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Review Article

Correlating Solubilities of Some Parabens in Supercritical Carbon Dioxide using Modified Wilson's Model

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Abstract

Modelling and measuring of solubilities of compounds in supercritical fluids is an important area of research and is gaining significant importance in the recent times. It is being exploited in the particle micronization. Parabens are some of the crucial industrial compounds as their roles in the cosmetics, food, pharmaceutical etc., industries are indispensable. The present work deals with the inception of new model correlations for the solubilities of ethyl, methyl and propyl parabens in Supercritical Carbon Dioxide ($ScCO_2$), wherein, the correlation constant's predictions were compared with the existing data reported in the literature [Asghari-Khiavi, M.; Yamini, Y. J. Chem. Eng. Data 48,61-65 (2003); Li, W.; Jin, J.; Tian, G.; Zhan, Z. Fluid Phase Equilb. 264, 93-98 (2008); Cheng,K-W.; Tang, M.; Chen, Y.-P. Fluid Phase Equilib. 201, 79-96 (2002)]. The solubility model used in this work was based on thermodynamic solid- liquid phase equilibrium criteria. In the present model, $ScCO_2$ was considered as an expanded liquid and the activity coefficient of the solute at infinite dilution is represented with the Wilson's model. Correlation efficacy of the model was evaluated with corrected Akaike's information criterion (AIC_c). From the correlation results, the present model was able to correlate the data below 6.13%, 7.93% and 4.04% and the corresponding AICc were -793.145, -356.868 and -462.107 for methyl, ethyl and propyl parabens respectively. Further, conventional density model proposed by Chrastil has been evaluated for comparison. The correlation results of Chrastil model were 10.09%, 5.217% and 11.12% and the corresponding AICc were -773.932, -301.787, -526.112 for methyl, ethyl and propyl paraben respectively.

Keywords: Chrastil model; Ethylparaben; Methylparaben; Modified wilson's model; Propylparaben; Solid liquid equilibrium criteria

Introduction

Parabens are the esters of para hydroxyl benzoic acids. They are extensively used in pharmaceutical, food, personal hygiene etc., industries as preservative compounds, additives and bacterial and mold growth inhibitors in the cosmetic industry. Methylparaben's industrial usage as an anti-fungal agent in both the personal hygiene and cosmetic industries and as a food preservative (E218) is noticeable. For ethylparaben, its anti-fungal and anti-microbial properties are appreciable along with its usage as a phytoestrogen and as a plant metabolite. In the case of propylparaben, its industrial uses are common as a food preservative and as a preservative, specifically in the water-based cosmetics. It is to be noted that paraben compounds have low solubility in the aqueous phase but they tend to dissolve in a maximum number of systems at temperatures above 333.15 K. At room temperature, the above parabens are solids. Their utilization, effectively, is managed by controlling the particle's size of the compound. This is generally known as micronization of particles. The process of micronization may is effectively performed with organic solvents or supercritical solvents. The process that utilizes supercritical fluids is known as green process and it is given due importance. In nature we have several supercritical compounds, however, carbon dioxide is increasingly being used and it is represented as $ScCO_2$. It has impressive solubility characteristics and distinctive physical properties such as alterable density, non-flammability, low cost for more purity, non-toxicity, inert nature, precise and efficient separation as a green solvent and more. Supercritical solvents dissolve paraben compounds to varying extent depending on pressure and temperature. The is a limited amount of paraben solubility data in $ScCO_2$ is available in literature and measuring solubility at every

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point is a difficult task, therefore, the modelling the solubility data is essential [1-4].

In this work, a new four parameter solubility model based on solid liquid phase equilibrium criteria is evaluated. For comparison, popular Chrastil model [5] is considered and the efficacy of the model is evaluated in terms of corrected Akaike's information criterion (AIC_c). More details about the models and AIC_c are presented in the following sections.

