MODELLING STUDIES OF THE DIFFUSIVITY AND INTERSOLUBILITY OF SEMI VOLATILE ORGANIC COMPOUNDS IN WATER

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ABSTRACT

Semi-volatile organic compounds (SVOCs) are hazardous contaminants found in several products - ranging from personal care products to plastic products and the environment. Their chemical migration into food substances, raising environmental and health concerns, has been well documented. The dispersion/diffusion and solubility of SVOCs in food simulants is an indicator of their migration from food packaging materials. Here, we employed molecular dynamics simulations to investigate molecular mass transfer/diffusivity and intersolubility of three (S)VOCs from various sources into water. The simulation results illustrated that the molecular weight of SVOCs affects their dispersion and solubility in water. SVOC molecules are also much easier to diffuse into water at higher temperatures and longer time periods. The intersolubility of SVOCs in water according to the Flory-Huggins parameter (χ) and Hildebrand solubility parameter (δ) occurs in the following order: methyl isocyanate > caprolactam > naphthalene. The solubility of SVOCs increases with temperature, as evident by the decreasing δ_{SVOCs} and χ_{svocs}. These results will play a key role in expanding the knowledge base of chemical migration of small molecules into food simulants.

Keywords: *molecular dynamics simulation, SVOCs, Flory-Huggins parameter, plastic packaging, chemical migration*

INTRODUCTION

SVOCs are hazardous contaminants that are used in the manufacture of personal care products, plastics and industrial components, or are contaminants in their own right. They can be found in building materials, indoor and outdoor air, furniture, wastewater from industries, drinking water etc. Examples of SVOCs include polycyclic aromatic hydrocarbons, phthalates and pesticides, etc., and they pose public health concerns in our everyday lives [1, 2]. Humans are exposed to SVOCs through various means, such as inhalation, water and food intake. The result is that these compounds are possible human carcinogens and endocrine disruptors. Over exposure to specific SVOCs also potentially presents significant threats to animal and human health, such as asthma, allergic, reproductive and neurological diseases [2, 3]. SVOCs have thus garnered the interest of researchers.

Food packaging products made of paper, wood and plastic are widely used because of their low cost, durability, and lightweight, etc. However, the widespread nature of such packaging materials also leads to many concerns, such as chemical migration of (S)VOCs. Chemical migration occurs when harmful substances (usually additives and preservatives) present in food packaging materials (paper, plastic, wood etc.) migrate into the food. Pacos et al. [4] and Muncke [5] identified four ways by which chemical migration can occur: (i) by direct contact of food with packaging material, (ii) indirectly through the gas phase between the material surface and the food surface, (iii) transfer of (S)VOCs present on external packaging surface not intended to contact the food, such as components from printing inks or lacquers, and (iv) a fractional transfer of the substances most likely present in the environment migrating into the headspace of the packaging. The presence of a head-space in the food package also influences chemical migration (this could be the main route by which environmental VOCs migrate into food) [4, 6]. Aside from this, there may also be substances transferred from the packaging matrix to the surroundings. The focus of this paper is on the last two routes, (iii) and (iv), of chemical migration. For these routes, the migrant molecules diffuse away from the packaging interface and move into the bulk food. The migration at these stages, just like routes (i) and (ii) are driven mainly by entropy, a measure of the randomness of a system.

In the field of food packaging safety, solubility and diffusion coefficients are important factors that are influential to the dispersion of chemical migrants into food, thus affecting the rate of migration. (i.e., when a substance is dispersed in a matrix, diffusion occurs simultaneously with its solubilization) [7 - 9]. As such, this paper aims to study the diffusivity and solubility of three different SVOCs with well-documented health effects - naphthalene (NAPH), methyl isocyanate (MIC), and caprolactam (CAP) (with different migration routes), in water (Figure 1).

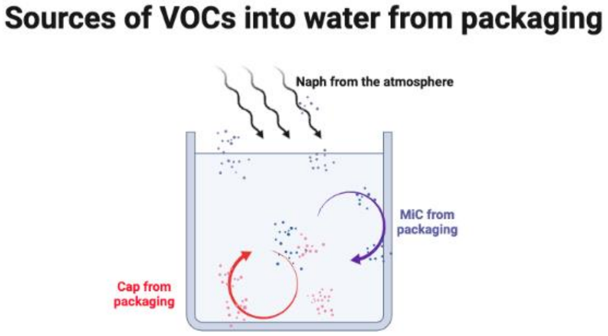


Figure 1. Migration routes of the selected SVOCs into water (created with BioRender.com)

Naphthalene vapor is an environmental contaminant with increased levels in air at places exposed to paint and repellents. The naphthalene levels in milk drinks stored in low-density polyethylene bottles (in naphthalene-prevailing environments) were observed to increase with storage time [10]. Caprolactam, which is a polyamide material used to contain food during cooking, produces bitter tastes in food, although it is relatively non-toxic on oral administration. Residual caprolactam has been found to migrate into boiling water [6]. Isocyanates are used in the manufacture of plastic materials intended to come into contact with foods. Other types of isocyanates, for example, MICs are used in the manufacture of pesticides [11].

