# The mutual diffusion coefficient of the methanol-*n*-hexane mixture around the coexistence line

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## Abstract

A comparison between experimental and calculated mutual diffusion coefficients is presented for the methanol-*n*-hexane mixture, around the coexistence line. For the experimental data, we used previous reported values, as well as our own measurements performed with the Taylor dispersion technique between 288 and 313 K, for several concentrations. For theory, we used the mean-field kinetic variational theory, i.e., the exact van der Waals theory. We reproduced the experimental values, in a semiquantitative way. The mean-field theory uses attractive interaction parameters which can be estimated when the binary system is classified according to the Scott and van Konynenburg scheme used for classifying binary phase diagrams. As a by-product, our method can give a mean-field theory spinodal curve prediction. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

There are very few mixture models which can be handled almost without approximations, giving explicit equations which relate the molecular parameters of the binary mixture to the mutual diffusion coefficient, $D$, (MDC). One of these is the van der Waals binary mixture model. In previous reports [1,2], we demonstrated this in the framework of the mean-field kinetic variational theory [3]. There, the MDC was related to the classification scheme devised by van Konynenburg and Scott [4–6] to study fluid phase equilibria in binary systems. The link between the MDC and fluid phase equilibria can be traced to the fact that MDC is equal to the free energy curvature of the binary mixture, modulated by a compressibility factor and other factors related to the dynamics of two-particle

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collision. The free energy curvature in a binary mixture is also responsible for the specific characteristics of the equilibrium phase diagrams. Our final formula has a practical advantage; the explicit dependence of the tail contribution is handled in such a way that the structure of the equations is the same as that given in the revised Enskog theory for hard-spheres (RET) [7,8]. This makes the task of developing numerical solutions for calculating MDC's easier. In particular, comparisons between the mean-field kinetic variational theory and the RET are very simple using our framework, since we only need to turn off the tail contributions to recover the MDC as given in the RET [8].

From the experimental point of view, the concentration dependence of the MDC over the whole concentration range is not easily obtained, although there are many applicable experimental techniques. However, understanding the shape of a $D$ vs. $X_2$ (mole fraction of component 2) diagram on molecular terms is a difficult issue. The shape depends on many molecular parameters, apart of those variables that determine the thermodynamic state: density, concentration, and temperature. Here is where our method can be of help. In our model, the $D$ vs. $X_2$ can be explicitly calculated, so we can understand how the different molecular parameters affect such diagrams.

In particular, we have shown that our method predicts, in a semiquantitative way, the concentration behavior of the MDC over the whole concentration range, for homogeneous binary mixtures of types I and II by the Scott and van Konynenburg scheme [1,2]. This work is a step further in that direction. It is not common to find predictions of MDC's in the literature when a coexistence line is present, since many predictive methods cannot deal with phase transitions. The aim of this paper is to show the capability of our method to predict the MDC of the system methanol-$n$-hexane around the coexistence line. Of course, we are not trying to give the correct behavior of $D$ close to the consolute point, since mean-field theories give only classical critical exponents. Our procedure can also give a spinodal curve prediction. This well defined spinodal curve exists only in the mean-field case. Other methods for describing non-equilibrium, one-phase states do not yield a unique spinodal curve. Nevertheless, it is useful to employ the mean-field description with caution since it provides a simple basis for characterizing metastable behavior, predicting a sharp distinction between metastable and unstable states.

The MDC of the methanol-$n$-hexane system has been measured by Clark and Rowley [9] as a function of composition at five temperatures, with a temperature-jump cell and a Gouy interferometer. They also report the critical exponent. However, only two temperatures were evaluated below the consolute temperature in their study. Therefore, additional temperatures measurements are needed to make a comparison with theory below the consolute temperature. We report additional measurements below the consolute point in both the methanol rich region and the $n$-hexane rich region.

The outline of the paper is as follows. In Section 2, we review the KVT I, i.e., the van der Waals theory of transport processes, as well as the most important features of the Scott and van Konynenburg scheme. In Section 3, we will present an experimental section, and in Section 4 the results and a discussion.

