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

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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.

Keywords: Diffusion coefficient, mixture, methanol, n–hexane

1 INTRODUCTION

There are very few model mixtures for which theory can be handled almost without approximations, giving explicit equations which relate the molecular parameters of the binary mixture to the mutual diffusion coefficient, D_{11}, (MDC). One of these is the van der Waals binary model mixture. In previous reports,[1] we showed how to do that, in the framework of the mean-field kinetic variational theory[2]. There, the MDC was related to the classification scheme devised by Scott and van Konynenburg [3, 4] to study fluid phase equilibria in binary systems in a systematic way. 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 collision. On the other hand, 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)[5, 6]. This make easier the task of developing numerical solutions for calculating MDC's. In particular, comparisons between the mean-field kinetic variational theory and the RET are very simple within our framework, since we only need to turn off the tail contributions to recover the MDC as given in the RET[6].

¿From the experimental point of view, the concentration dependence of the MDC along the whole concentration range is not easily obtained, although there are many well suited experimental techniques. However, understanding what determines the shape of a D_{11} vs X_2 (mole fraction of component 2) diagram on molecular terms is

a different and difficult issue. They depend 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_{11} vs X_2 can be explicitly calculated, and 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, in the whole concentration range, for homogeneous binary mixtures of types I and II in the Scott and van Konynenburg scheme[1]. This work is a step further in that direction. It is not quite common to find in the literature predictions of MDC's when a coexistence line is present, mainly because predictive methods can not 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_{11} close to the consolute point, since mean-field theories give only classical critical exponents. For the same token, our procedure can 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 with caution, the mean-field description and the sharp distinction between metastable and unstable states because it provides a simple basis for characterizing limiting types of behavior.

The MDC of the methanol-n–hexane system has been measured by Clark and R.L. Rowley[7] as a function of composition at five temperatures, with a temperature-jump cell and a Gouy interferometer. They found the critical exponent. However, in their study only two temperatures were evaluated below the consolute temperature. Therefore, in order to make a comparison with theory, below the consolute temperature, additional temperatures measurements were needed. We made some 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 II, we review the KVT I, i.e. the van der Waalsian theory of transport processes, as well as the most important features of the Scott and van Konynenburg scheme. In section III, we will present a experimental section, and in section IV 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 turned out to be extremely fruitful for 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 γ^{-1}. If the properties of this model are analyzed in the limit of $\gamma \to 0$, the van der Waals equation, combined with the Maxwell equal-area construction, is obtained [8]. Besides, the van der Waals theory has been developed to understand fluid phase equilibria in binary mixtures, revealing a rich variety of behaviors accounting for most of the types of fluid phase equilibria shown by actual mixtures, in a qualitative way [3, 4]. This model has also been used to understand a long list of related problems such as the theory of capillarity[9], nonuniform fluids,[10] interphase properties,[11] density fluctuations,[12] mutual diffusion coefficients,[1] and thermal diffusion factors [13].

The kinetic variational theory, first obtained by Karkheck et al [2], is defined by a set of coupled nonlinear mean-field kinetic. Those 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, $f_i(\mathbf{r}_1, \mathbf{v}_1, t), (i = 1, 2)$, are the following:

$$\left[\frac{\partial}{\partial t}+\mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\right] f_i(\mathbf{r}_1,\mathbf{v}_1,t)=\mathbf{C}^{RET}(f_i,f_j)+$$
$$\frac{1}{m_i}\sum_{j=1}^{2}\int_{r_{12}>\sigma_{ij}}^{\infty} d\mathbf{r}_2 \quad n_j(\mathbf{r}_2,t)g_{ij}^{HS}(\mathbf{r}_1,\mathbf{r}_2\mid\{n_k\})\frac{\partial}{\partial \mathbf{r}_1}\varphi_{ij}^{tail}\cdot\frac{\partial}{\partial \mathbf{v}_1}f_i(\mathbf{r}_1,\mathbf{v}_1,t) \tag{1}$$

where $f_i(\mathbf{r}_1,\mathbf{v}_1,t)$ is the average number of particles of component i, (with mass m_i) at the position $\mathbf{r}_1$, at the velocity $\mathbf{v}_1$, and at time t. $n_i=\int d\mathbf{v}_1 f_i(\mathbf{r}_1,\mathbf{v}_1,t)$. The $g_{ij}^{HS}(\mathbf{r}_1,\mathbf{r}_2\mid\{n_k\})$'s are the radial distribution functions of a binary hard-sphere mixture and φ_{ij}^{tail} are the attractive tails. The collision term $\mathbf{C}^{RET}(f_i,f_j)$ has exactly the form of that which appears in the revised Enskog theory introduced by van Beijeren and Ernst [5].