In recent years, molecular dynamics (MD) simulation has been used to provide molecular and thermodynamic insights by studying atomic-level molecular interactions, velocities and energies, as well as movement of atoms and molecules (e.g., the diffusion and migration of small molecules) [12, 13]. As such, simulations have been used successfully to predict solubility parameters, diffusion coefficients, and interaction energy of substances. Using MD simulations, Zheng et al., studied the diffusion of vitamin C in water. The results showed that at higher temperature and lower concentration the normal diffusions appear relatively late [14]. Xiang and Andersen used MD simulation to study the solubility and hydrogen bonding interactions of drug dispersions [15, 16]. Zhang et al. studied the leaching, diffusion and solubility of bisphenol A from polycarbonate (PC) into water [12]. The diffusion of five kinds of chemical additives in polypropylene (PP) has also been investigated by Wang et al [17]. The movements of the additives in PP cell models at different simulation time suggested that for a long time, the additive molecules vibrate rather than hop until they find an equal or larger transport channel to diffuse [17]. Chen and Hu used mathematical models to study the dynamics of SVOCs transport in the air and interactions with airborne particles and observed that the concentration of di-2-ethylhexyl phthalate (DEHP) depended on the molecular weight; a larger size led to smaller mass transfer coefficients [3].

Although there have been some MD simulation studies reporting valuable insights into the chemical migration/diffusion of various substances into food simulants, no study (to the best of our knowledge) has reported on MD simulation of the dispersion/diffusivity and solubility of NAPH, CAP and MIC in water. Motivated by this, the objective of this paper is to study the mass transfer/diffusivity and intersolubility of already migrated VOCs into water and in the headspace of food packaging containers (considering routes (iii) and (iv)) by a series of all-atom MD simulation models.

METHODS

Models

To study the migration of three kinds of SVOCs in water, we created various models of water-CAP, water-MIC and water-NAPH. The molecular models of the compounds studied in this work were sketched in Materials Studio 2019 software package (Accelrys Software Inc., USA), according to the molecular structure and properties illustrated in Table 1 and Figure 2 [18]. To obtain the proper structure of the models, we began by constructing and dispersing three molecules of each SVOCs randomly. The size of each simulation box was 30.67 Å × 40.14 Å. Geometry optimization of the molecular models was carried out using the smart algorithm embedded in Material Studio software to ensure that the system reaches equilibrium, and the structures of the molecules are reasonable. COMPASS II forcefield was employed in all simulations. The random amorphous cell construction of 1000 water molecules generates an interface for diffusion/migration and interaction energy observations of three molecules of each SVOC in water. For intersolubility studies, 200 water molecules and varying numbers of SVOC molecules were used in an amorphous cell model (see section “Interaction by CED, Flory-Huggins and Hildebrand parameter”).

Table 1. Physical properties of selected SVOCs [18]

SVOC	Physical property
Caprolactam	Molecular formula: $C_6H_{11}NO$ Average mas: 113.15 g/mol
Naphthalene	Molecular formula: $C_{10}H_8$ Average mass: 128.17 g/mol
Methyl isocyanate	Molecular formula: C_3H_3NO Average mass: 57.06 g/mol

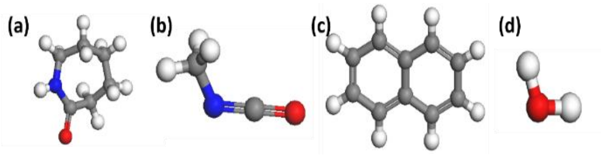
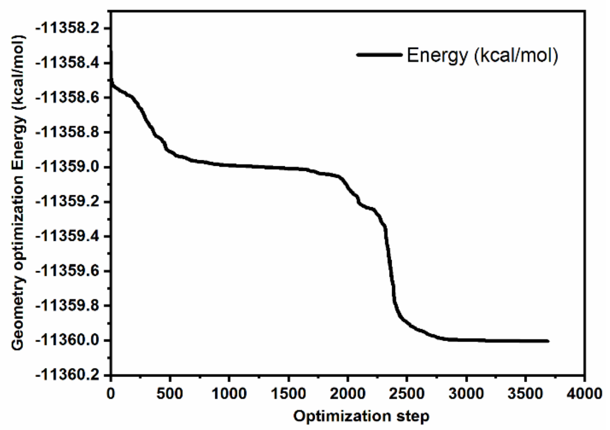


Figure 2. The molecular structures and properties of the studied compounds: a) CAP, b) MIC, c) NAPH, d) water [18]

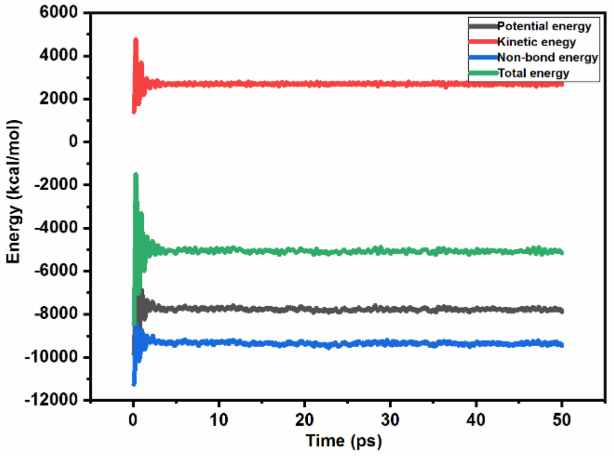
Simulation details

The widely used COMPASS II MD force field was applied to describe interactions among CAP, MIC, NAPH and water molecules. The