## 2. Theory

### 2.1. Kinetic theory for the van der Waals mixture

More than a century ago, van der Waals developed a simple model which was capable of describing the main properties of realistic fluids. In modern language, a rigorous formulation can be

given by writing the molecular pair interaction in the form $V(r) = V^S(r) + \gamma V^L(\gamma r)$, where $V^S$ refers to the short-range reference system, while $V^L$ is the long-range part of the potential, with range $\gamma^{-1}$. If the properties of this model are analyzed in the limit of $\gamma \to 0$, the van der Waals equation and the Maxwell equal-area construction is obtained [10]. The van der Waals theory has also been developed to predict fluid phase equilibria in binary mixtures, revealing a rich variety of behaviors which account for most of the types of fluid phase equilibria observed in actual mixtures, in a qualitative way [4–6]. This model has also been used to understand many related phenomena such as the theory of capillarity [11], nonuniform fluids [12], interphase properties [13], density fluctuations [14], mutual diffusion coefficients [1,2], and thermal diffusion factors [15].

The kinetic variational theory, first obtained by Karkheck et al. [3], is defined by a set of coupled nonlinear mean-field kinetic expressions. These equations were derived for a system of particles interacting through a pair potential consisting of a hard-sphere part plus a smooth but, otherwise arbitrary attractive tail. The set of equations for the two single particle distribution functions defined in a binary mixture, $f_i(r_1, v_1, t)$, $(i = 1, 2)$, are given by:

$$\left[ \frac{\partial}{\partial t} + v_1 \cdot \frac{\partial}{\partial r_1} \right] f_i(r_1, v_1, t) = C^{\text{RET}}(f_i, f_j) + \frac{1}{m_i} \sum_{j=1}^{2} \int_{r_{12} > \sigma_{ij}}^{\infty} dr_2 \, n_j(r_2, t) g_{ij}^{\text{HS}}(r_1, r_2 | \{n_k\})$$

$$\times \frac{\partial}{\partial r_1} \varphi_{ij}^{\text{tail}} \cdot \frac{\partial}{\partial v_1} f_i(r_1, v_1, t) \tag{1}$$

where $f_i(r_1, v_1, t)$ is the average number of particles of component $i$ (with mass $m_i$), at the position $r_1$, at the velocity $v_1$, and at time $t$. $n_i = \int dv_1 f_i(r_1, v_1, t)$. The $g_{ij}^{\text{HS}}(r_1, r_2\{n_k\})$'s are the radial distribution functions of a binary hard-sphere mixture and $\varphi_{ij}^{\text{tail}}$ are the attractive tails. The collision term $C^{\text{RET}}(f_i, f_j)$ has exactly the form which appears in the revised Enskog theory introduced by van Beijeren and Ernst [7].

The Kac limit can be found using the mean field terms of Eq. (1) ($\sigma_{ij} \to 0$, $g_{ij} \to 0$). Then, kinetic equations for the $f_i$ can be obtained that embody the exact thermodynamic description of a system interacting with a potential consisting of a hard-sphere core and an infinitely weak long-range attraction, i.e., the van der Waals interaction [3]. We shall call this theory KVT I.

Explicit expressions for the transport coefficients up to the Navier–Stokes level can be directly obtained by expanding the heat, the momentum and the mass fluxes to linear order in the gradients [1,2]. This is done by solving Eq. (1) in the Kac limit, in the form $f_i = f_i^{(0)}[1 + \Phi_i]$ through the Chapman–Enskog development. Here, the $f_i^{(0)}$ are the local Maxwell distribution functions, and $\Phi_i \sim \mathcal{O}\nabla$. The thermal conductivity and the viscosities are identical to those given in the RET [8]. The diffusion and thermal diffusion coefficients exhibit an explicit dependence on the tail strength [1,2]. Following the method of solution presented in Refs. [1,2], the independent mass flux relative to the local center of mass velocity can be obtained, in a binary system, by substituting the solution for the $f_i$ to the first order in the gradients into the expression:

