Supplementary material:

Mosquito repellent thermal stability, permeability and air volatility

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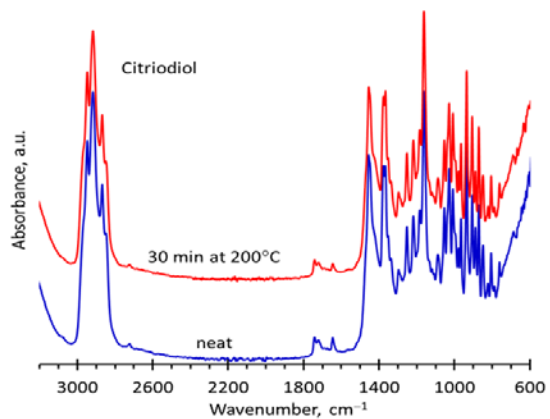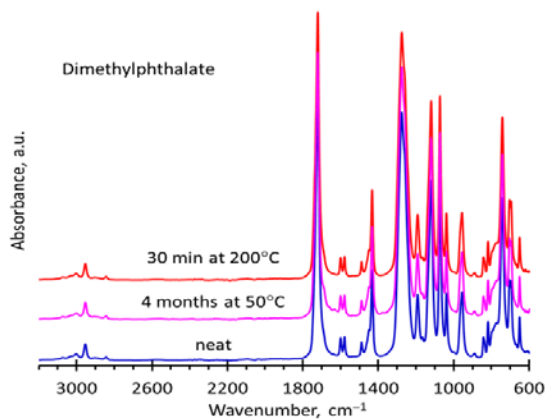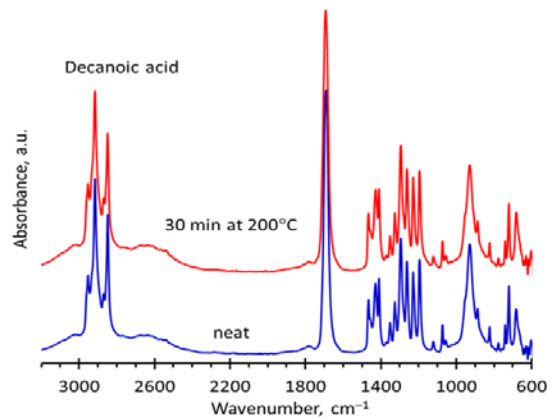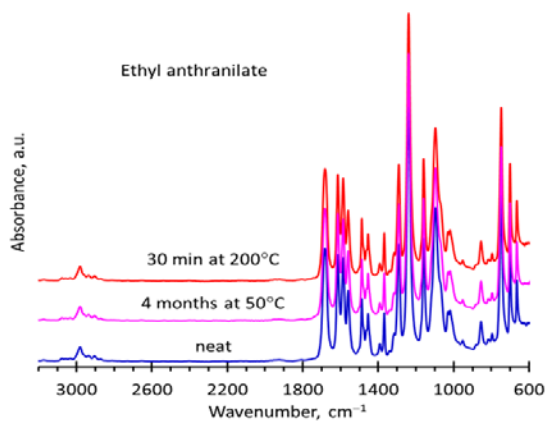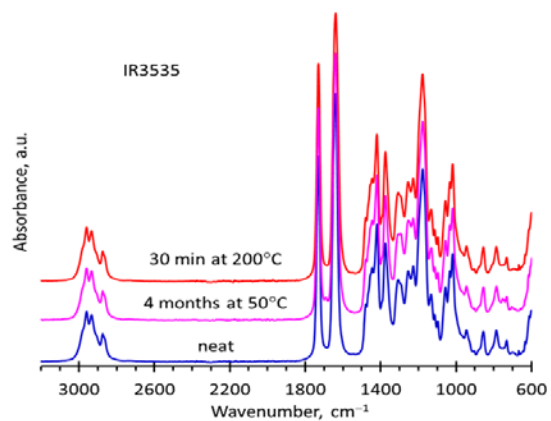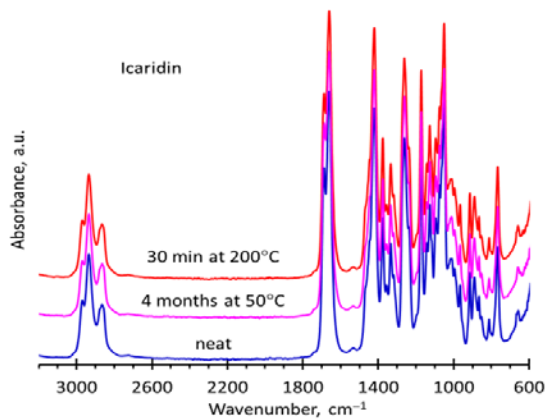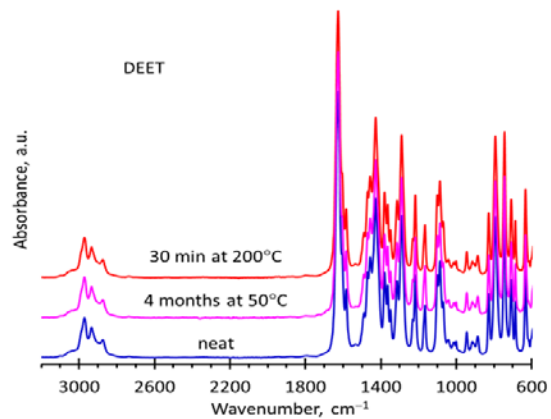
Figure S-1: FTIR spectra profiles of the mosquito repellents before and after thermo-oxidative stability testing, showing the same structure and demonstrating the stability of the mosquito repellents during analysis: DEET; Icaridin; IR3535; ethyl anthranilate; decanoic acid; dimethyl phthalate and Citriodiol. The repellents were heated for 30 min at 200 °C and for four months at 50 °C in an open container.