Nose-Hoover thermostat was used to control the temperature of the system. All simulations were carried out at a pressure of 1 bar. A vacuum layer of 20 Å was placed above the model layers to eliminate interactions caused by periodic boundary conditions. All SVOC-water models were pre-equilibrated for MD simulations. The layer docking MD model [19] was employed, by randomly dispersing (i.e., docking) three molecules of each SVOC on 1000 molecules of water layer. Each model was then subjected to geometry energy optimization using the smart algorithm embedded in Material Studio. Then, four isothermal and isochoric (NVT) annealing circles from 300 to 600 K and then back to 300 K (at 300, 450, 600, 450, and 300 K intervals) were conducted to eliminate unreasonable configurations [12]. MD simulations were conducted by NVT ensemble at 25 - 100 ps employing the accuracy of Ewald summation, and a time step of 1.00 fs. The simulation temperatures were varied accordingly at 300.15, 323.15, 373.15, 393.15 and 433.15 K. In all instances, the temperatures were selected to encompass simulated cold and hot water conditions. Using the dynamic energies of MIC as an example, Figure 3a shows that after geometry optimization procedure, the equilibrium system energy clearly converges after 2500 iterations. The change in energy after NVT MD simulation time at 300.15 K also indicates that the kinetic, potential, and non-bond and total energies fluctuate randomly around a constant value (Figure 3b), and this validated the thermodynamic equilibrium state of our MD model. Taken together, the role of temperature and time on the movement/dispersion of volatile compound molecules (assumed to have already been leached from plastic packaging into water) was studied at a molecular level and analysed to reveal the molecular diffusivity and solubility. The results are discussed in following sections.



a)



b)

Figure 3. MD energies of MIC system after geometry optimization (a) and NVT simulation at 300.15 K (b)

RESULTS AND DISCUSSION

Temperature enhances SVOC diffusivity in water

Using MD models, we studied the migration/diffusivity of CAP, MIC and NAPH (from plastic packaging and the environment) in water at different temperatures. Temperature is an important factor that has been reported to affect the migration/diffusion of volatile molecules. In this study, the effect of temperature was investigated at 300.15, 373.15, 393.15 and 433.15 K at a constant time step of 75 ps.

By visual analysis of Figure 4, the effect of temperature on the dispersion/diffusivity of all SVOCs can be clearly observed. Specifically, at room temperature (300.15 K), the movement of caprolactam molecules on the water layer was limited after 75 ps; however, one molecule each of MIC and NAPH moved across the interface (both into solution and the simulation box - the headspace) and possibly dissolved into the solution. As temperature increases from 300.15 to 433.15 K, significant movements of water and SVOC molecules are observed. This is because at higher temperatures, the molecules are energized to move faster and haphazardly. This can be interpreted as agitation of molecules during boiling, subsequently inducing the movements of volatile compounds. The diffusion of MIC is particularly significant with an increase in simulation temperature. This can be attributed to the small molecular size of the MIC molecule. The diffusion/migration of CAP and NAPH were almost similar, implying that the molecular weight of SVOC played a huge factor in their diffusion/chemical migration - in the order MIC (57.05 g/mol) > NAPH (128.17 g/mol) ≈ CAP (131.16 g/mol). Duplicate simulations were performed to further confirm the robustness of the results. At higher temperatures (boiling water), SVOCs are more likely to diffuse/migrate faster in drinking water. The results are in line with MD simulation observations that the molecules of certain endocrine disruptors much more easily migrate into food simulants (ethanol, water, and palmitic acid) at higher temperatures [12]. Wang et al. also observed experimentally and by MD simulation that the migration of DEHP plasticizers from poly(vinylidene chloride) (PVDC) into heptane, ethanol and water food simulants increase with the increase of migration temperature and migration time, probably because the high temperature increases the movement of PVDC molecular chains which is beneficial to the movement of DEHP [13].

