Fluid Phase Equilibria xxx (2017) 1–15

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

On fundamentally-based and thermodynamically-consistent description of dilute multicomponent solutions: Formal results, microscopic interpretations, and modeling implications

Ariel A. Chialvo

Knoxville, TN 37922-3108, USA

ARTICLE INFO

Article history:
Received 25 August 2017
Received in revised form
27 October 2017
Accepted 29 October 2017
Available online xxx

Keywords:
Multicomponent solutions
Maxwell relations
Gibbs-Duhem relation
Kirkwood-Buff
Henry's constant

ABSTRACT

We propose a thermodynamically consistent truncated composition expansion, around the infinite dilute quaternary reference system, to describe the thermodynamic behavior of dilute mixed solutes dissolved in mixed-solvents. The development involves the thermodynamically necessary second-order composition expansion of the species partial molar quantities, whose expansion coefficients encompass true molecular meaning based on their underlying links with the solvation properties of the corresponding infinite dilute reference system. Thus, we provide a rigorous molecular-based interpretation of the expansion coefficients in terms of precisely defined microscopic quantities that describe the mixed-solvent environment around all species in solution. Consequently, the proposed second-order truncated composition perturbation expansion applies to any type of quaternary system regardless of its aggregation state, in particular, it converges to the rigorous expressions for quaternary mixtures of imperfect gases obeying the truncated virial equation $z = 1 + BP/kT$, and it reduces naturally to its second-order truncated ternary and binary counterparts through the identification, and consequent manipulation, of the molecular asymmetries among species giving rise to the system nonidealities. Finally, we highlight the origin and key implications of the thermodynamic inconsistencies encountered in currently used first-order truncated expansions.

1. Introduction

Dilute solutions are systems of considerable theoretical and practical interest, *e.g.*, they are crucial to the microscopic foundation of the underlying solvation thermodynamics and the subsequent macroscopic modeling aimed at the description of observed behaviors and the correlation of experimental data. On the one hand, novel separations rely on our ability to tune the solvation behavior of species in solution for a variety of applications including food and pharmaceutical processing [1–5], capture of environmental carbon dioxide and flue gases [6–8], water reforming for energy generation and chemical synthesis [9,10], as well as synthesis and processing of novel materials [11]. On the other hand, all these processes either take place in or involve media with simultaneous solvation of gases, non-polar and ionic species whose behavior can only be interpreted, and consequently described, by macroscopic correlations through a fundamental understanding of the solvation processes in terms of microstructural changes undergone by the fluid environment [12].

For the sake of argument, let us consider a dilute solution comprising N_u solute particles and $N_v = N - N_u$ solvent particles, to be characterized by a solute mole fraction $x_u < 0.01$. Consequently, $N_u < 0.01N$ solute particles will contribute less than $1 \times 10^{-4}N^2$ and less than $4.95 \times 10^{-3}N^2$ $uu-$ and $uv-$ interactions, respectively, in comparison with the overwhelming number of more than $0.9801N^2 vv-$interactions. Therefore, it becomes clear that dilute solutions can be characterized by relatively negligible solute-solute interactions — about 20 and 10^4 smaller than the number of solute-solvent and solvent-solvent interactions, respectively, in our representative illustration — a useful condition to help the analysis of the solute-solvent interactions as sources of solution non-idealities. In fact, this scenario supports the idea of an infinite dilute solution as a handy reference system and, consequently, leads to the foundations of perturbation composition expansions around the corresponding infinite dilute reference, *i.e.*, the basis behind the successful formalism for the molecular-based analysis of solvation phenomena in compressible media [13,14].

E-mail address: ovlaich@gmail.com.

https://doi.org/10.1016/j.fluid.2017.10.031

Please cite this article in press as: A.A. Chialvo, On fundamentally-based and thermodynamically-consistent description of dilute multicomponent solutions: Formal results, microscopic interpretations, and modeling implications, Fluid Phase Equilibria (2017), https://doi.org/10.1016/j.fluid.2017.10.031

The modeling of dilute solutions involving low compressibility solvents has traditionally involved the determination of limiting behavior for the solute activity coefficients, as well as their temperature/pressure derivatives and, occasionally, the corresponding composition slope of their composition dependence at infinite dilution [15–18]. These thermodynamic quantities played a crucial role either as parameterization targets for the excess Gibbs free energy models [19–21] or as key indicators of consistency of the proposed models to describe the actual type of deviations from the ideal solution reference. The latter becomes crucial in detecting the presence of extrema in the composition dependence of activity coefficients, whose immediate outcome translates into the simultaneous occurrence of positive and negative deviations from solution ideality [17].

In contrast, the modeling of dilute solutes in highly compressible solvents, *i.e.*, typically associated with solubility enhancement and related phenomena, has frequently been carried out in terms of mechanical partial molar quantities of the infinite dilute solute and the corresponding pure solvent counterparts [12,22–31]. The choice of these partial molar properties at infinite dilution followed a simple rationale: the partial molar quantities are (*a*) directly associated to the pressure and temperature first derivatives of the corresponding chemical potentials, making possible the development of microscopically-based and well-behaved correlations that obey automatically known limiting behavior for the pair correlation functions describing the system structure, (*b*) rigorously linked to volume integrals over the microstructure of the solvent around the infinite dilute solute, *i.e.*, Kirkwood-Buff total correlation function integrals [32], whose resulting macroscopic modeling will capture the relevant underlying physics through truly molecular-based parameters [29], and (*c*) straightforwardly split into solvation (short-ranged) and compressibility-driven (long-ranged) contributions, whose magnitudes can be unambiguously determined from experimental measurements, a feature that avoids the unnecessary burden of modeling diverging quantities [14,28,33].

