

Expanded liquid model for phase equilibria in systems with specific CO₂ – polymer interactions

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Abstract

A lattice-based model for solutions with solute-solvent association is extended to the calculation of phase equilibria in polymer-CO₂ systems. The model requires a maximum of two adjustable parameters to correlate both cloud point and sorption data. Moreover, one of these parameters can be obtained from spectroscopic data. Application of the model is demonstrated for the calculation of cloud point curves of several polymer-CO₂ systems. Good agreement with experiment was obtained, with average deviations between calculated and experimental cloud points of 1.3 % and sorption data of about 10%.

The modified gART-L model

The gART-L model was proposed by Sukhadia¹, Variankaval and others²⁻³ as a simple reformulation of the Flory-Huggins model to account for specific interactions between polymer segments and solvent molecules. Their expression for the Gibbs energy of mixing ΔG_m is given by:

$$\begin{aligned}
\frac{\Delta G}{nRT} = & \alpha\mu\Phi_2\chi_a + \Phi_2\{1-\Phi_2(1+\alpha\mu)\}[(z-2-\mu)\alpha \\
& + (1-\alpha)(z-2)]\chi_u + \frac{\Phi_2}{x}\ln\Phi_2 + \left(\frac{1-\Phi_2(1+\mu\alpha)}{(1+\mu\alpha)}\right)\ln\{1-\Phi_2(1+\mu\alpha)\} \quad (1) \\
& - \Phi_1\ln\frac{\Phi_1}{\Phi_1-\mu\alpha\Phi_2} + \mu\alpha\Phi_2\ln\frac{\mu\alpha\Phi_2}{\Phi_1-\mu\alpha\Phi_2} + \Phi_2(1-\alpha)\ln(1-\alpha) + \alpha\Phi_2\ln\alpha
\end{aligned}$$

where z is the lattice coordination number (= 10), R is the gas constant, T is the temperature, Φ_1 and Φ_2 are volume fractions of CO₂ and polymer, and n is the total number of moles. There are five characteristic quantities in eq.(1): the solvent-solute binding ratio μ ; the association ratio α ; the number of segments x ; and the specific interaction parameters for association χ_a and for dispersion, χ_u . The binding ratio μ is assumed to be 1 throughout this work because only one CO₂ molecule is able to associate with a functional group in the polymers investigated. The specific interaction parameter for association χ_a (which is related to the enthalpy of association ΔH_a) can be obtained from FTIR spectra of the polymer-CO₂ mixture at the conditions of interest. The enthalpy of association, in turn, is related to the equilibrium constant K for the association reaction as follows:

$$\ln\frac{K}{K_0} = \frac{-\Delta H_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (2)$$

where K_0 is the equilibrium constant for association at a reference temperature T_0 (say, 300 K). In the above expression, ΔH_a has been assumed to be independent of T over the range of temperatures of many studies. K can therefore be calculated at any temperature if ΔH_a and K_0 are known. Knowledge of the equilibrium constant K also yields the association ratio α . The dispersion parameter χ_u is estimated from the solubility parameter of the non-polar analog (or homomorph) of the polymer.

The segment number x is generally obtained from the ratio of the molar volumes of the solvent (CO₂) and the solute (polymer) at ambient conditions. This somewhat arbitrary ratio works well for liquids, since liquid volumes are not significantly affected by pressure. However, it is quite inadequate at supercritical CO₂ conditions, because the molar volume of CO₂ changes dramatically with pressure above its critical point. In the present work, the polymer molar volumes were obtained from the Tait equation and CO₂ properties from a cubic equation of state. The modified gART-L model incorporating the pressure was then used to calculate phase equilibria and sorption behavior in CO₂-polymer systems. Note that the model requires a knowledge of two characteristic parameters (ΔH_a and K_θ) in the calculations. The remaining quantities in the models either have fixed values or they can be calculated from ΔH_a and K_θ . The number of parameters can be further reduced if ΔH_a is obtained from FTIR spectra.

Results for cloud point behavior of polymer-CO₂ mixtures

Cloud point data for the systems poly(butylmethacrylate) (PBMA)-CO₂ and PVAc-CO₂ were correlated using ΔH_a values obtained from FTIR measurements. A single adjustable parameter K_θ was obtained by fitting these data. Calculated results were in good agreement with experimental data using one adjustable parameter.

The model was also used to calculate cloud point curves in poly (acrylate) – CO₂ systems using two adjustable parameters. The model was able to correlate the data well

The solubility of CO₂ in polymers was also predicted using the parameters obtained by fitting cloud point curves. Reasonable agreement was obtained between predicted values and experimental sorption data (error in the range 5 - 20%). Note that

there are no adjustable parameters in the sorption calculations, so the agreement may be regarded as reasonable.