



Prediction of Solubility of β -Carotene as a Component in a Multicomponent System in High-Pressure Carbon Dioxide

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PAPER INFO

Paper history:

Received 05 September 2018

Received in revised form 12 December 2018

Accepted 03 January 2019

Keywords:

Prediction

Solubility

β -carotene

EoS

ABSTRACT

Solubility prediction of high molecular weight molecules in high-pressure solvents is an interesting field of research. Sometimes the solubility data are not available for several components due to lacking of valid equipments. Therefore, an accurate prediction technique can help the researchers. According to the literature, the simple Equations of State (EoSs) such as Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and the others require some data such as intermolecular energy parameters, critical properties, acentric factors, and molar refractions. Since these data are not available for a lot of high molecular weight molecules, there are some limitations in applying them. Furthermore, the calculations are more complicated when the high molecular weight molecule is a polar one due to the interference of polar factors in the calculations process. The polar factors for this kind of molecules are not available or cannot easily be calculated. One of these polar biomolecules is β -carotene. In this research, the solubility of β -carotene in high-pressure carbon dioxide was calculated by a two-parameter EoS and compared with the experimental data although it had already been successfully used for binary systems. The results showed that the two-parameter Mohsen-Nia-Modarress-Mansoori (MMM) EoS was an accurate model for the solubility prediction in supercritical and near critical conditions for the multicomponent systems. The binary coefficients of β -carotene and carbon dioxide in various pressures and temperatures were obtained by the genetic algorithm from the literature.

doi: 10.5829/ije.2019.32.02b.03

NOMENCLATURE		Z	Compressibility factor
a	Attraction parameter	ϕ	Fugacity coefficient
b	Repulsive parameter	Subscripts and Superscripts	
K	Binary interaction parameter	c	Critical
P	Pressure (bar)	V	Vapor
R	Gas constant	S	Solid
T	Temperature (K)	sat	Saturated
v	Molar volume (L/mole)	i	Component i
y	Mole fraction	j	Component j

1. INTRODUCTION

Supercritical fluid extraction is an advanced, clean and green technology currently used in various processes such as production of extracts from fruits, hops, nuts, spices and the other natural products [1, 2]. Supercritical fluids present unique characteristics which make them excellent solvents. They usually have relatively high

density, high selectivity, low viscosity and high diffusivity. These appropriate properties allow them to achieve high extraction rates [1, 3].

Among many supercritical solvents for extractions, carbon dioxide has the excellent properties such as low critical temperature (304.1 K), moderate critical pressure (7.38 MPa), low cost, and availability in purified form. Furthermore, it is inert, non-flammable, non-toxic, and

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can be easily removed from the extract [2]. Phase equilibrium data (in particular solubility ones) are the basis for the design and optimization of the supercritical extraction processes [4, 5].

One of the red or orange pigments found in some fresh fruits and vegetables is β -carotene. It is common to extract β -carotene from fruits abundant in carotenoids. β -carotene is an antioxidant that has medical characteristics. It is pro-vitamin A and enhances the immune system in the human body and may exert a key protective action against many diseases [6].

In fact, many vegetables are sources of carotenoids which can be extracted by supercritical fluid extraction (SFE) [7, 8]. Figure 1 shows the structure of β -carotene.

Understanding the phase behavior of solutes and solvents over a range of pressure and temperature is necessary for the development of supercritical fluid extraction. Considering the pressure and temperature of the process, calculation of solubility of solutes in supercritical solvents is useful in supercritical fluid extraction [3, 9, 10].

In general, the models used for calculation of solubility are classified into two different groups. They are theoretical models (by applying EoSs) and empirical correlations (density based equations). However, the theoretical models use different equations with various mixing rules but, the cubic equations are more used for calculation of solubility in the supercritical fluid because of their unique properties such as flexibility, reliability and their proper speed of calculations [11-17]. In contrast, the cubic EoSs have limited predictive capability, and they are not accurate for the complex systems [18]. Furthermore, EoSs need the critical pressure and temperature of compounds, vapor pressure and density data of solutes for calculation of solubility of solutes in the supercritical solvents [19-21]. Some three-parameter EoSs such as Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) require the acentric factors while Riazi-Mansoori (RM) requires molar refraction data, as well [7, 22]. The experimental critical properties, acentric factors and molar refractions are not available for some high molecular weight biomolecules such as β -carotene [7, 23, 24] although there are some theoretical methods for estimation of them. Lydersen, Edmister and Eisenlohr (or Vogel) methods are almost accurate techniques for assessment of critical properties, acentric factors and molar refractions calculations, respectively [7, 24].

In this work, the Mohsen-Nia-Modarress-Mansoori (MMM) as a two-parameter EoS is applied to predict the solubility of β -carotene in high-pressure carbon dioxide as a solvent.

