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Compressible Lattice Model for Phase Equilibria in CO_2 + Polymer Systems

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We present a compressible lattice model for representation of both low-pressure and high-pressure phase equilibria in CO_2 + polymer systems. The model explicitly accounts for weak complex formation in these systems, using two parameters that are obtained by fitting experimental cloud point pressures or sorption equilibria. In addition, one of these parameters may be obtained from Fourier transform infrared (FTIR) spectroscopy measurements. We demonstrate the application of this model to the prediction of low-pressure sorption behavior in the CO_2 + poly(vinyl acetate) (PVAc) system, using parameters obtained from high-pressure cloud point data. In addition, we show that we are able to predict the sorption behavior of CO_2 + PLGA copolymer systems using a single parameter obtained from CO_2 + poly(lactic acid) (PLA) cloud point data, together with enthalpies of association obtained from FTIR measurements.

1. Introduction

CO_2 + polymer phase behavior is of interest in several applications, including drug encapsulation, particle precipitation, and the manufacture of polymer foams and membranes.[1−4] In these applications, the morphology of the polymer product often is dependent on the processing path through single-phase and two-phase regions of the phase diagram. There is experimental evidence[5] to suggest that CO_2 forms weak complexes with carbonyl groups in polymers and, thereby, significantly affects their phase behavior. Unfortunately, popular thermodynamic models such as the Flory−Huggins equation and the Sanchez−Lacombe equation of state do not explicitly account for these weak interactions. Consequently, there is theoretical as well as practical interest in models that incorporate weak interactions, especially for applications at high pressures that are typical of supercritical processes.

Among the models that specifically account for specific polymer + solvent interactions at high pressures are several versions of the SAFT equation of state[6−8] and the lattice model for compressible associated solutions presented by Ozkan and Teja.[9] The SAFT equation generally requires two temperature-dependent or molecular-weight-dependent parameters to correlate cloud point behavior in systems that contain CO_2.[10,11] The Ozkan and Teja model, on the other hand, is able to correlate CO_2 + polymer phase equilibria using two parameters that are not dependent on temperature or molecular weight. In addition, it is also possible to obtain one of these parameters from Fourier transform infrared (FTIR) spectra.[9] Ozkan and Teja also showed that it is possible to predict the low-pressure CO_2 sorption behavior in polymers using their model with parameters obtained from high-pressure cloud point data. However, agreement with the experiment was only qualitative (with reported average absolute deviations (AADs) of ±20%−25%).

In the present study, we propose a modification of the Ozkan and Teja model, to improve the simultaneous representation of high-pressure (cloud point) and low-pressure (sorption) behavior and demonstrate the application of the modified model to CO_2 + poly(vinyl acetate) (PVAc). We then extend the model to CO_2 + poly(lactide-co-glycolide) (PLGA) copolymer systems, using new experimental measurements for CO_2 sorption in these copolymers. We have chosen to study these U.S. Food and Drug Administration (FDA)-approved copolymers because they are of interest in drug delivery applications and also because the PLGA backbone contains carbonyl repeat groups that are capable of forming weak complexes with CO_2.

2. Modified Lattice Model

The thermodynamic model of Ozkan and Teja[9] is based on lattice theory and accounts explicitly for complex formation between a polymer segment P and μ molecules of solvent S, according to the reaction

$$\mathrm{P} + \mu\mathrm{S} \Leftrightarrow \mathrm{PS}_{\mu} \tag{1}$$

The solvent + polymer mixture is assumed to consist of associated and unassociated polymer segments, as well as associated and unassociated solvent molecules. The formation of complexes restricts a certain number of solvent molecules to specific lattice sites, whereas unassociated solvent molecules are distributed randomly on the lattice. The total number of configurations is then calculated to yield an entropy of mixing, which is combined with an enthalpy of mixing based on two types of contacts (due to association and dispersion) to yield the following expression for the Gibbs energy of mixing (ΔG^{mix}):