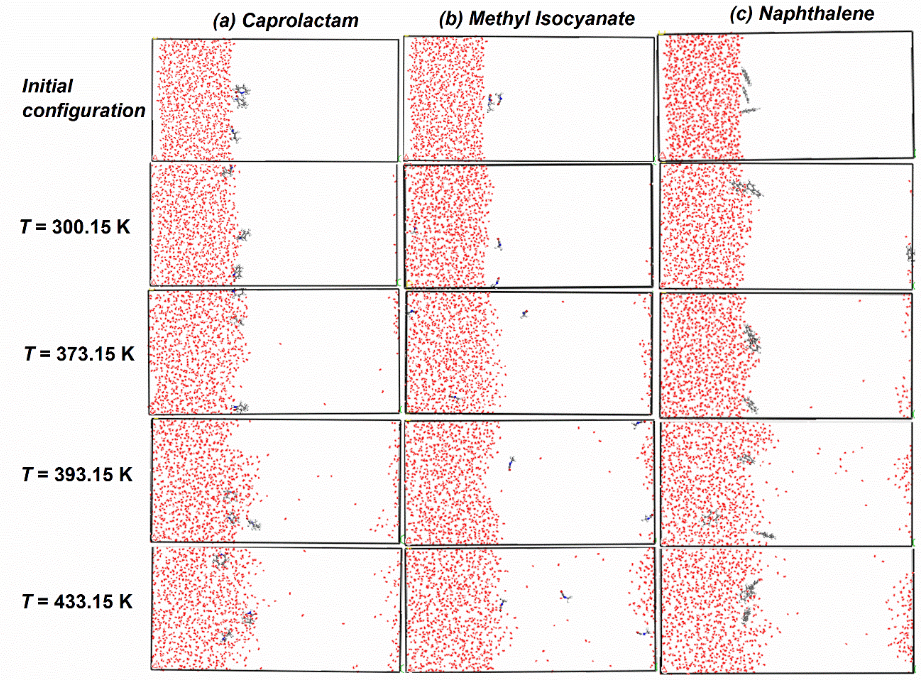


Figure 4. MD simulation depicting the evolution of SVOC dispersion with respect to simulation temperature: a) CAP, b) MIC, c) NAPH. (Red dots represent water molecules and black dots represent SVOCs)

The interaction of SVOCs with water molecules can be calculated by the difference in potential energy, E_p, of the SVOC-water mixture and the E_p of the single components. This value can be used to quantify their migration away from the water layer into the solution headspace.

$$Ep_{\mathrm{int}} = Ep_{\mathrm{total}} - (Ep_{\mathrm{water}} + Ep_{\mathrm{SVOCs}}) \quad (1)$$

It can be seen from Table 2 that all the interaction energies display negative values, indicating attracting forces between atoms and molecules. However, the interactions of MIC with water are far lower than CAP and NAPH, at all simulation temperatures. Furthermore, and especially for MIC, the interaction/binding energies are much lower at higher temperatures. The lower interaction with water molecules at higher temperatures confirms the movement or dispersion/diffusion of SVOCs further away into the simulation box, as seen in Figure 4. This also is attributable to the lower molecular weight of MIC. Here, we took a relatively unconventional approach to explain the dispersion/diffusion of SVOCs in water, mainly due to the simulation model we employed. Usually, by employing an amorphous cell model, the interaction energies are directly correlated to migration/diffusion intensity [14, 20]. However, to explicitly visualize the translational movement in the diffusion of molecules, we employed a layer docking approach in this work.

Table 2. Calculated interaction energies (kcal/mol) of SVOCs and water molecules

Temp/ K	Ep_{total}	Ep_{water}	Ep_{SVOC}	Ep_{int}
Caprolactam				
300.15	-7853.32	-7775.58	-44.8807	-32.8584
373.15	-6640.02	-6555.99	-37.722	-46.3061
393.15	-6077.31	-6009.17	-33.7392	-34.4076
433.15	-5445.33	-5375.14	-28.1228	-42.075
Methyl isocyanate				
300.15	-7885.9	-7890.65	18.46195	-13.7174
373.15	-6501.57	-6497.25	18.17702	-22.5059
393.15	-6268.14	-6290.89	26.11211	-3.3618
433.15	-5471.21	-5489.63	22.90646	-4.48265
Naphthalene				
300.15	-7446.22	-7800.64	384.3491	-29.9261
373.15	-6242.32	-6612.34	394.2219	-24.1999
393.15	-5132.31	-5504.3	400.7573	-28.7647
433.15	-4963.58	-5340.12	401.2055	-24.6625

Diffusion intensity estimated by MSD

The dispersion or diffusivity of SVOC molecules can be quantified using the mean square displacement (MSD) that is defined by the Einstein's diffusion equation [14]:

$$D_a = \frac{1}{6N_a}\lim_{x\to\infty}\frac{d}{dt}\sum_{i=1}^{N_a}\langle r_i(t)-r_i(t_1)\rangle^2 \quad (2)$$

The term $\langle r_i(t)-r_0(t_1)\rangle^2$ is the MSD, and by linear fitting of its values, the slope (D_α), which reflects the translational mobility or movement intensity of molecules, can be obtained; $r(t)$ denotes the position vector of the particles, and the angular brackets denote an ensemble average. MSDs can be obtained using the "Forcite" module of Materials Studio (Figure 5). Higher MSD value means better diffusivity or dispersion intensity. It can be observed from Figure 5 that the diffusivity of all 3 SVOCs is enhanced at higher temperatures. The results further cement the idea that the chemical migration of SVOCs into water increases with temperature. Taking the temperature effects on the diffusion ability of SVOCs into accounts, and since most food packaging materials are used at relatively high temperatures (about 170 °C [21]), the exposure of SVOCs is thus more likely with hot foods. We suggest that non-volatile additives and preservatives with higher molecular sizes should be recommended to manufacturers to slow down dispersion and chemical migration into food substances from food packaging materials.

