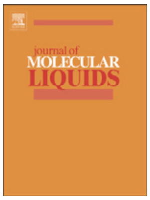
Journal of Molecular Liquids 217 (2016) 103–111

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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



Partial molar volume of nonionic surfactants in aqueous solution studied by the KB/3D-RISM–KH theory

M. Holovko [a], A. Kovalenko [b,c], F. Hirata [d,*]

[a] Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1, Svientsitskii Str., Lviv 79011, Ukraine
[b] National Institute for Nanotechnology, National Research Council of Canada, 11421, Saskatchewan Dr., Edmonton, AB T6G 2M9, Canada
[c] Department of Mechanical Engineering, University of Alberta, 10-203 Donadeo, Innovation Centre for Engineering, 9211-116 Str., Edmonton, AB T6G 1H9, Canada
[d] College of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

ARTICLE INFO

Article history:
Received 19 December 2015
Received in revised form 27 January 2016
Accepted 4 February 2016
Available online 20 February 2016

Keywords:
Aqueous solutions
Amphiphilic molecules
Nonionic surfactants
Partial molar volume
Kirkwood–Buff equation
3D-RISM–KH molecular theory of solvation
Hydration structure

ABSTRACT

Description of self-assembly by means of atomistic models without coarse-graining and empirical adjustment is the most challenging problem in statistical mechanics of liquids. Partial molar volume (PMV) is a thermodynamic property related to effective solvation forces spontaneously driving self-assembly of amphiphilic molecules in solution. We calculate the PMV of several ethylene glycol derivatives, in particular, alkyl polyoxyethylene ethers $H(CH_2)_{m-1}(CH_2OCH_2)_nCH_2OH$ commonly known as C_mE_n nonionic surfactants, in aqueous solution at infinite dilution by using the Kirkwood–Buff (KB) equation and the three-dimensional reference interaction site model with the Kovalenko–Hirata closure relation (3D-RISM–KH) integral equation theory of molecular liquids. Special attention is paid to the infinite dilution case since direct measurement of PMV of monomeric surfactants is hindered by their very low critical micelle concentration (cmc). The PMVs obtained from the KB/3D-RISM–KH approach are in good qualitative agreement with experimental data for ethylene glycol derivatives in water at 5; 25; and 45 °C.

1. Introduction

Alcohol ethoxylates are a major class of nonionic surfactants widely used in laundry detergents, household and industrial cleaners, agriculture, cosmetics, textile, oil, and other process industries. A molecule of alcohol ethoxylates $H(CH_2)_{n-1}(CH_2OCH_2)_mCH_2OH$ commonly denoted as C_nE_m consists of a hydrophobic linear alkyl chain $CH_3(CH_2)_{n-2}$ and a hydrophilic tail of m ethylene oxide groups (CH_2OCH_2) attached to the alcohol group CH_2OH. Due to the amphiphilic character of such molecules, they tend to dissolve in both aqueous and oil phases, reduce the surface tension of liquids and can form micellar or more complex self-assembly [1]. The effective forces spontaneously driving self-assembly of alcohol ethoxylate molecules originate from an interplay of the hydrophobic attraction of alkyl chains at the interface with water which induces aggregation of the molecules, and the hydrophilic repulsion of the ethylene oxide and alcohol groups which keeps them in contact with water [2].

Important thermodynamic properties of solution are related to the partial molar volume (PMV) of solute molecules. At infinite dilution of solute molecules, their PMV corresponds to the so-called apparent volume of the solute. The apparent volume V^{app} can be split up as [3, 4]

$$V^{app} = V^{int} + \Delta V, \qquad (1)$$

where V^{int} is the intrinsic volume which includes the Van der Waals volume of the solute molecule, internal voids, and a part of the empty space from the boundary region between the solute and solvent. The difference between the apparent and intrinsic volumes ΔV is related to the solvation effects caused by solute–solvent effective interactions. Since the hydration water near hydrophilic groups is denser than bulk water due to electrostatic attraction and water in a hydrophobic shell has a more open structure due to weak interaction of a hydrophobic solute with water, ΔV for hydrophilic groups is negative and for hydrophobic groups is positive [3, 4].

