is considered to be 0, the change in solvent concentration can be calculated as follows:²⁷

$$\frac{\partial c_{\text{solv}}}{\partial t} = \nabla \left(c_{\text{mix}} D_{\text{MS}} \frac{x_{\text{solv}}}{(1 - x_{\text{solv}})RT} \nabla \mu_{\text{solv}} \right)$$
(8)

where μ_{solv} is the chemical potential of the solvent in the network and $c_{solv/mix}$ is the concentration of the solvent (solv) or of the mixture (mix). D_{MS} is the Maxwell-Stefan diffusion coefficient, and its temperature dependence is considered via a classical Arrhenius approach as follows:

$$D_{\rm MS} = D_{\rm MS,\infty} \ e^{-E_{\rm A,D}/(RT)} \tag{9}$$

2.3. Numerical Approach. To discretize the time step of the Maxwell-Stefan equation, an explicit Euler scheme was applied. In this process, the spatial cuboid domain was discretized according to eqs 10-13,³⁹ where the indices *i*, *j*, and *k* represent each coordinate in the 3-dimensional space. It was assumed that the grid length Δz remained constant throughout the swelling process and is the same in all directions. The molar concentration is equivalent to the molar density and is calculated along with the chemical potential. In the case of 2D calculations, the terms $N_{i,j,k+0.5}$ and $N_{i,j,k-0.5}$ are set to 0. The 1D case is treated similarly, by also setting the terms $N_{i,j+0.5,k}$ and $N_{i,j-0.5,k}$ to 0.

$$\frac{\partial c_{\text{solv}}}{\partial t} = \frac{1}{\Delta z} (N_{i+0.5,j,k} - N_{i-0.5,j,k} + N_{i,j+0.5,k} - N_{i,j-0.5,k} + N_{i,j,k+0.5} - N_{i,j,k-0.5})$$
(10)

$$N_{i+0.5,j,k} = (c_{\text{mix}})_{i+0.5,j,z} \frac{(\mathbf{x}_{\text{solv}})_{i+0.5,j,k}}{(1 - (\mathbf{x}_{\text{solv}})_{i+0.5,j,k})RT} \\ \left[\frac{(\mu_{\text{solv}})_{i,j,k} - (\mu_{\text{solv}})_{i+1,j,k}}{\Delta z}\right]$$
(11)

$$(\mathbf{x}_{\text{solv}})_{i+0.5,j,z} = \frac{((\mathbf{x}_{\text{solv}})_{i+1,j,k} + (\mathbf{x}_{\text{solv}})_{i,j,k})}{2}$$
(12)

$$(c_{\min})_{i+0.5,j,z} = \frac{((c_{\min})_{i+1,j,k} + (c_{\min})_{i,j,k})}{2}$$
(13)

The time step (Δt) was adjusted according to the greatest change (u) per step in the grid, utilizing a Courant– Friedrichs–Lewy (CFL) condition as outlined in eq 14. The CFL number was set to 0.5 to ensure suitable accuracy and numerical stability.

$$CFL \ge \frac{u\Delta t}{\Delta z^2}$$
 (14)

2.4. Boundary Conditions. Concerning the boundary conditions, in the case of swelling, the solvent uptake in the outermost layer of cells is assumed to occur instantaneously. Hence, the equilibrium value for the solvent uptake is applied as a Dirichlet boundary condition. In the case of drying, evaporation is also considered to be instantaneous, meaning that the solvent concentration at the system boundary remains constantly zero throughout the calculation. The starting condition for a drying simulation involves a completely swollen polymer sample, i.e., with a uniform equilibrium solvent concentration x_{solv} across the whole sample, at room temperature.

3. EXPERIMENTAL METHODS

3.1. Materials. Details about the chemicals used are provided in Table 3, which includes information about the

Table 3. Chemicals Used in This Work

| chemical | CAS Reg. No. | supplier | purity (mass fraction) |
|-------------|--------------|-----------|------------------------|
| cyclohexane | 110-82-7 | Honeywell | 99.7% |
| heptane | 142-82-5 | Honeywell | 99.0% |
| isopropanol | 67-63-0 | Honeywell | 99.9% |

supplier and purity levels. All chemicals were employed as received without any additional purification steps. Deionized water was used for the swelling experiments in water.

3.2. Polymer Preparation. The investigated silicone was an addition cure specialty silicone coating produced by the CHT Group (Tübingen, Germany), in which the polymer was synthesized from two starting mixtures, mixed in a 1:1 mass ratio. To avoid bubbles in the final samples, the combined mixture was evacuated multiple times before polymerization was initiated by heating up to 105 °C for one hour. Afterward, the hardened polymer was removed from the mold and cut into flexible, transparent rectangular cuboids. To remove residual solvents from the starting material, the samples were dried at 105 °C for at least 2 weeks, until no further mass decrease was measurable.