Theory (expanded liquid model)

According to solid-liquid phase equilibrium criteria, at equilibrium, fugacity of the solute (paraben) in the solid phase is equal to fugacity of solute in the liquid phase. Density of $ScCO_2$ is close to that of the liquid's density, therefore, the supercritical gas phase can be treated approximately as an expanded liquid. When solubility of $ScCO_2$ in solid phase is negligible, solubility of solid component in $ScCO_2$, at infinite dilution is expressed as [6,7].

$$y_2 = \frac{1}{\gamma_2^{\infty}} \frac{f_2^S}{f_2^L} \qquad (1)$$

Where, γ_2^{∞} is the solute's activity coefficient at infinite dilution in $ScCO_2$; f_2^S / f_2^L is the ratio of fugacity of pure solid and liquid, [8].

$$\ln\left(\frac{f_2^S}{f_2^L}\right) = \frac{\Delta H_2^m}{RT}\left(\frac{T}{T_m} - 1\right) - \int_{T_m}^{T} \frac{1}{RT^2}\left[\int_{T_m}^{T} \left[\Delta C_p\right] dT\right] dT \qquad (2)$$

Where, ΔC_p is the net change of heat capacities between the solid and $ScCO_2$ phases. On substitutingeq.(2) in eq.(1) we get, eq (3)

$$y_2 = \frac{1}{\gamma_2^{\infty}} \exp\left[\frac{\Delta H_2^m}{RT}\left(\frac{T}{T_m} - 1\right) - \int_{T_m}^{T} \frac{1}{RT^2}\left[\int_{T_m}^{T} \left[\Delta C_p\right] dT\right] dT\right] \qquad (3)$$

The final expression for solubility depends on the activity coefficient and the integral expression in the eq.(3) When the integral term in eq. (3) is neglected and the expression for the solubility is

$$y_2 = \exp\left[\frac{\Delta H_2^m}{RT}\left(\frac{T}{T_m} - 1\right)\right] / \gamma_2^{\infty}$$

in order to use eq (3), we need an appropriate model for activity coefficient. In this work, a modified Wilson's activity coefficient model is used. The relevant equations are presented as follows [6,7].

$$\ln(\gamma_2^{\infty}) = 1 - \Lambda_{12} - \ln(\Lambda_{12}) \qquad (5)$$

Where,

$$\Lambda_{12} = \frac{v_2}{v1} exp\left(-\frac{\lambda_{12}}{RT}\right) \qquad (6)$$

$$\Lambda_{21} = \frac{v_2}{v1} exp\left(-\frac{\lambda_{21}}{RT}\right) \qquad (7)$$

(8)

$$\Lambda_{12} = v_2 \rho_{c1} \rho_r exp\left(-\frac{\lambda_{12}^{'}}{T_r}\right)$$

$$\Lambda_{12} = \frac{1}{v_2 \rho_{c1} \rho_r} exp\left(-\frac{\lambda_{21}^{'}}{T_r}\right) \qquad (9)$$

$$\lambda_{12}^{'} = \frac{\lambda_{12}}{RT_{c1}} \quad \text{and} \quad \lambda_{21}^{'} = \frac{\lambda_{21}}{RT_{c1}}$$

$$v_2 = \alpha\rho_r + \beta \qquad (10)$$

v_1 and v_2 are molar volumes of the solute and solvent respectively; On combining eqs.(6) to (10), we get

$$\Lambda_{12} = (\alpha\rho_r + \beta)\rho_{c1}\rho_r exp\left(-\frac{\lambda_{12}^{'}}{T_r}\right) \qquad (12)$$

$$\Lambda_{21} = \frac{}{(\alpha\rho_r + \beta)\rho_{c1}\rho_r} exp\left(-\frac{\lambda_{21}^{'}}{T_r}\right) \qquad (13)$$

$\lambda_{21}^{'}$ and $\lambda_{12}^{'}$ are the energies of interaction between the molecules respectively Finally, the expression for dilute activity coefficient is

$$\ln\left(\gamma_2^{\infty}\right) = 1 - (\alpha\rho_r + \beta)\rho_{c1}\rho_r exp\left(-\frac{\lambda_{12}^{'}}{T_r}\right) - \ln\left(\frac{1}{(\alpha\rho_r + \beta)\rho_{c1}\rho_r} \exp\left(-\frac{\lambda_{21}^{'}}{T_r}\right)\right) \qquad (14)$$

Combining eq.(3) and eq.(14) gives an expression for solubility.

$$y_2 = \exp\left[\frac{\Delta H_2^m}{RT}\left(\frac{T}{T_m} - 1\right)\right] / \exp(1 - (\alpha\rho_r + \beta)\rho_{c1}\rho_r \exp\left(-\frac{\lambda_{12}^{'}}{T_r}\right) - \ln\left(\frac{1}{(\alpha\rho_r + \beta)\rho_{c1}\rho_r} \exp\left(-\frac{\lambda_{21}^{'}}{T_r}\right)\right)) \qquad (15)$$

Thus eq.(15) is a four parameter model.

