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Short communication

A comment on water’s structure using monomer fraction data and theories

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ABSTRACT

Monomer fraction data for water (and other compounds) can provide useful information about their structure and can be used in “advanced” equations of state, which account explicitly for association phenomena. Recent findings about the performance of association theories in representing the monomer fraction of water are reviewed. Three such theories are considered and all of them perform qualitatively similar. They can all represent phase equilibria for water solutions qualitatively well but with parameters which are not in good agreement with Luck’s famous monomer fraction data. While this could set the theoretical basis of these theories in doubt, we also show in this work that the findings with these association models are in agreement with a recently presented theory which links monomer fraction to dielectric constants. This new theory, like the three thermodynamic models, predicts more hydrogen bonding in water than Luck’s data (Angew. Chem. Int. Ed. Engl. 1980, vol. 19, pp. 28). Moreover, it appears that both the new theory and the three models provide evidence for the four-site association scheme for water and thus support that the tetrahedral structure of the water molecule is correct or at least that the tetrahedral structure is in agreement with several pure water physical properties, monomer fraction information and phase equilibria data in mixtures with alkanes.

1. Introduction

Water is the most important substance in the world; it covers two thirds of the Earth and our own cells include two thirds water by volume. Hundreds of books have been written about water and at the same time we know so little about it. In the words of Philip Ball: “No one really understands water. It’s still a mystery” [1,2].

Water has more than 50 exceptional properties, in the sense that their magnitude and/or their trends with temperature, pressure and composition do not follow what we know from other compounds.

Among the most exciting ones are the maximum of density at 4 °C (but also presence of minima at low temperatures [3]), high values of heat capacity, solubility parameter, dielectric constant and surface tension, low free-volume percentages (similar to those encountered for polymers) and maxima and minima of many thermodynamic properties as function of temperature, e.g., the minimum hydrocarbon solubility in water at room temperature (related to the hydrophobic effect) and the speed of sound.

Water’s hydrogen bonding and in particular its structure are often considered to be the prevailing explanations. But there is no consensus on which structure is correct and which one can interpret the large volume of available data. While numerous theories for water structure have been presented they are all under debate. It is unclear whether liquid water maintains the tetrahedral structure (as we know it from ice), possibly the most established opinion, or whether it should best be described by a two-state model, where most molecules are in the form of rings or chains [4,5] and literature is full with heated discussions [1,2].

The effect of salts [6], solid surfaces and biomolecules on water structure are not well understood either, but in this work we limit our discussion to the structure of pure “bulk” water and potential changes at different temperatures.

The mixture behavior of water with hydrocarbons (and other compounds) can provide additional information about its structure. It is now well-established that the immiscibility of water with alkanes is largely an entropic phenomenon associated with high

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positive values of the change in the standard molar Gibbs energy for the transfer of alkanes from pure liquids into water [7,8]. These are due to highly negative entropy changes. The prevailing interpretation is that pure water's closed packed semi-tetrahedral structure (with 3–3.5 hydrogen bonds/molecule) becomes more structured (with 4 hydrogen bonds/molecule) when alkanes are added in the solution [9,10]. Water molecules stick together when "enemies" (= alkanes) appear in the vicinity but water returns to its previous state when they disappear. This phenomenon is widely understood as the "hydrophobic effect".

This phenomenon also provides an explanation for the micellization of surfactants. The entropy change of micellization is high and positive, even though micelles are formed, and results to the observed negative Gibbs energy change of micellization. The positive entropy change is due to water returning to its "original less-structured" state (pure water) when the surfactants leave their pure form to create micelles.

Direct spectroscopic and other measurements could provide quantitative information on the degree of hydrogen bonding of water. There are problems both in the actual measurements and the interpretation of the data. Fig. 1 includes the first known data for water monomer fraction from Luck [17], data from other sources [28,29] and the most recent data from Mallamace et al. [3]. The data shown in Fig. 1 are measured with different methods (IR, NMR, X-ray scattering) and details are presented in the original references.

The data of Mallamace et al. [3] indicate the presence of much higher monomer fraction than the other sources. Actually, furthermore Mallamace et al. [3] report no tetrahedral water structure above room temperature, where non-monomeric water is partially hydrogen bonded with 1, 2 or 3 hydrogen bonds. This is a picture similar to the two-state "ring chain" model mentioned previously. This model has both supporters (e.g., Frosch et al. [6] report that only 43% of water has 4 hydrogen bonds) and opposers (e.g., Smith et al. [11] reporting that water creates tetrahedral and only 10% of the hydrogen bonds are broken).