$$J_i(r_1, t) = \int dv_1 m_i(v_1 - u) f_i(r_1, v_1, t).$$

The final result is as follows:

$$J_i^{(1)} = -\frac{\rho_i}{2n^2} \sum_{j=1}^{2} (1 - \delta_{jL}) \left[ \sum_{k=1}^{2} d_{i,0}^{(k)} \left( E_{kj} - \frac{P_j}{P_L} E_{kL} \right) \right] \frac{\partial n_j}{\partial r} \tag{2}$$

where the $J_i^{(1)}$ are the macroscopic mass fluxes, to the first order in the gradients, relative to the local center of mass velocity, $\delta_{jL}$ is a Kronecker delta, and $P_i = \sum_{j=1}^{2} E_{ji}$, where $E_{ji} = \left(\frac{n_i}{kT}\right)\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T, n_{k \neq j}}$. Those functions $P_i$ should not be confused with the pressure.

In binary mixtures, there is only one independent diffusion coefficient. The phenomenological expression for the mass flux $J_i^{\mathrm{ph}}$ (relative to the local center of mass velocity, $i = 1,2$), under the condition of no external forces, thermal and mechanical equilibrium ($\nabla T = \nabla p = 0$), is [16,17]:

$$J_i^{\mathrm{ph}} = - \sum_{j=1}^{2} \left(1 - \delta_{Lj}\right) D_{ij}^{\mathrm{CM}} \nabla \rho_j \tag{3}$$

In Eq. (3), $\rho_j$ is the mass density of component $j$, $T$ is the temperature, and $D_{ij}^{\mathrm{CM}}$ are the mutual diffusion coefficients in the center of mass reference system. Eq. (3) has been written in such a way that all the gradients occurring therein are independent. The choice of the component $L$ is arbitrary and, although it is not explicitly stated the $D_{ij}^{\mathrm{CM}}$ depend upon the choice of $L$ [16,17].

Comparing Eqs. (2) and (3) allows us to obtain the expression for the MDC of the van der Waals binary mixture in the KVT I, as follows [1,2]:

$$D_{11}^{\mathrm{CM}} = \frac{\rho_1}{2 m_1 n^2} \sum_{k=1}^{2} d_{1,0}^{(1)} \left[ E_{k1} - \left(\frac{P_1}{P_L}\right) E_{kL} \right]. \tag{4}$$

In Eq. (4), the $d_{1,0}^{(j)}$ are the coefficients that appear in the Sonine polynomial expansion. They depend on the hard core part only. The tail contribution in Eq. (4) comes through the chemical potential. In order to obtain practical results, one restricts the number of Sonine polynomials in the expansion. We shall adopt here the convention, usually called the Nth Enskog approximation, so only the first N Sonine polynomials are taken into account. For details see Refs. [1,2]. Eq. (4) can be used for calculating the MDC in binary mixtures, but if one is interested in comparisons with experimental MDC's of actual mixtures, we need to make a transformation, since the measured MDC's are measured relative to the mean volume velocity ($D^v$). Therefore, this relationship for binary mixtures is given by $D^v = (\rho v_2) D_{11}^{\mathrm{CM}}$, where $v_2$ is the partial specific volume of component 2. For details, see Ref. [1,2].

## 2.2. The Scott and van Konynenburg scheme

A very useful classification scheme was devised some time ago by van Konynenburg and Scott [4,5], who used the van der Waals equation in a systematic way to study the fluid phase equilibria of binary mixtures. They characterized the mixtures by three dimensionless parameters:

$$\xi = \frac{b_{22} - b_{11}}{b_{22} + b_{11}}, \quad \zeta = \frac{\dfrac{a_{22}}{b_{22}^2} - \dfrac{a_{11}}{b_{11}^2}}{\dfrac{a_{11}}{b_{11}^2} + \dfrac{a_{22}}{b_{22}^2}}, \quad \Lambda = \frac{\dfrac{a_{11}}{b_{11}^2} - \dfrac{2 a_{12}}{b_{11} b_{22}} + \dfrac{a_{22}}{b_{22}^2}}{\dfrac{a_{11}}{b_{11}^2} + \dfrac{a_{22}}{b_{22}^2}}.$$

