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Reprint of “Correlation/prediction of sorption, swelling, and cloud points in CO_2 + polymer systems”☆

Mohammad Z. Hossain, Amyn S. Teja*

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, 30332-0100, USA

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ABSTRACT

We have previously presented an associated lattice fluid equation of state (ALF EOS) and shown that the equation is able to predict the solubility of CO_2 in polymers and, simultaneously, the extent of swelling of the polymer due to CO_2 using a single parameter obtained from one solubility isotherm. In the present study, we show that cloud point curves in CO_2 + polymer systems (at higher pressures) may also be predicted using the same value of the parameter. In addition, we show that the single parameter does not depend on temperature, pressure, or polymer molecular weight.

1. Introduction

CO_2 has been known to play an important role as a solvent and/or reactant during polymer synthesis and processing, as well as in pharmaceutical processing and other applications [1–3]. Therefore, the volumetric (swelling) and phase behavior (solubility/sorption, cloud points) of CO_2 + polymer systems are of great practical importance in the design of equipment and determination of optimum conditions of operation in these applications [1–4]. There is evidence to suggest that CO_2 interacts with electron donating functional groups in polymers to form weak Lewis acid – base or EDA (Electron Donor Acceptor) complexes [5–7], and it is also known that these complexes have a significant effect on the phase behavior of CO_2 + polymer systems [8–10]. However, complex formation is rarely considered explicitly in thermodynamic models, with the notable exception of versions of the Statistical Association Fluid Theory (SAFT) [11–14] and some lattice fluid models [15,16]. Most of the SAFT and lattice fluid models, however, require two or more adjustable parameters to correlate data [11,12,17–20] and are therefore limited in their predictive capability. More recently, complex formation has been explicitly taken into account in a Compressible Lattice Model (CLM) proposed by Ozkan and Teja [21] and extended by Kasturirangan et al. [22,23] and Yuan and Teja [24]. They showed that cloud point and sorption behavior of CO_2 + polymer systems could be correlated using their model with one adjustable parameter per binary system. However, it was not possible to describe volumetric properties such as swelling using the CLM model. To overcome this limitation, an Associated Lattice Fluid Equation of State (ALF EOS) [4,10,25] was developed by combining the Guggenheim-Huggins-Miller lattice partition function [26] and the CLM partition function for association [27,28]. The ALF EOS includes two physically meaningful association parameters that do not depend on temperature, or molecular weight. It was also demonstrated that one of these parameters can be obtained via independent *in situ* ATR-FTIR measurements [8,29,30], thus reducing the number of adjustable parameters in the EOS to one. The resulting model proved successful in describing the sorption and swelling behavior of many CO_2 + polymer systems over a wide range of temperatures, using a parameter obtained by fitting a single sorption isotherm [10]. In the present work, we explore the ability of the ALF EOS to predict cloud point behavior of CO_2 + polymer systems (at high pressures) using the parameter determined by fitting a single sorption isotherm (at much lower pressures). If successful, this predictive capability of the ALF EOS will allow users to simulate polymer processes using a minimum of experimental data.

2. Associated lattice fluid equation of state (ALF EOS)

The Associated Lattice Fluid Equation of State (ALF EOS) is derived from the partition function that combines the association contribution of the CLM model [27,28] with the Guggenheim-Huggins-Miller lattice partition function [26]. Details of the derivation can be found in references [4,10,25]. The analytical form of the EOS is given by:

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* Corresponding author.
E-mail address: amyn.teja@chbe.gatech.edu (A.S. Teja).

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$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{\hat{r}}\right)\tilde{\rho}\right] = 0 \tag{1}$$

with

$$\tilde{\rho} = \frac{\rho}{\rho^*} = \frac{\rho\hat{r}v^*}{M};\quad \tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{\varepsilon^*};\quad \tilde{T} = \frac{T}{T^*} = \frac{TR}{\varepsilon^*};\quad \tilde{v} = \frac{1}{\tilde{\rho}} = \frac{1}{1-f_0}$$

