Surface tension of methane–nitrogen solutions: 2. Description in the framework of the van der Waals gradient theory

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A B S T R A C T

Surface tension, adsorption, partial profiles of density, the position of dividing surfaces in the interfacial layer and the Tolman length of methane–nitrogen solutions have been calculated in the context of the van der Waals gradient theory (GT). Equations of state have been built up for pure methane and nitrogen, which describe stable, metastable and unstable regions and parameters of liquid-gas phase equilibrium. A one-liquid model of a solution has been used for determining the density of the Helmholtz free energy of a homogeneous system. The influence parameters of methane and nitrogen have been calculated from data on their surface tension. It has been found that in a first approximation they are independent of temperature. The problem of determination of the mixture cross influence parameter is discussed. The results of calculations of surface tension are compared with experimental data [V.G. Baidakov, M.N. Khotienkova, V.N. Andbaeva, A.M. Kaverin. Capillary constant and surface tension of methane–nitrogen solutions: 1. Experiment. Fluid Phase Equilib. 301 (2011) 67–72].

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1. Introduction

Surface phenomena play an important role in many industrial processes, such as extraction, distillation, adsorption, heat exchange in boiling, etc. Being one of the main thermodynamic parameters of a two-phase system, the surface tension essentially determines the work of fluctuation formation of a new-phase nucleus, the flow of liquid through capillary structures, etc.

In recent years, there has been a considerable increase in the number of papers on measuring the surface tension of liquids of different classes [1–5]. However, the amount of the experimental data obtained is as yet limited and does not allow satisfying the requirements of engineering to a sufficient extent. Numerical methods of calculation of this parameter are developed along with the experimental methods of calculating surface tension. Some of the most widespread computing methods are the parachore method [6,7], the principle of corresponding states [8,9], the perturbation theory [10], the method of density functional [11,12] and the gradient theory [13,14].

The gradient theory (GT) of inhomogeneous fluids has its origin in the van der Waals work [13] and is widely used for determining

the surface and the interfacial tension of hydrocarbons and their mixtures [15], polymeric fluids [16], aqueous solutions [17], etc. One of the advantages of this theory is its relative simplicity. To describe the properties of an interface in the framework of the GT, it is sufficient to know the density of the Helmholtz free energy of a homogeneous fluid and the influence parameter. The Helmholtz free energy may be determined by building up an equation of state that describes the regions of stable, metastable and unstable states of a homogeneous fluid, and the influence parameter may be calculated on the basis of molecular-statistical representations or with the use of empirical relations.

The present paper describes the properties of the liquid–gas interface of methane–nitrogen solutions in the framework of the GT. Previously [4] we measured the capillary constant and determined the surface tension for this solution in a wide range of temperatures and concentrations.

The paper in constructed as follows. The first section is an introduction. The second examines the fundamental tenets of the gradient theory. The third section describes the results of construction of the functional of the excess thermodynamic potential and a technique of determination of the influence coefficients. The results of calculation of the surface tension of solution, the density distribution in an interfacial layer, adsorption and some other parameters are presented in the fourth section. The conclusion sums

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up the results, and the appendix gives equations of state for nitrogen and methane that describe stable, metastable and unstable states of these substances.

2. The van der Waals gradient theory for two-component solutions

Let us examine a two-component system with a flat interface. The Helmholtz free energy of such a system may be presented as follows [15]:

$$F = A \int_{-\infty}^{+\infty} \left(f_0\left(\overrightarrow{\rho}\right) + \frac{1}{2} \sum_i \sum_j \kappa_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right) dz, \tag{1}$$

where A is the interface area, $f_0(\overrightarrow{\rho})$ is the density of the Helmholtz free energy of a homogeneous fluid, $\overrightarrow{\rho}$ is the vector of partial densities with components ρ_i ($i = 1, 2$), κ_{ij} is the matrix of the influence parameters, and z is the axis of a rectangular system of coordinates directed from liquid into vapor perpendicularly to the interface. From the requirements of stability of a two-phase system follows the positive value of the influence coefficients. Otherwise the formation of inhomogeneity would be an energy-efficient process leading to a decrease in the free energy.

The influence parameters of pure components κ_{ii} are determined through the second moment of the direct correlation function [18]. Since the direct correlation function has a weak dependence on the density, in a first approximation κ_{ij} may be considered only temperature functions.