Chrastil Model

Chrastil [5] has proposed a solubility model based on solvato complex theory which was the first density-based model and it is being used for a variety of solute-solvent systems. Chrastil model is represented according to the following equation in terms of mole fraction

$$y_2 / mole\ fraction = \frac{M_{ScF}}{M_{Solute}} \left(\rho_1 / kg \cdot m^{-3}\right)^{k-1} \exp\left(A_1 + B_1 / T/K\right) \Big/ \left[1 + \frac{M_{ScF}}{M_{Solute}} \left(\rho_1 / kg \cdot m^{-3}\right)^{k-1} \exp\left(A_1 + B_1 / T/K\right)\right] \qquad (15)$$

The model constants in eqs (12), (13) and (14) are estimated with following objective function (OF) eq.(15) [4-9].

$$OF = \sum_{i=1}^{N} \frac{\left|y_{2i}^{\exp} - y_{2i}^{calc}\right|}{y_{2i}^{\exp}} \qquad (16)$$

The results are reported in terms ofaverage absolute relative deviation percentage (AARD %).

$$AARD(\%) = \left(100 / N_i\right) \sum_{i=1}^{N} \frac{\left|y_{2i}^{\exp} - y_{2i}^{cal}\right|}{y_{2i}^{\exp}} \qquad (16)$$

If meltingenthalpy (ΔH_2^m) and melting point (T_m) a suitable group contribution method such as Jain et al. [10] may be used.The regression is done with MATLAB's inbuilt fminsearch algorithm.

Table 1: Correlation constants of modified Wilson's model and Chrastil model.

Name of the model/Compound	Correlation constants				AARD %
Modified Wilson's model					
	α	β	$\lambda_{12}^{'}$	$\lambda_{21}^{'}$	
Methylparaben	6.6982×10^{-4}	5.0734×10^{-3}	0.16784	9.3740	6.13
Ethylparaben	-9.0137×10^{-4}	3.7672×10^{-3}	-1.3686	12.746	7.93
Propylparaben	-6.6627×10^{-4}	1.5332×10^{-2}	0.41238	11.172	4.04
Chrastil model					
	k	C_1	C_2		
Methylparaben	3.877	-10.15752	-5170.3		10.09
Ethylparaben	3.3749	-8.5741	-4770.5		5.217
Propylparaben	5.5618	-14.791	-7099.6		11.12

Table 2: Statistical parameters of modified Wilson's model and Chrastil model.

Model/Compound	SSE	AIC	AIC_c
Modified Wilson's model			
Methylparaben	8.28×10^{-8}	-794	-793.145
Ethylparaben	4.04×10^{-10}	-359	-356.868
Propylparaben	4.09×10^{-9}	-464	-462.107
Chrastil model			
Methylparaben	1.34×10^{-7}	-775	-773.932
Ethylparaben	1.59×10^{-8}	-304	-301.787
Propylparaben	1.94×10^{-10}	-528	-526.112

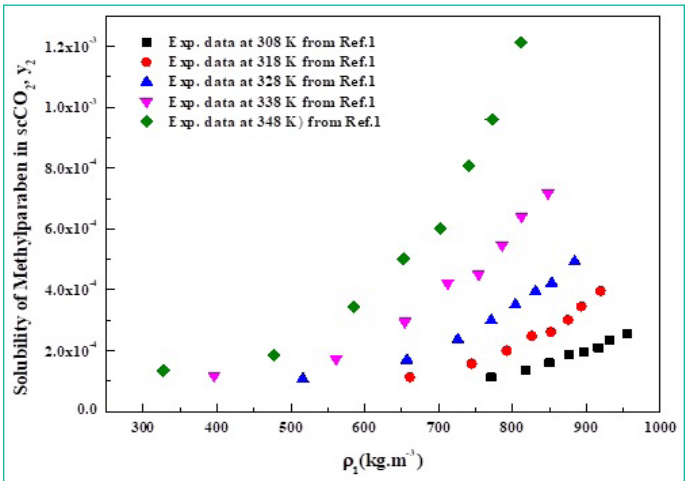

Figure 1: Solubility of Methylparaben in $ScCO_2$ [1].