Here $\tilde{\rho}$, $\tilde{P}$, and $\tilde{T}$ are the reduced density, pressure, and temperature; ρ^*, P^*, T^* are the characteristic density, pressure, and temperature; and ρ, P, T are the system density, pressure and temperature, respectively. In addition, $\tilde{v}$ is the reduced volume, ε^* is the characteristic energy per segment, v^* is the characteristic volume per segment, $\hat{r}$ is the average segment number per molecule ($=r_1$ or r_2 for the two pure components), M is the molecular weight, R is the universal gas constant, and f_0 represents the fraction of holes in the lattice. It should be added here that the ALF EOS is of the same form as the Sanchez Lacombe (SL) EOS for pure substances [15]. However, for mixtures, the average lattice energy per segment in the ALF EOS is given by:

$$\varepsilon_m^* = \phi_1\varepsilon_1^* + \phi_2\varepsilon_2^* - RT\left[\alpha\phi_2\chi_\alpha + \phi_2(\phi_1 - \alpha\phi_2)(z-2-\alpha)\chi_u\right] \tag{2}$$

where ϕ_1 and ϕ_2 are the volume fractions of the solvent and solute, respectively; α is the association ratio (or the fraction of solute segments that are associated with solvent molecules), and z is the coordination number. Eq. (2) contains two contributions that can be attributed to association (represented by χ_a) and dispersion (represented by χ_u). These are given by:

$$\chi_u = \frac{\varepsilon_1^* + \varepsilon_2^* - 2\varepsilon_{12}^*}{(z-2-\alpha)RT} \tag{3}$$

$$\chi_\alpha = \frac{\Delta H_a}{RT} \tag{4}$$

In Eq. (3), the cross-interaction energy ε_{12}^* may be further expressed as:

$$\varepsilon_{12}^* = (1-k_{ij})\sqrt{\varepsilon_1^*\varepsilon_2^*} \tag{5}$$

where k_{ij} is a binary interaction coefficient that accounts for the non-ideality of cross-interactions in the absence of association. If the solvent and polymer segments are of about the same size, we may set $k_{ij} = 0$ for simplicity in the following discussion. Eq. (3) then becomes:

$$\chi_u = \frac{\left(\sqrt{\varepsilon_1^*} - \sqrt{\varepsilon_2^*}\right)^2}{(z-2-\alpha)RT} \tag{6}$$

In Eq. (4), ΔH_a is the enthalpy of complex formation and is related to the equilibrium constant K for the complexation reaction via the van't Hoff equation [6] via:

$$\ln\left(\frac{K}{K_0}\right) = \frac{\Delta H_a}{RT}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{7}$$

where K_0 is the equilibrium constant for the complexation reaction at an arbitrary reference temperature T_0 ($=298.15$ K in this work).

Eqs. (1)–(7) represent the governing equations of the ALF model. The equations incorporate pure component constantsρ^*, P^*, T^* (or equivalently, ε^*, v^* and r_i) as well as mixture quantities ε_m^*, v_m^* and $\hat{r}$. For binary mixtures, ε_m^* is obtained using Eq. (2), and v_m^* and $\hat{r}$ are obtained using:

$$v_m^* = \phi_1 v_1^* + \phi_2 v_2^* \tag{8}$$

$$\frac{1}{\hat{r}} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2(1+\alpha)} \tag{9}$$

Note that there are two mixture parameters in Eqs. (1)–(7), namely ΔH_a and K_0. We obtain ΔH_a using the methods discussed in the results section and treat K_0 as the only adjustable parameter in our calculations.

The chemical potential of pure gas phase CO_2 (assuming no polymer dissolves in the gas phase) and of CO_2 (component 1) dissolved in a polymer (component 2) can be obtained from the following expressions [4,10]:

Table 1
Characteristic constants of the ALF and SL equations for pure components.

Polymer	T^*/K	P^*/MPa	ρ^*/kg m^{-3}	ε^*/J mol^{-1}	v^*/cm^3 mol^{-1}	Ref.
PVAc	592.0	504.2	1282.7	4922.3	9.76	[4,10]
PLA	641.6	547.7	1330.1	5334.7	9.74	[4,10]
$PLGA_{50}$	638.0	536.6	1458.5	5304.6	9.89	[4,10]
PBMA	624.3	409.6	1124.8	5190.7	12.67	[4,10]
CO_2	308.6	574	1505.0	2565.7	4.47	[31]

Note: The value of parameter r is obtained from $r = \frac{\tilde{\rho}M}{\rho v^*}$ which is 6.54 for CO_2.

