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Numerical study of non-isothermal adsorption of Naphthalene in supercritical CO_2: Behavior near critical point

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ABSTRACT

In this study, adsorption in a model binary mixture is investigated near the critical point in a side-heated cavity. The diverging behavior of the equilibrium constant and the Piston effect are taken into account and their influence on the adsorption process is pointed to. The modeling is based on numerical integration of the differential equations, considering the Navier–Stokes equations coupled with the energy and mass diffusion balances. By means of this model, the temperature, density and adsorbed concentration profiles are drawn at different times. Some fundamental concepts about the system's response to the heating are illustrated. The results reveal that the adsorption process is influenced by the combined effect of several parameters, such as the gravity and the proximity to the critical point. In particular, the adsorbed amount exhibits a reversed dependency on the wall heating very close to the critical point, which confirms the complexity of such a process in binary systems near critical conditions.

1. Introduction

The supercritical state was first reported in 1822 by Baron Gagniard de la Tour [1], but only one hundred years later, supercritical techniques have received increased attention and have been used in analytical and on an industrial scale. This state is achieved when the temperature and the pressure of a substance is set over their critical values. So the properties of a supercritical fluid range between those of a liquid and a gas and the distinction between the liquid and the gas phases is not possible. Some of the properties of a supercritical fluid are more liquid-like, whereas others are more gas-like.

Moreover, very close to the critical point, some properties diverge and others tend to zero. In fact, a small raise in pressure remarkably increases the fluid density and this effect diminishes with increasing distance from the critical point. On the other hand, a supercritical fluid has a higher diffusion coefficient and lower viscosity and surface tension than a liquid solvent, which leads to a more favorable mass transfer. Supercritical fluids exhibit very interesting qualities with regard to their physicochemical properties as well as ecology and economy. They are used as an alternative to organic liquid solvents in several applications such as cleanings [2–4]. Adsorption technologies using supercritical fluids have been also focused due to their potential applications including analytical extractions, activated carbon regeneration and soil remediation. Several studies have investigated the supercritical adsorption characteristics of many systems [5–12]. When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms.

In the framework of isothermal supercritical adsorption, there have been numerous publications in literature dealing with the modeling of adsorption equilibrium using the most common adsorption isotherm models, i.e. the Langmuir, the Freundlich and the Redlich–Peterson models [6,7,13–16]. All the experimental conditions used correspond to thermodynamic states relatively beyond the critical point because the adsorption equilibrium is influenced by the system temperature, pressure and by the supercritical fluid properties in the vicinity of the critical point. In contrast, supercritical adsorption systems close to the solvent's critical point have received much less explicit attention in the open literature. The experimental studies in this area are scarce. A thermodynamic analysis of near critical binary mixtures was established by Afrane and Chimowitz [17]. The authors studied the adsorption thermodynamics of dilute solutes adsorbing from high pressure supercritical fluid using the Henry's law. However, set under high pressures, the results showed an extremely weak dependence to pressure and to the composition of the supercritical solvent phase. In chromatography, the proximity to the critical point was early reviewed by Van Wasen et al. [20]. The authors pointed out the unusual behavior of equilibrium partition coefficients in the near-critical region. Many other works also showed interesting features of data in this region [21,22];

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Table 1
Pure component properties.

	T_c (K)	ρ_c (kg m^{-3})	P_c (bar)	M (kg mol^{-1})	ω	υ_b (cm^3 mol^{-1})	E_a (J/mol)
CO_2 (1)	304.21	467.8	73.8	4.401×10^{-2}	0.225	–	–
Naphthalene (2)	748.40	314.9	40.5	1.282×10^{-1}	0.302	155	101.4

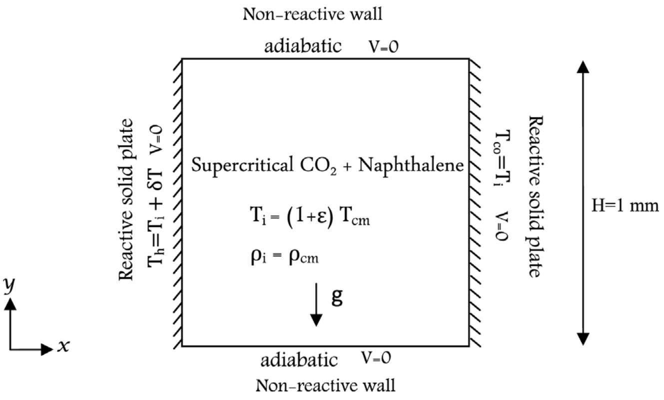

Fig. 1. Physical configuration.

in particular, papers by Schmitz et al. [23] and Klesper and Schmitz [24] provided striking evidence of the highly nonlinear behavior of equilibrium coefficients with respect to pressure and temperature variations, as the critical point of the fluid phase is approached. We believe that an adequate explanation of the thermodynamic basis of these phenomena in adsorption process taking into account both temperature and pressure effects is necessary. And it is also important to show the influence of the divergent character of thermodynamic properties and transport coefficients in near-critical systems on adsorption system behavior.