$$\begin{aligned}\Delta G^{\mathrm{mix}} = {} & \alpha\mu\phi_2\chi_{\mathrm{a}} + \phi_2\{1 - \phi_2(1 + \alpha\mu)\}[(z - 2 - \mu)\alpha + \\ & (1 - \alpha)(z - 2)]\chi_{\mathrm{u}} + \frac{\phi_2}{\xi}\ln\phi_2 + \left[\frac{1 - \phi_2(1 + \mu\alpha)}{1 + \mu\alpha}\right] \\ & \ln[1 - \phi_2(1 + \mu\alpha)] - \phi_1\ln\frac{\phi_1}{\phi_1 - \mu\alpha\phi_2} + \\ & \mu\alpha\phi_2\ln\frac{\mu\alpha\phi_2}{\phi_1 - \mu\alpha\phi_2} + \phi_2(1 - \alpha)\ln(1 - \alpha) + \alpha\phi_2\ln\alpha\end{aligned} \tag{2}$$

where z is the lattice coordination number (assumed to be 10 in this work), R is the gas constant, T is the temperature, n is

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the total number of moles, and ϕ_1 and ϕ_2 are the volume fractions of CO_2 and the polymer, respectively. The five characteristic parameters in eq 2 include the solvent−polymer segment binding ratio (μ), the association ratio (α), the number of segments (ξ), and the two interaction parameters for association (χ_a) and dispersion (χ_u). The interaction parameter for association χ_a also can be expressed in terms of an enthalpy of association (ΔH_a), as follows:

$$\chi_a = \frac{\Delta H_a}{RT} \tag{3}$$

with ΔH_a being related to the equilibrium constant K for the binding reaction, via

$$\ln \frac{K}{K_0} = \frac{-\Delta H_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{4}$$

where K_0 is the equilibrium constant for association at a reference temperature T_0 (280 K in this work). In the above expression, ΔH_a has been assumed to be independent of T over the temperature range of interest. The equilibrium constant K is also related to the association ratio α, or the fraction of associated segments per molecule, as follows:

$$\alpha = \frac{(1 + K) - \sqrt{(1 + K)^2 - 4\phi_1\phi_2 K(1 + K)}}{2\phi_2(1 + K)} \tag{5}$$

where ϕ_1 and ϕ_2 are volume fractions of the polymer and solvent, respectively. Therefore, χ_a and α can be replaced by ΔH_a and K_0 in the model.

The binding ratio has a value of $\mu = 1$ when only one CO_2 molecule is able to associate with a functional group in the polymer segment, as is the case for all systems investigated in the present study.

The dispersion parameter χ_u can be estimated from the solubility parameters δ_1 and δ_2 of CO_2 and the nonpolar analog (or homomorph) of the polymer as follows:

$$\chi_u = \frac{V_1(\delta_1 - \delta_2)}{RT(z - \mu\alpha - 2)} \tag{6}$$

where the functional group in the polymer molecule that interacts with CO_2 is substituted with a nonpolar group to obtain the homomorph. In eq 6, V_1 is the molar volume of CO_2 and the other quantities have been defined previously.

In the Flory−Huggins theory, the segment number (ξ) is calculated from the ratio of molar volumes of the polymer and the solvent under ambient conditions. However, to account for the compressibility of the lattice, Ozkan and Teja allowed the segment number to vary with temperature and pressure. In their model, ξ is given as

$$\xi = \frac{V_2[T,P]}{V_1[T,P]} \tag{7}$$

where V_2 is the volume of the polymer and V_1 is the molar volume of CO_2. According to eq 7, ξ (and, hence, the entropy of mixing) changes with temperature and pressure, which means that the number of possible lattice configurations also changes with the temperature and pressure to allow for the flexibility of the polymer chain. The use of eq 7 allowed Ozkan and Teja to calculate both cloud point and sorption behavior using the same set of parameters. However, agreement with experiment was only qualitative when sorption behavior was predicted using parameters obtained from cloud point data. Therefore, we may conclude that eq 7 does not properly account for compressibility effects. According to Hilderbrand,[12] the probability of finding a molecule in a given volume is dependent on the free volume, which suggests that the entropy of mixing (and, therefore, the segment number ξ) must also be dependent on the free volume. The development of the UNIFAC−FV model[13] also suggests that the ratio of free volumes provides a better representation of entropic effects in polymer solutions. The free volume (V_f) is equal to the molar volume (V) minus the volume occupied by the molecules (V_j). The latter may be approximated by the hard core or van der Waals volume (V^{vdW}). Alternatively, as suggested by Bondi,[14] we may use the molar volume V^0 at 0 K to estimate V_j. The molar volume V of the polymer may be calculated from the expression proposed by van Krevlen,[15]

