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Solubility of triclocarban in pure alkanols at different temperatures

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Abstract−Triclocarban solubility in six pure alcohols was determined in the temperature interval from 278.15 to 318.15 K. The experimental solubility data were correlated by the Wilson, the nonrandom two liquid (NRTL) and the universal quasi-chemical (UNIQUAC) models. The data are well fitted with all three models for the six pure alcohols studied here. Also, *ab initio* geometry optimization of triclocarban was performed using the density functional theory (DFT) based on DMol^3 method.

Key words: Solid-liquid Equilibrium, Triclocarban, Alcohol

INTRODUCTION

Triclocarban (3,4,4′-trichlorocarbanilide) is a synthetic substance with anti-bacterial and anti-fungal properties that is widely used in cosmetics, consumer health products [1,2] and household products [3,4]. Due to its molecular nature, triclocarban is unionized at pH below 11 [5].

Solid-liquid phase equilibrium (SLE) data are important in many chemical engineering processes such as extraction and purification. During these processes, the difference between the actual concentration and the saturation solubility, namely, super-saturation is the driving force for nucleation, growth and agglomeration phenomena that affect the morphology, filterability, crystal size distribution, and polymorphic distribution of the product. Therefore, solubility information in different solvents is essential for designing a crystallization process. Triclocarban can be purified by crystallization using various solvents, and obviously crystallization relies upon the solubility. Accordingly, solubility data in different solvents are very important in industrial applications including purification. Unfortunately, limited data are available on the solubility of triclocarban in solvents [6].

The concentration of a saturated solution of solute dissolved in solvent has been measured using a laser technique [7], an analytical method [8], and a gravimetric method [9]. The gravimetric method is simple and reliable, so it was selected for this study.

This study aims to measure the solubility of triclocarban in ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol as pure solvents. The experimental temperature ranges from 278.15 to 318.15 K and experimental pressure is atmospheric pressure. The solubility was measured using gravimetric measurement after drying the equilibrium solutions. To confirm the validity of the designed apparatus and the experimental procedure, we measured the solubility of *dl*-alanine in water. Experimentally determined *dl*-alanine solubility values were compared with those reported in the literature. In addition, the experimental results were correlated by the Wilson [10], the nonrandom two liquid (NRTL) [11], and the universal quasi-chemical (UNIQUAC) [12] models. And *ab initio* geometry optimization of triclocarban was investigated by the density functional theory (DFT) based on DMol^3 method.

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EXPERIMENTAL SECTION

1. Chemicals

Ethanol (min. 99.9%), 1-propanol (min. 99.9%), 1-butanol (min. 99.7%), 1-pentanol (min. 99.0%), 1-hexanol (min. 99.0%), *dl*-alanine (min. 99.0%), triclocarban (min. 99.0%) were supplied by Sigma Aldrich (St. Louis, MO, USA). 1-Heptanol (min. 98.0%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Water was passed through an ion exchanger and distilled. All chemicals were used without further purification.

2. Apparatus and Procedures

The solubility of solids was measured in a solubility measurement apparatus with an external thermostat in the temperature range between 278.15 and 318.15 K at atmospheric pressure. The numerical value of an expanded uncertainty of the measured pressure is 0.0360 bar. The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2, providing a level of confidence of approximately 95% [13]. All expanded uncertainty reported herein was estimated by the same method as mentioned above. The experimental temperature in the apparatus was controlled within ±0.05 K by a thermostat and measured with a digital thermometer (1502A/5618B). The numerical value of the expanded uncertainty of the measured temperature is 0.0118 K. The supersaturated solutions in the 50 ml glass tube were agitated with a magnetic stirrer for at least 48 hr. Then, samples of clear saturated solution were withdrawn by using a syringe (10 ml) through a filter (PTFE, 0.2 μm). The mass of the saturated (filtered) clear solution sample was recorded with an analytical balance (EPG 214). The numerical value of an expanded uncertainty of the measured weight is 0.000246

g. To evaporate all solvents, each solution sample was dried in a vacuum oven for at least seven days. To certify that no solvent remained, the mass of the samples was recorded repeatedly throughout the drying process. When all solvent of samples was evaporated, the samples were weighed and recorded. To improve reliability of the experimental results, the solubility experiments were performed more than three times for all data points. The mole fraction, x_1, was obtained with the following equation:

$$x_1 = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2} \quad (1)$$

where W_1 and W_2 represent the mass of solute and solvent, respectively. And M_1 and M_2 are the molecular weight of solute and solvent, respectively.

