Fluid Phase Equilibria 278 (2009) 41–53

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Quantification of thermodynamics of aqueous solutions of poly(ethylene glycols): Role of calorimetry

Lalaso V. Mohite, Vinay A. Juvekar*

Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

ARTICLE INFO

Article history:
Received 2 May 2008
Received in revised form
16 November 2008
Accepted 2 January 2009
Available online 19 January 2009

Keywords:
Polyethylene glycols
Calorimetry
Enthalpy of mixing
Activity
Binodal curve

ABSTRACT

A correlation based on generalized Flory-Huggins model, which relates the activity data of aqueous poly(ethylene glycol) (PEG) solutions at low temperatures to the binodal curve in the LCST region, has been developed. The temperature dependent parameters of the model are estimated by regression of the experimental data of the enthalpy of mixing of aqueous PEG solutions, obtained using isothermal titration calorimetry. The temperature independent parameters are estimated from the data of the activity of PEG solutions at a single temperature. An attempt to develop a similar correlation based on the hydrogen bond model has been unsuccessful. It is also shown that the correlation based on the activity data alone, does not have the ability to predict the binodal curve and the use of the enthalpy data is essential for this purpose.

1. Introduction

Poly(ethylene glycol) (PEG) is an industrially important nonionic polymer. Its hydrophilic ethereal oxygen atoms interact strongly and favorably with water through hydrogen bonds. As a result, it is completely miscible with water at moderate temperatures. The interaction between PEG and water progressively weakens with increasing temperature due to the reduction in the enthalpy of hydrogen bond and finally, above the lower critical solution temperature (LCST), phase separation occurs. This phase behavior is utilized in diverse applications including the separation of biomolecules [1,2] and metal ions [2,3], bioconversion [4], and organic synthesis [4]. To understand and optimize these applications, thermodynamic properties of aqueous solutions of PEG need to be quantified. This requires both the accurate experimental data and a good model which allows prediction of properties of the system in the range of temperature and composition in which experimental data are not available.

A large number of experimental studies have been reported in the literature on the thermodynamic properties of aqueous PEG solutions. These include activity of water in the solution and phase separation behavior. The data obtained from these studies are well documented by Wohlfarth [5]. The most widely used methods for activity measurements are vapor pressure osmometry [6], laser-light scattering [7], isopiestic method [7,8], dew point method [9], and sedimentation technique [10]. Different methods of measurements differ in terms of their accuracy as well as the range of temperature and composition in which each is applicable. Every technique has a relatively narrow range of temperature and polymer compositions over which it is accurate. For example, the sedimentation technique is accurate only at lower temperatures (<313 K) [10], whereas vapor pressure osmometry is valid only above the temperature of about 313 K [6].

Regarding the phase separation studies, the coexistence curves for aqueous PEG solutions are obtained from the cloud-point data. The cloud point is measured by using either thermo-optical analysis method [11,12] or through visual observations [13–15].

Several models have been used for predicting the behavior of aqueous PEG solutions viz. those based on the osmotic virial expansion [7], those based on equations of state [16,17], the group contribution schemes [18], and those based on the lattice mean field theory [11,14–16,19–24]. Among these models, those based on the mean field theory are most widely used. Two types of mean field models are reported. The first is the modified form of the Flory-Huggins theory [11,14–16,19] and the second accounts for the thermodynamics of hydrogen bond formation [20–24]. A good thermodynamic model should be able to relate the activity of PEG solutions at low temperatures with its phase behavior at high temperatures. Unfortunately, models described above use two separate sets of parameters, one to correlate the low-temperature activity data for PEG solutions and the other to correlate the phase separation data. The parameters obtained from the activity data in the

---

* Corresponding author. Tel.: +91 22 25767236; fax: +91 22 25726895.
E-mail address: vaj@che.iitb.ac.in (V.A. Juvekar).

0378-3812/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2009.01.003

low-temperature range (278–343 K) are not suitable to predict LCST and the coexistence curve of PEG. This failure stems from inaccuracies in either the models or the experimental data. A very high accuracy of the low-temperature activity data is needed since the data need to be extrapolated over a wide interval of the temperature beyond the range of the measurement and small inaccuracies in the parameter estimates are magnified. Same can be said about the inaccuracies in the model. The task is made difficult by the fact that each activity measurement technique has a relatively narrow range of temperature over which it is accurate. The data obtained using two or more technique needs to be combined in order to extend the range of temperature. This procedure is also a source of error.

One possible way to overcome this difficulty is to supplement the activity data with the measurements of the partial molar enthalpy of water (or PEG) in the solution. Partial molar enthalpy is related to the derivative of the chemical potential with respect to temperature, through Gibbs-Helmholtz equation. This derivative dependence on temperature results in a better temperature-extrapolation ability of the partial molar enthalpy than that of the chemical potential (or the activity coefficient) itself. A calorimeter could be used for the measurement of the enthalpy of mixing of PEG and water, from which the partial molar enthalpies of the constituents could be derived. These could then be used to estimate the model parameters which predict temperature dependence of the activity coefficient. Another advantage of the calorimetric technique is that it is accurate over a wider range of temperature (278–348 K).

Calorimetry therefore appears suitable for correlating low-temperature activity data of PEG to the phase behavior data. The main objective of the present work is to verify this expectation. If such a correlation is found, it can be used for predicting the thermodynamic data in the range of temperature and concentration, where experimental measurements cannot be performed by the available techniques. It can also be used as a benchmark for comparing various methods of measurement of activity of PEG solution and also for discriminating different models for thermodynamics of PEG–water system.