The Kac limit can be done in the mean field terms of equations (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 [2]. 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]. This is done by solving equations (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 [6]. The diffusion and thermal diffusion coefficients exhibit an explicit dependence on the tail strength [1]. Following the method of solution presented in Ref.[1], the independent mass flux relative to the local center of mass velocity, in a binary system can be obtained substituting the solution for the f_i to the first order in the gradients into the expression:

$$\mathbf{J}_i(\mathbf{r}_1,t)=\int d\mathbf{v}_1 m_i\left(\mathbf{v}_1-\mathbf{u}\right)f_i(\mathbf{r}_1,\mathbf{v}_1,t)$$

The final result is as follows:

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

where the $\mathbf{J}_i^{(1)}$ are the macroscopic mass fluxes to the first order in the gradients, relative to the local center of mass velocity, 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 $\mathbf{J}_i^{ph}$ (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 [14, 15]:

$$\mathbf{J}_i^{ph} = -\sum_{j=1}^{2}(1-\delta_{Lj})D_{ij}^{CM}\nabla\rho_j \tag{3}$$

In equations (3), ρ_j is the mass density of component j, T is the temperature, D_{ij}^{CM} are the mutual diffusion coefficients. Equations (3) have been writing 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}^{CM} depend upon the choice of L.[14, 15]

Comparing equations (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]:

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

In equations (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 equations (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, i.e., only the first N Sonine polynomials are taken into account. For details see Ref.[1]. 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_{11}^{v}). Therefore,

the relationship between them for binary mixtures is given by $D_{11}^{v} = (\rho v_2) D_{11}^{CM}$, where v_2 is the partial specific volume of component 2. For details see Ref[1].

2.2 The Scott and van Konynenburg scheme

Studies of fluid phase equilibria have shown that there are continuous transitions between phase diagrams that exhibit gas-liquid, liquid-liquid, and gas-gas phase separations. Critical lines are often observed to change continuously from one type of the phase separation to another. When the lines representing a single degree of freedom (pure-component vapor pressure curves, three-phase lines, critical lines, etc.) are plotted on P-T diagrams, the resulting graphs fall naturally into several different categories, providing a convenient basis for classification of the fluid phase equilibria.

A very useful classification scheme has been devised some time ago by Scott and van Konynenburg,[3] 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:

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

For $\xi = 0, \zeta$ is related to the difference in critical temperatures or pressures of the pure components, and Λ is related to the molar heat of mixing. The van der Waals constants a_m and b_m for the mixture depend on mole fraction x_i, as follows:

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

The constants 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,[3] we have used the cross size parameter as $b_{12} = (b_{11} + b_{22})/2$.

On the basis of the selected parameters Λ and ζ, and on the P-T diagrams resulting from their calculations Scott and van Konynenburg grouped fluid phase equilibria diagrams into five types, see Fig. 1. 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.

The usefulness of the above scheme relies in that it gives a qualitative description of the properties of the liquid mixtures, and very rarely yields non-physical results. The fluid phase of binary mixtures can be qualitatively discussed in terms of interaction parameters and changes of thermodynamic properties near the critical points. Therefore, a very natural extension of the work of Scott and van Konynenburg is to use this scheme to describe the behavior of the MDC [1].

3 Experimental section

3.1 Instrument design and operation

The Taylor dispersion technique is based on the dispersion, 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 normal, 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 [16]. Furthermore, they presented detailed criteria for the design of a practical instrument for measuring MDC's. In the present paper, we followed that work in order to design a measuring instrument, and the details of our instrument were presented in Ref. [17].

Alizadeh et al. derived expressions for the volume-fixed MDC for an ideal instrument, in terms of the first ($\bar{t}$) and second (σ^2) temporal moments of the distribution

of the dispersed pulse. These expressions can be written as:

$$D_1^V = \frac{(1+2\zeta)}{\zeta}\frac{a_0^2}{48\bar{t}_{id}}$$

where

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

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. [16] and [17].

In addition, Alizadeh et al [16]. derived a set of corrections for this ideal instrument in order to include the deviations of a practical instrument. They found that the ideal moments have to be corrected according to $\bar{t} = \bar{t}_{\text{exp}} + \sum \delta\bar{t}_i$ and $\sigma^2 = \sigma_{\text{exp}}^2 + \sum \delta\sigma_i^2$, where $\bar{t}_{\text{exp}}$ and σ_{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. [16] and [17].