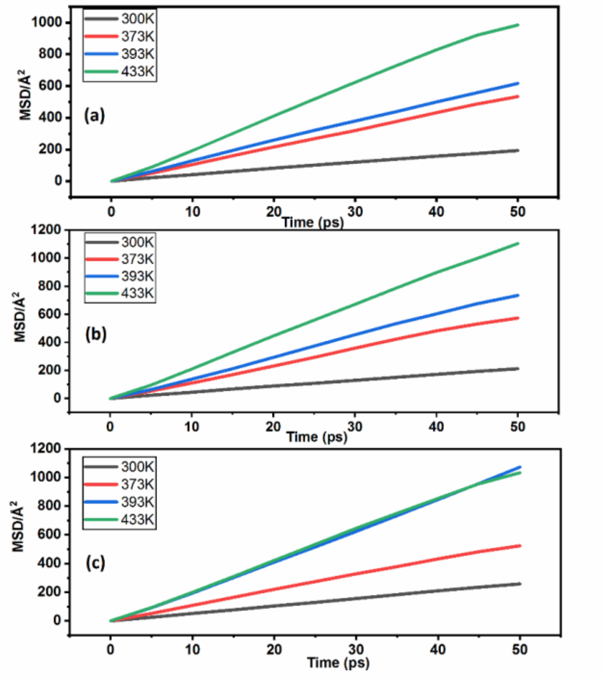


Figure 5. Temperature effect on diffusivity of SVOCs: a) CAP, b) MIC, c) NAPH in water

Time dependence of SVOC dispersion in water

On the one hand, while we have ascertained that the diffusion of SVOCs in water is greatly affected by temperature (i.e., at simulated cold and hot water conditions), we also prepared another set of simulation models to observe how the evolution of time affects the diffusion of SVOCs. The simulations were carried out at 25, 50, 75 and 100 ps. As represented in Figure 6, at smaller simulation time (25 ps), in all three SVOCs, only MIC molecules moved away from the water layer. With an increase in simulation time from 25 to 100 ps, further movement of molecules across and into the water layer was observed. Although the diffusion/migration of all three SVOCs was not as vigorous as that observed with temperature effects, similar trends could be observed. MIC diffused much more prominently than CAP and NAPH, again demonstrating that molecular weight plays a significant role in the diffusion of SVOCs in water.

The diffusion of SVOC molecules is observed in our model to be limited and not so much dependent on time as shown by the time dependent SVOC dispersion (Figure 6) and MSD (Figure 7), compared with temperature. However, this means that with increasing use of SVOC-containing substances for longer periods of time, migration and dispersion in food substances could increase. Our molecular level studies conform with experimental observations of Pelto-Huikko et al. who studied the migration of VOCs from cross-linked polyethylene (PEX) pipes into drinking water during the first five years of use [22]. The stagnation time of the drinking water in contact with the PEX material before the actual water sample was taken had a major impact on analysed migration of organic compounds. The amount of VOCs that were able to migrate from PEX materials into the drinking water increased when the stagnation time increased. Shaikh et al. also confirmed experimentally the time dependence of chemical migration in drinking water. Although the levels of some percolated compounds were below the allowable levels, their accumulation during lengthy consumption can potentially increase the exposure to harmful constituents in water. As a prevention step, they recommended the use of sorbent filtration kits for household drinking water [23].

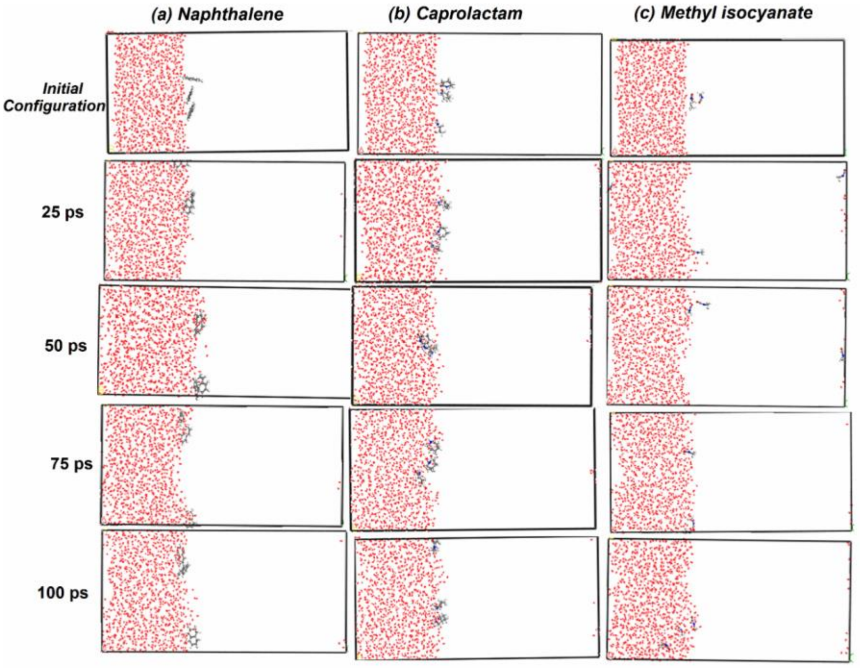


Figure 6. MD simulation depicting the evolution of SVOC dispersion with respect to simulation time: a) NAPH, b) CAP, c) MIC (Red dots represent water molecules and black dots represent SVOCs)

