

MODELING OF THE SOLUBILITY IN SUPERCRITICAL CARBON DIOXIDE OF SOME SOLID SOLUTE ISOMERS USING THE EXPANDED LIQUID THEORY.

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Abstract

One of the most important research fields of supercritical fluid technology is the solubility of solids in supercritical fluids. Solubility data is fundamental to the development of new supercritical applications as biodiesel production and refrigeration, and the enhancement of existing applications including environmental pollution, extraction and purification of pharmaceuticals, food and natural products, and natural gas industry. Hence, the ability to correlate and predict the solubility of solids in supercritical fluids is of utmost importance. In this work, we propose to correlate and predict the solubility in supercritical CO₂ of disubstituted aromatic isomers of hydroxybenzoic acid with a new model based on the expanded liquid theory, in which the solid–fluid equilibrium is modeled using the local composition model of UNIQUAC in which the interaction parameters are related to the solvent reduced density with an empiric exponential form equations. The experimental solubility data of o-hydroxybenzoic acid, p-hydroxybenzoic acid, m-hydroxybenzoic acid and mixed isomers (m-hydroxybenzoic acid+p-hydroxybenzoic acid) are used for evaluating the correlation and prediction capabilities of this new model. The results obtained using the proposed model show good agreement with the experimental data used.

Keywords: supercritical fluid, aromatic isomers, correlation, prediction, solubility.

Résumé

L'un des domaines de recherche les plus importants de la technologie des fluides supercritiques est la solubilité des solides dans les fluides supercritiques. Les données de solubilité sont fondamentales pour le développement de nouvelles applications supercritiques comme la production de biodiesel et la réfrigération et l'amélioration des applications existantes, y compris la pollution de l'environnement, l'extraction et la purification des produits pharmaceutiques, des aliments et des produits naturels, et de l'industrie du gaz naturel. Par conséquent, la possibilité de corréler et de prédire la solubilité des solides dans les fluides supercritiques est d'une importance capitale. Dans ce travail, nous proposons la corrélation et la prédiction de la solubilité dans le CO₂ supercritique des isomères de l'acide hydroxybenzoïque avec un nouveau modèle basé sur la théorie du liquide expansible, où l'équilibre solide-fluide est modélisé en utilisant le modèle de composition locale UNIQUAC dans lequel les paramètres d'interaction sont liés à la densité réduite du solvant supercritique par des équations empiriques de forme exponentielle. Les données expérimentales de solubilité des acides o-hydroxybenzoïque, p-hydroxybenzoïque, et m-hydroxybenzoïque et mélanges d'isomères (m-hydroxybenzoïque + p-hydroxybenzoïque) sont utilisés pour l'évaluation des capacités corrélatives et prédictives de ce nouveau modèle. Les résultats obtenus en utilisant le modèle proposé sont en bon accord avec les données expérimentales utilisées.

Mots clés : Fluide supercritique, isomères aromatiques, corrélation, prédiction, solubilité.

ملخص

واحدة من مجالات البحث الأكثر أهمية لتكنولوجيا السوائل فوق الحرجة هو ذوبان المواد الصلبة فيها. بيانات الذوبان من الأمور الأساسية لتطوير تطبيقات جديدة مثل إنتاج وقود الديزل الحيوي والتبريد وتحسين التطبيقات الموجودة، بما في ذلك التلوث البيئي، واستخراج وتنقية الأدوية والمواد الغذائية والمنتجات الطبيعية وصناعة الغاز الطبيعي. ولذلك، فإن القدرة على التنبؤ وربط قابلية ذوبان المواد الصلبة في السوائل فوق الحرجة هو أمر بالغ الأهمية. في هذا العمل، نقترح الارتباط والتنبؤ لذوبان أيزومرات من حمض الهيدروكسيبنزويك في ثاني أكسيد الكربون فوق الحرج مع نموذج جديد يستند إلى نظرية السائل قابل للتمديد، حيث يتم على غرار استخدام نموذج UNIQUAC للتوازن. يتم استخدام البيانات التجريبية من ذوبان 2-حمض الهيدروكسيبنزويك، 3-حمض الهيدروكسيبنزويك، 4-حمض الهيدروكسيبنزويك وخليط من أيزومرات (2-حمض الهيدروكسيبنزويك+3-حمض الهيدروكسيبنزويك) لتقييم قدرات هذا النموذج الجديد. النتائج التي تم الحصول عليها باستخدام النموذج المقترح في اتفاق جيد مع البيانات التجريبية المستخدمة.