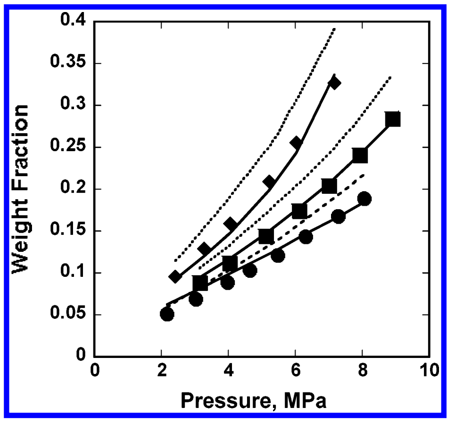

Figure 1. Sorption data and predictions for CO_2 + poly(vinyl acetate) (PVAc) (molecular weight of $M_W = 100\,000$): (◆) 313.15, (■) 333.15, and (●) 353.15 K.[19] Dashed lines are predictions of the Ozkan and Teja[9] model, and solid lines are predictions of the modified model.

$$V = V^{vdW}(1.3 + 10^{-3}T) \tag{8}$$

so that, when $T = 0$ K, $V^0 \rightarrow 1.3V^{vdW}$. Kouskoumvekaki et al.[16] have suggested that V^0 is closer to 1.2 V^{vdW} for many polymers. Therefore, in the present work, we propose that the segment ratio ξ be obtained as follows:

$$\xi = \frac{V_2[T,P] - 1.2V_2^{vdw}}{V_1[T,P] - V_1^{vdw}} \tag{9}$$

V_1 may be calculated from an equation of state (such as that of Patel and Teja[18] used in our calculations) and V_2 may be calculated using the Tait equation or the group contribution modified cell model (GCMCM) of Sato et al.[17]

3. Representation of Both Low-Pressure and High-Pressure Phase Behavior

To compare the original Ozkan and Teja model with the modified model, we have calculated cloud point and sorption equilibria in the CO_2 + PVAc system, using parameters reported by Ozkan and Teja[9] from a correlation of cloud point data. We found that the modified model could correlate cloud point pressures in the CO_2 + PVAc system ($K_0 = 1.75$) with an average absolute deviation (AAD) of 2.0%, compared with an AAD of 2.4%, which was reported by Ozkan and Teja.[9] In addition, sorption equilibria in the CO_2 + PVAc system could be predicted with an AAD of 4%, which represents a significant improvement over the AAD of 22% that was reported by Ozkan and Teja.[9] Sorption predictions are shown in Figure 1. Note

Table 1. Polymer Properties

polymer	source	average molecular weight
polylactide, PLA	Aldrich	75000−120000
poly(methyl methacrylate), PMMA	Aldrich	100000
poly(lactide-co-glycolide)		
85:15, $PLGA_{15}$	Aldrich	50000−75000
65:35, $PLGA_{35}$	Sigma	40000−75000

that no adjustable parameters were used in these calculations, and that cloud point pressures were on the order of 1000 bar, whereas sorption pressures were on the order of 10 bar. Therefore, we may conclude that the modified model is able to extrapolate phase equilibria over a range of pressures.

In the following sections, we describe the application of the modified model to CO_2 + PLGA copolymer systems for which cloud point pressures have been reported in the literature.[20] Because no measurements of sorption equilibria in these systems have been published, we also have measured CO_2 sorption in these copolymers using a quartz crystal microbalance (QCM).[16] Therefore, our sorption measurements serve to further test the capabilities of the model.