The solute PMV is usually measured by extrapolation of its concentration dependence to infinite dilution. However, for alcohol ethoxylate aqueous solutions, such direct experimental measurement of PMV of monomeric surfactants is hindered by a very low critical micelle concentration (cmc) of these substances. In order to avoid this problem, empirical and theoretical approaches were proposed. In particular, in the so-called additive group (AG) approach, the PMV of a C_nE_m molecule is considered to be an additive sum of the PMVs of the CH_3, $(n-2)CH_2$, mCH_2OCH_2, and CH_2OH constituting groups. The PMVs of these groups were found from experimental measurements in a series of dilute

---

[*] Corresponding author.
E-mail addresses: holovko@icmp.lviv.ua (M. Holovko), andriy.kovalenko@nrc-cnrc.gc.ca (A. Kovalenko), hirataf@fc.ritsumei.ac.jp (F. Hirata).

http://dx.doi.org/10.1016/j.molliq.2016.02.016
0167-7322/

aqueous solutions of simpler molecules. For example, the PMVs of such groups as CH_3, CH_2, CH_2OCH_2, and CH_2OH necessary for calculation of PMVs of alcohol ethoxylate molecules in aqueous solutions were obtained in the AG approach by reconstruction of the experimental values of PMVs of ethylene glycol derivatives $HOCH_2(CH_2OCH_2)_{n-1}CH_2OH$, $H(CH_2OCH_2)_{n+1}H$, and $H(CH_2)_{n-1}CH_2OCH_2CH_2OH$ with $n = 1-4$ in water at temperatures 5, 25, and 45 °C [5].

The values obtained for the PMVs of the groups were successfully used to calculate the PMVs of monomeric molecules $C_{12}E_m$ with $m = 6;7;8$ in aqueous solutions [6]. However, although the AG method apparently succeeds in predicting the PMV itself, it is basically incapable of providing a molecular picture of PMV as a thermodynamic quantity.

The problem of describing PMV of molecules in aqueous solutions is a challenging problem in statistical mechanics of liquids. One of such ways of describing the PMV of solute molecules in water is based on scaled particle theory (SPT) [7, 8] which yields an approximate expression for the chemical potential of a nonpolar particle in nonpolar fluid. By taking the pressure derivative of this chemical potential, an analytical expression for the PMV of a nonpolar solute particle was obtained and the intrinsic volume of ions in aqueous solutions was successfully extracted [9]. However, SPT has essential difficulties when applying it to surfactant molecules in water because it is not clear how to include electrostatic effects in the SPT approach.

Another approach is based on the Kirkwood–Buff (KB) solution theory [10]. In this theory, the PMV of a solute is given by

$$V^{\mathrm{u}} = k_{\mathrm{B}}T\chi_T^0 - 4\pi\int_0^{\infty} r^2 \mathrm{d}r \left(g^{\mathrm{uv}}(r) - 1\right) \tag{2}$$

where χ_T^0 is the isothermal compressibility of the solution, $g^{\mathrm{uv}}(r)$ is the radial distribution function (RDF) between solute "u" and solvent "v", k_{B} is the Boltzmann constant and T is the solution temperature.

Recently, the KB theory was combined with computer simulation in a study of the volumetric properties of the C_8E_6 molecule in aqueous solution [4]. The apparent volume V^{app} of the solute molecule was calculated from the expression Eq. (2). The intrinsic volume V^{int} of the solute molecule was calculated as the volume of the Voronoi region of the solute molecule. It was shown that the hydration water contribution to the apparent volume ΔV is negative for lower temperatures and becomes positive for higher temperatures.

However, the KB theory in the form Eq. (2) treats only spherical species in simple liquids. The expression Eq. (2) can be generalized to such complex solute molecules as C_nE_m in molecular solvents, including water, in the framework of the Ornstein–Zernike type integral equation theory of liquids [11]. Well suitable for this aim is the reference interaction site model (RISM) [12–16], also called molecular theory of solvation [17], which operates with the site–site representation of correlation functions and can treat molecules of arbitrary geometry. The RISM integral equation complemented with the hypernetted chain (HNC) closure relation [14–17] had been combined with the KB theory [17–19] and applied to calculate the PMVs of different molecules in aqueous solution, including ions [18, 19], hydrocarbons [20, 21], and biomolecules [22–24]. The three-dimensional version of the RISM formalism (3D-RISM theory) yields the solvation structure in terms of 3D maps of correlation functions of solvent interaction sites around a solute molecule, including density distributions [25–34]. Complemented with the Kovalenko–Hirata (KH) closure approximation [29, 32, 34], the 3D-RISM–KH theory properly accounts for chemical functionalities by representing in a single formalism both electrostatic and non-polar features of solvation, such as hydrogen bonding, hydrophobic hydration and interaction, structural solvent, preferential solvation, salt bridges, desolvation, and other associative and steric effects in various chemical, soft matter, supramolecular, and biomolecular systems (see the citations in Refs. [34–36]). The KB method using the 3D correlation functions obtained from the 3D-RISM–KH integral equations accurately predicts the PMV of various biomolecules [37–45].