Under the above circumstances, a successful molecular-based formalism for the description of the behavior of infinite dilute solutions becomes the natural reference to build the composition dependence of the residual partial molar quantities of the species of the actual system, regardless of its compressible nature. The obvious approach for this purpose involves isothermal-isobaric truncated composition perturbation expansions around the infinite dilute system [22,26,27,34,35], and, regardless of the dilute nature of the mixtures, their modeling must comply with essential thermodynamic requirements such as the Gibbs-Duhem relation (GDR) [36].

Truncated composition perturbation expansions have been frequently invoked in the study of dilute binary solutions, whose GDR also implies compliance with Maxwell relations (MR) (see Appendix A of Ref. [37]), *i.e.*, the exactness of the corresponding differentials and consequent path independence for any finite change of the state variables. However, as we have discussed elsewhere [37,38], the development of consistent truncated composition perturbation expansions for multicomponent systems requires the explicit enforcement of the MR in addition to the GDR; otherwise, the resulting modeling expressions will not describe state functions but rather path-dependent quantities and consequently will be thermodynamically inconsistent (*vide infra*).

Therefore, our first goal here is to derive a thermodynamically consistent truncated composition expansion, around the infinite dilute reference quaternary system, to describe the thermodynamic behavior of dilute mixed solutes dissolved in mixed-solvents. This task requires (*a*) the development of a second-order composition expansion of the species partial molar quantities, rather than the prototypical first-order counterpart, as a crucial prerequisite to comply with the GDR and MR, and (*b*) not only the identification of the expansion coefficients but also ascribing true molecular meaning to them based on the underlying links with the solvation properties of the infinite dilute reference system. Consequently, our second goal is to provide a rigorous molecular-based interpretation of the derived expansion coefficients in terms of precisely defined microscopic quantities that describe the mixed-solvent environment around the species in solution. Then, our third goal is to show that, due to the well-defined nature of the expansion coefficients, the proposed second-order truncated composition perturbation expansion applies to any type of quaternary system regardless of its aggregation state; furthermore, the expansion reduces naturally to its second-order truncated ternary and binary counterparts, *i.e.*, without appealing to any foreign assumption.

Thus, to pursue these goals we follow the subsequent outline. In section 2 we derive the isothermal-isobaric second-order truncated composition perturbation expansion for the species fugacity coefficients of quaternary systems comprising dilute mixed-solutes in mixed-solvents. Then, in section 3, we identify the macroscopic (thermodynamic) meaning and provide explicit microscopic interpretation of the expansion coefficients in terms of total correlation function integrals over the microstructure of the corresponding infinite dilution reference system. Moreover, in section 4 we illustrate how the proposed perturbation expansion converges to the rigorous expressions for quaternary mixtures of imperfect gases obeying the truncated virial equation $z = 1 + BP/kT$ and discuss how the formalism reduces naturally to its second-order truncated ternary and binary counterparts. Finally, in section 5 we discuss the origin as well as the central implications of the thermodynamic inconsistencies encountered in currently used first-order truncated expansions that render those expansions invalid.

2. Isobaric-isothermal composition truncated perturbation expansion of the partial molar properties of species in dilute quaternary solutions

In this section we derive the second-order truncated composition series expansion of the species fugacity coefficients under thermodynamic consistency dictated by Gibbs-Duhem and the exactness of the differential of the resulting Gibbs free energy function also known as the Maxwell relations. With this purpose, let us assume a quaternary mixture of a solvent (1), a cosolvent (2), a solute (3), and a cosolute (4) at constant temperature, pressure, and solvent-to-cosolvent ratio of mole fractions $(T, P, r = x_2/x_1)$, *i.e.*, a system whose composition is given by the independent mole fractions x_3 and x_4 as follows:

$$x_1 = (1 - x_3 - x_4)/(1 + r) \tag{1}$$

$$x_2 = r(1 - x_3 - x_4)/(1 + r) \tag{2}$$

For this system we can write the following second-order composition expansion for the species fugacity coefficients:

$$\begin{aligned}
\ln\widehat{\phi}_1(T,P,x_3,x_4,r) &= \ln\widehat{\phi}_1^{\otimes} + a_1x_3 + b_1x_4 + c_1x_3^2 + d_1x_4^2 + e_1x_3x_4 \\
\ln\widehat{\phi}_2(T,P,x_3,x_4,r) &= \ln\widehat{\phi}_2^{\otimes} + a_2x_3 + b_2x_4 + c_2x_3^2 + d_2x_4^2 + e_2x_3x_4 \\
\ln\widehat{\phi}_3(T,P,x_3,x_4,r) &= \ln\widehat{\phi}_3^{\infty} + a_3x_3 + b_3x_4 + c_3x_3^2 + d_3x_4^2 + e_3x_3x_4 \\
\ln\widehat{\phi}_4(T,P,x_3,x_4,r) &= \ln\widehat{\phi}_4^{\infty} + a_4x_3 + b_4x_4 + c_4x_3^2 + d_4x_4^2 + e_4x_3x_4
\end{aligned} \tag{3a-d}$$

with the obvious notation

Please cite this article in press as: A.A. Chialvo, On fundamentally-based and thermodynamically-consistent description of dilute multicomponent solutions: Formal results, microscopic interpretations, and modeling implications, Fluid Phase Equilibria (2017), https://doi.org/10.1016/j.fluid.2017.10.031