Ternary Liquid Diffusion Coefficients Near Plait Points

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Mutual diffusion coefficients were measured as a function of temperature above the 30°C plait point of the water + 2-propanol + cyclohexane system using a Gouy interferometer and a new temperature-jump procedure. The four independent diffusion coefficients were found to decrease rapidly along the constant plait-point line as the temperature approached the consolute or plait temperature. Effective critical exponents were found to be 0.55 for the individual diffusion coefficients and 1.31 for the determinant of the diffusion coefficient matrix. The measured diffusion coefficients satisfy all stability requirements, although cross diffusion coefficients were found to be as large as main diffusion coefficients and a negative value was obtained for the water main diffusion coefficient in the component representation utilized in this work.

KEY WORDS: critical exponents; diffusion coefficients; Gouy interferometry; plait points; ternary liquid systems.

1. INTRODUCTION

Nonequilibrium thermodynamics indicates that the driving force for isothermal molecular diffusion processes is a gradient of chemical potential [1–3]

\[ \mathbf{J}_i = - \sum_{j=1}^{n} \Omega_{ij} \nabla \mu_j; \quad i = 1, 2, \ldots, n \]  

where \( \mathbf{J}_i \) is the molar flux of component \( i \) relative to the center of volume or Fickian reference frame, \( n \) is the number of components, \( \mu_i \) is the

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chemical potential of component \(i\), and \(\Omega'_{ij}\) are Onsager coefficients. As discussed by Miller [1] neither the fluxes (usually constant-volume experiments) nor the chemical potential gradients (Gibbs-Duhem relation) are independent. Transformation to independent fluxes and forces is desirable so that the Onsager coefficients will satisfy reciprocity. In terms of independent fluxes and forces, Eq. (1) becomes

\[
J_i = - \sum_{j=1}^{n-1} \Omega'_{ij} Y_j; \quad i = 1, 2, \ldots, n-1
\]  

where the \(\Omega'_{ij}\) constitute a set of Onsager coefficients which satisfy reciprocity, and the independent driving forces are given by

\[
Y_j = \sum_{k=1}^{n-1} a_{jk} \nabla \mu_k
\]

In the above equation,

\[
a_{jk} = \delta_{jk} + \bar{v}_j c_k / \bar{v}_n c_n
\]

\(\delta_{jk}\) is the Kronecker delta, \(\bar{v}_j\) is the partial molar volume, and \(c_k\) is the molarity.

Phenomenologically, the mole flux can be written in terms of diffusion coefficients, \(D_{ik}\), as a generalized form of Fick's law

\[
J_i = - \sum_{k=1}^{n-1} D_{ik} \nabla c_k; \quad i = 1, 2, \ldots, n-1
\]

While Eq. (5) is convenient, Eqs. (1) and (2) describe the true driving force; therefore, the interpretation of diffusion coefficients in multi-component, highly nonideal systems must be done carefully. It is particularly enlightening to compare Eqs. (2) and (5) to obtain the relationship between diffusion and Onsager coefficients,

\[
D_{ik} = \sum_{j=1}^{n-1} \sum_{l=1}^{n-1} \Omega'_{ij} a_{jl} \mu_{lk}; \quad i, k = 1, 2, \ldots, n-1
\]

where

\[
\mu_{lk} = (\partial \mu_l / \partial c_k)_{T, P, c_m \neq k}
\]

and \(\mu_{lk}\) is the so-called thermodynamic factor [3].