In this paper, we apply the KB/3D-RISM–KH approach to calculate the PMVs of surfactant molecules C_nE_m in water at different temperatures. The results obtained are compared with the experimental data for simpler ethylene glycol derivatives [5] and with the prediction from the AG approach for more complex molecules C_nE_m [6]. We also interpret the PMV behavior by analyzing the 3D site correlation functions of water around the solute surfactant molecules. The paper is organized as follows. In Section 2, we summarize the method combining the KB approach and the 3D-RISM–KH theory. The microscopic models of molecules C_nE_m are reviewed in Section 3, and the results for their PMVs in aqueous solution are presented and discussed in Section 4.

2. Kirkwood–Buff relation and 3D-RISM integral equation theory

Within the Kirkwood–Buff (KB) theory combined with the three-dimensional reference interaction site model (3D-RISM) integral equation approach, the partial molar volume of a solute molecule immersed in molecular solvent is expressed in terms of the 3D solute–solvent site correlation functions by the relation [37, 45]

$$V^{\mathrm{u}} = k_{\mathrm{B}}T\chi_T^0\left(1 - \sum_{\gamma\in\mathrm{v}} \rho_\gamma^{\mathrm{v}} c_\gamma^{\mathrm{uv}}(\mathbf{k}=0)\right), \tag{3}$$

where indices "u" and "v" denote solute and solvent species, respectively, ρ_γ^{v} is the number density of site γ of solvent molecules, $k_{\mathrm{B}}T$ is the Boltzmann constant times the solution temperature, and $c_\gamma^{\mathrm{uv}}(\mathbf{k})$ is the 3D direct correlation function between the whole solute molecule and solvent site γ in the reciprocal space at zero wavevector which is calculated as $c_\gamma^{\mathrm{uv}}(\mathbf{k}=0) = \int \mathrm{d}\mathbf{r}\ c_\gamma^{\mathrm{uv}}(\mathbf{r})$. (In a general case of solvent mixture, γ enumerates all interaction sites on all sorts of solvent species "v".) The isothermal compressibility of pure solvent χ_T^0 is obtained in the site–site RISM approach as [39, 45]

$$k_{\mathrm{B}}T\chi_T^0 = \left[\rho^0\left(1 - \sum_{\alpha\gamma\in\mathrm{v}} \rho_\alpha^{\mathrm{v}} c_{\alpha\gamma}^{\mathrm{vv}}(k=0)\right)\right]^{-1} \tag{4}$$

in terms of the radial direct correlation function $c_{\alpha\gamma}^{\mathrm{vv}}(k)$ between interaction sites α and γ of solvent molecules in the reciprocal space at zero wavevector which is calculated as $c_{\alpha\gamma}^{\mathrm{vv}}(k=0) = 4\pi\int_0^{\infty} r^2 \mathrm{d}r\ \ c_{\alpha\gamma}^{\mathrm{vv}}(r)$, and $\rho^0 = \sum_{\mathrm{v}} \rho^{\mathrm{v}}$ is the total number density of solvent molecules.

The 3D distribution functions of solvent interaction sites around the solute molecule are determined from the 3D-RISM integral equation [25–34]

$$h_\gamma^{\mathrm{uv}}(\mathbf{r}) = \sum_\alpha \int \mathrm{d}\mathbf{r}' c_\alpha^{\mathrm{uv}}(\mathbf{r}-\mathbf{r}')\chi_{\alpha\gamma}^{\mathrm{vv}}(r') \tag{5}$$

for the 3D total and direct correlation functions $h_\gamma^{\mathrm{uv}}(\mathbf{r})$ and $c_\gamma^{\mathrm{uv}}(\mathbf{r})$ of solvent site γ around the solute molecule, where the radially dependent site–site susceptibility of pure solvent $\chi_{\alpha\gamma}^{\mathrm{vv}}(r)$ is an input to the 3D-RISM theory.

To be solved, the 3D-RISM integral equation has to be complemented with another relation between the total and direct correlation functions called a closure which also involves the interaction potential between interaction sites of solution species specified with a molecular force field. The exact closure has a nonlocal functional form which can be expressed as an infinite diagrammatic series in terms of multiple integrals of the total correlation function [11]. However, these diagrams are cumbersome and the series are poorly convergent, which renders the exact closure computationally intractable. Therefore, it is replaced in practice with amenable approximations with analytical features that properly represent physical characteristics of the system, such as long-range asymptotics and short-range features of the correlation functions related to the solvation structure and thermodynamics. Examples of closure relations