4. Sorption Measurements

Coleman-grade CO_2 (purity of >99.999%) was obtained from National Welders Co. and used as received. Polymers were obtained from the sources listed in Table 1 and also were used as received. Polymer films were prepared by dip coating a polished gold-coated QCM wafer (International Crystal Manufacturing Company, Inc., AT cut at 35° 25′, with a nominal resonant frequency of 5 MHz) in a 5 wt % solution of polymer in acetone for ~1 min, and then withdrawing the wafer at a controlled rate. The coated wafer was dried under vacuum at 80 °C for 1 h and then subjected to CO_2 for 30 min at a pressure corresponding to the maximum pressure of the subsequent experiment. The CO_2 preconditioning step was undertaken to remove any residual solvent after drying and to relieve internal stresses. The thickness of the polymer film coating was ~500 nm, obtained by dividing the frequency change of the crystal (6000 MHz) by the quantity represented by twice its mass sensitivity constant (2×56.6 Hz μg^{-1} cm^2). The factor of 2 was used because the wafer was coated on both sides with the polymer. The wafer was then placed in a custom-built high-pressure cell and connected to an oscillator circuit (Maxtek, Model PLO-10) via a high-pressure electrical feed through (Conax Buffalo Technologies, Model PL-16-A2-G). The oscillator circuit included a 225 MHz Universal Frequency Counter (Agilent, Model 53131A) to read the frequency of the vibrating crystal. The thick-walled cylindrical high-pressure cell (inner diameter (ID) of 63.5 and a depth of 200 mm, with an inside volume of 25 cm^3) was designed for a maximum working pressure of 50 MPa. A thermocouple (Omega, Model KQIN-116V-12) was placed in the cell to measure any variations in temperature. CO_2 was added to the cell using a syringe pump (ISCO, Inc., and Model 260 D), and the pressure inside the cell was monitored with a pressure transducer (Omega, Model PX302-10KGV). The entire assembly was placed in a constant-temperature water bath (Neslab).

The total mass of polymer deposited on the wafer (Δm) was determined from measurements of the change in the oscillation frequency of the crystal before and after coating ($F - F_0$). These measurements yield the overall frequency change due to mass loading, viscous coupling, pressure, and roughness:

$$F - F_0 = \Delta F_M + \Delta F_P + \Delta F_\eta + \Delta F_R \qquad (10)$$

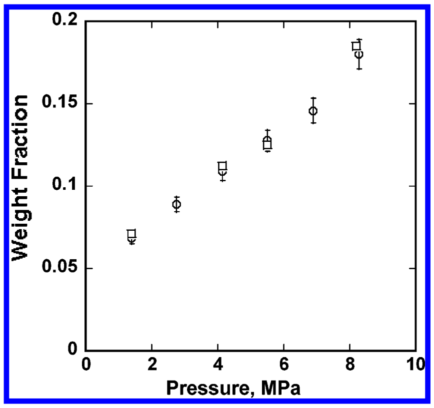

Figure 2. Sorption data for CO_2 + poly(methyl methacrylate) (PMMA) at 313 K: (□) experimental data of Aubert[25] and (○) this work.

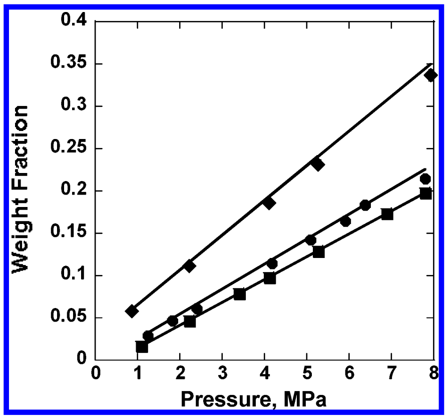

Figure 3. Sorption predictions for CO_2 + poly(lactic acid) (PLA): (◆) experimental data at 313.15 K, (●) experimental data at 333.15 K, and (■) experimental data at 344.15 K. Solid lines represent predictions of the modified model.