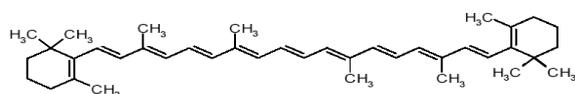


Figure 1. Structure of β -carotene

This equation only requires the critical pressure and temperature of the components. The critical data are calculated by Lydersen's method [24, 25]. Furthermore, genetic algorithm is used to solve the system of equations and find out the binary coefficients, and then solubility data [26]. A solution generated by a genetic algorithm is called a chromosome and collection of them is called population. In genetic algorithm, some chromosomes in the population may produce new chromosomes. Furthermore, a few of them may mutate. The chromosomes that are maintained for the next generation have higher fitness value. In fact, they will have the greater probability of reselection in the next generation. The genetic algorithms use random sampling methods to create generations of random candidate solutions. After several generations, the chromosome will converge to a final value which is the best solution to the problem. Considering random sampling methods, solution of genetic algorithm may slightly differ in every run of calculations due to the acceptable method precision [26]. The genetic algorithm is applied several times to find the best results for the solubility according to the experimental data illustrated in the literature. In fact, the calculations are done several times. Then, closest results to the experimental data are reported when they are very close to each other.

2. EQUILIBRIUM OF SUPERCRITICAL PHASE

The equality of the fugacity of the solid solute in supercritical and solid phases describes the solubility of the solid in the supercritical phase:

$$f_i^{solid} = f_i^{supercritical}(T, P, \{y_i\}) \quad (1)$$

where, f_i is the fugacity, T is the temperature, P is the pressure and y_i is the mole fraction in the supercritical phase. The solubility of the solid in the supercritical phase can be calculated by Equation (1) when the system temperature and pressure data are known.

The fugacity in the solid phase can be obtained by neglecting the supercritical fluid solubility in the solid phase, assuming the constant solid molar volume and considering the saturation fugacity coefficient of solid to be unity:

$$f_i^{solid} = P_i^{sat} \exp\left\{\frac{v_i^s(P - P_i^{sat})}{RT}\right\} \quad (2)$$

where, P_i^{sat} denotes the vapor pressure of solid at temperature T , v_i^s is the molar volume of solid and R is the universal gas constant.

Fugacity for component i in the supercritical phase can be written as follows:

$$f_i^{supercritical} = P\phi_i^{supercritical}y_i \quad (3)$$

The solubility of component i in vapor phase (y_i) at supercritical condition is defined as follows:

$$y_i = \left(\frac{P_i^{sat}}{\phi_i^{supercritical} P} \right) \exp \left\{ \frac{v_i^s (P - P_i^{sat})}{RT} \right\} \quad (4)$$

Equation (4) can be rewritten as follows:

$$\phi_i^{supercritical} = \left(\frac{P_i^{sat}}{y_i P} \right) \exp \left\{ \frac{v_i^s (P - P_i^{sat})}{RT} \right\} \quad (5)$$

The fugacity coefficient of the condensed phase in the supercritical fluid ($\phi_i^{supercritical}$) can be derived from an EoS as follows:

$$RT \ln \phi_i^{supercritical} = \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z \quad (6)$$

$$\text{where, } Z = \frac{Pv}{RT}$$

where, ϕ shows the fugacity coefficient of the solute in the supercritical phase and Z is the compressibility factor of the supercritical phase [22].

The MMM EoS is expressed as follows [27]:

$$P = \frac{RT(v+1.3191b)}{v(v-b)} - \frac{a}{T^{0.5}v(v+\sum_i y_i b_{ii})} \quad (7)$$

Mixing rules:

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (8)$$

$$b = (1/4)(3 \sum_i \sum_j y_i y_j b_{ij} + \sum_i y_i b_{ii}) \quad (9)$$

$$a_{ii} = 0.48748 R^2 T_{cii}^{2.5} / P_{cii} \quad (10)$$

$$b_{ii} = 0.064662 R T_{cii} / P_{cii} \quad (11)$$

$$a_{ij} = (1 - K_{ij})(a_i a_j)^{1/2} \quad (12)$$

Therefore:

$$\phi_i^{supercritical} = \exp \left\{ 2.3191 \left[\frac{3(2 \sum_j y_j b_{ij} - \sum_i \sum_j y_i y_j b_{ij}) + b_{ii}}{4(v-b)} - \ln \left(1 - \frac{b}{v} \right) \right] - \ln Z + \frac{a}{RT^{1.5} \sum_i y_i b_{ii}} \left[\left(\frac{b_{ii}}{\sum_i y_i b_{ii}} - \frac{2 \sum_j y_j a_{ij}}{a} \right) \ln \left(1 + \frac{\sum_i y_i b_{ii}}{v} \right) - \frac{b_{ii}}{v + \sum_i y_i b_{ii}} \right] \right\} \quad (13)$$

The critical properties of the components in the extraction of β -carotene from CPO by high-pressure carbon dioxide as a solvent are shown in Table 1. The solubility data are extracted from the literature [28].