Table 2
Binary parameters for CO_2 + polymer X systems (obtained by fitting one sorption isotherm).

X	M/kg/mol	K_0	ΔH_a/kJ mol^{-1}	^{a} AAD%	^{b} AAD%	Data Ref
PVAc	330	0.10	−9.3[29]	2.90	–	[32]
PLA_H	110	0.20	−8.8[29]	0.39	–	[22]
$PLGA_{50}$	100	0.09	−8.5[29]	1.00	1.26	[33]
PBMA	100	0.18	−8.3 [30]	0.81	–	[35]

a – Sorption calculation; b – Swelling ratio calculation; K_0 – [10].

$$\frac{\mu_1^{G,pure}}{RT} = \frac{r_1}{RT}\left[-\tilde{\rho}_1\varepsilon_1^* + \frac{Pv_1^*}{\tilde{\rho}_1}\right] + r_1\left[\left(\frac{1-\tilde{\rho}_1}{\tilde{\rho}_1}\right)\ln(1-\tilde{\rho}_1) + \frac{1}{r_2}\ln\tilde{\rho}_1\right] \tag{10}$$

$$\begin{aligned}\frac{\mu_1^L}{RT} &= \frac{Pr_1}{RT\tilde{\rho}}[-f_0v^* + v_1^*] - r_1f_0 + \frac{r_1}{\hat{r}}f_0 + \ln(1-f_0)\\ &\quad - \frac{1}{RT}[r_1\tilde{\rho}(1-\tilde{\rho})\varepsilon^* + r_1\varepsilon_1^*\tilde{\rho}]\\ &- \frac{r_1\phi_2}{r_2} + (\beta_1\phi_2\chi_a + \phi_2[\{-\beta_1\phi_2 + \phi_2(1+\alpha)\}(z-\alpha-2)\\ &\quad - \beta_1(\phi_1 - \alpha\phi_2)]\chi_u)\tilde{\rho}\\ &+ \left[\frac{1}{1+\alpha} - \frac{\beta_1}{(1+\alpha)^2}\right]\ln(\phi_1 - \alpha\phi_2) + \frac{\phi_1 - \alpha\phi_2}{1+\alpha}\left(\frac{1-\beta_1\phi_2}{\phi_1-\alpha\phi_2} - 1\right) - \ln\left(\frac{\phi_1}{\phi_1 - \alpha\phi_2}\right)\\ &\quad - 1\\ &+ \phi_1\left(\frac{1-\beta_1\phi_2}{\phi_1-\alpha\phi_2}\right) + \beta_1\phi_2\ln\left(\frac{\alpha\phi_2}{\phi_1-\alpha\phi_2}\right) + \alpha\phi_2\ln\left(\frac{\beta_1}{\alpha} - \frac{1-\beta_1\phi_2}{\phi_1-\alpha\phi_2}\right) + \beta_1\phi_2\ln\left(\frac{\alpha}{1-\alpha}\right)\end{aligned} \tag{11}$$

with, $\beta_1 = \frac{\alpha(1+K)-K}{(1+K)(2\alpha\phi_2-1)}$

Eqs. (10) and (11) can be used to calculate the solubility of CO_2 in a polymer by equating the chemical potential of pure CO_2 in the gas phase (obtained from Eq. (10)) to the chemical potential of CO_2 dissolved in the polymer (obtained from Eq. (11)). We assume that at low pressures, the gas phase is pure CO_2. The extent of swelling of a polymer due to CO_2 can be estimated using the expression

$$S_w = \frac{V}{V_0} \times 100\% \tag{12}$$

where V_0 and V are the volume of the dry polymer and the CO_2 + polymer solution, respectively (obtained using Eq. (1)). The cloud point behavior of CO_2 + polymer systems is obtained by equating the chemical potentials of CO_2 in the two (mixed) phases using Eq. (11).

3. Results and discussion

As noted above, the characteristic constants P^*, ρ^*, and T^* (or ε_i^*, v_i^*, and r_i) for the pure components of interest must be available in order to apply the ALF EOS. These constants were obtained by fitting *PVT* data in our previous work [4,10] and are listed for the polymers of interest in Table 1. It is worthwhile to note here that the characteristic constants of the ALF EOS are almost the same as the SL EOS constants for many polymers [4,10]. Small differences in values for the two sets of