RESULTS AND DISCUSSION

The solubility of *dl*-alanine in water was measured between 278.15 K and 328.15 K to check the reliability of the solid-liquid equilibrium measurement apparatus and the experimental procedure. *Dl*-alanine is inexpensive and easy to obtain. Also, the experimental data of *dl*-alanine that can be used as a reference are diverse and abundant. So, we selected *dl*-alanine for the solubility measurement as a reference. Fig. 1 and Table 1 summarize the results compared to those obtained by Dalton and Schmidt [14] for each temperature. Our results are in good agreement with the literature, which leads us to conclude that this apparatus is reliable.

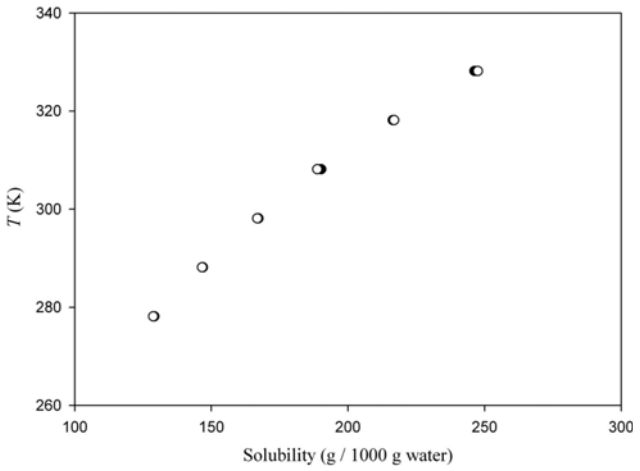


Fig. 1. Solubility of dl-alanine in pure water. ○, this work; ●, literature [14].

Table 1. Solubility of *dl*-alanine in pure water

T (K)	Literature [14] (g/kg solvent)	Solubility (g/kg solvent)	Standard deviation	Mole fraction, x_1
278.15	129.1	128.7	0.176	0.0254
288.15	146.9	146.6	0.187	0.0288
298.15	167.2	166.8	0.183	0.0326
308.15	190.2	188.8	0.195	0.0368
318.15	216.4	216.9	0.164	0.0420
328.15	246.3	247.5	0.175	0.0477

The solubility data for triclocarban in various alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol), between 278.15 K and 318.15 K are presented in Table 2 along with

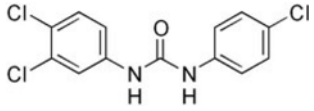
Table 2. Experimental solid-liquid equilibrium data for triclocarban (1)+pure alcohols (2) expressed in mole fractions at temperatures from 278.15 K up to 318.15 K

Alcohols	T (K)	Mole fraction	Expanded uncertainty
Ethanol	278.15	0.000491	0.0000156
	283.15	0.000663	
	288.15	0.000884	
	293.15	0.001172	
	298.15	0.001527	
	303.15	0.001985	
	308.15	0.002574	
	313.15	0.003276	
	318.15	0.004172	
1-Propanol	278.15	0.000669	0.0000202
	283.15	0.000887	
	288.15	0.001198	
	293.15	0.001563	
	298.15	0.002043	
	303.15	0.002635	
	308.15	0.003402	
	313.15	0.004290	
	318.15	0.005471	
1-Butanol	278.15	0.001004	0.0000250
	283.15	0.001355	
	288.15	0.001746	
	293.15	0.002251	
	298.15	0.002883	
	303.15	0.003655	
	308.15	0.004630	
	313.15	0.005785	
	318.15	0.007208	
1-Pentanol	278.15	0.001574	0.0000299
	283.15	0.002025	
	288.15	0.002539	
	293.15	0.003205	
	298.15	0.003976	
	303.15	0.004910	
	308.15	0.006081	
	313.15	0.007430	
	318.15	0.009062	
1-Hexanol	278.15	0.002268	0.0000349
	283.15	0.002807	
	288.15	0.003454	
	293.15	0.004238	
	298.15	0.005112	
	303.15	0.006206	
	308.15	0.007502	
	313.15	0.008981	
	318.15	0.010789	