الكلمات المفتاحية : السوائل فوق الحرجة، أيزومرات العطرية، الارتباط والتنبؤ، الذوبان.

I- INTRODUCTION

During the past few years, widespread attention has been focused on supercritical fluids due to their potential application in extraction processes in food processing, pharmaceutical and petroleum industries, etc. The main advantages of supercritical fluid extraction over conventional extraction methods include increased speed, easy solvent separation and better recovery, and reduction in both solvent usage and solvent waste generation. The most widely used supercritical fluid is carbon dioxide because it is nontoxic, nonflammable and relatively inexpensive, and possesses reasonable critical properties ($t_c=30^\circ\text{C}$ and $P_c=72\text{atm}$) as well as a high solvent power for a wide range of nonpolar and intermediately polar organic compounds. The solubility of a solute in a supercritical fluid is perhaps the most important thermophysical property that must be determined and modeled for an efficient design of any extraction procedure based on supercritical solvents. The determination of solubilities of a wide variety of solids and liquids of low volatility in supercritical carbon dioxide has received considerable attention in recent years. However, despite the vital importance of the solubility data of isomeric compounds from chemical, biochemical, pharmaceutical and industrial points of view, there is still a lack of fundamental solubility and mass-transfer data available in the literature to facilitate the development of commercial-scale processes. Since the experimental determination of the solubilities of various solutes in supercritical fluids at each operating condition is tedious, time-consuming and not reported in literatures, there is a considerable interest in mathematical models that can accurately predict the solubilities of solid solutes in supercritical fluids [1].

Aromatic isomers serve as raw materials for a wide variety of chemical, pharmaceutical, and polymer products; in some cases the individual isomers are difficult to obtain in pure form, and frequently the separation involves an *ortho-para* pair [2] because in most cases the solute-solute interactions lead to an enhancement in the solubilities of components relative to their respective binary systems [3]. As a consequence, there is now a greater need to understand the solubility behaviour of such systems. Therefore it is essential to have a model that not only can accurately correlate but also predict phase equilibrium properties.

Some of the models that have been used for correlating solubility data can be classified in two classes, equations of state based models (EOS) [4] and empirical models [5]. EOS based models require the prior knowledge of a certain number of parameters such as the critical properties (temperature and pressure), acentric factor and the sublimation pressure of the solid solute. These parameters are not available and are often calculated using group contribution methods, which

could lead to solubility error prediction. Due to the lack of information on these properties, empirical models are used for the correlation of experimental solubility data. These models are known as density-based models and consist of equations that contain constants that are empirically adjusted for each compound. Although simple, these models rely much on the knowledge of the thermodynamic behaviour of the supercritical solvent rather than of the solute, and are mostly capable of correlating rather than predicting the solubility. They are used for quantitative determination of the solute solubility in supercritical phase at equilibrium, and do not provide qualitative information about the solute-solvent interaction.

In this work we will test the methodology previously used [6] that correlates and predicts the solubility of solids in supercritical carbon dioxide based on the expanded liquid model theory [7, 8]. This theory does not require the knowledge of the solute critical properties and sublimation pressure.

In this case the supercritical phase is considered as an *expanded liquid* and is modeled using excess Gibbs energy models such as Margules, Van Laar, and local composition based models i.e. Wilson, NRTL and UNIQUAC. In this study we focus on the use of the UNIQUAC model that has been widely used in modeling vapour-liquid and liquid-liquid equilibrium data. This model does not only take the size and nature of the molecules into consideration, but also accounts for the strength of solute-solvent intermolecular forces. And because the primary concentration variable is the surface fraction rather than mole fraction, the UNIQUAC model is applicable to solutions containing small or large molecules, including polymers.

2. MODEL DEVELOPMENT

The supercritical phase is considered as an expanded liquid phase in equilibrium with the solid phase. The solvent solubility in the solid phase is considered to be negligibly small to consider the solid fugacity to be that of the pure solid. To estimate the solid solubility in the supercritical phase, the knowledge of the activity coefficients are required. These coefficients are determined from the knowledge of the component fugacities, thus when the equilibrium of the pure solid and the supercritical phase is reached, we have:

$$f_2^s = f_2^{\text{SCF}} = f_2^L \quad (1)$$

f_2^s is the fugacity of the solute in the solid phase considered as pure solid and equal to f_2^{os} , f_2^L is the fugacity of the solid solute in the supercritical phase and is equal to:

$$f_2^L = \gamma_2 Y_2 f_2^{oL} \quad (2)$$

Equation (1) could be written as follows:

$$f_2^{os} = \gamma_2 Y_2 f_2^{oL} \quad (3)$$

Where γ_2 , Y_2 and f_2^{oL} are the activity coefficient, the solid solubility represented in mole fraction and the fugacity of the pure solid solute in the expanded liquid phase respectively. According to Prausnitz *et al.* [9], we have:

$$\ln\left(\frac{f_2^{os}}{f_2^{oL}}\right) = \frac{-\Delta H_2^f}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right) - \frac{\Delta C_p}{RT} \left(\frac{T - T_m}{T}\right) + \frac{\Delta C_p}{R} \ln\left(\frac{T}{T_m}\right) \quad (4)$$