The values of $\bar{t}_{\text{exp}}$ and σ_{exp}^2 were determined with a nonlinear fitting program of the digitized values corresponding to the analogical signal of 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, Co.) 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 δX_1 is a small correction described in Refs. [16] and [17].

4 Results and Discussion

In table 1, we present some results for the MDC's of the methanol-n–hexane system, at several temperatures and n–hexane mole fractions. All worked 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 $\bar{t}_{\rm exp}$ and $\sigma^2_{\rm exp}$ and after considering the mentioned corrections, we obtained a mean precision better than 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 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 R.L. Rowley. The two values are within the experimental error.

In order to make the numerical calculations, it is necessary to define the set of parameter to be used in the mean-field theory. We have used the following set: m_1, m_2, a_{22}, b_{22}, Λ, ξ, ζ, n, T, and X_2. Once this set is given, the other interactions parameters can be obtained [1]. 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, a difficult problem is 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 σ (L-J length), plus an attractive L-J tail. The a_{ij}'s and b_{ij}'s can be estimated through standard formulas. The parameters Λ, ξ,and ζ were selected to fall into type II phase diagrams of the Scott and van Konynenburg scheme. Thus, the initial set of interacting parameters were modified for the 313 K mixture, in such a way that one can obtain the experimental shape of the D_{11} 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 of parameters affect the D_{11} vs X_2 diagrams, we were not interested in developing a procedure to obtain the best set of parameters that match the experimental data completely. This is matter of a forthcoming work. In figure 2 presents a comparison between experimental data, coming from this work and from the

work of Clark and R.L. Rowley, 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_{ij}'s which were varied a little bit, since the hard-core must be temperature dependent.

In figure 3, 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 $D_{11} = 0$, the spinodal curve (curvature of the free energy=0). Inside the spinodal curve, we set the D_{11} equal to zero to avoid misunderstandings. But, 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, due to the lack of thermodynamic instability of the system to remain as an homogeneous phase.

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Figure Captions

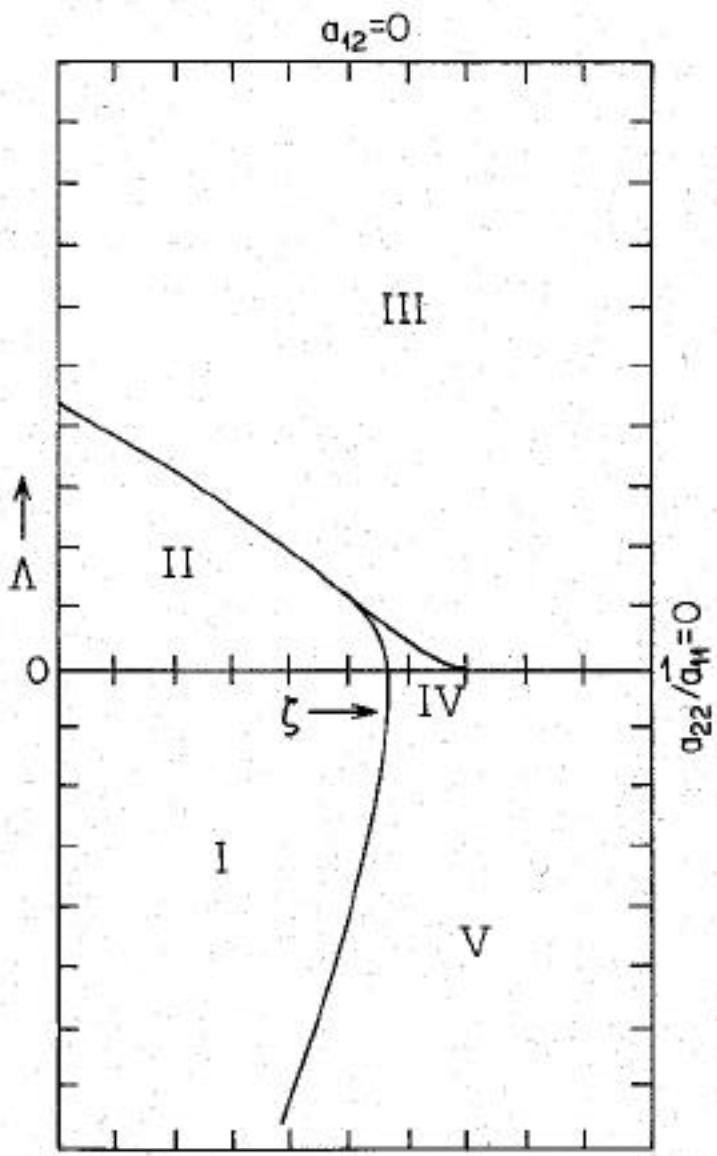
Figure 1. Classification of Scott and van Konynenburg. (a) Values of Λ and ζ defining the main regions of similar phase diagram (modified form Ref. [3]. The shield region is not shown. (b) Sketches of the pressure-temperature projections of the six possible types of fluid phase equilibria exhibited by binary mixtures [modified from K.E. Gubbins, K.S. Shing, and W.B. Street. J. Phys. Chem. **87**,5473 (1983)]. The vapor-pressure curves of pure components are shown as solid curves. The gas-liquid-liquid three-phase lines are shown as dash-dot, and the gas-liquid and liquid-liquid critical lines are shown dashed. The U and L are upper and lower critical end points, respectively.