The van der Waals constants $a_m$ and $b_m$ for the mixture depend on mole fraction $x_i$, as follows:

$$a_m \sum x_1 x_j a_{ij}, \text{ and } b_m = \sum x_i x_j b_{ij}.$$

The constant $a_{11}$ and $a_{22}$ measure the attractive forces between pairs of molecules of the pure components 1 and 2, respectively, and $a_{12}$ is the corresponding parameter for the interaction between molecules 1 and 2. The constants $b_{ij}$ are the size parameters for the pure components and for mixed pairs, respectively. Here, in agreement with the Scott and van Konynenburg convention [4,5], we have used the cross-size parameter as $b_{12} = (b_{11} + b_{22})/2$.

On the basis of the selected parameters $\Lambda$ and $\zeta$, and the P–T diagrams resulting from their calculations, van Konynenburg and Scott grouped fluid phase equilibria diagrams into five types, see [4,5]. The diagrams were distinguished mainly by the configuration of the critical lines and the three-phase lines on the P–T graphs. They recognized a sixth type of diagram that occurs in some aqueous systems, but it was not among those predicted by the van der Waals equation. This scheme is useful since it gives a qualitative description of the properties of the liquid mixtures while it very rarely yields non-physical results. Therefore, a very natural extension of the work of van Konynenburg and Scott is to use this scheme to describe the behavior of the MDC [1,2].

## 3. Experimental section

### 3.1. Instrument design and operation

The Taylor dispersion technique is based on the spreading, by the joint action of convection and molecular diffusion, of an injected binary-mixture pulse in a laminar flowing stream of the same mixture at slightly different composition. Under adequate conditions, the pulse concentration profile will eventually become Gaussian, and the center of gravity of the profile will move with the mean velocity of the laminar flow. The theory for the development of an ideal equipment to measure MDC's using this method was revised by Alizadeh et al. [18]. Furthermore, they presented detailed criteria for the design of a practical instrument for measuring MDC's. In the present paper, we followed that work to design a measuring instrument. The details of our instrument were presented in Ref. [19].

Alizadeh et al. [18] derived expressions for the fixed-volume MDC for an ideal instrument, in terms of the first ($\bar{t}$) and second ($\sigma^2$) temporal moments of the distribution of the dispersed pulse. These expressions can be written as:

$$D^v = \frac{(1 + 2\zeta)}{\zeta} \frac{a_0^2}{48\bar{t}_{id}},$$

where

$$\zeta = \frac{2\sigma_{id}^2 - \bar{t}_{id}^2 + \left\{ \bar{t}_{id}^4 + 4\bar{t}_{id}^2 \sigma_{id}^2 \right\}^{1/2}}{\left\{ 8\bar{t}_{id} - 4\sigma_{id}^2 \right\}} + \delta\zeta.$$

Here, $a_0$ is the capillary radius, and $\delta\zeta$ is a correction due to the use of weaker condition on the diffusion time. For details, see Refs. [18,19].

In addition, Alizadeh et al. [18] derived a set of corrections for this ideal instrument that account for the deviations of a practical instrument. They found that the ideal moments have to be corrected

according to $\bar{t} = \bar{t}_{exp} + \Sigma \delta \bar{t}_i$ and $\sigma^2 = \sigma_{exp}^2 + \Sigma \delta \sigma_i^2$, where $\bar{t}_{exp}$ and $\sigma_{exp}^2$ denote the experimentally determined moments, and the $\delta \bar{t}_i$ and the $\delta \sigma_i^2$ are the corrections to be applied. For details, see Refs. [18,19].