Prausnitz *et al.* [9] stated that to a fair approximation, the heat capacity terms can be neglected. Equations (3) and (4) then combined to yield an expression for the solute solubility:

$$Y_2 = \frac{1}{\gamma_2} \exp\left[\frac{-\Delta H_2^f}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad (5)$$

ΔH_2^f is the enthalpy of fusion, T_m is the melting point temperature of the solid solute.

Since the solid solubility in the supercritical phase is very small, it can be assumed that the activity coefficient of the solid solute is the one at infinite dilution and that the density of the solution is that of the pure solvent, i.e. CO₂. Thus equation (5) becomes:

$$Y_2 = \frac{1}{\gamma_2^\infty} \exp\left[\frac{-\Delta H_2^f}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad (6)$$

The activity coefficient of the solid solute at infinite dilution γ_2^∞ was calculated using the UNIQUAC model which consists of two parts, a combinatorial part $\gamma_2^{C,\infty}$ that attempts to describe the dominant entropic contribution, and a residual part $\gamma_2^{R,\infty}$ that is due primarily to intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only pure-component data. The residual part, however, depends also on intermolecular forces; the two adjustable binary parameters a_{12} and a_{21} , therefore, appear only in the residual part [9]:

$$\ln \gamma_2^\infty = \ln \gamma_2^{C,\infty} + \ln \gamma_2^{R,\infty} \quad (7)$$

$$\ln \gamma_2^{C,\infty} = 1 - \frac{r_2}{r_1} + \ln \frac{r_2}{r_1} - q_2 \frac{z}{2} \left(1 - \frac{r_2 q_1}{r_1 q_2} + \ln \frac{r_2 q_1}{r_1 q_2} \right) \quad (8)$$

Here q and r are the surface area and volume parameters; z is the coordination number that is usually taken equal to 10. The residual part at infinite dilution is given by the following equation [9]:

$$\ln \gamma_2^{R,\infty} = q_2 (1 - \ln \tau_{12} - \tau_{21}) \quad (9)$$

Where

$$\tau_{12} = \exp(-\Delta u_{12}/RT) = \exp(-a_{12}/T)$$

$$\tau_{21} = \exp(-\Delta u_{21}/RT) = \exp(-a_{21}/T) \quad (10)$$

Δu_{12} and Δu_{21} are characteristic energies and are related to the interaction parameters a_{12} and a_{21} through equation (10). Finally combining equations (9) and (10) leads to:

$$\ln \gamma_2^{R,\infty} = q_2 \frac{a_{12}}{T} + q_2 \left(1 - e^{\frac{-a_{21}}{T}} \right) \quad (11)$$

Equation (11) could be written in reduced form by introducing the reduced temperature, thus we obtain:

$$\ln \gamma_2^{R,\infty} = q_2 \frac{a'_{12}}{T_r} + q_2 \left(1 - e^{\frac{-a'_{21}}{T_r}} \right) \quad (12)$$

with

$$a'_{12} = \frac{a_{12}}{T_c} \quad \text{and} \quad a'_{21} = \frac{a_{21}}{T_c} \quad , \quad T_c \text{ is the solvent critical temperature.}$$

The binary interaction parameters a'_{12} and a'_{21} are related to the energy of interaction between the solid solute and the solvent in the supercritical phase, and cannot be kept constant and specifically at high pressure conditions. Therefore to take into account the pressure and temperature effects, these parameters are assumed to be density dependant and were fitted to the following equations:

$$a'_{12} = \alpha_{12} \cdot \exp(\beta_{12} \cdot \rho_r) \quad (13a)$$

$$a'_{21} = \alpha_{21} \cdot \exp(\beta_{21} \cdot \rho_r) \quad (13b)$$

ρ_r is the reduced density of the solvent equal to ρ/ρ_c where ρ_c is its critical density, α_{12} , β_{12} , α_{21} and β_{21} are the regressed parameters of the model.

