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:
\[
\frac{\Delta G_m}{nRT} = \alpha \Phi_1 \chi_a + \Phi_2 \{1 - \Phi_2 (1 + \mu \alpha)\} \right\} (z - 2 - \mu) \alpha \\
+ (1 - \alpha) (z - 2) \chi_u + \Phi_2 \frac{1}{x} \ln \Phi_2 + \left( \frac{1 - \Phi_2 (1 + \mu \alpha)}{1 + \mu \alpha} \right) \ln \{1 - \Phi_2 (1 + \mu \alpha)\} \\
- \Phi_1 \ln \frac{\Phi_1}{\Phi_1 - \mu \alpha \Phi_2} + \mu \alpha \Phi_2 \frac{\ln \Phi_2}{\Phi_1 - \mu \alpha \Phi_2} + \Phi_2 (1 - \alpha) \ln (1 - \alpha) + \alpha \Phi_2 \ln \alpha
\]

where \(z\) is the lattice coordination number (= 10), \(R\) is the gas constant, \(T\) is the temperature, \(\Phi_1\) and \(\Phi_2\) are volume fractions of CO\(_2\) and polymer, and \(n\) is the total number of moles. There are five characteristic quantities in eq.(1): the solvent-solute binding ratio \(\mu\); the association ratio \(\alpha\); the number of segments \(x\); and the specific interaction parameters for association \(\chi_a\) and for dispersion, \(\chi_u\). The binding ratio \(\mu\) is assumed to be 1 throughout this work because only one CO\(_2\) molecule is able to associate with a functional group in the polymers investigated. The specific interaction parameter for association \(\chi_a\) (which is related to the enthalpy of association \(\Delta H_a\)) can be obtained from FTIR spectra of the polymer-CO\(_2\) 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:

\[
\ln \frac{K}{K_0} = -\frac{\Delta H_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)
\]

where \(K_0\) is the equilibrium constant for association at a reference temperature \(T_0\) (say, 300 K). In the above expression, \(\Delta H_a\) 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 \(\Delta H_a\) and \(K_0\) are known. Knowledge of the equilibrium constant \(K\) also yields the association ratio \(\alpha\). The dispersion parameter \(\chi_u\) 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 (CO$_2$) 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 CO$_2$ conditions, because the molar volume of CO$_2$ changes dramatically with pressure above its critical point. In the present work, the polymer molar volumes were obtained from the Tait equation and CO$_2$ 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 CO$_2$-polymer systems. Note that the model requires a knowledge of two characteristic parameters ($\Delta H_a$ and $K_0$) in the calculations. The remaining quantities in the models either have fixed values or they can be calculated from $\Delta H_a$ and $K_0$. The number of parameters can be further reduced if $\Delta H_a$ is obtained from FTIR spectra.

**Results for cloud point behavior of polymer-CO$_2$ mixtures**

Cloud point data for the systems poly(butylmethacrylate) (PBMA)-CO$_2$ and PVAc-CO$_2$ were correlated using $\Delta H_a$ values obtained from FTIR measurements. A single adjustable parameter $K_0$ 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) – CO$_2$ systems using two adjustable parameters. The model was able to correlate the data well.

The solubility of CO$_2$ 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.