ELSEVIER

Biophysical Chemistry 51 (1994) 393–396

Biophysical
Chemistry

Excluded volume effect in solvation thermodynamics: simple Lennard-Jones model

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Received 28 January 1994; accepted 2 February 1994

Abstract

Using the Ornstein–Zernike equation for Lennard-Jones mixtures, it is shown that the chemical potential, entropy, and potential energy of a solute can vary linearly with its volume. Simple size dependence appears only for sufficiently large solutes and weak solute–solvent interactions.

Key words: Thermodynamics; Ornstein–Zernike equation; Lennard-Jones mixtures; Solute–solvent interactions

1. Introduction

Hydration of nonpolar solutes draws attention in the current literature spanning from the sophisticated computer simulations (e.g. Refs. [1–4], and references therein) to the simple solvation models in which the nonpolar solute–solvent contributions to the solvation energy are reduced to the linear dependence on the solvent-accessible surface (SAS) [5–7]. While the latter theories may provide rather accurate results, it is also known that the scaled particle theory [8], in which the chemical potential is assumed to be a solute-size polynomial of the third degree, describes quite successfully the solvaton of nonpolar solutes [9,10]. This means that the solute volume can be a leading parameter in simple solvation models [11]. Immediate checking of the size dependence of the nonpolar solvation energies is complicated because the true nonpolar data are available basically for the linear alkanes whose either volume or surface area are proportional to the carbon number [11]. An important role of the volume effect can be corroborated by the expression for the excess entropy of non-interacting particles which is proportional to their excluded volume [3,12]. For such a system, the free energy is clearly proportional to the particle volume. In this communication, we consider solvation effects in a simple model with the Lennard-Jones pair interactions which may reflect some properties of hydration [13]. The traditional statistical method of calculating the free energy employs the functional integration [14]. We use an alternative approach which allows for expressing the chemical potential via a simple integral [15–18] over the solution to the Ornstein–Zernike equation [18,19].

2. Theory

We consider a Lennard-Jones fluid with the pair potential

$$\phi_{\alpha\beta} = (4\epsilon_{\alpha\beta})\left[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}\right], \qquad (1)$$

SSDI 0301-4622(94)00061-N

where $\phi_{\alpha\beta}$ is given in kT units; α, $\beta = u$, v (solute and solvent indexes respectively), and the conventional mixing rules are used for describing the solute-solvent interactions: $\sigma_{\alpha\beta} = 0.5(\sigma_\alpha + \sigma_\beta)$, $\epsilon_{\alpha\beta} = (\epsilon_\alpha \epsilon_\beta)^{1/2}$.The excess Gibbs chemical potential of a molecule can be calculated via the general expression [15,16]

$$\mu_\alpha = -kT\sum_\beta n_\beta \int \{h_{\alpha\beta}(r) - w_{\alpha\beta}(r) - 0.5\ h_{\alpha\beta}(r) \times [w_{\alpha\beta}(r) + B'_{\alpha\beta}(r)]\}\ \mathrm{d}r \tag{2}$$

where summation is performed over all molecular species that constitute the mixture, $g_{\alpha\beta} = 1 + h_{\alpha\beta} = \exp(-\phi_{\alpha\beta} + w_{\alpha\beta})$ is the pair correlation function, $B'_{\alpha\beta}$ is the functional that has been estimated in Ref. [16]

$$B'_{\alpha\beta} = \tfrac{1}{3} B_{\alpha\beta}, \tag{3}$$

$B_{\alpha\beta}$ is the bridge functional determined by the direct correlation function, $c_{\alpha\beta}$,

$$c_{\alpha\beta} = h_{\alpha\beta} - w_{\alpha\beta} + B_{\alpha\beta}. \tag{4}$$

The relation between the pair and direct correlation functions is imposed by the Ornstein–Zernike equation [18,19]

$$h_{\alpha\beta}(1,2) = c_{\alpha\beta}(1,2) + \sum_\gamma n_\gamma \int c_{\alpha\gamma}(1,3) h_{\beta\gamma}(2,3)\ \mathrm{d}3. \tag{5}$$

Within the hypernetted chain approximation, $B'_{\alpha\beta} = B_{\alpha\beta} = 0$, and Eq. (2) coincides with the expression given by Singer and Chandler [14] and employed in Refs. [21,22]. We use the Martynov–Sarkisov closure [23]

$$B_{\alpha\beta} = -0.5\ w_{\alpha\beta}^2, \tag{6}$$

which is more accurate than the hypernetted chain and Percus–Yevick equations for the simple fluids with the short-range pair potentials [23–26] and for the site–site model of the hydrocarbon–water system [17]. For highly diluted solutions ($n_u \ll n_v$),

$$\mu_u = -n_v kT \int [h_{uv} - w_{uv} - 0.5\ h_{uv}(w_{uv} + \tfrac{1}{6} w_{uv}^2)]\ \mathrm{d}r \tag{7}$$

and the Ornstein–Zernike equation for mixtures [26] has the form

$$w_{uv} = n_v \int c_{uv}(1,3) h_{vv}(2,3)\ \mathrm{d}3 - 0.5\ w_{uv}^2, \tag{8}$$

$$w_{vv} = n_v \int c_{vv}(1,3) h_{vv}(2,3)\ \mathrm{d}3 - 0.5\ w_{vv}^2. \tag{9}$$

The potential energy of a solute is easily calculated using the Ornstein–Zernike solution

$$u_u = U_u/kT = 0.5\ n_v \int \phi_{uv}(r) g_{uv}(r)\ \mathrm{d}\boldsymbol{r}. \tag{10}$$