3. ISOMERS SOLUBILITY CALCULATION :

The surface area and volume parameters are calculated as the sum of the group volume and area parameters (R and Q) given by the UNIFAC group specifications [9], since the solutes are isomers they have the same functional groups so they have the same surface area and volume parameters ($r_2=4.6869$ and $q_2=3.624$). These parameters and properties listed in Table 1, together with those of carbon dioxide listed in Table 2 are used to calculate the combinatorial part of the activity coefficient from equation (8).

In other hand, equation (12) is used to calculate the residual part of the solid solute activity coefficient. Thermodynamic properties of the solid solute listed in Table 1 are used together with equations (7), (8), and (12) to estimate the solubility y_2 using equation (6).

The interaction parameters a'_{12} and a'_{21} are then regressed according to equations (13a) and (13b). The regression is based on minimizing the error between the regressed and experimental solubility data. The error is calculated as the *average absolute relative deviation* (AARD) according to equation (14):

$$\text{AARD}(\%) = \frac{1}{N} \left| \sum_{i=1}^n \frac{y_{2(\text{exp})} - y_{2(\text{reg})}}{y_{2(\text{exp})}} \right| \times 100 \quad (14)$$

Where N is the number of experimental solubility data of each isomer.

Table 1. Isomers fusion properties

Component	$T_m(\text{K})$	$\Delta H_2^f(\text{J/mol})$	solubility reference
<i>m</i> -hydroxybenzoic acid	476 [10]	36500 [10]	[2],[3]
<i>p</i> -hydroxybenzoic acid	488,1[10]	30990 [10]	[2],[14]
<i>o</i> -hydroxybenzoic acid	432 [11]	19585 [11]	[2],[3],[13],[14]

Table 2. Solvent physical properties

Solvent	$T_c(\text{K})$	$P_c(\text{bar})$	$\rho_c(\text{mol/cm}^3) \times 100$	r_1	q_1	Ref
CO ₂	304.2	73.83	1.063	1.296	1.261	[9],[12]

4. CORRELATION RESULTS

The interaction parameters a_{12} and a_{21} are regressed through the optimization of the adjustable parameters α_{12} , β_{12} , α_{21} and β_{21} . These fitting parameters are evaluated by minimizing the objective function given in equation (14).

The analysis of the model results is done through statistical calculations. Table 3 provides the quantitative results of the regression for the proposed model. The AARD is listed for each isomer and for each temperature together with the adjustable parameters values and the overall absolute deviations. Each isomer parameters are obtained by fitting them on its own and whole solubility data. The overall deviations values obtained are generally low and so indicate a good correlation capability of the model.

Table 3. Regression results

Component	N	T(K)	α_{12}	β_{12}	α_{21}	β_{21}	AARD (%)
<i>m</i> -hydroxybenzoic acid	16	318	4,24	-0,292	6497,8-14,5	1,91	8,23
		328					30,1
		373					11,32
		overall					
<i>o</i> -hydroxybenzoic acid	84	308	2,83	-0,288	2,35	-2,2	8,6
		313					7,48
		318					11,04
		328					5,74
		373					41,95
		overall					10,37
<i>p</i> -hydroxybenzoic acid	16	318	4,57	-0,292	6100,3-14,9	2,28	6,35
		328					30,4
		373					10,84
		overall					

From table 3 and figure 1 we can see clearly that the greatest values of AARD are noted at high temperatures especially for $T=373\text{K}$. These can be probably attributed to the very important phenomenon occurring in some high-pressure-mixtures and which is the melting point depression [15], [16].

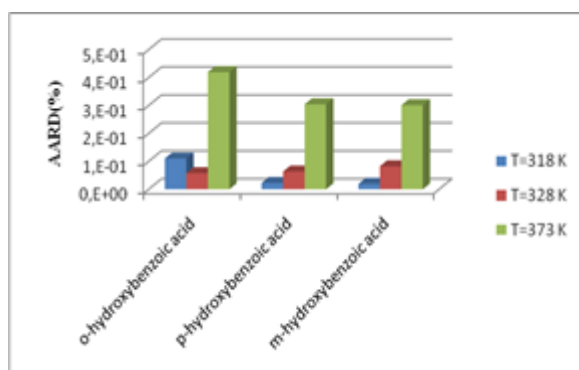


Figure 1. Comparison of the average absolute deviation for the isomers at three different temperatures

Under the influence of high-pressure carbon dioxide, organic solids may undergo melting point depression [17] which lead to the exhibition of fluid-liquid equilibria and so affect the measured solubility data.