Figure 2.Comparison between experimental and calculated MDC's. Upper panel: 313.1 K, medium panel 303.1 K, and lower panel 293.1 K.

Figure 3. $3D$ plot of calculated MDC's using the kinetic variational mean field theory versus T and X_2. In this plot we included the coexistence line (continuous line). The spinodal curve can be seen as the first points where the MDC's vanishes on a isotherm.

Table 1. Experimental Results

Temperature (K)	n–Hexane mole fraction	$D_{11}^{v} \times 10^{9}$ (m^2/s)
283.15	5.7116×10^{-6}	1.86
	0.05159	1.32
	0.90307	1.62
	0.95026	1.96
	0.9998	5.45
293.15	0.00003	2.30
	0.05162	1.60
	0.90269	1.57
	0.9545	2.21
	0.9971	5.71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II
Λ
0
ζ
IV
1
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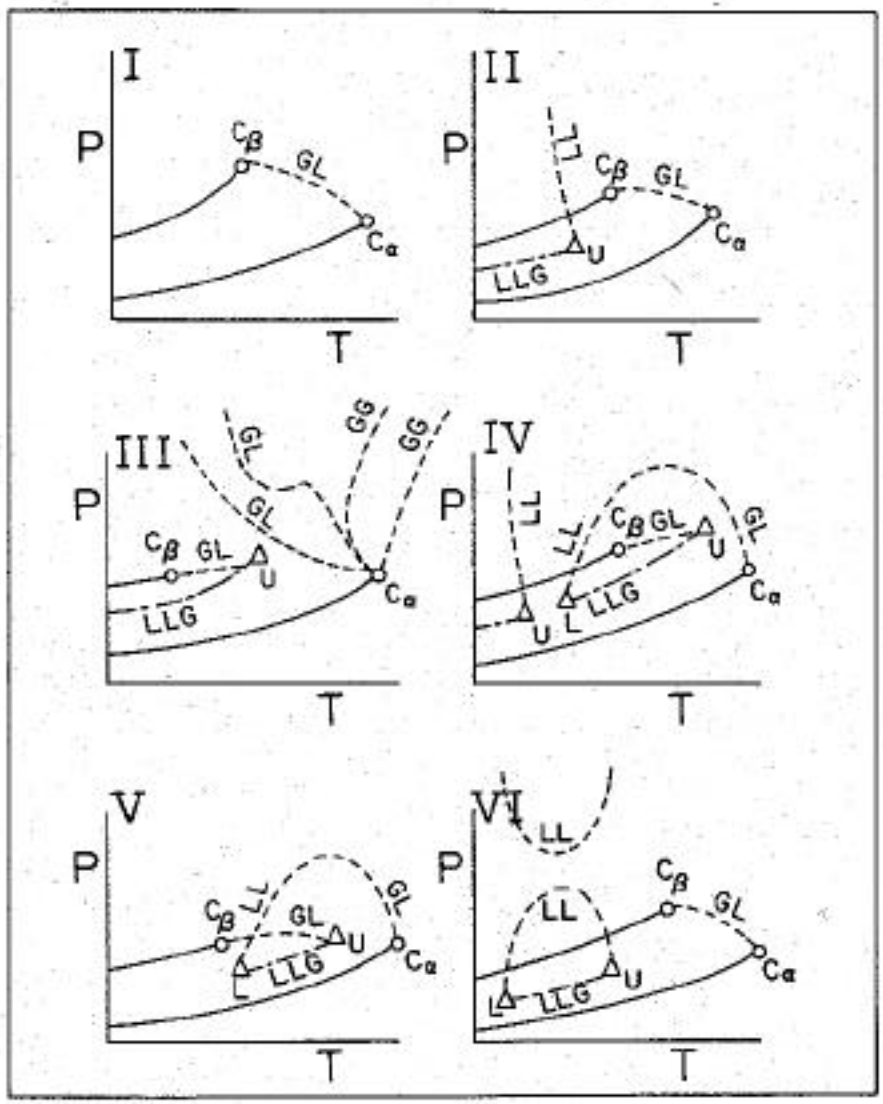
I
V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P
Cβ
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Cα
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II
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U
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VI