This is precisely the aim of this paper. For this purpose, adsorption of a model solute from supercritical CO_2 was investigated in a small side-heated cavity by means of 2D numerical simulations. Naphthalene was chosen as a model solute because its phase equilibria with CO_2 has been thoroughly studied [18,19]. There are extensive data available for this system that have been confirmed. The first section of the paper is devoted to the mathematical modeling of the problem and the numerical method used for the simulations. The modeling of the adsorption reaction at the solid boundaries is exposed in details. Then, the effect of the mass fraction and the proximity to the critical point are discussed for wide temperature and pressure conditions. The results show a strong dependence to temperature and pressure variations when the critical point is approached. We ended up with the effect of Damköhler number on the adsorbed mass fraction.

2. Mathematical modeling

2.1. Problem under investigation

The problem we consider is that of a dilute solute (Naphthalene in this case, named species 2) in supercritical CO_2 (named species 1). The physical properties of each pure compound are given in Table 1. The Naphthalene–CO_2 mixture is enclosed in a square cavity of height $H = 1$ mm and subjected to the earth gravitational field g. The cavity vertical walls are made of activated carbon (see Fig. 1). The activated carbon was chosen as a model adsorbent for this problem allowing as considering an adsorption reaction at the solid–fluid interface. Here, we emphasize that the chosen mixture as the adsorbent material is only generic since the aim of this study is to qualitatively investigate the influence of the proximity to the critical point on an adsorption reaction. Initially, the fluid is considered in thermodynamic equilibrium at a constant temperature T_i slightly above the mixture critical temperature $T_{cm} = 307.65$ K such that $T_i = (1+\varepsilon)T_{cm}$, where ε defines the dimensionless proximity to the critical point ($\varepsilon \ll 1$), and the density is equal to the mixture critical density $\rho_{cm} = 470$ kg m^{-3}. The critical properties, T_{cm} and ρ_{cm} correspond to the LCEP ("Lower Critical EndPoint") of the mixture and are slightly above the critical point of CO_2 ($T_{c1} = 304.21$ K, $\rho_{c1} = 467.8$ kg m^{-3}). A weak gradually heating is then applied at the solid plate ($x = 0$). The hot temperature is noted $T_h = T_i + \delta T$ where δT is about hundreds mK, while maintaining the other side at its initial temperature T_i (noted T_{co}). An adiabatic boundary condition was applied to the non-reactive walls.

2.2. Governing equations

The mathematical model is based on the 2D time-dependent and compressible Navier–Stokes equations, coupled with energy and mass diffusion equations including the supplemental Peng–Robinson equation of state. In order to reduce computational costs, a low Mach number approximation is used [25]. This approximation is valid since Mach numbers about 10^{-4} are obtained. Thus, the total pressure is split into two parts: a homogeneous thermodynamic part $P_{th}(t)$, which appears in the equation of state and in the energy equation and only depends on time t, and a non-homogeneous dynamic part $P_{dyn}(x, y, t)$, appearing in the momentum equation and which varies with time and space. In this study, the dynamic pressure is strongly smaller than the thermodynamic part. Consequently, the total pressure is little different from the thermodynamic pressure and the evolution of P_{th} governs that of the total pressure. In [38], a modification of the low Mach number approximation was proposed to account for the strong stratification of fluids near the critical point. We tested this modification and we noted that, for the present problem, the results obtained with and without the modification were the same. Therefore, the original approximation [25] was used for the simulations reported in this paper.

The dimensionless formulation was obtained using T_{cm} as characteristic temperature, ρ_i as characteristic density, $\rho_i(R/M_1)T_{cm}$ (with R is the perfect gas constant ($R = 8.3145$ J mol^{-1} K^{-1})) as characteristic pressure, H as characteristic length, the time scale of the piston effect as characteristic time, $t_{PE} = t_d/(\gamma_m - 1)^2$, where t_d is the characteristic time of thermal diffusion, γ_m the capacity ratio of the mixture (see Appendix A) and H/t_{PE} was taken as the characteristic velocity. The transport properties such as the dynamic viscosity μ, the isochoric specific heat capacity C_V, the thermal conductivity λ and the diffusion coefficient D_{21} were dimensionless, relative to their respective initial values (μ_i, λ_i, C_{vi}, $(D_{21})_i$). Thus, the governing equations in a dimensionless form are:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 \qquad (1)$$

$$\rho \frac{\partial \mathbf{V}}{\partial t} + \rho \mathbf{V} \cdot \nabla \mathbf{V} = -\nabla P_{dyn} + \frac{1}{Re} \Delta \mathbf{V} + \frac{1}{3Re} \nabla(\nabla \cdot \mathbf{V}) + \frac{1}{Fr} \rho \qquad (2)$$