1. Vapour pressure equations for pure compounds

Vapour pressure is an important thermo-physical property in numerous chemical processes and product design applications (Mohammadzadeh and Zahedi, 2008). It can be determined experimentally using different techniques. However, with the increasing number of compounds, the calculations require a considerable investment in time and cost. Many correlations for estimating vapour pressure can be used to complement existing experimental measurements – numerous correlations are available that can be used to estimate or correlate the vapour pressure of pure liquids as a function of temperature. The present study addresses the four best-known equations namely: (i) the Wagner equation (Poling et al., 2001); (ii) the Antoine equation; (iii) the Cox equations (Roháč et al., 1999, Gobble et al., 2014) and (iv) the Myrdal and Yalkowsky equation (Myrdal and Yalkowsky, 1997).

1.1.The Wagner equation

The Wagner equation has contributed greatly to vapour pressure data reduction. This is attributed to the fact that it can represent, with a very high accuracy, the experimental data for many substances over the entire liquid-vapour range, from the triple point to the critical point (Wu and Liu, 2005, Forero G and Velásquez J, 2011). The vapour pressure of decanoic acid was reported in the form of the Wagner equation (Ambrose and Ghiassee, 1987). The Wagner equation also extrapolates well with temperature and it is represented by equation (1) as follows:

$$ln\, P_r = (A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5)/T_r \qquad (1)$$

where, $P_r = P/P_c$ the reduced vapour pressure; $T_r = T/T_c$ is the reduced temperature; $\tau = 1 - T_r$; *A, B, C,* and *D*, are the Wagner parameters and are listed in the Table 3 for decanoic acid.

Table 1: Parameters of the Wagner equation used for the decanoic acid (Ambrose and Ghiassee, 1987).

Temperature range (K)	Pc/kPa	Tc/K	A	B	C	D
246-726	2229.784	726.0	-9.0706	2.77535	-11.10141	-2.43545

1.2. The Antoine equation

The Antoine equation is considered most appropriate for correlating vapour pressures over the so-called medium-pressure region that spans the pressure range from approximately 1 to 200 kPa (Roháč et al., 1999). The equation is stated in equation (2) for decanoic acid and in equation (3) for dimethyl phthalate.

$$log_{10}(P_A) = A - [B/(T + C)] \tag{2}$$

$$ln(P_A) = A - [B/(T + C)] \tag{3}$$

where P_A is the vapor pressure in (kPa); *T* is the absolute temperature in (K); *A, B,* and *C* are the Antoine constants which depend on both the compound and the measurement temperature range. The Antoine equations were used to correlate the vapour pressures of decanoic acid (Kahlbaum, 1894) and dimethyl phthalate (Roháč et al., 1999). The constants for decanoic acid and dimethyl phthalate are listed in Table 2.

Table 2: Antoine equation constants and temperature range used for the decanoic acid (Kahlbaum, 1894) and dimethyl phthalate (Roháč et al., 1999).

Compound	Equation form	Temperature range (K)	A	B	C
Decanoic acid	3	426.0 - 460.3	2.4645	733.581	-256.708
Dimethyl Phthalate	4	466 - 552	14.82359	4660.937	-99.1086

1.3. The Cox equation

The Cox equation was previously used to correlate the vapour pressure of dimethyl phthalate (Gobble et al., 2014, Roháč et al., 1999). The Cox equation (equation (4)) is also known to extrapolate well with temperature (Gobble et al., 2014).

$$ln(P/P_o) = [1 - (T_o/T)exp\{A_0 + A_1 T + A_2 T^2\}] \tag{4}$$

where P is the vapour pressure in (kPa); T is the absolute temperature in (K); T_o is a constant reference temperature (K); P_o is the constant pressure (kPa); A_0, A_1, and A_2 are the Cox parameters listed in Table 3.