The values of $\bar{t}_{exp}$ and $\sigma_{exp}^2$ were determined with a nonlinear fitting program of the digitized values from a differential refractometer (Waters 402). This instrument was used to determine the temporal shape of the injected pulse, in the region where it has a linear response, to the concentration difference between the cells. Data acquisition was carried out using a data acquisition board (PC-LabCard, Advantech) and a Printaform PC. The diffusion coefficient obtained corresponds to the mole fraction concentration given by:

$$X_{1r} = X_{1f} + \delta X_1.$$

where $X_{1f}$ is the flowing-stream composition, and $\delta X_1$ is a small correction described in Refs. [18,19].

## 4. Results and discussion

In Table 1, we present some results for the MDC's of the methanol-$n$-hexane system at two temperatures and $n$-hexane mole fractions. All temperatures are below the consolute temperature. We followed the common practice of employing the reproducibility of the results of a series of experiments, under nominally identical experimental conditions, as a measure of the precision of the observations. Hence, we determined the values of $\bar{t}_{exp}$ and $\sigma_{exp}^2$ and after considering the mentioned corrections, we obtained a mean precision better than $\pm 1.5\%$. Taking into account several uncertainties related to the cross-section area and the length of the diffusion tube, etc., the overall accuracy of the reported diffusion coefficients is estimated to be of $\pm 2.5\%$. At 313.1 K, we also measured the MDC at infinite dilution to compare our measurements with those reported values due to Clark and Rowley [9]. The two values are within the experimental error.

In order to make the numerical calculations, it is necessary to define the set of parameters to be used in the mean-field theory. We have used the following set: $m_1$, $m_2$, $a_{22}$, $b_{22}$, $\Lambda$, $\xi$, $\zeta$, $n$, $T$, and

Table 1
Experimental results

| Temperature (K) | $n$-Hexane mole fraction | $D^v \times 10^9$ (m$^2$/s) |
|---|---|---|
| 288.15 | $5.7116 \times 10^6$ | 1.86 |
|  | 0.05159 | 1.32 |
|  | 0.90307 | 1.62 |
|  | 0.95026 | 1.96 |
|  | 0.9996 | 5.45 |
| 293.15 | 0.00003 | 2.30 |
|  | 0.05171 | 1.60 |
|  | 0.90269 | 1.57 |
|  | 0.9545 | 2.21 |
|  | 0.9971 | 5.71 |

$X_2$. Once this set is given, the other interactions parameters can be obtained [1,2]. In particular, the cross interaction parameter $a_{12}$:

$$a_{12} = \frac{[1 - \xi][1 - \Lambda]}{[1 + \xi][1 + \zeta]} a_{22}.$$

With the theory developed above, the MDC was calculated for the methanol-$n$-hexane binary mixture as a function of the concentration and temperature, in the ninth Sonine approximation. When predictions for actual fluids are done, it is difficult to obtain a reliable set of interaction parameters. Here, an initial set of parameters was estimated as follows: each component was modeled as a hard-sphere of diameter $\sigma$ (L–J length), plus an attractive L–J tail. The $a_{ii}$'s and $b_{ii}$'s can be estimated through standard formulas [20]. The parameters $\Lambda$ and $\zeta$ were selected to fall into type II phase diagrams of the van Konynenburg and Scott scheme, since the mixture probably belongs to that type. Thus, the initial set of interacting parameters was modified for the 313 K mixture, so one can obtain the experimental shape of the $D^v$ vs. $X_2$ diagrams. In this way, we arrived to a final set of interacting parameters. Since, our main interest was to understand how the different parameters affect
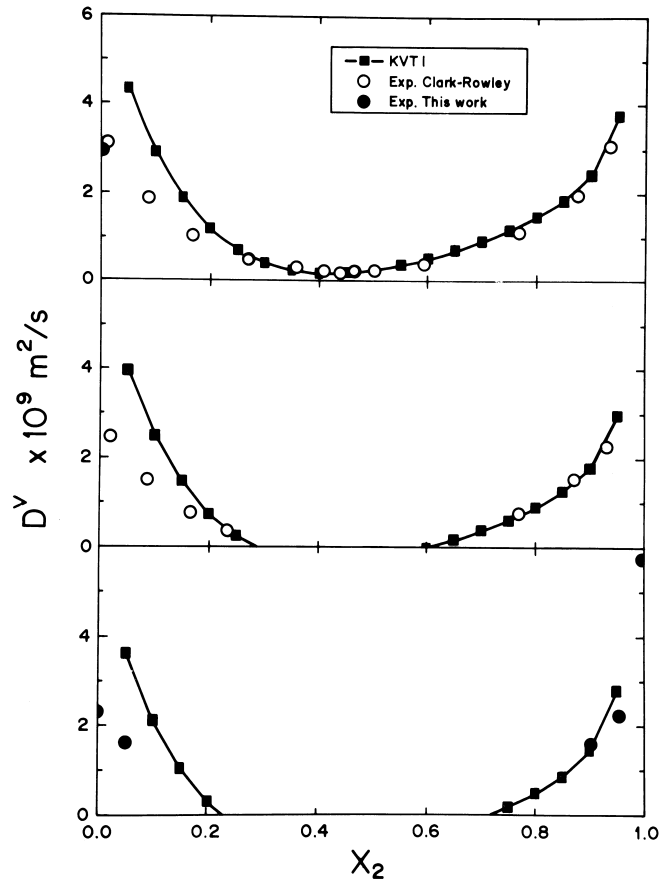


Fig. 1. Comparison between experimental and calculated MDC's. Top panel: 313.1 K, middle panel: 303.1 K, and lower panel: 293.1 K.
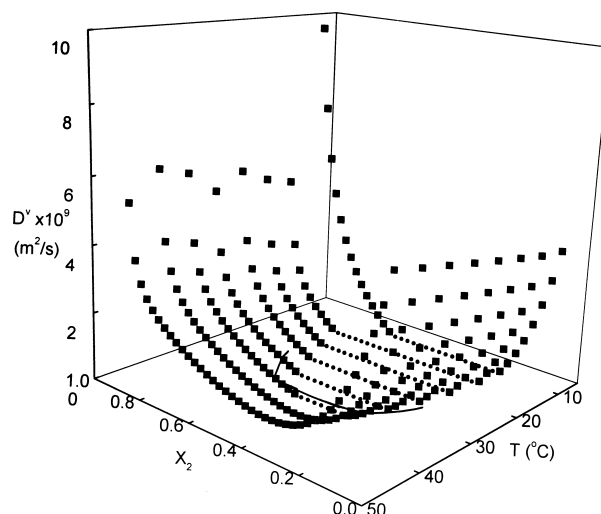
Fig. 2. 3D plot of calculated MDC's using the kinetic variational mean field theory vs. $T$ and $n$-hexane mole fraction. In this plot we included the coexistence line (continuous line). The spinodal curve can be seen as the first points where the MDC's vanish on the isotherms.

the $D^v$ vs. $X_2$ diagrams, we were not interested in developing a procedure to obtain the best set of parameters that match the experimental data. Fig. 1 presents a comparison between our experimental data, some experimental values of Clark and Rowley [9], and our calculations. The agreement is quite good and semiquantitative mainly in the hexane-rich region. Here, we used the same parameters obtained for the 313 K mixture, except for the $b_{ii}$'s which were increased a little bit to match the experimental values, since the hard-core must be temperature dependent.

In Fig. 2, we present a 3D plot of our kinetic mean field predictions for the methanol-$n$-hexane system for a small range of temperatures (283–318 K). Here, the coexistence line was also included. Inside this coexistence line, we can find the geometric locus where the MDC's reach the value $D^v = 0$, the spinodal curve (curvature of the free energy = 0). Inside the spinodal curve, we set the $D^v$ equal to zero to avoid misinterpretation. As expected, our actual calculations gave negative values for the MDC's. This is in agreement with the point of view of a mean field theory where diffusion inside the spinodal curve must help to nucleate a new phase.

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