3.3. Swelling Measurement. The swelling of the polymer samples was conducted gravimetrically by measuring the increase in mass over time using a Sartorius Secura 26-1CEU

microbalance with a linearity error of 0.01 mg. For this purpose, the polymer samples were immersed in a vessel containing the solvent of interest. During the weighing process, the samples were quickly removed from the vessel and dried with paper before being measured on the microbalance. Given that the polymer samples began to dry immediately upon removal from the solvent, each step of the measurement process must be executed as quickly as possible to increase accuracy. This measurement procedure was repeated until equilibrium was reached, which was indicated by the constant mass of the samples after the three measurements. Furthermore, an antistatic device was utilized to enhance the measurement accuracy by reducing electrostatic forces.

3.4. Drying Measurement. Drying was also measured gravimetrically by using the same microbalance for one sample. In the preparation, the polymer sample was swollen in 2-propanol at room temperature (25 $^{\circ}$ C), and the swelling equilibrium was established analogously to the swelling experiments. The drying experiment began when the sample was placed on the microbalance and its weight was then automatically measured every 60 s.

3.5. Density Measurement. The density of the polymer sample was determined by using the pycnometer method. This procedure involved measuring the weight of the sample, the empty pycnometer vessel, and the vessel filled with both a working fluid and the sample. Additionally, the volume of the vessel was obtained by weighing the working fluid, which had a known density determined using an Anton Paar SVM 3000 Stabinger viscometer. For the measurements, water was used as the working liquid for the dried polymer, while for each sample the same fluid was used as in the swelling experiments, respectively. The polymer's density was measured twice, each measurement requiring the polymer sample to be cut into small pieces. To eliminate any potential air bubbles, an ultrasonic bath was utilized.

4. RESULTS AND DISCUSSION

4.1. Swelling Equilibria. First, the silicone PC-SAFT parameters, reported in Table 1 and Table 2, were adjusted to the swelling equilibrium state of silicone in the different solvents. The model effectively represents the final solvent uptake at various temperatures, as demonstrated in Figure 1. At 20 °C, the model predicted a total uptake of 975.4 mg/g for heptane and 192.6 mg/g for isopropanol. The highest deviation between experimental and theoretical values was observed for heptane (3.8% higher) and isopropanol (3.6% lower). Water exhibited the lowest uptake compared to the other solvents due to its high polarity contrasting with the low polarity of silicone. The minimal water uptake slightly increased from 1.16 mg/g (calculated 1.01 mg/g) at 55 °C to 1.33 mg/g (calculated 1.28 mg/g) at 70 °C and further to 1.54 mg/g (calculated 1.50 mg/g) at 80 °C. The data are presented in the Supporting Information (Table S1). Hereby, it has to be stated that defects in the polymer network as well as polydispersity of silicon chains are not considered by the model, so the model parameters are polymer charge dependent. Due to the high experimental deviation caused by the low uptake, diffusion measurements were not conducted for water.

4.2. Density. Investigating the densities of the dried samples at room temperature, we found the experimental value to be 1014 kg/m³, while the calculated density was 1060 kg/m³, resulting in a deviation of 4.5%. The calculated density exhibited a decrease of 2.0% at 50 °C and 4.3% at 80 °C



Figure 1. Comparison of observed and predicted solvent uptake in silicone for water (red line), isopropanol (blue line), heptane (black line), and cyclohexane (green line) at ambient pressure. The lines represent the calculated uptake, and the symbols represent the measured solvent equilibrium, respectively.

relative to its room temperature value. The observed trend is consistent with the experimental density changes seen in long-chain polydimethylsiloxane, which decreased by 1.9% at 55 °C and 5.2% at 80 °C.⁴⁰

The experimental density of the swollen silicone in isopropanol was constantly decreasing with the higher uptake at higher temperatures: 960 kg/m³ at 50 °C, 942 kg/m³ at 65 °C, and 915 kg/m³ at 80 °C. The model was capable of calculating the densities of the swollen samples accurately with a slight underestimation of 1.9% at 50 °C, 2.7% at 65 °C, and 2.2% compared to the experimental values. The measured density of the swollen silicone in heptane was 853 kg/m³ at 50 °C, with a slightly larger overestimation by the model, at 6.2%. The decrease in the swollen sample was associated with a visible increase in the sample volume.