Table 2. Continued

Alcohols	T (K)	Mole fraction	Expanded uncertainty
1-Heptanol	278.15	0.003046	0.0000392
	283.15	0.003637	
	288.15	0.004410	
	293.15	0.005251	
	298.15	0.006315	
	303.15	0.007502	
	308.15	0.008959	
	313.15	0.010510	
	318.15	0.012456	

Table 3. Some physicochemical properties of triclocarban and alcohols

Molecular structure	M (g/mol)	$\Delta_{fus}H$ (kJ/mol)	$_{fus}T$ (K)
	315.58	41.94	528.20

Component	r	q	v (m^3/kmol)
Triclocarban[a]	10.064	7.516	0.220
Ethanol[b]	2.105	1.972	0.059
1-Propanol[b]	2.780	2.512	0.075
1-Butanol[b]	3.454	3.048	0.092
1-Pentanol[b]	4.129	3.592	0.109
1-Hexanol[b]	4.803	4.132	0.125
1-Heptanol[b]	5.477	4.672	0.142

[a]Literature [16,17]
[b]Literature [16]

the expanded uncertainty for the data points.

The melting temperature and fusion enthalpy of triclocarban were measured by using a differential scanning calorimeter (TA instrument Q100). The melting temperature and fusion enthalpy value of triclocarban were 528.20 K and 41.94 kJ/mol, respectively. The van der Waals (VdW) volume, VdW area, and liquid molar volume of alkanol were taken from the DIPPR 801 database [15]. VdW volume, VdW area, and liquid molar volume of triclocarban were obtained by the group contribution method [16,17]. The physicochemical properties of triclocarban and pure alcohols are summarized in Table 3.

According to the solid-liquid phase equilibrium theory, the temperature dependence of solid solubility in pure solvents is described as [18]

$$\ln(x_1\gamma_1)=\frac{\Delta_{fus}H}{RT}\left(\frac{T}{T_m}-1\right)-\frac{\Delta C_p}{R}\left(1-\frac{T_m}{T}+\ln\left(\frac{T_m}{T}\right)\right) \quad (2)$$

where x_1 is the solubility of a solid in a liquid phase, γ_1 is the activity coefficient of the solid, $\Delta_{fus}H$ is the molar enthalpy of fusion of the solid and T_m is melting temperature of the solid. In Eq. (2), ΔC_p at melting temperature can be considered equal to zero, which is an assumption used commonly for the estimation of solubility [18,19]. This assumption is based on empirical observations. Therefore, a simplified form of this equation can be used:

$$\ln(x_1\gamma_1)=\frac{\Delta_{fus}H}{RT}\left(\frac{T}{T_m}-1\right) \quad (3)$$

In this study, the Wilson, NRTL, UNIQUAC models were used to derive the solute activity coefficient, γ_1.

The Wilson equation for the activity coefficient is given by

$$\ln\gamma_1=-\ln(x_1+\Lambda_{12}x_2)+x_2\left(\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2}-\frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right) \quad (4)$$

where

$$\Lambda_{12}=\frac{v_2}{v_1}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right),\ \Lambda_{21}=\frac{v_1}{v_2}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right) \quad (5)$$

The Wilson model has two adjustable parameters: $\Delta\lambda_{12}=\lambda_{12}-\lambda_{11}$, $\Delta\lambda_{21}=\lambda_{21}-\lambda_{22}$.

The NRTL model for the activity coefficient is given by

$$\ln\gamma_1=x_2^2\left[\frac{\tau_{21}G_{21}^2}{(x_1+G_{21}x_2)^2}+\frac{\tau_{12}G_{12}}{(G_{12}x_1+x_2)^2}\right] \quad (6)$$

where

$$G_{12}=\exp(-\alpha_{12}\tau_{12}),\ G_{21}=\exp(-\alpha_{12}\tau_{21}),\ \tau_{12}=\frac{\Delta g_{12}}{RT},\ \tau_{21}=\frac{\Delta g_{21}}{RT} \quad (7)$$

The NRTL equation contains three adjustable parameters: Δg_{12}, Δg_{21}, and α_{12}. The parameter α_{12} is related to the non-randomness in the mixture and varies from 0.2 to 0.47. In this study, α_{12} was set to 0.3, so the NRTL equation has two adjustable parameters [19].