To the state of thermodynamic equilibrium corresponds the minimum of the Helmholtz free energy on condition that the number of particles is retained. Minimization of the functional (1) leads to a system of Euler-Lagrange equations that determine the density distribution in an interfacial layer:

$$\sum_j \frac{d}{dz}\left(\kappa_{ij}\frac{d\rho_j}{dz}\right) - \frac{1}{2}\sum_j \sum_k \frac{\partial \kappa_{kj}}{\partial \rho_i}\frac{d\rho_k}{dz}\frac{d\rho_j}{dz} = \frac{\partial \omega}{\partial \rho_i}, \tag{2}$$

$$\omega\left(\overrightarrow{\rho}\right) = f_0\left(\overrightarrow{\rho}\right) - \sum_i \rho_i \mu_{i\,\alpha}, \tag{3}$$

$\mu_i = (\partial f_0/\partial \rho_i)_{T,V,\rho_j}$ is the chemical potential of the component i, the index α refers to one of the coexistent bulk phases. If the influence parameters are independent of density and are only temperature functions, from (2) and (3) we have

$$\sum_j \kappa_{ij}\frac{d^2\rho_j}{dz^2} = \mu_i\left(\overrightarrow{\rho}\right) - \mu_{i\alpha}. \tag{4}$$

The boundary conditions for this equation are the following: $\rho(-\infty) = \rho_L$, $\rho(+\infty) = \rho_V$, where ρ_L and ρ_V are the equilibrium densities of the liquid and vapor phases.

After multiplication of both parts of Eq. (4) by Refs. $\partial\rho_i/\partial z$, summation over i and integration we will have,

$$\frac{1}{2}\sum_i \sum_j \kappa_{ij}\frac{\partial \rho_i}{\partial z}\frac{\partial \rho_j}{\partial z} = \Delta\omega, \tag{5}$$

where $\Delta\omega(\overrightarrow{\rho}) = \omega(\overrightarrow{\rho}) - \omega_\alpha$, $\omega_\alpha = -p_\alpha$ and p_α is the saturation pressure.

The surface tension may be calculated as,

$$\sigma = \int_{-\infty}^{+\infty} \sum_i \sum_j \kappa_{ij}\frac{\partial \rho_i}{\partial z}\frac{\partial \rho_j}{\partial z}dz = 2\int_{-\infty}^{+\infty} \Delta\omega dz. \tag{6}$$

Let us turn in Eq. (6) from integration with respect to the variable z, which varies in the range $(-\infty, +\infty)$ to the variable ρ_n, which decreases monotonically from Ref. ρ_L to ρ_V. Then Eq. (5) may be rewritten as

$$\frac{1}{2}\sum_i \sum_j \kappa_{ij}\frac{d\rho_i}{d\rho_n}\frac{d\rho_j}{d\rho_n}\left(\frac{d\rho_n}{dz}\right)^2 = \Delta\omega, \tag{7}$$

Whence,

$$dz = \sqrt{\frac{\sum_i \sum_j \kappa_{ij}\frac{d\rho_i}{d\rho_n}\frac{d\rho_j}{d\rho_n}}{2\Delta\omega}}d\rho_n \tag{8}$$

Combining Eqs. (6) and (8), we have,

$$\sigma = \int_{\rho_L}^{\rho_V} \left(2\Delta\omega\sum_i \sum_j \kappa_{ij}\frac{d\rho_i}{d\rho_n}\frac{d\rho_j}{d\rho_n}d\rho_n \right)^{1/2} \tag{9}$$

As distinct from (6), integration in (9) is performed with respect to density, which varies from Ref. ρ_L to ρ_V.

3. Model

3.1. Equation of state

In calculating the density of the Helmholtz free energy of a homogeneous solution use is usually made of cubic equations of state whose parameters are functions of the composition and are found with the help of the appropriate rules of mixing. The Peng-Robinson [19,20], Soave-Redlich-Kvong [21], and cubic-plus-association [22,23] equations are used widely as such equations. The small number of free parameters in these equations makes it possible to obtain classical van der Waals loops on the dependence $p(\rho)$ at temperatures lower than the critical one. The pressure on a subcritical isotherm in the region of a liquid-gas phase transition is a hypothetical pressure, which would be in the fluid if at the given temperature it were in equilibrium and had a uniform density. The function $p(\rho)$ must satisfy the Maxwell rule, describe the metastable states of liquid and vapor to the boundary of their essential instability (spinodal) and convey correctly the critical parameters of the substance. It is, however, impossible to satisfy all these requirements in the framework of a cubic equation of state with an acceptable accuracy.

By this reason, in recent years, methods of building up multiparameter equations of state for pure liquids and solutions capable of reproducing the first and the second derivatives of the thermodynamic potential of such systems with a high degree of accuracy have been developed intensively [24–26].

In the framework of a one-liquid model the density of the Helmholtz free energy of a homogeneous binary mixture may be presented as follows [24]:

$$f(\rho, T, x) = f^{id}(\rho, T, x) + f^r(\delta, \tau, x) + f^m(\delta, \tau, x), \tag{10}$$

where x is the concentration of the second component of the mixture ($x = x_2$) expressed in mole fractions, $f^{id}(\rho,T,x)$ is the free energy of a unit volume of an ideal gas mixture, $f^r(\delta,\tau,x)$ is the contribution of intermolecular interactions to the free energy