4.3. Diffusion. The calculated solvent uptake can be compared with the experimental results by analyzing the change in the total mass of the samples. To do this, the mass uptake is calculated for each grid point cell, and then, the arithmetic mean is computed across the entire sample. For all calculations, only the Maxwell-Stefan diffusion model is applied as the glass transition temperature is significantly lower than the investigated temperature range. This assumption is consistent with all measured swelling curves because there is no linear diffusion behavior visible in any experimental curve. In Figure 2, the swelling of a silicone sample calculated in 1D, 2D, and 3D is compared with experimental results at 80 °C. Since all polymer samples were cuboids, the diffusion time and behavior depend strongly on the length of each side. For the recalculation of dimensionless²³ diffusion to dimensional diffusion, each side must be considered. In the 1D case, it is always the shortest diameter because this is the minimum distance that a solvent needs to diffuse. The 2D case considers the two shortest diameters for the same reason, while in the 3D case, all diameters are considered. In this regard, it is important that the relationship between all of the sides in the dimensionless calculations is the same as that of the measured samples. For the sake of comparability, the lengths of the dimensions (x = 20 mm, y =20 mm, and z = 8.5 mm) were chosen based on the mean values of each side for the investigated polymer samples. Computationally, the smallest diameter of the samples was set to 50 grid points, and the other diameter was set to 124 grid points during the 1D, 2D, and 3D calculations.

The Maxwell-Stefan diffusion coefficients were adjusted to achieve the best correlation between the experimental and calculated swelling curves at each dimension, respectively. The 3D calculated swelling curve is the closest to the measured swelling curve, while the 1D curve is the farthest. However, the experimental behavior can still be sufficiently described in all dimensions. The experimental diffusion is better represented by taking more geometric aspects into account. For example, the mass increment on the surface at the polymer edge at the beginning is much higher than that at a surface grid point somewhere in the middle. Therefore, the solvent uptake at the edges is significantly faster than that in the middle, which is



Figure 2. Comparing measured (\blacksquare) and calculated solvent uptake of silicone in heptane and isopropanol at 80 °C over time in 1D (red line), 2D (blue line), and 3D (green line).

also reflected in the calculated concentration profiles. This effect, for instance, is completely neglected in the 1D calculation.

Considering different dimensions greatly affected the calculation of diffusion coefficients in Table 4. Taking the

Table 4. Comparison of the Diffusion Coefficient at Different Dimensions at 80 $^{\circ}\mathrm{C}$

| dimension | heptane m ² /s | isopropanol m²/s |
|-----------|---------------------------|------------------------|
| 1D | 2.45×10^{-10} | 3.95×10^{-10} |
| 2D | 1.85×10^{-10} | 3.00×10^{-10} |
| 3D | 1.45×10^{-10} | 2.34×10^{-10} |

3D case as the best representation of diffusion, the dimensionally affected deviation differs by >28% and even more so in 1D by >69% for both heptane and isopropanol. The deviation did not differ much between both solvents, which indicates that the geometric effect is mostly solvent-independent, especially considering that both heptane and 2-propanol differ significantly in their polarity. Given that diffusion calculations are often kept one-dimensional for the sake of simplicity, the calculated diffusion coefficients are highly susceptible to being overestimated because the diffusion coefficient is higher at 1D and 2D than at 3D. In higher dimensions, a greater amount of solvent can be absorbed at once, requiring lower dimensions to compensate with faster diffusion speeds to achieve a similar uptake behavior. In this regard, modeling in 1D and 2D could also lead to results similar to those of 3D, which strongly depends on the geometry. For example, in polymer foils, the diffusion at the edge is negligible, resulting in almost 1D diffusion behavior. This also significantly reduces the calculation time. Even when using multithreading on 30 cores each operating at 2.10 GHz, 3D calculations still take a few days.

An important factor not currently considered is the volume change of the silicone sample. This is crucial when accounting for the remaining deviation between the 3D calculated and measured diffusion. During the swelling process, the volume of the sample expands due to the additional space required for the solvent within the polymer. This results in continuous pubs.acs.org/jced

expansion of the grid length at each grid point until equilibrium is reached. Consequently, the change in mass slightly decreases further due to the increased distance the solvent must diffuse. The implications of this are that since the coefficients were adjusted based on the lowest mean deviation between experimental data points and the modeled solvent uptake curve, the model tends to underestimate the solvent uptake at the beginning and overestimate it toward the end. Despite the higher-dimensional effects, the results still accurately represent the underlying principles, proving the concept's validity even without considering the volume change.