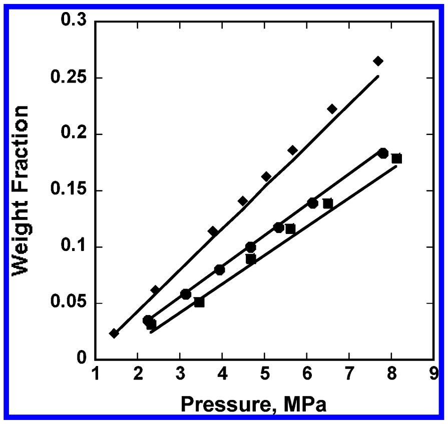

Figure 4. Sorption predictions for CO_2 + $PLGA_{15}$: (◆) experimental data at 313.15 K, (●) experimental data at 333.15 K, and (■) experimental data at 344.15 K. Solid lines represent predictions of the modified model.

where ΔF_M is the frequency change due to mass loading and is related to Δm via Saubrey's equation:

$$\Delta F_M = \frac{-2\Delta m F_0^{\,2}}{A\sqrt{\rho_q \mu_q}} \qquad (11)$$

Here, F_0 is the resonant frequency of the crystal, A the active area of the crystal (between electrodes), ρ_q the density of the quartz, and μ_q the shear modulus of the quartz.

The frequency change due to viscous coupling (ΔF_η) was calculated using the equation proposed by Kanazawa and

Gordon:[21]

$$\Delta F_{\eta} = -0.5C_{\mathrm{m}}(\pi F_0)^{0.5}(\rho_{\mathrm{f}}\eta_{\mathrm{f}}) \tag{12}$$

where ρ_{f} and η_{f} are the density and shear viscosity of the fluid surrounding the crystal, respectively, and C_{m} is the mass sensitivity constant ($C_{\mathrm{m}} = 56.6$ Hz μg^{-1} cm^2 for a 5 MHz crystal). Filiâtre et al.[22] have shown that this equation can be applied to a QCM crystal that is immersed in a fluid.

The frequency change due to pressure was calculated using the following relation proposed by Park et al.:[23]

$$\Delta f_{\mathrm{p}} = F_0\beta P \tag{13}$$

where $\beta = (1.095 - 0.002T) \times 10^{-5}$ MPa^{-1} (where T is given in degrees Celsius) at temperatures between -10 °C and 75 °C.

The frequency change due to roughness was ignored, because smooth crystals (rms of <5 nm)[24] were used in our experiments.

5. Results and Discussion

5.1. Sorption Measurements. We have validated our method by measuring the sorption of CO_2 in poly(methyl methacrylate) (PMMA). The data are plotted in Figure 2, together with the published data of Aubert.[25] The two sets of measurements generally agree within their experimental uncertainties, thus confirming the validity of our measurements.

Measured sorption data for the CO_2 + poly(lactic acid) (PLA), CO_2 + PLGA$_{15}$, and CO_2 + PLGA$_{35}$ polymer systems (where the subscript denotes the glycolide content in the copolymer) are presented in Table 2 and shown in Figures 3−5. Our results show that the solubility of CO_2 in the polymer decreases as the glycolide content increases. For example, the solubility of CO_2 in PLA at 4 MPa and 60 °C is 11 wt % and decreases to 4 wt % in PLGA$_{35}$ under the same conditions. The solubility also decreases as the temperature increases in all cases.

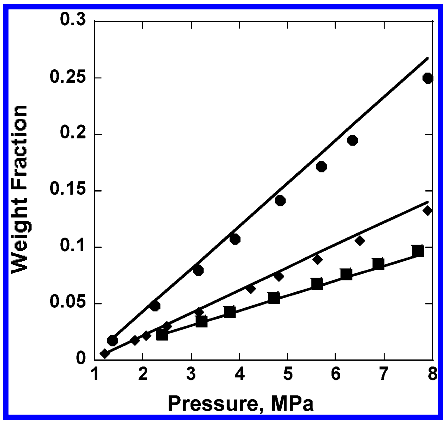

Figure 5. Sorption predictions for CO_2 + PLGA$_{35}$: (◆) experimental data at 313.15 K, (●) experimental data at 333.15 K, and (■) experimental data at 344.15 K. Solid lines represent predictions of the modified model.