In the present work, the enthalpy of mixing of the aqueous solutions of PEG has been measured using isothermal titration calorimeter. The range of temperature covered is 288.15–348.15 K and that of the concentration is 0–53% (w/w). We have used generalized Flory-Huggins theory and hydrogen bond model of Dormidontova [23] to correlate both the activity as well as the calorimetry data. It is important to note that the calorimetric data alone are insufficient for computing the activity because, when the expression for the activity is substituted in the Gibbs-Helmholtz equation, temperature independent parameters in the expression are eliminated during the differentiation and thus cannot be estimated using the calorimetry data. Hence, the calorimetry data needs to be supplemented with the activity data in order to determine the temperature independent coefficients.

Using the correlations based on the two models viz. generalized Flory-Huggins theory and hydrogen bond model of Dormidontova [23], and using the activity data obtained from different techniques, an attempt has been made to predict the coexistence curve for PEG–water system in the region of LCST. The work is presented as follows. We first describe the models for thermodynamic of PEG solution. We then present the methodology to estimate the coefficients of these models from the data on the enthalpy of mixing and the activity of water in the PEG solutions. Next, we present the results of the experiment on measurements of the enthalpy of mixing of aqueous solutions of PEG. This is followed by the analysis of the results to obtain the model parameters. The different models are then discriminated based on the accuracy, and the best model is arrived at. Finally, the selected model has been used to grade the quality of the reported solution activity data.

2. Models for solution thermodynamics

2.1. Generalized Flory-Huggins model

According to the generalized Flory-Huggins model, the total free energy of polymer solution, F, is given by [25]

$$\frac{F}{RT} = \frac{n_p}{r_p}\ \ln(\phi_p) + n_w\ \ln(1-\phi_p) + g n_w \phi_p + n_p \frac{\mu_p^0}{RT} + n_w \frac{\mu_w^0}{RT} \tag{1}$$

In the above equation, n_p and n_w represent the moles of polymer and water in the aqueous PEG solution, respectively. The number of Kuhn segments in PEG chain is represented by r_p. μ_p^0 and μ_w^0 are the chemical potential of pure polymer and pure water, respectively. The term g is the generalized Flory-Huggins parameter and should be considered as the function of the volume fraction of the polymer, ϕ_p, and temperature, T. We have considered g to be independent of r_p. In the range of chain lengths of PEG investigated in this work, the entropic term in the Flory-Huggins model (the first term on the right of Eq. (1)) is adequate to account for the effect of the chain length. The dependence of g on r_p needs to be considered only for short chain polymers where the end-group effect is significant.

The expressions for the chemical potential of water and polymer segment in the polymer solution can be obtained from Eq. (1) as follows:

$$\begin{aligned}\frac{\mu_w-\mu_w^0}{RT} &= \left(\frac{\partial(F/RT)}{\partial n_w}\right)_{n_p}\\ &= \ln(1-\phi_p) + \phi_p\left(1-\frac{\upsilon_w}{r_p \upsilon_p}\right) + g\phi_p^2 - (1-\phi_p)\phi_p^2\frac{\partial g}{\partial \phi_p}\end{aligned} \tag{2}$$

$$\begin{aligned}\frac{\mu_p-\mu_p^0}{RT} &= \left(\frac{\partial(F/RT)}{\partial n_p}\right)_{n_w} = \frac{1}{r_p}\ \ln(\phi_p) + (1-\phi_p)\left(\frac{1}{r_p}-\frac{\upsilon_p}{\upsilon_w}\right)\\ &\quad + g\frac{\upsilon_p}{\upsilon_w}(1-\phi_p)^2 + (1-\phi_p)^2\phi_p\left(\frac{\upsilon_p}{\upsilon_w}\right)\frac{\partial g}{\partial \phi_p}\end{aligned} \tag{3}$$

where υ_p and υ_w are the partial molar volumes of polymer segment and water, respectively. The ratio of υ_p to υ_w is assumed to be independent of the polymer concentration and temperature.

The activity of water in the solution can be obtained using Eq. (2) as

$$\begin{aligned}\ln a_w &= \frac{\mu_w-\mu_w^0}{RT}\\ &= \ln(1-\phi_p) + \phi_p\left(1-\frac{\upsilon_w}{r_p\upsilon_p}\right) + g\phi_p^2 - (1-\phi_p)\phi_p^2\frac{\partial g}{\partial \phi_p}\end{aligned} \tag{4}$$

We define the chain length independent activity of water, β_w, as

$$\ln \beta_w = \ln a_w + \frac{\upsilon_w}{r_p\upsilon_p}\phi_p = \ln(1-\phi_p) + \phi_p + g\phi_p^2 - (1-\phi_p)\phi_p^2\frac{\partial g}{\partial \phi_p} \tag{5}$$

The advantage of using the chain length independent activity is that the relation between β_w and ϕ_p for the solutions of different chain lengths of PEG molecules could be represented by a single curve.

The partial molar enthalpies of species (polymer segment and water) are related to the respective chemical potentials by the Gibbs-Helmholtz equation:

$$h_i - h_i^0 = -RT^2\frac{\partial(((\mu_i-\mu_i^0)/RT))}{\partial T} \quad (i = w \text{ or } p) \tag{6}$$