Fluid Phase Equilibria xxx (2017) 1–9

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

GC-MOSCED: A group contribution method for predicting MOSCED parameters with application to limiting activity coefficients in water and octanol/water partition coefficients

Pratik Dhakal, Sydnee N. Roese, Erin M. Stalcup, Andrew S. Paluch*

Miami University, Department of Chemical, Paper and Biomedical Engineering, 650 E. High Street, Oxford, OH 45056 USA

ARTICLE INFO

Article history:
Received 7 September 2017
Received in revised form
8 November 2017
Accepted 16 November 2017
Available online xxx

Keywords:
Phase-equilibria
Solubility parameter
Group contribution
Limiting activity coefficient
Infinite dilution activity coefficient

ABSTRACT

The **MO**dified **S**eparation of **C**ohesive **E**nergy **D**ensity (MOSCED) is a solubility parameter based method that can both quantitatively predict limiting activity coefficients and can additionally be used to qualitatively understand the underlying molecular-level interactions for intuitive solvent selection and formulation. However, before predictions may be made, MOSCED parameters must be available. Here we propose a group contribution method (GC-MOSCED) to predict parameters devoid of experimental data. Predictions of limiting activity coefficients in water and octanol/water partition coefficients made using GC-MOSCED are found to be in close agreement with MOSCED using existing parameters. We additionally propose a relation between MOSCED parameters and enthalpy of vaporization, and demonstrate the ability of GC-MOSCED to predict enthalpy of vaporization. An interactive software suite has also been developed to facilitate the calculation of GC-MOSCED parameters.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Phase-equilibria thermodynamics is a subject of fundamental importance in both the biological and physical sciences. The ability to model and predict phase-equilibria is crucial for the design of industrial separation processes, which may constitute 40–70% of the both the capital and operating cost of a chemical plant [1]. Separation processes are expensive. Separation processes are non-spontaneous processes and require an external "separating agent," typically either energy or a solvent [1]. It stands that even a small improvement upon existing technologies could lead to significant cost savings. Conventional engineering design schemes to improve performance and reduce costs often neglect the molecular-level details of the system of interest. However, it is these molecular-level details upon which the entire process is built. It is for this reason that "Ullmann's Encyclopedia" stresses that significantly greater improvements may be expected if molecular-level insight is incorporated in conventional design schemes [2].

The **MO**dified **S**eparation of **C**ohesive **E**nergy **D**ensity (MOSCED) is a solubility parameter based method to predict limiting (or infinite dilution) activity coefficients [3,4]. As a solubility parameter based method, its use is particularly attractive because in addition to making quantitative predictions, MOSCED may be used to understand the underlying molecular-level driving forces for intuitive solvent selection and formulation. A major improvement of MOSCED over similar solubility parameter methods is that it splits the association term, allowing MOSCED to better capture the physics of solvation of associating compounds. An assessment of the association term was provided in our recent work [5].

The specific case of predicting limiting activity coefficients is important for the design of separation processes. First, limiting activity coefficients are a direct measure of solute-solvent intermolecular interactions, and correspond to the maximum deviation from ideality. Limiting activity coefficients may therefore be used to quantify the affinity of a solute for a solvent, and are commonly used to calculate separation factors for extraction processes and relative volatilities for distillation for use in solvent selection and design. Furthermore, a comparison of limiting activity coefficients in a binary mixture may be used to predict the presence of an azeotrope [6]. Limiting activity coefficients may additionally be used to parameterize an excess Gibbs free energy model to make phase-equilibria calculations [5–8].

However, MOSCED is limited in that parameters must exist before predictions may be made. At present, MOSCED is parameterized for 130 organic solvents and water [4]. In order to expand

* Corresponding author.
E-mail address: MOSCED@MiamiOH.edu (A.S. Paluch).

https://doi.org/10.1016/j.fluid.2017.11.024
0378-3812/© 2017 Elsevier B.V. All rights reserved.

Please cite this article in press as: P. Dhakal, et al., GC-MOSCED: A group contribution method for predicting MOSCED parameters with application to limiting activity coefficients in water and octanol/water partition coefficients, Fluid Phase Equilibria (2017), https://doi.org/10.1016/j.fluid.2017.11.024

the MOSCED parameter database, reference limiting activity coefficients are required. For a novel solvent, sufficient data may not be available. Previously, we have demonstrated the ability of molecular simulation and electronic structure calculations to predict MOSCED parameters of nonelectrolyte solids [9–13]. Here we propose an efficient group contribution method (GC-MOSCED) to predict parameters devoid of experimental data, based on the 130 organic solvents for which MOSCED parameters exist. Not only does this allow us to predict MOSCED parameters and ultimately phase-equilibria, but it additionally adds an additional layer of molecular-level design. The method assumes group additivity of the cohesive energy and molar volume. The molecular interactions modeled using MOSCED may therefore additionally be interpreted in terms of contributions from specific functional groups.

In the present study the proposed GC-MOSCED model is used to predict limiting activity coefficients of organics in water and octanol/water partition coefficients. We focus on solvation in water both because of its important as a solvent and MOSCED was previously found to perform worst when water is the solvent [4]. Comparison is made to predictions using existing MOSCED parameters. Overall, predictions using the two methods are found to be in good quantitative agreement. Additionally, we propose an expression to relate the MOSCED parameters to the cohesive energy (or ultimately the enthalpy of vaporization), and use this expression to confirm the reasonableness of the GC-MOSCED parameters.