Table 3: Parameters of the Cox equation and range of temperature used for the dimethyl phthalate (Roháč et al., 1999, Gobble et al., 2014).

Temperature range (K)	T_o/K	P_0/kPa	A_0	A_1	A_2
324 - 552	555.799	101.325	3.076854	-0.001650657	1.17163E-06

1.4. The Myrdal and Yalkowsky equation

Recent research findings have indicated that the available vapour pressure values of compounds in the literature have some inconsistencies. Therefore the reproducibility of the data depends on the experiments and the method used to determine the vapour pressure (Nhlapo, 2013). The Myrdal and Yalkowsky equation is widely used to estimate the vapour pressure of liquid compounds (Myrdal and Yalkowsky, 1997). In this work, the Myrdal and Yalkowsky equation was used to estimate the vapour pressure of the repellents. The formula is given by equation (5) as follows:

$$log_{10}(P) = -\frac{[86.0+0.4\tau+1421HBN](T_b-T)}{19.1T} + \frac{[-90.0-2.1\tau]}{19.1T} + \left(\frac{T_b-T}{T} - ln\frac{T_b}{T}\right) \tag{5}$$

where, T_b is the boiling point in (K); the parameters τ and HBN which characterize the molecular structure representing the torsional bond and the hydrogen bond number. The effect of hydrogen bonding is determined by n(-OH), n(-COOH), and n(-NH_2), all representing the number of functional groups of alcohols, carboxylic acids, or primary amines, respectively. M_{WA} is the

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molecular weight of the repellent. The parameters τ and *HBN* are determined using the semi-empirical equations described in equation 6 and equation 7.

$$HBN = \frac{\sqrt{n(-OH)+n(-COOH)}+0.33\sqrt{n(-NH_2)}}{Mw} \tag{6}$$

$$\tau = SP3 + 0.5SP3 + 0.5RING - 1 \tag{7}$$

where *SP3* is the Σ non-ring, non-terminal sp^3 atoms (e.g. CH_2, CH, C, NH, N, O, S) , *SP2* is Σ non-ring, nonterminal sp^2 atoms (=CH, =C, =N, C=O) and RING is Σ independent single, fused or conjugated ring system (Jain and Yalkowsky, 2006). In the torsional bond, terminal groups such as -CH3, -NH2, -OH, -CN-, -F-, -Cl-, Br-, -I-, = O, = CH2 and 2N as well as non-terminal *sp.* Hybrid carbons are not included. Also, not included are carbon atoms with three identical groups. Compounds with a negative value of τ are assigned a value of zero, and for compounds containing aliphatic cyclic rings such as cyclohexane, a value of -2 per ring is added (Jain et al., 2004).

1.5. Diffusion coefficients (D_{AB})

Several methods are used for estimating diffusion coefficient in low-pressure for binary gas systems such as the equations proposed by Arnold, Gilliland, Fuller, Wilke and Lee, Bairley, Chen and Othmer (Poling et al., 2001). However, in this work, the equation proposed by Wilke and Lee was used to estimate the diffusion coefficient of repellents. The Wilke-Lee equation proposed was used due its reliability (Wilke and Lee, 1955). The equation is presented in equation (8) as follows:

$$D_{AB} = \frac{\left[3.03-\left(\frac{0.98}{\sqrt[2]{M_{AB}}}\right)\right](10^{-3})T^{\frac{3}{2}}}{P\sqrt[2]{M_{AB}}\,\sigma_{AB}^2\Omega_D} \tag{8}$$

where D_{AB} ($cm^2 \cdot s^{-1}$) is the binary diffusion coefficient, T (K) is the temperature, M_{w_A} and M_{w_B} are molecular weights of substances A (repellent) and B (air), these are represented in $g \cdot mol^{-1}$, P is the pressure in bar. $M_{w_{AB}}$ is obtained by using equation 9.

$$M_{w_{AB}} = 2[\frac{1}{M_{w_A}} + \frac{1}{M_{w_B}}]^{-1} \tag{9}$$

The scale parameter σ_{AB} is obtained from equation (10).

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{10}$$

where each component is written by equation (11)

$$\sigma = 1.18\, V_b^{1/3} \tag{11}$$

V_b is the liquid molar volume at the normal boiling temperature (T_b), which can be obtained from experimental data or estimated using empirical methods. For decanoic acid, dimethyl phthalate, DEET and ethyl anthranilate, the method proposed by Rackett (Poling et al., 2001) to determine the pure saturated-liquid molar volume was used. The equation used is presented by equation (12).

$$V_b = V_c z_c^{(1 - T_b/T_c)^{2/7}} \tag{12}$$

where V_c is the critical volume; z_c is the critical compressibility factor; T_c is the critical temperature in (K). The molar volumes V_b and V_c have units of $cm^3 \cdot mol^{-1}$.