In this work we analyze the monomer fraction of water using thermodynamic theories and a recently developed theory relating the monomer fraction with the dielectric constant.

2. Monomer fraction from theories against Luck's experimental data

Many modern thermodynamic theories are presented in the form of advanced equations of state, having additive contributions to account for the van der Waals (attractive) interactions, repulsion and hydrogen bonding. Some of these models are based on perturbation, chemical or quasi-chemical theories. Examples of the former are PC-SAFT and CPA and of the latter type NRHB. Description of the models can be found in the original publications and in review books (e.g., Kontogeorgis and Folas [12], see also Ref. [14]).

These models have a theoretical background on molecular physics which via their association term enables them to estimate the monomer fraction which can then be compared to the experimental data. This has been reported in the literature [13–15,19–22]. The parameters of these association theories are rarely fitted directly to these monomer fraction data; instead they are obtained from physical properties like vapor pressure and liquid density in order to ensure that the models can be subsequently used for phase equilibrium and other engineering calculations. On the other hand, these thermodynamic theories cannot a priori predict the hydrogen bonding structure of a molecule but have the possibility to account for different schemes, e.g., oligomer and 3D structures, which can be checked against experimental data.

All these theories are quite sensitive on the parameter estimation and in reality several parameter sets for pure compounds can be obtained which all can fit two or three physical properties equally well. As several "optimum" parameters are obtained this way, it was originally thought or hoped (e.g., Refs. [13] and [27]) that monomer fraction data could be used for determining the "most correct" parameter set.

The model parameters are in practice often tested against mixture data, e.g., water–alkanes LLE in the case of water. Despite their different physical background and different functional forms of their equations, it is now well-established that most/all of these advanced models (and certainly the three ones mentioned above; CPA, PC-SAFT and NRHB) can describe reasonably well difficult phase equilibria such as liquid–liquid equilibria of water–alkanes over extensive temperature ranges (a single temperature independent interaction parameter is used—satisfactory results are obtained also in the absence of adjustable parameters). A typical example is shown in Fig. 2. It is possibly the similarities of the hydrogen bonding terms of the various theories which is the underlying reason behind this similar performance. The equivalence of the hydrogen bonding contributions of chemical, quasi-chemical and perturbation theories has been very elegantly illustrated by Economou and Donohue [30,31].

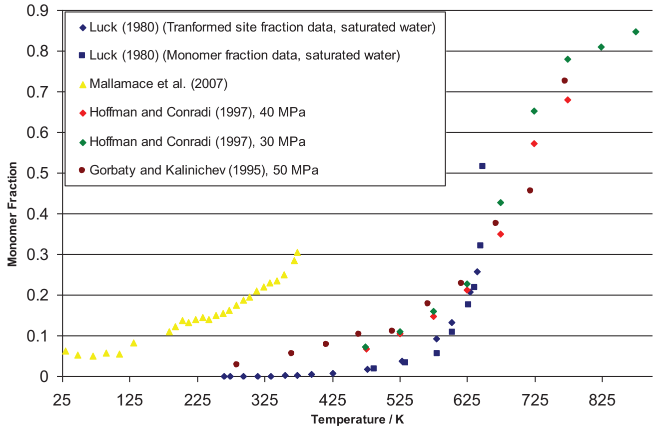

Fig. 1. Monomer fraction of water as function of temperature from different experimental techniques and sources.

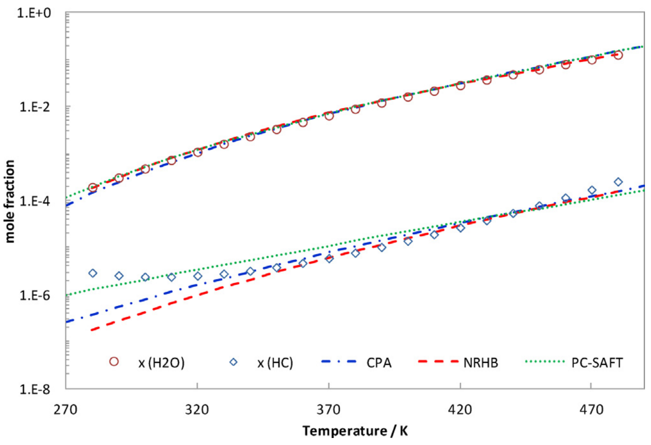

Fig. 2. LLE of water–hexane with CPA, PC-SAFT and NRHB. The parameters for the three models are shown in Tsivintzelis et al. [14] and Liang et al. [15]. Experimental data are taken from Tsonopoulos et al. [16]. All models use a single temperature-independent interaction parameter.

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