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Cβ
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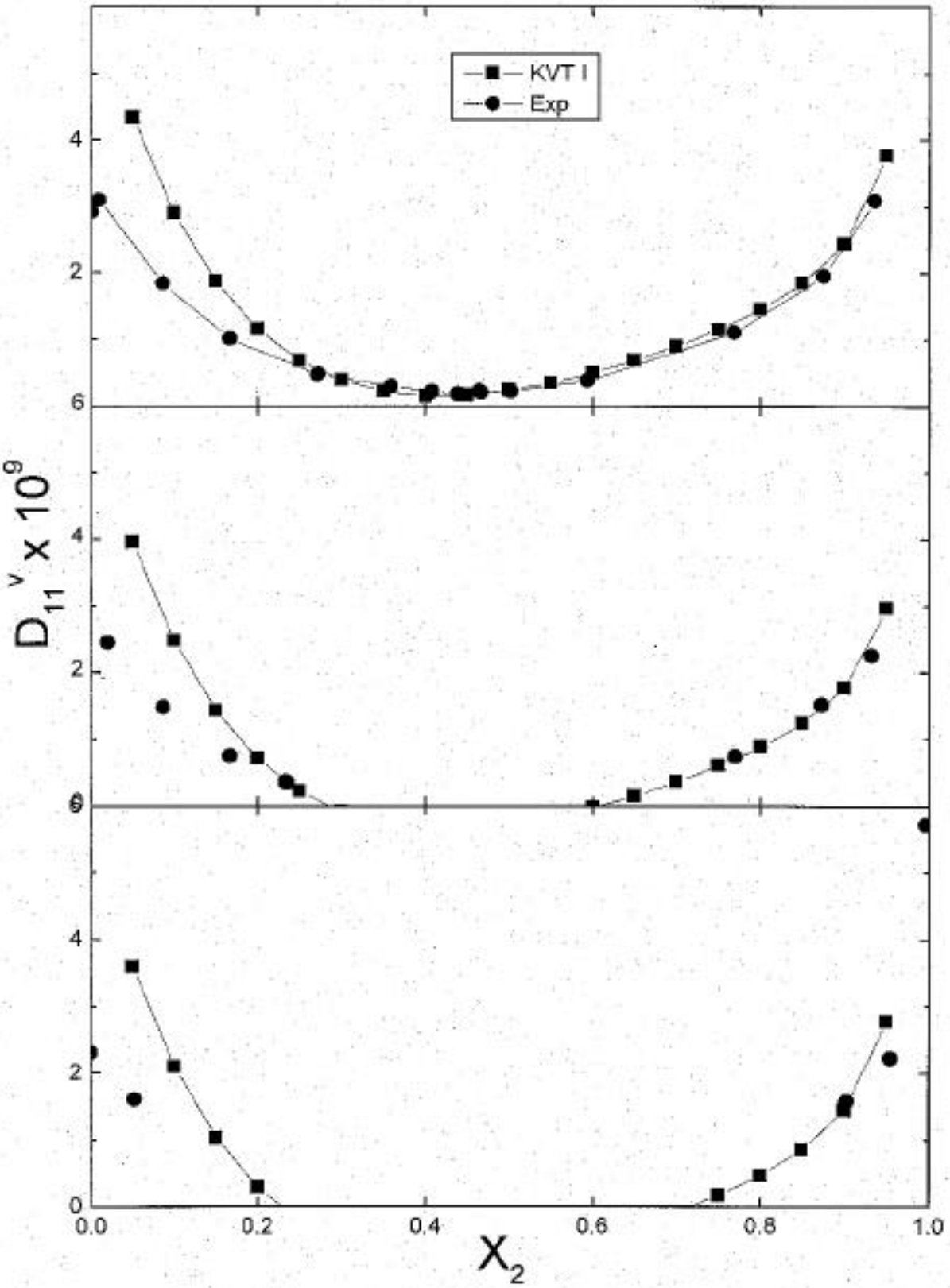
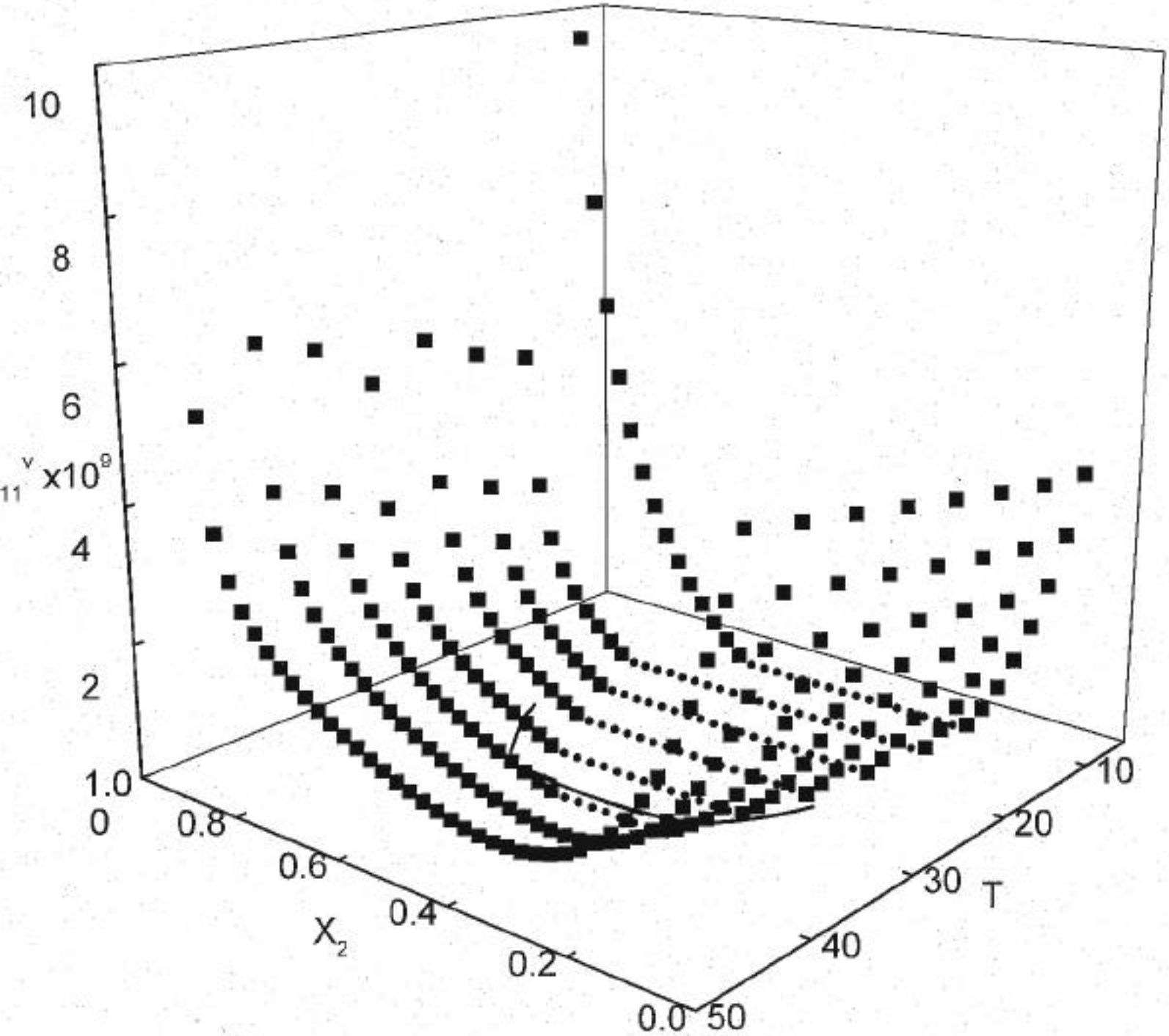
LLG
Cα
T


KVT I
Exp
$D_{11}^{v} \times 10^{9}$
X_2
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6


10
8
6
$_{11}^{v}$ x10^{9}
4
2
1.0
0
0.8
0.6
0.4
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X_2
10
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30
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50
T