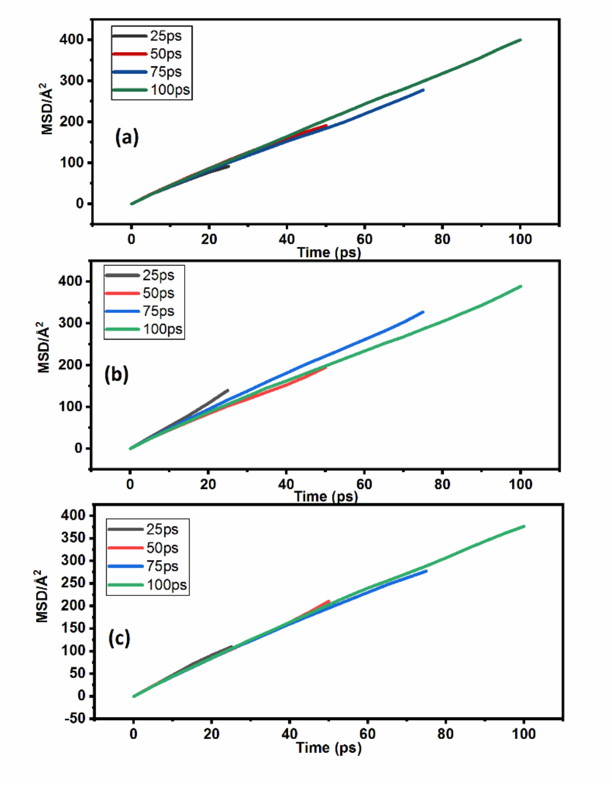


Figure 7. Time effect on diffusivity of SVOCs: a) CAP, b) MIC, c) NAPH in water

Interaction by CED, Flory-Huggins and Hildebrand parameter

The diffusivity of SVOCs into water was very clearly observed at different temperatures in section "Temperature enhances SVOC diffusivity in water". Next, we studied the temperature effects on intersolubility of SVOCs with water to provide more insights into their interactions with food simulants. The Flory-Huggins (F-H) interaction parameter, χ, is used to reflect the solubility between two substances, and calculated by a series of MD simulation models. The improved F-H theory considers the hydrogen bond interactions and polar interactions between simple systems. The reliability of the F-H parameter means it has successfully been used to characterize the strength of attractive interactions of organic molecules by MD simulations [12, 24]. F-H interaction parameter between SVOCs and water, $\chi_{\text{water-CAP}}$, $\chi_{\text{water-MIC}}$ and $\chi_{\text{water-NAPH}}$ can be calculated from the cohesive energy densities (CED) obtained by the "Forcite" analysis tool embedded in Materials Studio software. The CED is used to numerically estimate the degree of interaction between two components and represents the increase in energy per mole of a material [20].

Hildebrand solubility parameter is also commonly used to assess miscibility of the molecular species involved in a system. The electrostatic and polar solubility parameter components (δ) for water and SVOCs were calculated from the CEDs according to:

$$\delta = \sqrt{\text{CED}} \qquad (3)$$

The CED values were obtained for the simulated single components (water, CAP, MIC, and NAPH), and also a mixture of components (water-CAP, water-MIC and water-NAPH). Finally, the χ was obtained from the δ according to equation 4. Taking water-MIC model as an example, $\chi_{\text{water-MIC}}$ can be calculated using the following equations [16]:

$$\chi_{\text{water-MIC}} = \frac{\Phi_{\text{water-MIC}}}{RT}(\Delta\delta_{\text{water-MIC}})^2 \qquad (4)$$

where Φ is volume fraction V_r/V_T of each component. V_T is the total volume of the model of interest, V_r is a reference volume and assumed to be the volume of a single SVOC molecule (V_r is obtained from the simulation box volume in equilibrium state divided by the number of SVOC in a system). R is the gas constant and T is the temperature.

In all, 7 models of water, CAP, MIC, NAPH, water-CAP, water-MIC and water-NAPH were created (Table 3 and Figure 8) and studied at 6 different temperatures ranging from 300.15 to 433.15 K. To avoid unfavourable configurations, each model was annealed as described in section "Simulation details".