Lucien and Foster [14], have mentioned that with their experimental technique for measuring, in all of the systems investigated (pure and mixed) no melting point depression was observed.

However, Krukoniš and Kurnik [2] have reported measured solubilities of the hydroxybenzoic acid isomers at very high conditions: $T=373\text{K}$ and for pressures greater than 207 bar without indication to the melting point depression phenomenon.

5. PREDICTION RESULTS :

A number of aromatic isomers serve as raw materials for a wide variety of chemical, pharmaceutical, and polymer products and in most cases the individual isomers are difficult to obtain in pure form because binary solubility data present a limited picture of the complex interactions that can occur in the supercritical fluid phase [2]. Consequently, the separation involves a mixture of isomers and frequently an *ortho-para* pair. In this case of mixture solute-solute interactions lead to an enhancement in the solubility of components relative to their respective binary systems [4]. As a consequence, in literature there are several studies on the determination of solubilities of mixed isomers in supercritical carbon dioxide.

In this part, we attempt to predict the solubilities of mixed hydroxybenzoic acid isomers in supercritical carbon dioxide. In this case experimental solubility data provided by Lucien and Foster [3] for an equimolar mixture of the isomers *m*-hydroxybenzoic acid and *p*-hydroxybenzoic acid are used. The solubility data of the two isomers are very small and have an order of 10^{-6} . As a consequence, we can assume that the density of the supercritical phase is that of the pure solvent, and the activity coefficient of each isomer is the one at infinite dilution. In this case the only interaction parameters that are taken into account are those of *m*-hydroxybenzoic- CO_2 and *p*-hydroxybenzoic- CO_2 .

Therefore predicted solubilities are estimated using equations (6) to (13b) and interaction parameters for both *meta* and *para* isomers listed in table 3 are directly implemented to estimate the solubility of each isomer in the mixture.

Table 4. Prediction results

isomer	N	AARD (%)
<i>m</i> -hydroxybenzoic	12	4,3
<i>p</i> -hydroxybenzoic	12	5,8

The absolute average relative deviation (AARD) obtained are given in table 4. Figures 2a and 2b show a parity plot of the experimental versus predicted solubility data of mixed *m*-hydroxybenzoic and *p*-hydroxybenzoic isomers in supercritical CO_2 for two different temperatures, i.e. 318 and 328K.

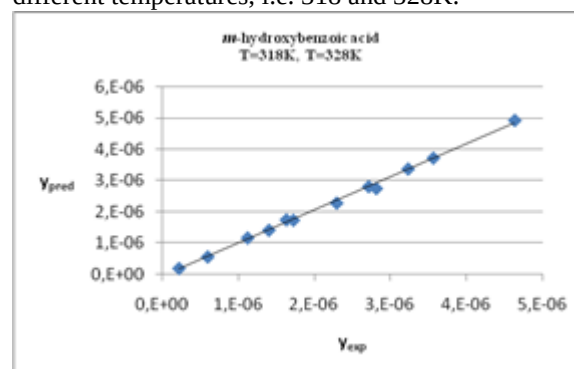


Figure 2 (a)

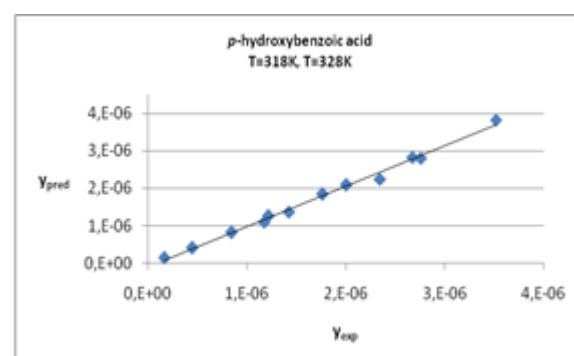


Figure 2 (b)

These figures, and results in table 4 show good agreement between measured solubility data and predicted ones and confirm predictive ability of the proposed model.

6. CONCLUSION

In this work, we have proposed the correlation and prediction of the solubility in supercritical CO₂ of disubstituted aromatic isomers of hydroxybenzoic acid with a new methodology based on the expanded liquid theory, in which the solid–fluid equilibrium is modeled using the local composition model of UNIQUAC. The advantages of this model include the following: it does not require the knowledge of critical properties of solid solutes and does take into account the binary interaction between solid solute and solvent. The results obtained using the proposed model show good agreement with the experimental data of isomers used.

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