The UNIQUAC model for the activity coefficient is given by

$$\ln\gamma_1=\ln\frac{\varphi_1}{x_1}+\frac{z}{2}q_1\ln\frac{\theta_1}{\varphi_1}+\varphi_2\left(l_1-\frac{r_1}{r_2}l_2\right)-q_1\ln(\theta_1+\theta_2\tau_{21})+\theta_2q_1\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}}-\frac{\tau_{12}}{\theta_1\tau_{12}+\theta_2}\right) \quad (8)$$

where

$$l_1=\frac{z}{2}(r_1-q_1)-(r_1-1),\ l_2=\frac{z}{2}(r_2-q_2)-(r_2-1) \quad (9)$$

$$\tau_{12}=\exp\left(-\frac{\Delta u_{12}}{RT}\right),\ \tau_{21}=\exp\left(-\frac{\Delta u_{21}}{RT}\right) \quad (10)$$

$$\varphi_1=\frac{x_1r_1}{x_1r_1+x_2r_2},\ \varphi_2=\frac{x_2r_2}{x_1r_1+x_2r_2},$$
$$\theta_1=\frac{x_1q_1}{x_1q_1+x_2q_2},\ \theta_2=\frac{x_2q_2}{x_1q_1+x_2q_2} \quad (11)$$

The UNIQUAC model has two adjustable parameters, Δu_{12} and Δu_{21}. The coordination number z is set to 10 [12].

A comparison between the experimental data and the calculated results is shown in Figs. 2, 3, and 4. The values of parameters and the average absolute deviation of mole fraction (AADx) are listed in Table 4. The AADx is defined as

$$AADx=\frac{1}{N}\sum_{j=1}^{N}\left|\frac{x_{1,j}^{exp}-x_{1,j}^{calc}}{x_{1,j}^{exp}}\right| \quad (12)$$

where N is the number of experimental points, $x_{1,j}^{calc}$ represents the solubility calculated from Eq. (3), and $x_{1,j}^{exp}$ represents the experimen-

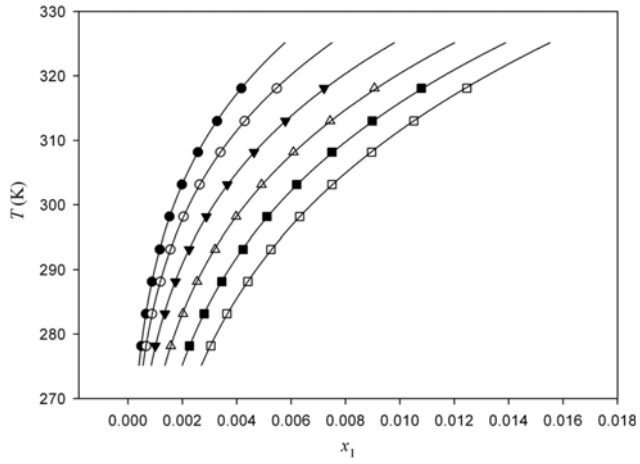


Fig. 2. Experimental solid-liquid equilibrium data and correlated data by the Wilson model for triclocarban (1)+pure alcohols (2) at temperatures from 278.15 K up to 318.15 K: ●, ethanol; ○, 1-propanol; ▼, 1-butanol; △, 1-pentanol; ■, 1-hexanol; □, 1-heptanol; solid curves, Wilson.

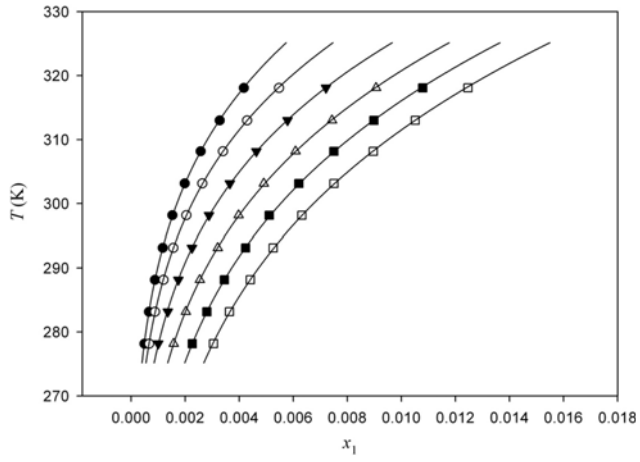


Fig. 3. Experimental solid-liquid equilibrium data and correlated data by the NRTL model for triclocarban (1)+pure alcohols (2) at temperatures from 278.15 K up to 318.15 K: ●, ethanol; ○, 1-propanol; ▼, 1-butanol; △, 1-pentanol; ■, 1-hexanol; □, 1-heptanol; solid curves, NRTL.

tal solubility values.