4.4. Temperature Dependency of the Diffusion **Coefficient.** The swelling of silicone at different temperatures is shown in Figure 3. The modeling was performed in 2D due to the lower computational time requirements compared to those in 3D. Interestingly, the diffusion speed of heptane was mostly temperature-independent in the sample, resulting in nearly identical diffusion curves. Indeed, the diffusion coefficients in heptane slightly increased, which is expected due to the higher thermal energy of the solvent molecules. However, the lower absorption capacity of heptane at higher temperatures suggests that with regard to the chemical potential heptane is less favorably absorbed, and this effect counteracts the faster diffusion, causing the measured swelling curves to be visibly overlapping within the investigated temperature range. In contrast, the diffusion of isopropanol was slower at all temperatures compared to heptane, which could be related to the lower uptake of isopropanol. However, the equilibrium uptake increases with temperature, and therefore, the mass increase for isopropanol is indeed higher from the beginning at higher temperatures.

Since the diffusion coefficients (Table 5) are temperaturedependent, the diffusion coefficients were expressed using a

| Table 5. Comparison of t | he Adjusted 2D-Diffusion |
|----------------------------|--------------------------|
| Coefficient at Different T | emperatures |

| temp °C | heptane m ² /s | isopropanol m²/s |
|---------|---------------------------|------------------------|
| 50 | 1.38×10^{-10} | 2.90×10^{-10} |
| 65 | 1.60×10^{-10} | 2.95×10^{-10} |
| 80 | 1.85×10^{-10} | 3.00×10^{-10} |



Figure 3. Comparing measured and calculated solvent uptake of silicone in heptane and isopropanol over time at 50 °C (blue line), 65 °C (red line), and 80 °C (green line) in 2D.

classic Arrhenius dependence as shown in eq (9). The defined diffusion parameters were set for heptane with $D_{\rm MS,\infty} = 4.334 \times 10^{-9} {\rm m}^2 \cdot {\rm s}^{-1}$ and $E_{\rm A,D} = 9266 J \cdot {\rm mol}^{-1}$, and for isopropanol with $D_{\rm MS,\infty} = 4.321 \times 10^{-10} {\rm m}^2 \cdot {\rm s}^{-1}$ and $E_{\rm A,D} = 1072 J \cdot {\rm mol}^{-1}$. The diffusion coefficients were fitted to achieve the best overlap with the experiments, respectively. Then, the Arrhenius parameters were determined using linear regression, yielding excellent coefficients of determination for both heptane ($R^2 = 0.9996$) and isopropanol ($R^2 = 0.9996$).

4.5. Drying. With a solid foundation for the description of solvent diffusion established, the goal is now to apply the same Maxwell-Stefan approach to describe the drying of polymers in all room dimensions. The diffusion constant of isopropanol at room temperature ($25 \,^{\circ}$ C) was calculated using the previously defined Arrhenius eq (9). Because the differences between the 1D, 2D, and 3D diffusion constants rely solely on geometric factors, it was reasonable to assume that the relationship between these constants at room temperature would be similar to that at 80 °C. With this assumption, the 1D and 3D diffusion coefficients were calculated from the 2D diffusion coefficient. The resulting diffusion curves were then compared to the experimental data shown in Figure 4.



Figure 4. Comparison of measured (\blacksquare), adjusted (—), and predicted (---) solvent evaporation from isopropanol-swollen silicone at room temperature (calc. 25 °C) over time represented in 1D (red line), 2D (blue line), and 3D (green line).

The differences in the shapes of the graphs between the 1D, 2D, and 3D approaches are as similar in Figure 4 as in Figure 2. Therefore, the geometric aspect in the drying process remains the same as that in the swelling process, as expected. The measured weight loss proceeded more slowly than the model's prediction; however, the model is still able to account for this by adjusting the diffusion coefficient, as shown in Table 6. In this regard, the diffusion coefficient during drying was 1.33 times lower than that during swelling. This factor was found to be consistent across all dimensions.

