Theor Chem Acc (2006) 115: 1–17
DOI 10.1007/s00214-005-0014-z

REGULAR ARTICLE

H. Gharibi · R. Behjatmanesh-Ardakani
S. M. Hashemianzadeh · S. M. Mousavi-Khoshdel
S. Javadian · B. Sohrabi

Study of thermodynamic parameters in amphiphilic systems by lattice Monte Carlo: effect of tails and heads

Received: 24 July 2004 / Accepted: 18 November 2004 / Published online: 9 November 2005

Abstract Results from three-dimensional lattice Monte Carlo simulations of amphiphile–solvent mixtures are presented. The chemical potential is derived from the monomer distribution in different clusters rather than using a Widom particle insertion approach. The effect of tail and head characteristics on the non-ideality of these systems, aggregation number, and premicellar phenomena is considered. The aggregation number and CMC behavior of the simulated amphiphilic systems are compared with existing experimental results for non-ionic amphiphiles. Two kinds of polydispersity changing with total concentration of surfactants are observed which are related to phase transition phenomena. Shape variations in clusters are studied by calculating the eigenvalues of the gyration matrix; it is shown that large clusters are non-spherical. With the Maclaurin's expansion of activity coefficient into volume fraction, the distribution of excess chemical potential with changing aggregation number is considered. Study of the degree of non-ideality of these amphiphiles reveals that asymmetric amphiphiles are characterized by greater non-ideality than symmetric amphiphiles. Goldstein's parameters are calculated taking non-ideality into consideration. The difference between the phenomenological model and the simulation data is investigated.

List of Symbols

n	Aggregation number
x_n	Mole fraction of cluster with aggregation number n
x_a	Total mole fraction of surfactant
V_s	Total volume fraction of surfactant
T	Tail part of amphiphile chain
H	Head part of amphiphile chain
h	Excess chemical potential in ideal condition
w	Water site
W	Rosenbluth weight
E	Energy of system
K_B	Boltzmann constant
ε	Interaction parameter between H–T and w–T sites
n_{Tw}	Number of tail–water interactions
n_{TH}	Number of tail–head interactions
$P_{acc.}$	Probability for acceptance of new configuration
β	Reduced temperature
$Z_s(i)$	Number of nearest water sites for site i
z	Coordination number
N_n	Number-average aggregation number
N_{wt}	Weight-average aggregation number
I_P	Polydispersity
n_{max}	Aggregation number at the maximum of monomer distribution
CMC	Critical micelle concentration
H_iT_j	An amphiphile chain with i sites in the head and j sites in the tail
C_jE_i	Non-ionic surfactant with j carbons and i ethoxylate groups
I_1, I_2, I_3	Three principal moments of inertia
$R^2_{r_i,r_j}$	Gyration matrix
$r_{i,cm}$	Position of the center of mass of a cluster in the i direction
l_1, l_2, l_3	Three characteristic lengths
μ_n	Chemical potential for cluster with aggregation number n
μ^0_n	Standard chemical potential of cluster with aggregation number n
f_n	Activity coefficient for a chain in cluster with aggregaion number n
f_1	Activity coefficient for monomer
μ^0_1	Standard chemical potential for monomer

H. Gharibi (✉) · R. Behjatmanesh-Ardakani
S. M. Mousavi-Khoshdel · S. Javadian · B. Sohrabi
Department of Chemistry, Tarbiat Modarres University,
P.O. Box 14155-4838, Tehran, Iran
E-mail: gharibi@irandoc.ac.ir

H. Gharibi
Iranian Information and Documentation Center (IRANDOC),
P.O. Box 13185-1371, Tehran, Iran

S. M. Hashemianzadeh
Department of Chemistry, College of Chemistry, Iran University
of Science and Technology, P.O. Box 16765-163, Tehran, Iran