The critical compressibility factor is obtained by equation (13):

$$z_c = \frac{P_c V_c}{R\, T_c} \tag{13}$$

where R is the gas constant and the critical parameters (T_c, V_c and P_c) were found in the literature and are listed in Table S-1.

Table S-1. Repellents name, critical temperature, critical volume and critical pressure and sources

Repellent	T_c /(K)	V_c/(m$^3 \cdot$ kg$\cdot$mol^{-1})	Pc/(kPa)	Source
DEET	778.19	0.620	2517.59	Cheméo (https://www.chemeo.com)
Ethyl anthranilate	812.12	0.484	3615.89	Cheméo (https://www.chemeo.com)
Dimethyl phthalate	831.50	0.540	3191.93	Cheméo (https://www.chemeo.com)
Decanoic acid	726.0	0.621	2161.74	Cheméo (https://www.chemeo.com)

The liquid molar volume at the normal boiling temperature for Icaridin and IR3535 was estimated using the additive method suggested by Schroeder (Poling et al., 2001). This method was used for these two repellents (Icaridin and IR3535) because the critical parameters (T_c, V_c and P_c) were not found in the literature.

The method uses the analogy of counting the numbers of carbon, hydrogen, oxygen, and nitrogen atoms, and then adding one (1) for each double bond (DB), two (2) for each triple bond (TB) and multiplying the sum by seven. The formula used is described by equation (14):

$$V_b = 7\left(N_C + N_H + N_O + N_N + N_{D_B} + 2N_{T_B}\right) + 31.5N_{Br} + 24.5N_{Cl}$$

$$+10.5N_F + 38.5N_I + 21N_S - 7^{\#} \tag{14}$$

The additive method has been extended to include halogens and sulphur. The last value in equation (15) given by ($^{\#}$) is counted once if the compound has one or more rings (Poling et al. 2001). The V_b is represented by $cm^3 \cdot mol^{-1}$.

The collision integral Ω_D is calculated from accurate relation proposed by Neufield (Poling et al., 2001) is given in Equation 15.

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} \tag{15}$$

where $T^* = kT/\varepsilon_{AB}$ and the A, B, C, D, E, F, G and H are parameters of the collision integral (Poling et al., 2001). All parameters are listed in Table S-2.

For each component, the $(\varepsilon/k)_{AB}$ is calculated using equation 16 while ε_{AB} is determined using a simple equation 17:

$$\varepsilon/k = 1.15T_b \tag{16}$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \tag{17}$$

with T_b as the normal boiling point (at 1 atm) in (K). For systems in which one component is air, $\sigma_{air} = 3.62$ Å and $\varepsilon/k_{air} = 97.0\ K$.

Table S-2: Parameters of the collision integral Ω_D (Poling et al., 2001)

A	B	C	D	E	F	G	H
1.06036	0.15610	0.19300	0.47635	1.03587	1.52996	1.76474	3.89411

2. Predicting repellent diffusion coefficients into air

The release rate of a pure volatile compound into air is determined by its air permeability. The release rate parameter is the product of the vapour pressure of the compound and its diffusion coefficient in air as described in equation (18) (Pieterse et al., 2006).

$$S_A = P_A D_{AB} \tag{18}$$

where S_A is the air permeability and is represented by (mPa·m^2·s^{-1}), P_A (kPa) is the vapour pressure and D_{AB} is the diffusion coefficient in (m^2·s^{-1}).

However, from equation (18) it was possible to calculate the experimental diffusion coefficient through the relation to air permeability. In this regard the experimental values of the evaporation rates obtained by TGA and vapour pressure were considered. The simple equation is given by equation (19) as follows:

$$D_{AB} = S_A / P_A \tag{19}$$

2.1. Vapour pressure correlations with experimental data in the literature

An effective repellent should have low volatility. Volatility is usually associated with vapour pressure, but in fact the diffusivity in air also contributes (Focke, 2003, Pieterse and Focke, 2003). The volatility controls the duration of the effective action of the repellent. Ambrose and Ghiassee Ambrose and Ghiassee (1987) published vapour pressure data for decanoic acid and Roháč et al. (1999) published data for dimethyl phthalate. Figure 3 compares the experimental data for decanoic acid and dimethyl phthalate with predictions made using the Antoine, Wagner, Cox and Myrdal and Yalkowsky equations. Figure 2 shows that the performance of the Antoine equation (2 and 3) was unsatisfactory. This equation can only fit real data well over smaller temperature intervals. However, the Wagner equation (1) gave good predictions for decanoic acid, and the Cox