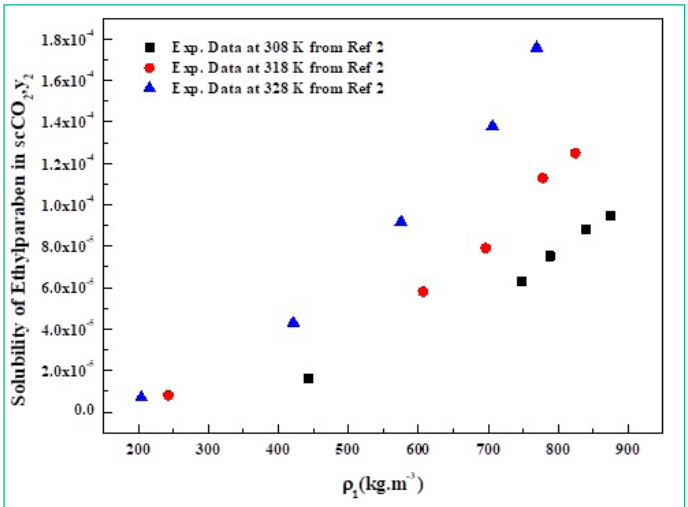

Figure 2: Solubility of Ethylparaben in $ScCO_2$ [2].

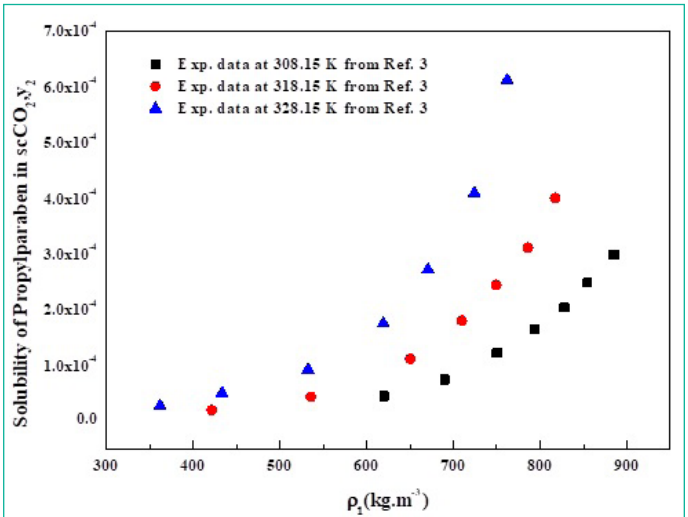

Figure 3: Solubility of Propylparaben in $ScCO_2$ [3].

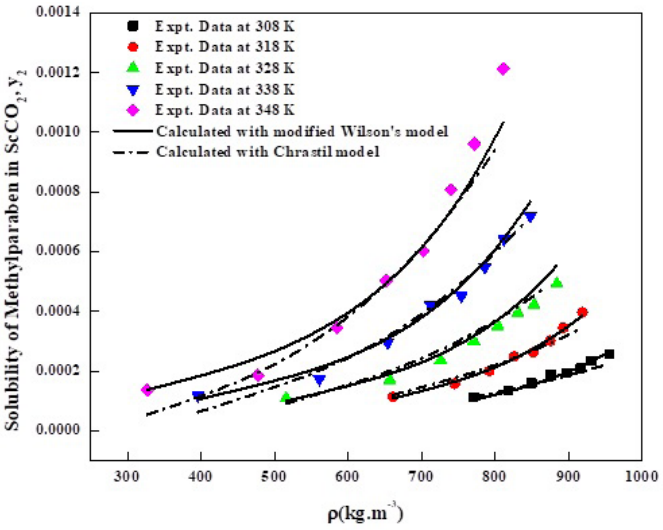

Figure 4: Solubility of Methylparaben vs $ScCO_2$ density. Symbols indicate experimental data at different temperatures obtained from literature. Solid lines are calculated modified Wilson's model. Dash-dot lines are calculated Chrastil model.