3. RESULTS AND DISCUSSION

The solubility of β -carotene in the vapor phase and the binary coefficient are found by the genetic algorithm. In fact, the genetic algorithm is applied several times to find the best results for solubility according to the experimental data illustrated in literature [28].

TABLE 1. Critical properties of the components in the extraction of β -carotene by high pressure carbon dioxide

Compound	T_c (K)	P_c (bar)	v^s (l/mol)	Ref.
Carbon dioxide	304.12	73.740	-	[28]
β -carotene	801.00	8.090	0.5368	[3]

Tables 2-4 show the solubility achieved by experiment, regular solution theory model (RSTM) and MMM EoS at temperatures of 353.2, 373.2 and 393.2 K, respectively. The average error was calculated based on the arithmetic mean of the calculated solubility data by MMM EoS and the experimental ones. Figures 2-4 clearly show the solubility of β -carotene in high-pressure carbon dioxide at various temperatures by experiment, RSTM and MMM EoS [28]. As shown in these evidences, MMM EoS can properly predict solubility of β -carotene in high pressure carbon dioxide (supercritical and near critical conditions) while the precision of solubility estimation is reduced in lower pressures (subcritical conditions). This confirms that the MMM EoS is valid and accurate for the solubility prediction in supercritical and near critical conditions for the multicomponent systems.

TABLE 2. Solubility of β -carotene in high pressure carbon dioxide and binary coefficient at 353.2 K

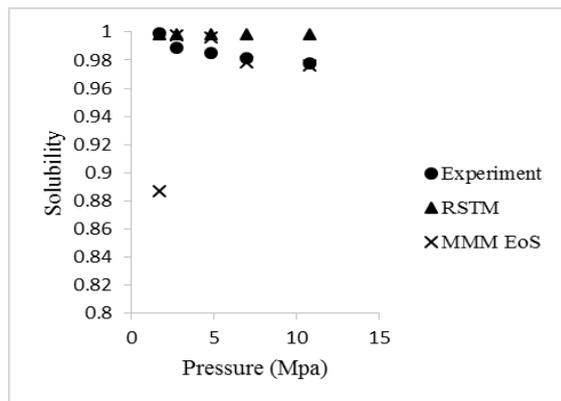
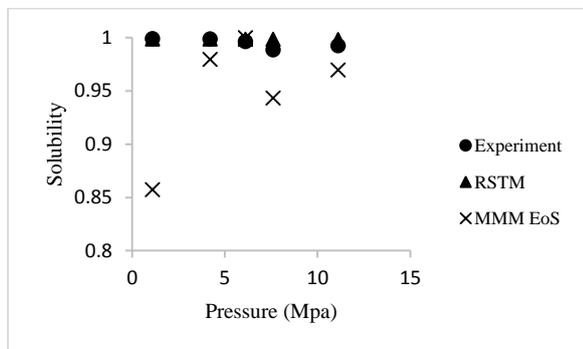
P (Mpa)	Experiment [28]	RSTM [28]	MMM EoS	Error (%)	Binary coefficient
10.8	0.9781	0.9981	0.9765	0.1596	0.4428
7	0.9814	0.9984	0.9785	0.2961	
4.8	0.9852	0.9986	0.9961	1.1053	
2.7	0.989	0.9987	0.9980	0.9145	
1.7	0.999	0.9988	0.8866	11.2506	
				Average error	2.7452

TABLE 3. Solubility of β -carotene in high pressure carbon dioxide and binary coefficient at 373.2 K

P (Mpa)	Experiment [28]	RSTM [28]	MMM EoS	Error (%)	Binary coefficient
11.1	0.9924	0.9981	0.9697	2.2878	0.9521
7.6	0.9886	0.9984	0.9433	4.5819	
6.1	0.9965	0.9986	1.0000	0.3511	
4.2	0.9988	0.9987	0.9795	1.9352	
1.1	0.999	0.9988	0.8573	14.1860	
				Average error	4.6684

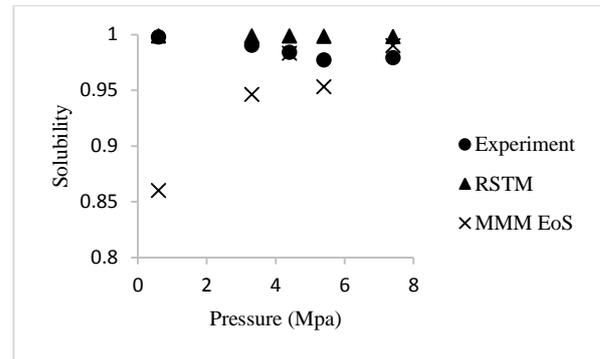
TABLE 4. Solubility of β -carotene in high pressure carbon dioxide and binary coefficient at 393.2 K