equation (4) gave satisfactory results for dimethyl phthalate. The Myrdal and Yalkowsky equation (5) performed well for estimating the vapour pressure for dimethyl phthalate but less so for decanoic acid.
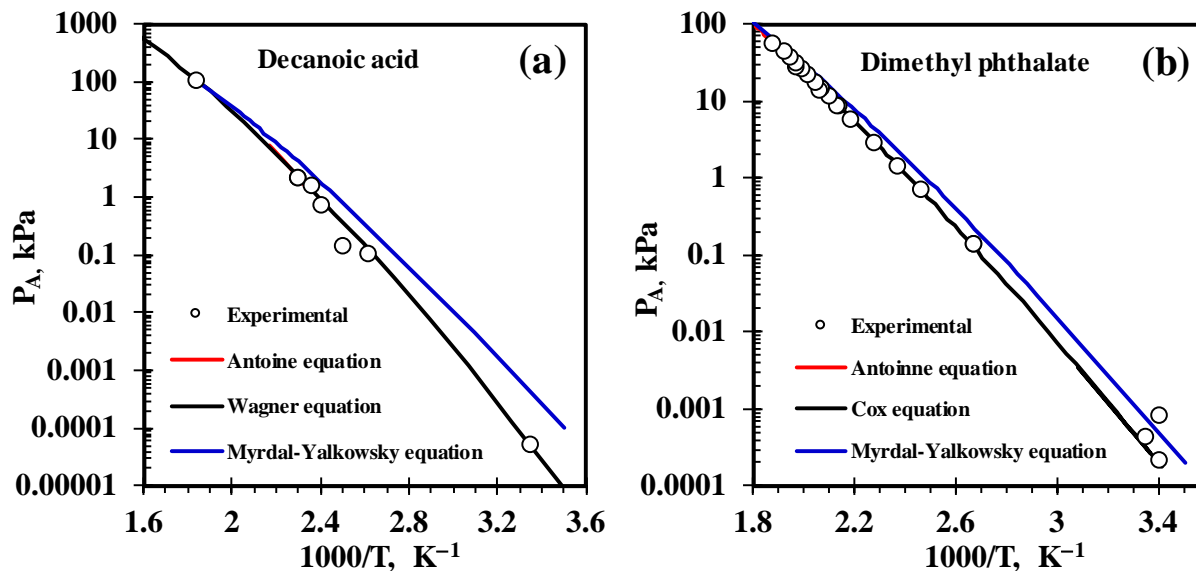

Figure 2: (a) Comparison of the experimental vapour pressure values reported by Baccanari et al. (1968), Weast and Grasselli (1989) and Lide and David (2009) with the values theoretically determined by equations (1), (2) and (5) for decanoic acid. (b) Comparison of the experimental vapour pressure values reported by Roháč et al. (1999), O'Neil (2013) and Daubert (1989) with the values theoretically obtained by equations (3), (4) and (5) for dimethyl phthalate.