Table. 3 Parameters of the simulation models for solubility estimation

Model	wt. %	No. of molecules	Cell parameter/Å	V_T /Å^3	V_r/Å^3	Φ
Single components						
water		200	18.15 x 18.15	5982.92	29.91	0.005
CAP		8	11.46 x 11.46	1503.25	187.91	0.125
MIC		16	11.49 x 11.49	1515.79	94.74	0.063
NAPH		7	11.42 x 11.42	1489.87	212.84	0.143
Mixed components						
Water-CAP	80:20	200:8	19.56 x 19.56	7486.18	935.77	0.125
Water-MIC	80:20	200:16	19.57 x 19.57	7498.72	468.67	0.063
Water-NAPH	80:20	200:7	19.55 x 19.55	7472.79	1067.54	0.143

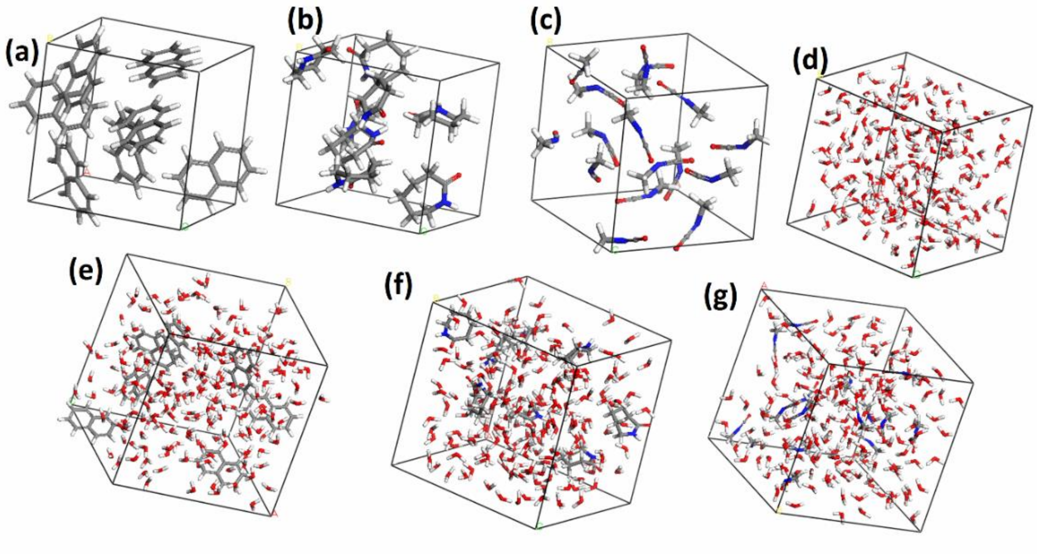


Figure 8. Models for solubility parameter calculation: a) 7 NAPH molecules, b) 8 CAP molecules, c) 16 MIC molecules, d) 200 water molecules, e) water-NAPH mixture, f) water-CAP mixture and g) water-MIC mixture

The calculated water-CAP, water-MIC and water-NAPH F-H interaction parameter, χ, and Hildebrand solubility parameter, δ, at six temperatures are listed in Table 4 and graphically displayed in Figure 9. In Flory-Huggins theory, larger χ values means worse solubility and smaller χ values indicate the solute (SVOCs) and solvent (water) are thermodynamically compatible. Additionally, the solubility of the two components is good if $\chi < 0.5$, and vice versa [12, 24]. As shown in Table 4 and Figure 9a, all SVOCs have smaller values of the χ (< 0.5) which can help access their solubility in water. It also shows that MIC is more soluble in water and may interact more with water molecules, followed by CAP and lastly, NAPH. Naphthalene (which is a non-polar and hydrophobic compound) shows the most insolubility with water (a polar solvent), according to the calculated χ values. Based on the χ values, the solubility of the SVOCs in water are in the order MIC > CAP > NAPH. Also, with an increase in temperature from 300.15 to 433.15 K, the χ values of all systems decrease, implying that the attractive interactions between water-SVOCs increase with temperature. This could also imply that the solubility of the SVOCs in water increases with temperature and could further explain the easy migration of MIC into water since it has the better solubility among the SVOCs.

Table 4. Hildebrand solubility and F-H interaction parameters of SVOCs in water

Temp/ K	δ_{water}	δ_{CAP}	δ_{NAPH}	δ_{MIC}	$\Delta\delta_{water-CAP}$	$\Delta\delta_{water-NAPH}$	$\Delta\delta_{water-MIC}$	$\chi_{water-CAP}$	$\chi_{water-MIC}$	$\chi_{water-NAPH}$
300.15	47.87	23.47	20.43	22.96	24.41	27.45	24.92	0.030	0.016	0.043
308.15	47.67	23.22	20.23	22.79	24.45	27.44	24.88	0.029	0.015	0.042
313.15	47.45	23.28	20.10	22.78	24.18	27.35	24.68	0.028	0.015	0.041
373.17	46.17	22.89	19.85	22.46	23.28	26.32	23.71	0.022	0.011	0.032
393.15	45.73	22.62	19.73	22.36	23.12	26.00	23.38	0.020	0.010	0.030
433.15	44.95	22.49	19.77	22.12	22.46	25.18	22.83	0.018	0.009	0.025