2. MOSCED

The limiting activity coefficient for component 2 in 1 (γ_2^∞) is calculated using MOSCED via the following series of equations [3,4]:

$$\ln\gamma_2^\infty = \frac{v_2}{RT}\left[(\lambda_1-\lambda_2)^2 + \frac{q_1^2 q_2^2\left(\tau_1^{(T)}-\tau_2^{(T)}\right)^2}{\psi_1} + \frac{\left(\alpha_1^{(T)}-\alpha_2^{(T)}\right)\left(\beta_1^{(T)}-\beta_2^{(T)}\right)}{\xi_1}\right]$$
$$+\ln\left(\frac{v_2}{v_1}\right)^{aa_2} + 1 - \left(\frac{v_2}{v_1}\right)^{aa_2}$$
$$aa_2 = 0.953 - 0.002314\left[\left(\tau_2^{(T)}\right)^2 + \alpha_2^{(T)}\beta_2^{(T)}\right]$$
$$\alpha_i^{(T)} = \alpha_i\left(\frac{293\ \mathrm{K}}{T}\right)^{0.8},\ \beta_i^{(T)} = \beta_i\left(\frac{293\ \mathrm{K}}{T}\right)^{0.8},\ \tau_i^{(T)} = \tau_i\left(\frac{293\ \mathrm{K}}{T}\right)^{0.4} \quad (1)$$
$$\text{where } i = \{1 \text{ or } 2\}$$
$$\psi_1 = \mathrm{POL} + 0.002629\,\alpha_1^{(T)}\beta_1^{(T)}$$
$$\xi_1 = 0.68(\mathrm{POL}-1) + \left[3.4 - 2.4\exp\left(-0.002687(\alpha_1\beta_1)^{1.5}\right)\right]^{(293\ \mathrm{K}/T)^2}$$
$$\mathrm{POL} = q_1^4\left[1.15 - 1.15\exp\left(-0.002337\left(\tau_1^{(T)}\right)^3\right)\right] + 1$$

where v_i is the (liquid) molar volume, λ_i, τ_i, α_i and β_i are the solubility parameters due to dispersion, polarity, and hydrogen bond acidity and basicity, respectively, where $i = \{1,2\}$, and the induction parameter, q_i, reflects the ability of the nonpolar part of a molecule to interact with a polar part. The terms ψ_1 and ξ_1 are empirical (solvent dependent) asymmetry terms to modify the residual contribution for polar and hydrogen bonding interactions, and aa_2 is an empirical (solute dependent) term to modify the size dissimilarity in the combinatorial contribution for polar and hydrogen bonding interactions. These additional empirical terms are not adjustable but are functions of the other parameters (τ_i, α_i, β_i and q_i). For all cases $aa_2 \leq 0.953$, effectively reducing the size dissimilarity and magnitude of the combinatorial contribution, with the value smaller for polar and associating compounds. R is the molar gas constant and T is the absolute temperature. The superscript (T) is used to indicate temperature dependent parameters, where the temperature dependence is computed using the empirical correlations provided in eq. (1). As suggested by the equations, MOSCED adopts a reference temperature of 293 K (20 °C). An equivalent expression for the limiting activity coefficient for component 1 in 2 (γ_1^∞) can be written by switching the subscript indices.

In the 2005 MOSCED parameterization, parameters were regressed for 130 organic solvents using 6441 reference infinite dilution activity coefficients. The root mean squared error (RMSE) for $\ln\gamma_2^\infty$ was 0.148, and the average absolute error (AAE) for γ_2^∞ was 10.6% [4,14]. With the MOSCED parameters for the 130 organic solvents fixed, the authors then regressed MOSCED parameters for water using reference infinite dilution activity coefficients for organic solutes in water, and obtained a much larger AAE for γ_2^∞ of 41.1% [4,14].

MOSCED is based on the theory that the cohesive energy may be separated into individual contributions (due to specific intermolecular interactions) which are additive [15–19]. MOSCED is a "modified" separation in that empirical asymmetry terms are introduced that improve the accuracy of the model. We therefore expect that we can relate the MOSCED parameters (partial solubility parameters) to the total cohesive energy (ΔU^{coh}). Following the work of ref. [19], which like MOSCED splits the association parameter, we use an expression of the form:

$$\Delta U^{\mathrm{coh}} = v\left(\lambda^2 + a_1\tau^2 + a_2\alpha\beta\right) \quad (2)$$

where a_1 and a_2 are constants that have been introduced to account for the empiricism introduced by MOSCED. In eq. (2) the cohesive

Please cite this article in press as: P. Dhakal, et al., GC-MOSCED: A group contribution method for predicting MOSCED parameters with application to limiting activity coefficients in water and octanol/water partition coefficients, Fluid Phase Equilibria (2017), https://doi.org/10.1016/j.fluid.2017.11.024

Download English Version:

https://daneshyari.com/en/article/6619155

Download Persian Version:

https://daneshyari.com/article/6619155

Daneshyari.com