2.2. The Myrdal and Yalkowsky equation

For most repellents, only a few discrete vapour pressure data points were found in the literature. In these cases, the vapour pressure variations with temperature were predicted with the Myrdal and Yalkowsky equation (5). A plot of the experimental and predicted vapour pressures is presented in Figure 3. The plot shows small differences between the predicted and experimental curves for Icaridin, DEET, ethyl anthranilate and IR3535. In summary, equation (5) proved satisfactory for estimating the vapour pressures of the liquid repellents.
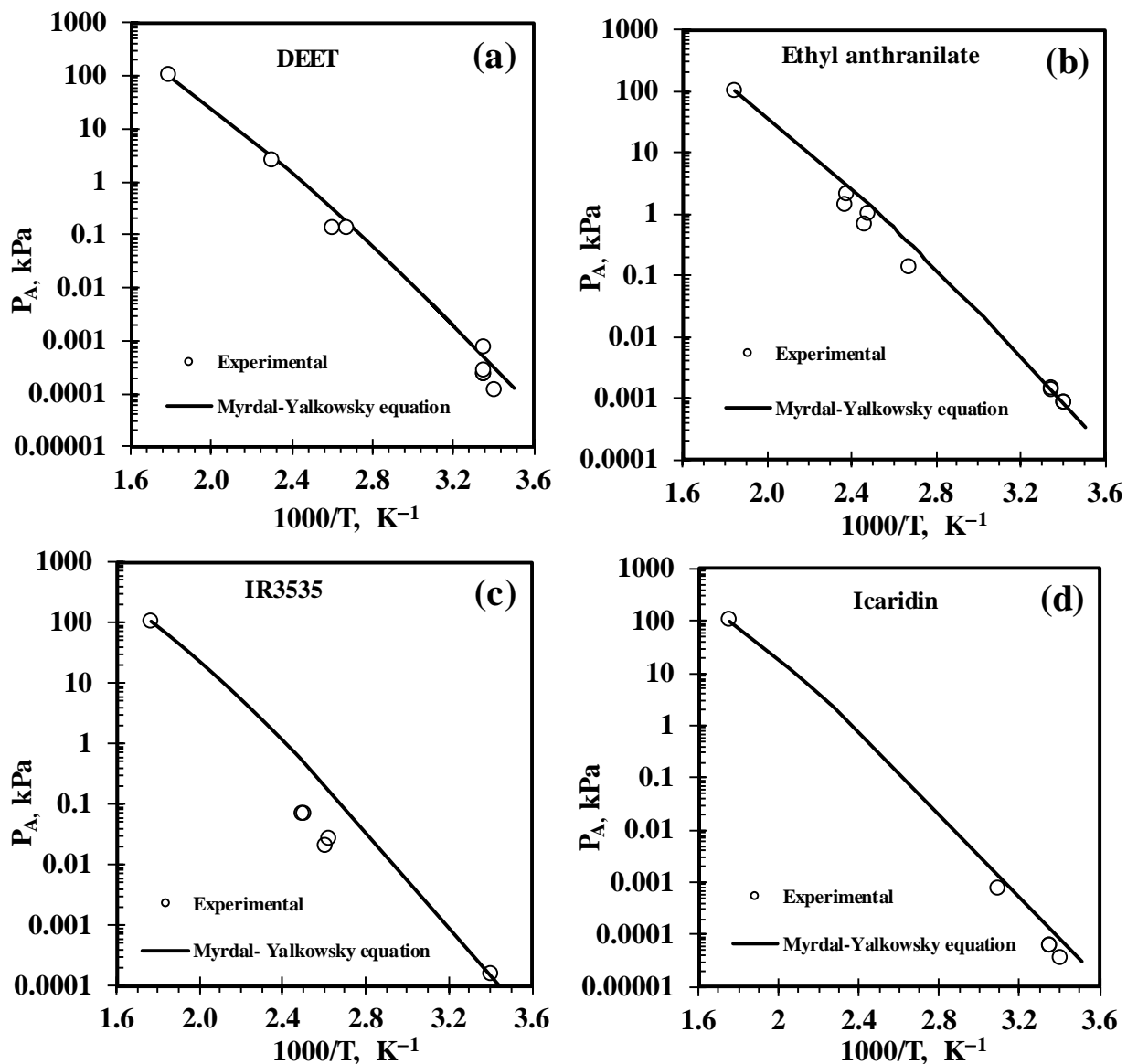
Figure 3: The experimental vapour pressure values for (a) DEET reported by Drapeau et al. (2011) and Haynes (2014); (b) ethyl anthranilate reported by Lide (2004), Api et al. (2015), Weast and Grasselli (1989), Milwaukee (1990), Islam et al. (2017); (c) IR3535 reported by O'Neil (2013) and (d) Icaridin reported by O'Neil (2013) are compared with the values estimated by equation (5).

2.3.Diffusion coefficient of repellents

Figures 4 and 5 show the predicted diffusion coefficients calculated using equation (8). From Figures 4 and 5 it can be seen that the predicted data correlated well with the experimental data. However, Figure 4 (d) revealed a significant difference between the predicted and the experimental data for ethyl anthranilate repellent at low temperatures. In contrast, the Wilke-Lee equation showed good agreement with the result for decanoic acid, dimethyl phthalate, DEET, IR3535 and Icaridin.