$\delta_{SVOC} = (J/cm^3)^{0.5}$

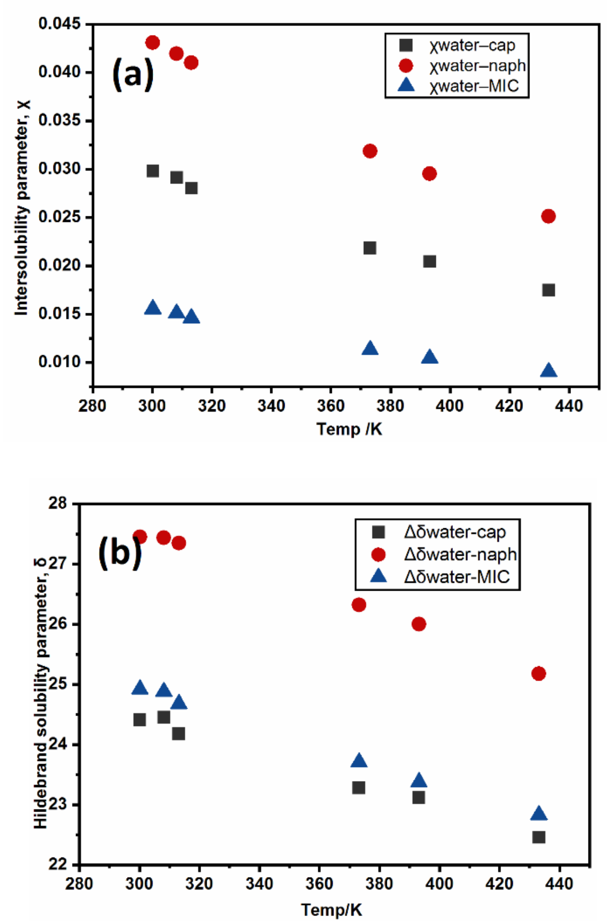


Figure 9. a) F-H intersolubility parameter, b) Hildebrand solubility parameter of SVOCs in water

The miscibility of a two-component system can be adjudged in two ways - when the differences in the two component solubility parameters, $\Delta\delta$, is less than 7.0 $(J/cm^3)^{0.5}$ and when the two substances have similar δ value [20]. On the contrary, substances with $\Delta\delta >$ 10.0 $(J/cm^3)^{0.5}$ are likely to be immiscible with each other. The two-component solubility parameter can further be used to predict the thermodynamic compatibility of SVOCs and water. Solubility parameters for water-SVOCs were calculated from MD simulations and reported in Table 4 and Figure 9b. It can be seen from Table 4, the solubility parameter calculated for water agreed with the well reported extremely high solubility parameter of water (δ = 47.9 $(J/cm^3)^{0.5}$) [20]. The δ values of all SVOCs are not close to that of water and $\Delta\delta_{SVOCs-water}$ are > 10.0, with $\Delta\delta_{water-CAP}$ and $\Delta\delta_{water-MIC}$ closer to 10 than $\Delta\delta_{NAPH.}$ It can also be seen from Table 4 that the δ of SVOCs decreases with increasing temperature. What this means is that, with increasing temperature, the solubility of SVOCs kept improving (i.e., approaching $\Delta\delta < 7.0$). The same observation was made for the F-H parameter where the interaction, and hence solubility, improves with increasing temperature.

The observed solubility parameters also show that MIC and CAP are more soluble in water than NAPH. This may be the reason (in addition to molecular weight) for the higher diffusion/migration abilities of MIC in water. Based on the predictions of the F-H interaction parameter, Hildebrand solubility parameter and the inferences made on the easier diffusivity of MIC into water as compared to CAP and NAPH, it can be deduced that in a system where all 3 SVOCs are present at the same temperatures and time period, MIC is much more likely to disperse quickly leading to a higher risk of exposure. In summary, the solubility of SVOCs was observed to improve with increasing temperature, as evident by the decreasing $\Delta\delta_{SVOCs}$ and χ as temperature increased.

CONCLUSION

Solubility and diffusivity are important factors that govern the dispersion of migrants into food, from food packaging materials, thereby affecting the rate of chemical migration. The chemical migration of substances from plastic, paper and wood packaging materials is an important health issue that has attracted extensive concerns. In this work, we performed a series of MD simulations to gain insights into the dispersion and solubility of CAP, NAPH and MIC in water food simulants. We carefully investigated effects of the temperature and time on the diffusivity and intersolubility of the above-mentioned SVOCs in water.

Taking all the results together, it was inferred that the molecular weight of SVOCs plays an important role in diffusion/dispersion in water; small-sized molecules were observed to be more easily dispersed in water, especially at simulated hot water conditions. The intersolubility, as a way of predicting the interactions between SVOCs and water was also observed to correlate with diffusion/dispersion of SVOCs. At higher temperatures and simulation times, both solubility and diffusivity increased. High temperatures correspond to high tendency of SVOC molecules to move into the bulk food and into the headspace of the packaging material. In summary, small sized volatile additives in food packaging are expected to diffuse/disperse easily with good solubility in water at higher temperatures and at longer time periods. With the observed temperature effects on the dispersion/diffusion intensity of SVOCs in our modelling studies, we suggest that non-volatile additives and preservatives with higher molecular sizes should be used by manufacturers to slow down dispersion and chemical migration into food substances. The results of our MD model throw more light on the chemical migration of SVOC molecules from plastics, wood, and paper packaging, etc.

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