Entropy can be calculated via the thermodynamic relations that require to take the temperature derivatives of the chemical potential [22]. There is no simple exact relation between the pair correlation functions and entropy since the latter depends on the higher order correlations [4,27]. However, the pair-correlation approximation proves to be quite accurate for applications [4,12,28]. Wihin this approximation for the infinitely diluted solution, the solute excess entropy (where the ideal gas term is neglected) equals

$$s_u = S_u/k = -0.5\ n_v \int [g_{uv}(r) \ln g_{uv}(r) - h_{uv}(r)]\ \mathrm{d}r \tag{11}$$

This expression clearly exhibits possible volume effects. Indeed, let us consider for a moment a gas of the noninteracting particles with the density n where each particle has a volume V_0. For such a model, $g(r)$ equals zero and unity inside and outside the particle volume, respectively. Therefore the excess entropy of a particle equals $s = -0.5\ nV_0$. Comparison [12] with the computer simulation data [29] shows that expressions (7) and (11) provide consistently accurate results for the dimensionless temperature $T^* = kT/\epsilon = 2.74$ and higher.

3. Results and discussion

Size effects can be studied in terms of the solute thermal radius (where the pair potential equals kT) [4]. We use the Lennard-Jones radius [9] that is an explicit factor for the dimensionless solvent density $\rho = n_v \sigma_v^3$ which governs the Ornstein–Zernike equation (8), (9) and the thermodynamical integrals (7), (10), (11). The solvent density was assigned the value 0.8 in all calculations. First, we consider a solute and solvent with the same interaction strength $\epsilon_u = \epsilon_v = 0.365$ (cf. with the water parameters at room temperature: $\rho = 0.71$, $T^* = 3.74$ [9]). The chemical potential, entropy and potential energy of the model considered are listed in Table 1 being multiplied by factor $(1+R)^{-3}$, where $R = \sigma_u/\sigma_v$. In this case, all thermodynamic parameters increase with R faster than R^3 even at $R = 20$. Let us consider now a weakly interacting solute ($\epsilon_u = 0.01$) in the same solvent. Then both potential energy and entropy are inclined to become linear with the solute excluded volume at $R > 8$, while the chemical potential still increases faster. The passage to the weakly interacting solvent ($\epsilon_v = 0.01$) strengthens the tendency for the solute thermodynamic parameters to become linear with their volume though even the ratio $R = 20$ is not sufficient for the chemical potential to become strictly linear with R^3. Hence, within the Lennard-Jones model, the solute chemical potential, which has basically enthalpic nature at $R > 1$, may rise as the cubic power of the solute size only asymptotically, and the speed of approaching this asymptote decreases with the interaction strength. Volume linearity of entropy (with the negative sign) has clear physical sense: increase of the excluded volume restricts a space for chaotic motions of molecules, and entropy being a negative value decreases [12]. It should be noted that these results, as well as the Ornstein–Zernike formalism, are valid in the thermodynamic limit (i.e. in the NVT ensemble where both the total particle number N and the volume of the system V approach infinity while the density N/V remains a finite constant) [19]. The difference between the thermodynamic parameters in the NVT and NPT ensembles is discussed in Refs. [3,22,30].

Realistic models of water solutions show that entropy plays an important role in hydration of nonpolar solutes [1,2] and increases quickly with the solute size [3,4]. Concerning the simple solvation models, it is interesting to note that the data for 140 small organic molecules [31] show that the consistent continuum model [32] provides practically the same nonpolar components of the solvation energy (differences do not exceed 0.2 kcal/mol) irrespective of whether they are fitted to the solute excluded volume or SAS. This is understandable since virtually all atoms of small molecules are exposed to water, so that their excluded volume and SAS are roughly proportional. In the recent experimental studies [33,34], the hydrophobic effect in proteins is discussed rather in terms of volumes than SAS. In the general case, however, the number of the protein sites effectively interacting with water may depend on SAS [35], so that protein hydrophobicity may be determined by a complex interplay of the volume and surface effects.

Table 1
Thermodynamical parameters of a Lennad-Jones solute [a]

R	$\epsilon_v = 0.365$, $\epsilon_u = 0.365$			$\epsilon_v = 0.365$, $\epsilon_u = 0.01$			$\epsilon_v = 0.01$, $\epsilon_u = 0.01$		
	μ_u/kT [b]	$-s_u$ [b]	$-u_u$ [b]	μ_u/kT [b]	$-s_u$ [b]	u_u [b]	μ_u/kT [b]	$-s_u$ [b]	u_u [b]
0.25	0.005	0.259	0.248	0.328	0.153	0.005	0.241	0.083	0.0025
0.5	0.182	0.251	0.227	0.419	0.152	0.015	0.262	0.081	0.0027
1.0	0.386	0.230	0.193	0.557	0.144	0.028	0.295	0.079	0.0030
2.0	0.610	0.197	0.157	0.707	0.126	0.041	0.332	0.075	0.0033
4.0	0.774	0.170	0.135	0.815	0.108	0.046	0.362	0.072	0.0035
8.0	0.867	0.144	0.131	0.878	0.097	0.045	0.379	0.070	0.0036
20.0	0.894	0.137	0.131	0.892	0.095	0.045	0.387	0.070	0.0036

[a] See notations in the text.

[b] Multiplied by factor $(1+R)^{-3}$.

Acknowledgement

We thank R.M. Fine, M.E. Paulaitis and A.A. Rashin for helpful comments.

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