Figure 4: Comparison of theoretically predicted diffusion coefficients (solid line) obtained by equation (8) and experimentally determined TGA diffusion coefficients calculated by equation (19) for: (a) decanoic acid; (b) dimethyl phthalate; (c) DEET; and (d) ethyl anthranilate.
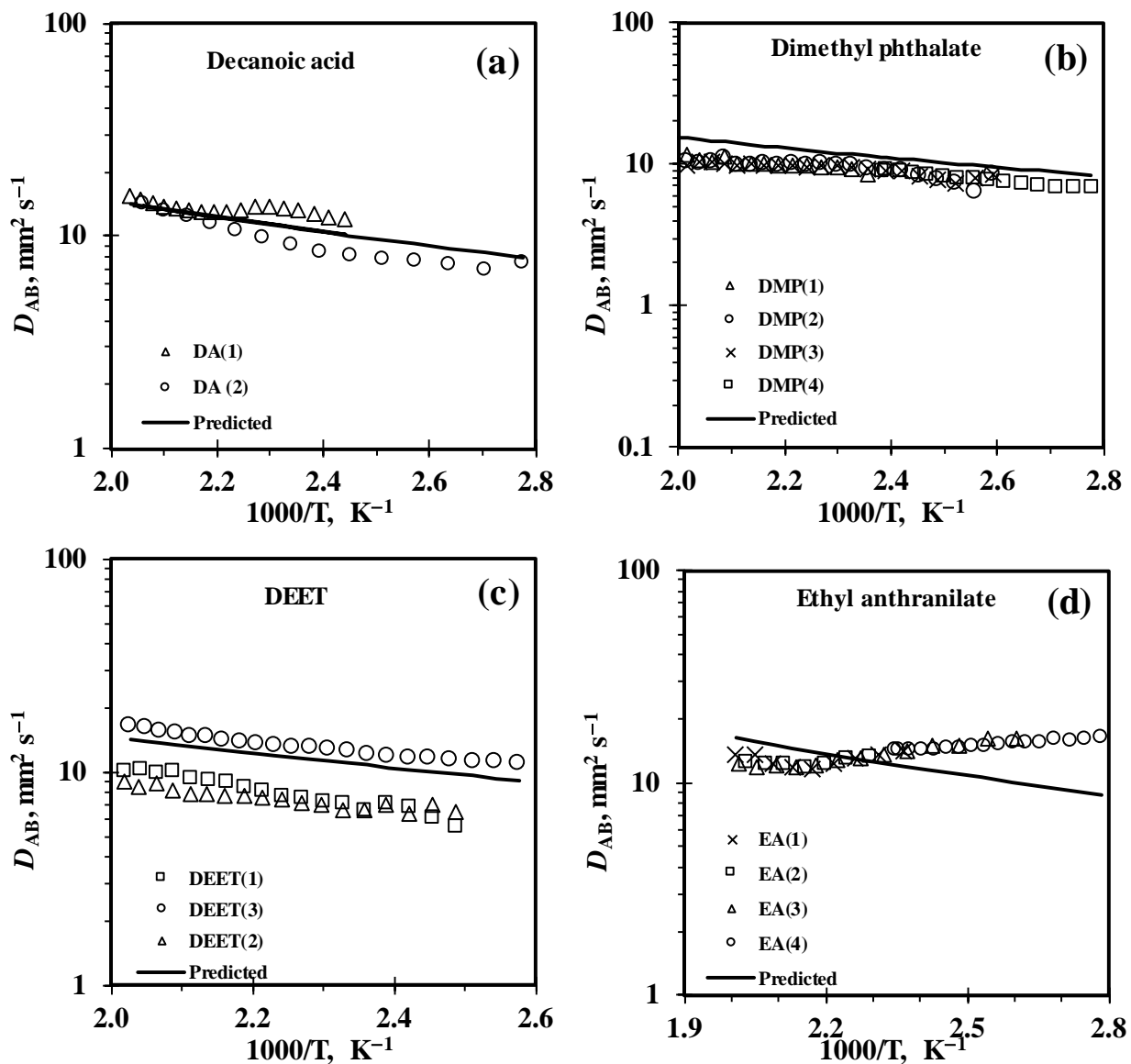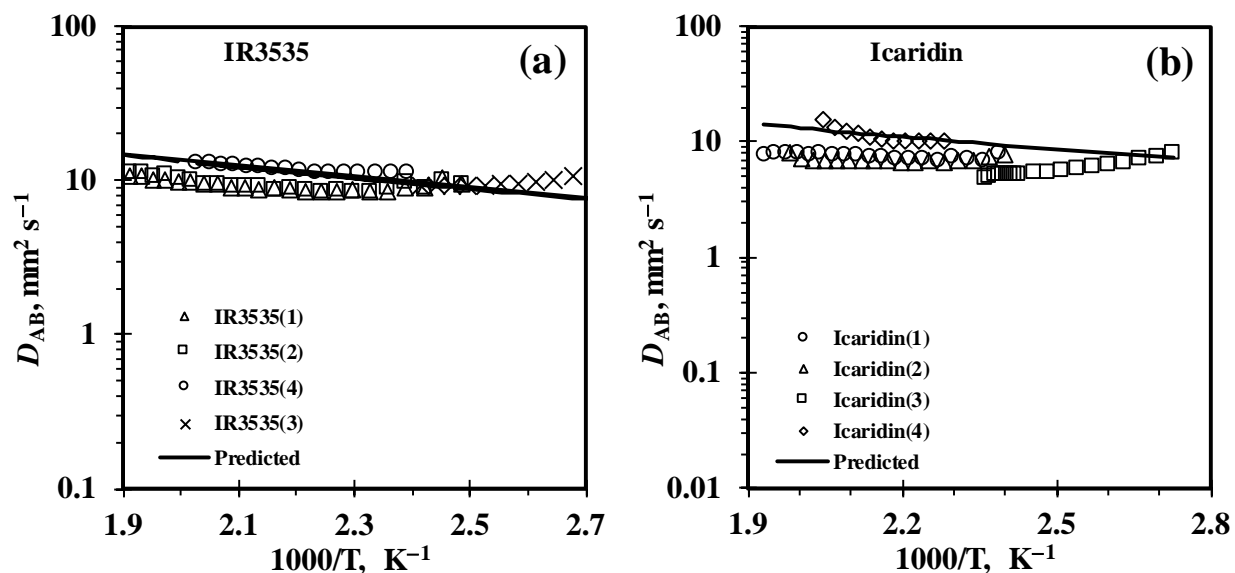
Figure 5: Comparison of theoretically predicted diffusion coefficients (solid line) obtained by equation (8) and experimentally determined TGA diffusion coefficients obtained by equation (19) for: (a) IR3535; (b) Icaridin.