As shown in Table 4, the average absolute deviation between calculated values and experimental data of triclocarban is less than 0.714%, 0.624%, and 0.627% for the Wilson, NRTL, and UNIQUAC model, respectively. All three correlation results are in good agreement with the experimental data.

As shown in Figs. 2, 3, and 4, the solubility is plotted versus temperature, and the figure shows that the solubility of triclocarban is the lowest in ethanol and the largest in 1-heptanol, and that of triclocarban increases with an increase of chain length of pure alkanols in all the temperature range and with temperature in selected solvents. The solubility of triclocarban decreases with a decrease in solvent polarity.

According to the molecular structure of triclocarban in Table 3, it has 'N-H' structure, which shows the clue of the possibility of

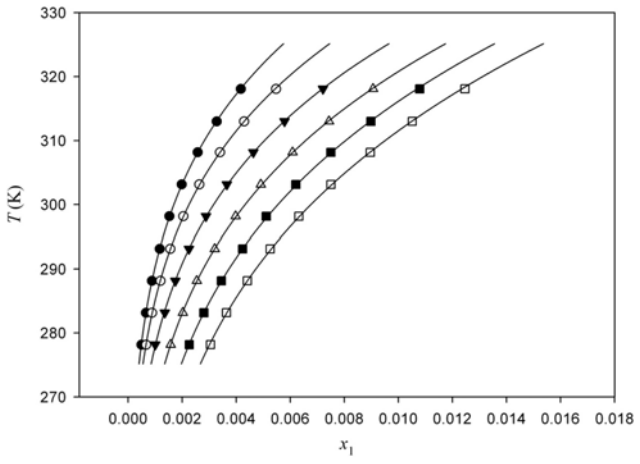


Fig. 4. Experimental solid-liquid equilibrium data and correlated data by the UNIQUAC for triclocarban (1)+pure alcohols (2) at temperatures from 278.15 K up to 318.15 K: ●, ethanol; ○, 1-propanol; ▼, 1-butanol; △, 1-pentanol; ■, 1-hexanol; □, 1-heptanol; solid curves, UNIQUAC.

Table 4. Interaction parameters for the activity coefficient models and average absolute deviation for liquid phase composition obtained by the correlation of solid-liquid equilibrium data in the studied systems

Model	Parameters		AADx (%)
	A_{12}[a]	A_{21}[a]	
Triclocarban (1)+ethanol (2)			
Wilson	−5653.444	3450.178	0.240
NRTL	−1202.348	−825.961	0.343
UNIQUAC	209.728	−139.621	0.296
Triclocarban (1)+1-propanol (2)			
Wilson	−5705.701	2784.448	0.442
NRTL	−807.342	−2041.072	0.488
UNIQUAC	132.814	−130.281	0.497
Triclocarban (1)+1-butanol (2)			
Wilson	4583.688	−1947.534	0.714
NRTL	−2995.781	496.351	0.624
UNIQUAC	177.699	−183.315	0.627
Triclocarban (1)+1-pentanol (2)			
Wilson	5600.822	−2609.093	0.584
NRTL	−4546.749	3236.821	0.420
UNIQUAC	293.267	−257.282	0.459
Triclocarban (1)+1-hexanol (2)			
Wilson	6226.472	−3114.868	0.431
NRTL	−5447.901	5220.092	0.372
UNIQUAC	402.951	−306.837	0.548
Triclocarban (1)+1-heptanol (2)			
Wilson	5555.354	−3374.025	0.385
NRTL	−5983.651	6487.984	0.450
UNIQUAC	−217.325	220.428	0.642

[a]Adjustable parameters: NRTL $A_{ij}=g_{ij}-g_{jj}$; UNIQUAC $A_{ij}=\Delta u_{ij}$; Wilson $A_{ij}=\lambda_{ij}-\lambda_{jj}$

