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Application of supercritical fluid processes



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ABSTRACT

The present work deals with the storage of Hydrogen where promising ways are based on the solubility of organic or inorganic compounds in supercritical fluids, inducing specific interactions to retain this non polluting energy vector.

Consequently the modeling of the solubility of polar organic compounds like Ortho Hydroxy benzoic acid (o-HBA), and Para Hydroxy benzoic acid (p-HBA), Dichloro diphenyl Trichloro ethane (DDT) and 2,4-Dichloro phenoxyacetic acid (usually referred to by its abbreviation, (2,4-D) as well as their mixtures, in supercritical fluids such as carbon dioxide, is presented.

For the two binary systems i.e. o-HBA-CO₂, DDT-CO₂ the model combining the cubic Redlich Kwong (RK) equation of state (EOS) with the van der Waals (VW) mixing rule (MR) at constant temperature of 313 K and a pressure range of 120–220bar, showed quite good results compared to the experimental values. However the model Redlich–Kwong–Soave (RKS)–Wong–Sandler (WS) provided a better correlation.

Similarly the model RK-WS gave better results for the solubility of o-HBA in CO₂ and for the mixture o-HBA–2,4-D in CO₂.

The obtained solubilities of p-HBA in supercritical carbon dioxide were found to be higher than that of o-HBA. This can be explained by the differences in the intermolecular interactions which are relatively weak for the case of o-HBA.

The results obtained from the combinations Patel–Teja (PT)-VW and PT-WS showed important deviations compared to the experimental values and this for all the considered systems.

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Introduction

Supercritical fluids have an interesting combination of liquid like density and solvency and gas like viscosity, diffusivity, compressibility, etc. This has greatly stimulated the development of various processes taking advantage of these properties. For instance hydrogen which is a non polluting energy vector requires great mass production and storage facilities, for subsequent uses. One of the most promising ways is metal hydrides, compared to pressure or liquefaction

based alternatives [1]. Magnesium a low cost and abundant metal has shown a great capacity for Hydrogen storage, particularly when its surface is modified by different methods using supercritical fluids. Also liquid organic hydrogen carriers such as the unsaturated heterocyclic aromatic compounds N-ethylcarbazole and dibenzyltoluene can store huge amounts of Hydrogen. They are hydrogenated or dehydrogenated again for storage or need of energy/hydrogen, respectively. Surely these operations do involve phase equilibria at high pressure, particularly solid–liquid phase equilibria. High pressure phase equilibria data are

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Table 1 – Parameters of the used equations of state [2,5].

Equation	u	w	b	A
Redlich Kwong (RK)	1	0	$\frac{0.08644RT_c}{p_c}$	$\frac{0.42748R^2T_c^{2.5}}{p_c T^{1/2}}$
Soave (RKS)	1	0	$\frac{0.08644RT_c}{p_c}$	$\frac{0.42748R^2T_c^2(1 + fw(1 - T_r^{1/2}))^2}{p_c}$ $fw = 0.48 + 1.574w - 0.176w^2$
Peng Robinson (PR)	2	-1	$\frac{0.0788RT_c}{p_c}$	$\frac{0.45724R^2T_c^2(1 + fw(1 - T_r^{1/2}))^2}{p_c}$ $fw = 0.37464 + 1.542274w - 0.2699w^2$

imperatively required for the design of processes which make use of these supercritical fluids. However these data are not always available and are often difficult to obtain experimentally, particularly with the large range of operating conditions that can be encountered. To remediate to this problem, development of new thermodynamic models or improvement of existing ones are still the main objective of a great number of research works reported in the literature. For instance some modifications brought to the traditional Peng Robinson equation of state have resulted in the development of a new equation by Soave which has been comparatively more successful in correlating data for various systems [2]. Wong and Sandler have developed a theoretically adequate mixing rule that is capable of extrapolating vapor–liquid equilibrium data at low pressure for the prediction of vapor–liquid data at high pressure. Unlike the VDW mixing rule, the WS mixing rule consists of binary interaction parameter that are not dependent on temperature, hence improving the solubility prediction.

Therefore in the supercritical conditions much efforts to improve solubility prediction, is necessary. Consequently in the present work a new combination EOS-MR is tested for the solubility prediction of solid compounds reported in the literature like o-HBA, p-HBA, DDT and 2,4-D, as well as their mixtures, in supercritical fluids such as carbon dioxide.

Thermodynamic modeling

The solubility of an organic solute in a supercritical fluid can be expressed as follows [3,4]:

$$P_i^s \exp\left(\int_{P_i^s}^P \frac{V_i^s}{RT} dP\right) = y_i^{sf} \phi_i^{sf} P \quad (1)$$

Table 2 – Parameters used to model the binary solubilities of organics in supercritical carbon dioxide [3].

System	T(K)	k_{ij}	$\ln \gamma_i^\infty$
o-HBA-CO ₂	318.	0.12	-36.96
p-HBA-CO ₂	318.	0.51	-18.60
DDT-CO ₂	313.1	0.61	-65.47
2,4-D-CO ₂	313.1	0.51	-38.96

with P_i^s the pressure at saturation of solid at given temperature (Bar), ϕ_i^{sf} the fugacity coefficient of supercritical fluid, V_i^s the volume of solid at saturation (cm³/mol), R: the universal gas constant (83.14 bar cm³/mol), T the system temperature (K), P the system pressure (bars), y_i^{sf} the solubility of solute in the supercritical fluid.

Cubic Equation of state

Two parameters equations of state [2,5]

Usual common two parameters cubic equations can be expressed by the following equation:

$$P = \frac{RT}{v-b} + \frac{a}{u^2 + ubv + wb^2} \quad (2)$$

The three well known cubic equations of state i.e. that of Peng Robinson (PR), Soave (RKS) and Redlich–Kwong (RK), are obtained with u and w taking integer values, as shown in Table 1. Also the parameters a and b appearing in Equation (2), are calculated in terms of critical properties as also shown in Table 1.

It is necessary to know the critical temperatures (T_c), pressures (P_c) and the acentric factor of each component.

An equivalent form of Equation (2) is:

$$Z^3 - (1 + b' - Ub')Z^2 + (a' + \omega b'^2 - Ub' - Ub'^2)Z - a'b' - \omega b'^2 - \omega b'^3 = 0 \quad (2)$$

With Z is the compressibility factor and $a' = \frac{aP}{(RT)^2}$; $b' = \frac{bP}{RT}$

Patel–Teja three parameters equations of state [3,6]

$$p = \frac{R \cdot T}{V - b} - \frac{a}{V(V + b) + c \cdot (V - b)} \quad (3)$$

with:

$$a = \Omega_a \cdot \left(\frac{R^2 T_c^2}{P_c}\right) \cdot \alpha(T_R), \quad b = \Omega_b \left(\frac{RT_c}{P_c}\right), \quad c = \Omega_c \left(\frac{R \cdot T_c}{P_c}\right)$$

$$\Omega_c = 1 - 3\zeta_c, \quad \Omega_a = 3 \cdot \zeta_c^2 + 3 \cdot (1 - 2 \cdot \zeta_c) \cdot \Omega_b + \Omega_b^2 + 1 - 3 \cdot \zeta_c$$

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