P (Mpa)	Experiment [28]	RSTM [28]	MMM EoS	Error (%)	Binary coefficient
7.4	0.9792	0.9981	0.9902	1.1258	0.3666
5.4	0.9773	0.9984	0.9531	2.4785	
4.4	0.984	0.9986	0.9834	0.0629	
3.3	0.9905	0.9987	0.9462	4.4689	
0.6	0.9978	0.9988	0.8602	13.7889	
			Average error	4.3850	

**Figure 2.** Solubility of β -carotene in high-pressure carbon dioxide (y_i) at 353.2 K**Figure 3.** Solubility of β -carotene in high-pressure carbon dioxide (y_i) at 373.2 K

Furthermore, RSTM could moderately predict the solubility in the wide range of pressure. RSTM which is an activity based model can properly legitimize the polar (even non-polar) systems behavior such as ethanol-octane (with various ratios) although it requires a computational calculations system due to having a lot of related equations and requiring several try-errors [29-32].

According to the literature, the statistical mechanically proper van der Waals mixing rules can improve prediction of highly polar mixture properties with the Peng-Robinson EoS. This method is general and may be applied as well to other cubic EoSs [33].

**Figure 4.** Solubility of β -carotene in high-pressure carbon dioxide (y_i) at 393.2 K

4. CONCLUSIONS

In the current research, the solubility of β -carotene from palm oil as a multicomponent system in high pressure carbon dioxide as a solvent was calculated using MMM EoS. The data were compared with the experimental and RSTM ones. The binary coefficient of β -carotene and carbon dioxide was found by the genetic algorithm, as well. It was concluded that MMM two-parameter EoS as non-dependence to critical properties and to acentric factor can properly estimate solubility data for a large biomolecule in supercritical and near critical conditions.

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Prediction of Solubility of β -Carotene as a Component in a Multicomponent System in High-Pressure Carbon Dioxide

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P A P E R I N F O

چکیده

Paper history:

Received 5 September 2018

Received in revised form 12 December 2018

Accepted 03 January 2019

Keywords:

Prediction

Solubility

β -carotene

EoS

تخمین میزان حلالیت مولکولهای سنگین وزن در حلالهای فشار بالا زمینه جذابی برای تحقیق و پژوهش است. گاهی اوقات بنا به دلایلی از جمله عدم دسترسی به تجهیزات مناسب، میزان حلالیت این مولکول ها در حلال را نمی توان به صورت تجربی اندازه گیری نمود. در چنین شرایطی تخمین انحلال پذیری به کمک معادلات حالت می تواند به محققین کمک قابل توجهی نماید. باتوجه به پیشینه پژوهش های انجام شده در این زمینه، معادلات حالت ساده نظیر Soave-Redlich-Kwong (SRK) و Peng-Robinson (PR) یا معادلاتی از این دست، به داده هایی نظیر پارامترهای وابسته به انرژی بین مولکولی، خواص بحرانی، ضرائب بی مرکزی و انکسار مولار نیاز دارند. از آنجا که این داده ها اغلب برای بسیاری از مولکولهای سنگین وزن در دسترس نیستند، در به کارگیری این معادلات حالت، محدودیت هایی وجود خواهد داشت. علاوه بر این چنانچه مولکول ها قطبی باشند، به علت حضور ضرائب قطبیتی، محاسبات، چندین برابر دشوارتر خواهد شد. ضرائب قطبیتی برای این دسته از مولکولها غالباً در دسترس نبوده و یا به آسانی قابل محاسبه نیستند. نتایج مطالعات نشان می دهد در چنین شرایطی، معادله حالت دو پارامتری MMM برای تخمین قابلیت انحلال سیستم های چندجزئی در شرایط بحرانی یا نزدیک به شرایط بحرانی، معادله ای دقیق است. به منظور اثبات این ادعا، در این پژوهش، میزان انحلال پذیری بتاکاروتن به عنوان یک مولکول سنگین و قطبی، در دی اکسید کربن فشار بالا با استفاده از معادله حالت MMM محاسبه شده و نتایج با داده های تجربی مقایسه گردیده است. همچنین، ضرائب تأثیر متقابل بتاکاروتن و دی اکسید کربن در دماها و فشارهای مختلف با استفاده از الگوریتم ژنتیک محاسبه شده اند.

doi: 10.5829/ije.2019.32.02b.03