forming a hydrogen bond. However, as shown in Table 2, the solubility is lower than expected when compared with that of triclosan, which has a similar structure to it [20]. So *ab initio* geometry optimizations in the framework of the density functional theory (DFT), as implemented in the DMol^3 code [21] were carried out to analyze this phenomenon qualitatively (DMol^3 is available from Accelrys, Inc., as part of Materials Studio). Exchange and correlation terms were treated within the generalized gradient (GGA) functional by Perdew et al. [22]. Core electrons were treated in a non-relativistic all-electron implementation of the potential. A double numerical quality basis set with polarization function (DNP) was considered, with a real-space cutoff of 3.7 Å. The tolerances of energy, gradient and displacement convergence were 0.0000054 eV, 0.000027 eV Å^{-1} and 0.00005 Å, respectively. The optimized, most stable triclocarban structure is shown in Fig. 5. To verify the optimized structure illustrated in Fig. 5 is global minimum, the total energy of various structures of triclocarban was calculated, of which results are listed in Table 5. According to the results, the structure shown in Fig. 5 can be considered as the most stable triclocarban structure that is thin plate shape. So this solid structure of triclocarban would be a more well-packed structure, and the intermolecular attractive interaction (such as hydrogen bond, dipole-dipole interactions, Debye force) will be stronger if we assume 0,0 conformation of triclocarban is dominant among nine geometries. Therefore, the interaction between triclocarban and alcohol might be weaker than that between triclocarban molecules (that is, degree of stabilized energy by interaction between triclocarban and alcohol was reduced); consequently, the solubility of triclocarban in alcohol seems to be considerably reduced.

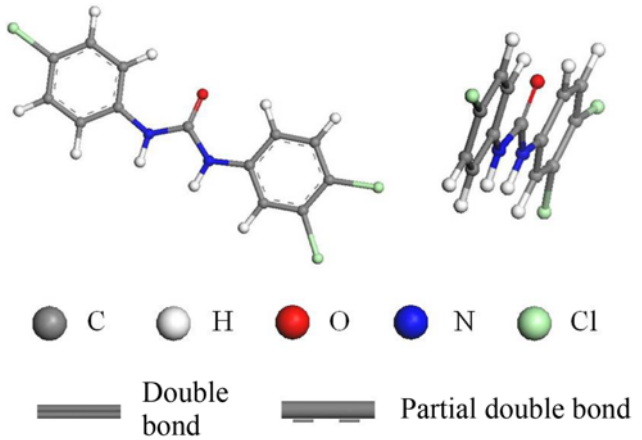
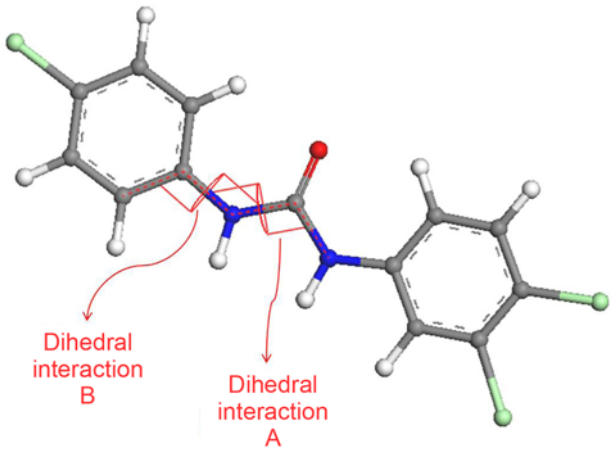


Fig. 5. Structure of triclocarban considered in the DMol^3 geometry optimization calculation.

Table 5. The total energy of various structures of triclocarban considered in the DMol^3 energy calculations



Dihedral interaction	0,0	0,1	0,2
kJ/mol	−5439667.42	−5439648.88	−5439651.40
	1,0	1,1	1,2
	−5439637.46	−5439619.22	−5439591.12
	2,0	2,1	2,2
	−5439631.82	−5439581.87	−5439615.89

A, B: dihedral interaction (0: trans, 1: −60° gauche, 2: 60° gauche)

CONCLUSIONS

SLE data for triclocarban in ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and 1-heptanol were measured from 278.15 to 318.15 K at 5 K intervals. The experimental solubility was determined using gravimetric measurements after drying the equilibrium solutions. The experimental solubility values of triclocarban in pure alcohols increase with an increase of temperature and with an increase of chain length of selected alkanols. The activity coefficient for solubility of triclocarban in pure alkanols was calculated with the Wilson, the NRTL and UNIQUAC models, and with them were correlated solubility data that were compared with the experimental ones. All three correlation results were in good agreement with the experimental data. *Ab initio* geometry optimization of triclocarban was carried out using the density functional theory (DFT) based DMol^3 method. According to the results, the most stable triclocarban structure is thin plate shape. So the interaction between triclocarban and alcohol might be weaker than that between triclocarban. Therefore, the solubility of triclocarban in alcohol seems to be considerably reduced. The challenge for the future is that more accurate and quantitative simulation is performed. And to do this, continued development of the simulator [23] is required.