There are several plausible explanations to account for the difference between experiment and predicted diffusion behavior. The first is related to volume change, which behaves inversely during drying compared to swelling. During drying,

Table 6. Adjusted and Predicted Diffusion Coefficients for Drying

| dimension | predicted m^2/s | adjusted m^2/s |
|-----------|------------------------|------------------------|
| unnension | predicted in 75 | udjusted in 75 |
| 1D | 3.69×10^{-10} | 2.85×10^{-10} |
| 2D | 2.80×10^{-10} | 2.10×10^{-10} |
| 3D | 2.18×10^{-10} | 1.60×10^{-10} |
| | | |

the volume decreases, which in turn reduces the distance between each grid point. However, this effect alone is not enough to fully account for the deviation between the experimental results and the model since this effect was completely neglected before in swelling without noticeable deviations. Another explanation is the formation of small cracks and pores on the surface, which could influence the mass loss. As reported by Robinson et al.,⁴¹ the swelling process can stimulate the formation of pores and enhance pore sizes within dense polydimethylsiloxane membranes. Consequently, they observed that the increase in the pore sizes led to an enhanced viscous flow of the solvent. It is important to note that viscous flow is not considered in the current model, as the mass transfer relies solely on the Maxwell-Stefan model, which depends exclusively on the gradient of the chemical potential.

Another possible explanation might be related to the boundary conditions. For both the swelling and drying processes, the concentration of the outermost cells was assumed to be constant, which completely neglected the effects of the interface. Therefore, the drying calculations were conducted under vacuum-like conditions, as the solvent rapidly left the polymer surface without accounting for interfacial effects. It should be noted that experimental drying was performed under standard atmospheric pressure. The modeling of boundaries was simplified in this study, as the primary focus was on accurately modeling the behavior of the solvent within the polymer at various dimensions. It is important to note that the internal conditions of the polymer sample should remain almost identical for both drying and swelling processes, suggesting that changes in the diffusion coefficient are most significant at the surface.

A closer look at the concentration profile reveals that during the initial few hours the model predicts a rapid decrease in mass near the surface. This results in the solvent concentration in the interior remaining relatively unchanged, encased by the nearly dried polymer layer, as depicted in Figure 5. The diffusion behavior during swelling can be considered the opposite of drying, where the solvent concentration increases toward the interior.

5. CONCLUSION

The solvent diffusion of different solvents with varying polarity was modeled by using 1D, 2D, and 3D thermodynamic model approaches. The solvent equilibrium was modeled using PC-SAFT with a network term, which also aided in deriving the chemical potential, which is the driving force for diffusion. As the measured temperature range was above the glass transition state, the Maxwell-Stefan diffusion approach alone proved sufficient for modeling all experimental data. Multidimensional modeling yielded a stronger correlation with experimental results, despite not accounting for volume changes. The diffusion coefficients were highly dependent on the geometries investigated, with significant differences observed among 1D, 2D, and 3D, regardless of solvent polarity. This suggests that

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Figure 5. Snapshots of the 3D drying profile of the isopropanol-swollen silicone at 25 °C.

3D modeling offers the most accurate results, albeit with increased computational times, as all polymer samples are three-dimensional objects. The temperature dependence of the diffusion coefficients for both 2-propanol and heptane was accurately described using a classic Arrhenius dependence. Interestingly, heptane's diffusion speed was initially similar across the investigated temperature range due to the lower solubility counteracting the higher thermal energy of the solvent molecules. However, the current Maxwell-Stefan diffusion-based model may not fully account for all effects during drying, emphasizing the need to consider additional factors, such as interface effects, in future studies. Overall, this study successfully demonstrated the importance of considering all spatial dimensions when modeling solvent diffusion to expediently improve the accuracy of the results. Finally, these results pave the way for the evaluation of a wide variety of polymer-solvent combinations, thus improving the prediction of the lifetime of polymer encapsulated electronics in harsh environments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.3c00406.

Details on the equilibrium swelling of the silicon network (PDF) $\,$

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Notes

The authors declare no competing financial interest.

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LATIN SYMBOLS

- a, Helmholtz free energy c, molar concentration CFL, Courant–Friedrichs–Lewy constant D_{MS}, Maxwell-Stefan diffusion coefficient
- $k_{\rm B}$, Boltzmann constant (=1.381 × 10⁻²³ J K⁻¹)
- k_{ij} , binary interaction parameter
- *m*, segment number
- *R*, universal gas constant (= $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
- T, temperature
- t, time
- *u*, greatest change per time step
- v, molar volume
- x, mole fraction
- X^{Ai} , fraction of nonbonded association sites
- Δz , grid length

Greek Symbols

 $\alpha_{\rm max}$ ratio of the maximum volume to the reference state volume

- Δ^{AiBj} , association energy
- ε , depth of the pair potential
- ε^{AB} , association energy
- κ^{AB} , association volume
- μ , chemical potential
- ρ , total number density
- σ , segment diameter
- ϕ , network functionality

Indices

assoc, association disp, dispersion elastic, elastic contribution hc, hard chain id, ideal max, maximum mix, mixture pol, polymer sol, solvent

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