5.2. Sorption Predictions. Figures 3−5 also show our predictions of sorption equilibria in CO_2 + PLGA copolymer systems, using a single value of K_0 ($K_0 = 1.16$) obtained by fitting cloud point pressures in the low-molecular-weight CO_2 + PLA system.[26] The ΔH_{a} values were obtained from FTIR measurements that were reported elsewhere (and are summarized in Table 3). As shown in Figures 3−5, we were able to predict the sorption behavior of the entire set of CO_2 + PLGA copolymer systems, using this single value of K_0 from just the cloud point data for the CO_2 + PLA system. The overall AAD between experimental and calculated solubilities was <6%, which is quite remarkable. The single value of K_0 required in the calculations suggests that the extent of complex formation at the reference temperature (280 K) is approximately the same in these systems.

Table 2. Measured Solubility of CO_2 in Polymers

CO_2 + PLA		CO_2 + PLGA$_{15}$		CO_2 + PLGA$_{35}$	
P (MPa)	weight fraction of CO_2	P (MPa)	weight fraction of CO_2	P (MPa)	weight fraction of CO_2
313.15 K					
0.862	0.0575	1.448	0.0236	1.38	0.0178
2.213	0.1109	2.427	0.0614	2.24	0.0487
4.103	0.1855	3.786	0.1138	3.13	0.0804
5.269	0.2316	4.482	0.1407	3.896	0.1074
7.931	0.3367	5.055	0.1628	4.848	0.1413
		5.662	0.1862	5.696	0.1715
		6.600	0.2224	6.351	0.1948
		7.700	0.2649	7.900	0.2499
333.15 K					
1.241	0.0292	2.248	0.0348	1.213	0.0054
1.813	0.0463	3.136	0.0586	1.848	0.0175
2.393	0.0609	3.931	0.0799	2.069	0.0217
4.172	0.1145	4.669	0.0997	2.503	0.0299
5.096	0.1421	5.343	0.1178	3.172	0.0426
5.917	0.1650	6.137	0.1391	4.241	0.0629
6.386	0.1830	7.800	0.1836	4.813	0.0738
7.800	0.2150			5.627	0.0893
				6.500	0.1059
				7.900	0.1325
344.15 K					
1.100	0.0163	2.317	0.0344	2.393	0.0235
2.213	0.0464	3.448	0.0627	3.206	0.0348
3.400	0.0786	4.669	0.0932	3.793	0.0431
4.103	0.0977	5.593	0.1163	4.703	0.0558
5.269	0.1292	6.496	0.1389	5.593	0.0683
6.896	0.1734	8.103	0.1790	6.206	0.0768
7.800	0.1978			6.862	0.0860
				7.689	0.0976

Table 3. Frequency Shifts and Corresponding ΔH_a Values from Fourier Transform Infrared (FTIR) Spectroscopy Measurements

system[a]	frequency shift, $\Delta\nu$ (cm^{-1})	$-\Delta H_a$ (kJ/mol)
D,L-PLA	3.6	3.57
D,L-PLGA$_{15}$	3.4	3.44
D,L-PLGA$_{25}$	3.3	3.23
D,L-PLGA$_{35}$	3.1	3.09

[a] Subscripts represent the percentage of glycolide in the backbone.

4. Conclusions

We have modified the lattice model of Ozkan and Teja[9] to calculate both cloud point and sorption equilibria in the CO_2 + poly(vinyl acetate) (PVAc) and CO_2 + poly(lactide-co-glycolide) (PLGA) systems, using a single set of parameters. Calculated equilibria were in good agreement with measured values, which confirmed that our modified model is able to extrapolate phase equilibria over a range of pressures. We have also measured the sorption equilibria in CO_2 + PLGA systems and shown that these equilibria can be predicted using information obtained from Fourier transform infrared (FTIR) spectra and a single parameter obtained by fitting cloud point pressures in a reference system (CO_2 + poly(lactic acid) (PLA), in our case).

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