Table S-3: Vapour pressures values reported in the literature are shown in table for all pure compound studied.

		Decanoic acid
T/K	P_A (kPa)	Source
298.15	4.88E-05	(Baccanari et al., 1968). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
381.15	0.100	(Lide and David, 2009)
		URL: https://wikivividly.com/wiki/Decanoic_acid#cite_note-pubchem-2
398.15	0.133	CAMEO CHEMICALS. https://cameochemicals.noaa.gov/chemical/17804
415.15	0.667	CAMEO CHEMICALS. https://cameochemicals.noaa.gov/chemical/17804
422.2	1.50	(Weast and Grasselli, 1989). URL: https://webbook.nist.gov/chemistry/
433.15	2.03	https://wikivividly.com/wiki/Decanoic_acid#cite_note-pubchem-2
541.85	101.325	CAMEO CHEMICALS https://cameochemicals.noaa.gov/chemical/17804

Dimethyl phthalate

T/K	P_A (kPa)	Source
293.15	0.0002	CAS-No. 131-11-3, Sigma-Aldrich Co., Dimethyl Phthalate
298.15	0.0004	(Daubert, 1989)
		URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~Ycadp8:2
373.15	0.1300	CAS-No. 131-11-3, Sigma-Aldrich Co., Dimethyl Phthalate
373.45	0.1333	(Roháč et al., 1999)
404.93	0.6666	(Roháč et al., 1999)
420.76	1.3332	(Roháč et al., 1999)
437.15	2.6664	(Roháč et al., 1999)
455.95	5.3329	(Roháč et al., 1999)
466.106	8.3710	(Roháč et al., 1999)
467.15	7.9993	(Roháč et al., 1999)
474.85	11.1130	(Roháč et al., 1999)
481.441	13.9670	(Roháč et al., 1999)
483.15	13.3322	(Roháč et al., 1999)
487.539	16.8560	(Roháč et al., 1999)
493.754	20.3600	(Roháč et al., 1999)
500.261	24.6530	(Roháč et al., 1999)
505.85	26.6645	(Roháč et al., 1999)
506.556	29.4960	(Roháč et al., 1999)
512.673	34.9410	(Roháč et al., 1999)
518.54	40.9170	(Roháč et al., 1999)
530.95	53.3289	(Roháč et al., 1999)
555.2	101.3250	(Roháč et al., 1999)
556.85	101.3250	(O'Neil, 2013)
		URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~Ycadp8:2

DEET

T/K	P_A (kPa)	Source
293.15	1.10E-04	(Haynes, 2014). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
298.15	7.47E-04	(Drapeau et al., 2011)
298.15	2.67E-04	Blaine RL (1976). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
298.15	2.30E-04	CAS-No. 134-62-3, Sawyer Co., DEET
298.15	2.27E-04	URL: https://www.cdpr.ca.gov/docs/risk/rcd/deet.pdf
384.15	1.33E-01	CAMEOChemicals.URL: https://cameochemicals.noaa.gov/chemical/20199
433.15	2.533	(Haynes, 2014). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
558.15	101.325	CAMEOChemicals.URL: https://cameochemicals.noaa.gov/chemical/20199

Ethyl anthranilate

T/K	P_A (kPa)	Source
293.15	8.00E-04	(Api et al., 2015)
293.15	8.47E-04	(Api et al., 2015)
298.15	1.33E-03	(Islam et al., 2017)
298.15	1.37E-03	(Api et al., 2015)
373.4	0.13	(Weast and Grasselli, 1989). URL: https://webbook.nist.gov/cgi/cbook.cgi?
402.7	1	(Milwaukee, 1990). URL: https://webbook.nist.gov/cgi/cbook.cgi?
404.9	0.67	(Milwaukee, 1990). URL: https://webbook.nist.gov/cgi/cbook.cgi?
419.2	2	(Weast and Grasselli, 1989). URL: https://webbook.nist.gov/cgi/cbook.cgi?
420.8	1.33	(Weast and Grasselli, 1989). URL: https://webbook.nist.gov/cgi/cbook.cgi?
541.2	101.325	(Lide, 2004). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2

IR3535

T/K	P_A (kPa)	Source
293.15	1.50E-04	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
381.15	0.027	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
383.15	0.02	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
399.15	0.067	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
400.15	0.067	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
565.15	101.325	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2

Icaridin

T/K	P_A (kPa)	Source
293.15	3.40E-05	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
298.15	5.90E-05	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
323.15	7.10E-04	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2
569.15	101.325	(O'Neil, 2013). URL: https://toxnet.nlm.nih.gov/cgi-bin/sis/search2

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