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NOMENCLATURE

x_1 : mole fraction, Eq. (1)
solubility of a solid in a liquid phase, Eq. (2)
W_1 : mass of solute, Eq. (1)
W_2 : mass of solvent, Eq. (1)
M_1 : molecular weight of solute, Eq. (1)
M_2 : molecular weight of solvent, Eq. (1)
$\Delta_{fus}H$: molar enthalpy of fusion of the solid, Eq. (2)

T_m : melting temperature of the solid, Eq. (2)
Δg_{12}, Δg_{21} : adjustable parameters contained in the NRTL model, Eq. (7)
Δu_{12}, Δu_{21} : adjustable parameters contained in the UNIQUAC model, Eq. (10)
z : coordination number, Eq. (9)
N : number of experimental points, Eq. (12)
$x_{1,j}^{calc}$: correlated solubility value, Eq. (12)
$x_{1,j}^{exp}$: experimental solubility value, Eq. (12)

Greek Letters

γ_1 : activity coefficient of the solid, Eq. (2)
α_{12} : adjustable parameters contained in the NRTL model (related to the non-randomness in the mixture), Eq. (7)
$\Delta\lambda_{12}$, $\Delta\lambda_{21}$: adjustable parameters contained in the Wilson model, Eq. (5)

Superscripts

calc : calculation
exp : experiment

Subscripts

fus : fusion
m : melting

REFERENCES

1. D. L. Breneman, J. M. Hanifin, C. A. Berge, B. H. Kewick and P. B. Neumann, *Cutaneous Medicine for the Practitioner*, **66**, 296 (2000).
2. S. Luby, M. Agboatwalla, D. Feikin, J. Painter, W. Billhimer, A. Altaf and R. Hoekstra, *The Lancet*, **366**, 225 (2005).
3. O. Exner and H. M. Hoffmann, US Patent, 6,121,214 (2000).
4. L. R. Charlton and J. T. McGillycuddy, US Patent, 6,224,886 (2001).
5. A. C. Moffat, M. D. Osselton and B. Widdop, *Clarke's Analysis of Drugs and Poisons*, 3rd Ed., Vol. 2, Pharmaceutical Press, London (2004).
6. D. M. Arogón, A. Sosnik and F. Martínez, *J. Sol. Chem.*, **38**, 1493 (2009).
7. Q. S. Ki, Z. Ki and S. Wang, *J. Chem. Eng. Data*, **52**, 151 (2007).
8. D. Wei and L. Chen, *Fluid Phase Equilib.*, **277**, 9 (2009).
9. R. R. Fu, W. D. Yan and M. Zhu, *J. Chem. Eng. Data*, **49**, 262 (2004).
10. G. M. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964).
11. H. Renon and J. M. Prausnitz, *AIChE J.*, **14**, 135 (1968).
12. D. S. Abrams and J. M. Prausnitz, *AIChE J.*, **21**, 116 (1975).
13. B. N. Taylor and C. E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, 1994 Ed., NIST.
14. J. B. Dalton and C. L. A. Schmidt, *J. Biol. Chem.*, **103**, 549 (1933).
15. DIPPR 801 Database, Design Institute for Physical Property Data, American Institute of Chemical Engineers.
16. B. E. Polling, J. M. Prausnitz and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th Ed., McGrow-Hill, New York (2001).
17. L. Constantinou, R. Gani and J. P. O'Connell, *Fluid Phase Equilib.*, **103**, 11 (1995).
18. S. I. Sandler, *Chemical, Biochemical, and Engineering Thermodynamics*, 4th Ed., John Wiley & Sons, Inc., New Jersey (2005).
19. J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd Ed., Prentice Hall PTR, New Jersey (1999).
20. D. M. Aragón, M. A. Ruidiaz, E. F. Vargas, C. Bregni, D. A. Chiappetta, A. Sosnik and F. Martínez, *J. Chem. Eng. Data*, **53**, 2576 (2007).
21. B. Delley, *J. Chem. Phys.*, **113**, 7756 (2000).
22. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996).
23. J. Chang, *Korean Chem. Eng. Res.*, **49**, 361 (2011).