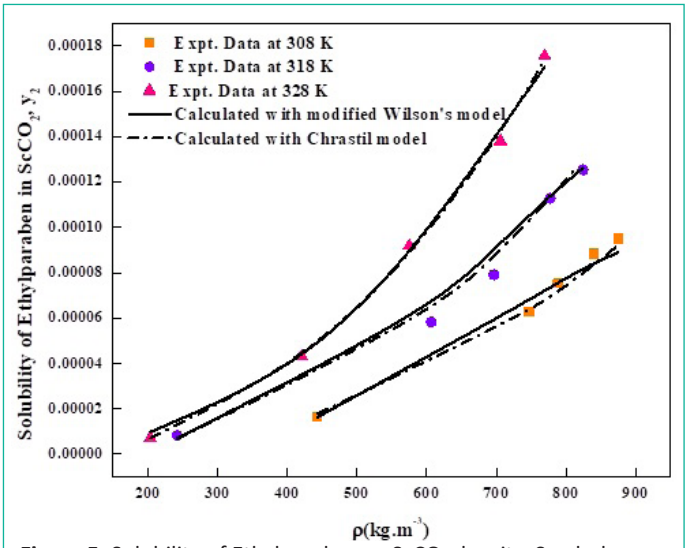

Figure 5: Solubility of Ethylparaben vs $ScCO_2$ density. Symbols indicate experimental data at different temperatures obtained from literature. Solid lines are calculated modified Wilson's model. Dash-dot lines are calculated Chrastil model.

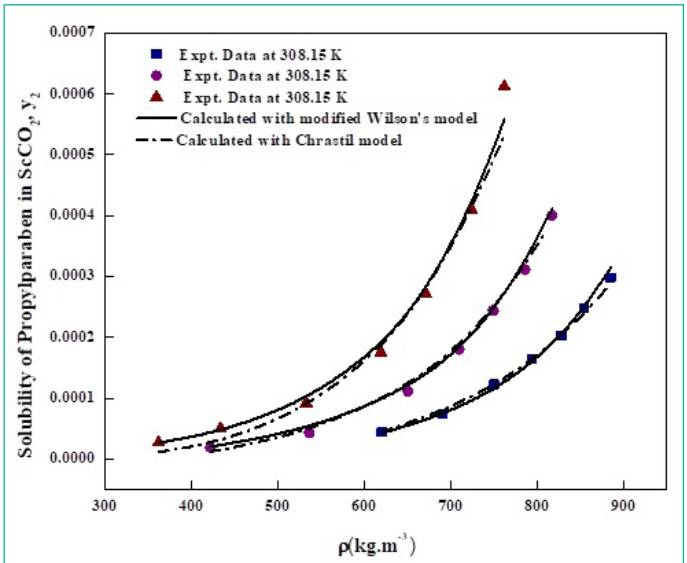

Figure 6: Solubility of Propylparaben vs $ScCO_2$ density. Symbols indicate experimental data at different temperatures obtained from literature. Solid lines are calculated modified Wilson's model. Dash-dot lines are calculated Chrastil model.

Results and Discussion

For modelling, the available solubility data of methyl (at 308, 318, 328 and 338 K), ethyl (at 308, 318 and 328 K) and propyl (at 308, 318 and 328 K) parabens are considered from the literature (Chen et al. [1], Asghari Khiavi and Yamini [2] and Li et al. [3]). Figure 1,2 and 3 show the solubility data of the parabens. The experimental data are modelled with modified Wilson's model and Chrastil model. The correlation results along with the statistical paramaters are reported in Table 2. Figures (4) to (6) indicate the correlating ability of the models. From the tables and figures, it is clear that modified Wilson's model is able to correlate the data better. The success of modifies Wilson's model may be attributed to its number of parameters. The statistical methodology is applied to know the best model. Since our experimental data set was less (less than 40 data points), we have considered the corrected Akaike's information criterion (AIC), and it is known as AIC_c [8,9]. The following expression denotes AIC_c

$$AIC_c = AIC + \frac{2Q(Q+1)}{N-Q-1} \qquad (17)$$

Where

$$AIC = N \ln\left(\sigma^2\right) + 2Q \qquad (18)$$

In eqs.(17) and (18),σ , N and Q represent the variance of deviations, number of observations, and model parameters, respectively. The calculated *AICc* values are shown in Table 1. From the AIC_c values, we can conclude that whichever the model is having the least value is the better model. From table 2 modifies Wilson's model is observed to be better for the 3 paraben compounds.

Conclusion

In this study, the new correlations for the solubility of the paraben compounds in $ScCO_2$are reported. The models used are modified Wilson's model and Chrastil model. Akaike's information criteria revealed that the modified Wilson's model shows better correlating ability than the Chrastil model.

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