Influence of the molecular interaction in the value of molecular volume for the isotropic-nematic transition of p-azoxianisol using the model HERSW in conjuntion with IPCM model

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Influencia de la interacción molecular en el valor del volumen molecular en la transición isotrópico-nemático del p-azoxianisol utilizando el modelo HERSW en conjunción con el modelo IPCM

Influència de la interacció molecular en el valor del volum molecular en la transició Isotròpic-Nemàtic del p-azoxianisol utilitzant el model HERSW en conjunció amb el model IPCM.

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RESUMEN

En este trabajo, analizamos el comportamiento experimental presión-temperatura en la transición de fase Isotrópico-Nemático para el cristal líquido p-azoxianisol a 1 atm utilizando un desarrollo para el modelo Convex Peg HERSW. Adicionalmente, obtenemos los valores del volumen molecular para las corazas duras y atractivas por medio de calculos cuánticos teóricos a los niveles PM3, PM6 y B3LYP/6-311++G considerando la interacción molecular alrededor de los cristales líquidos $(PAA)_5$. Se encontró que la mejor predicción de los datos experimentales aparecen cuando el efecto de la interacción molecular es considerada en el cálculo del volumen. Especificamente para a/b=3.7, V_0=70.86 Å^3 y a/b_λ=1.95 se obtuvo la mejor predicción.

Palabras clave: Transición de Fase, P-azoxianisol, Isotrópico-Nemático, Convex Peg, PAA.

SUMMARY

In this work, we analyzed the experimental pressure-temperature behavior in the Isotropic-Nematic phase transition for the liquid crystal p-azoxianisol at 1 atm using a development for the HERSW Conveg Peg model. Additionally, we obtained the values of the molecular volumes for the hard and attractive cores from theoretical quantum calculations at PM3, PM6 and B3LYP/6-311++G levels considering the molecular interaction among the liquid crystals $(PAA)_5$. We found that the best prediction for experimental data appears when the effect of the molecular interaction is considered in the volume calculation. Specifically for a/b=3.7, V_0=70.86 Å^3 and a/b_λ=1.95 the best prediction was obtained.

Keywords: Phase Transitions, P-azoxianisol, Isotropic-Nematic, Convex Peg, PAA.

RESUM

En aquest treball, analitzem el comportament experimental pressió-temperatura en la transició de fase isotròpica-nemàtica per al cristall líquid p-azoxianisol a 1 atm utilitzant un desenvolupament per al model Convex Peg HERSW. Addicionalment, obtenim els valors del volum molecular per les cuirasses dures i atractives mitjançant càlculs quàntics teòrics als nivells PM3, PM6 i B3LYP/6-311++G considerant la interacció molecular al voltant dels cristalls líquids $(PAA)_5$. Es va trobar que la millor predicció de les dades experimentals apareix quan es considera l'efecte de la interacció molecular en el càlcul del volum. Específicament, per a/b=3.7, V_0=70.86 Å^3 y a/b_λ=1.95 es va obtenir la millor predicció.

Paraules clau: Transició de fase, p-azoxianisol, Isotròpic-Nemàtic, Convex Peg, PAA.

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INTRODUCTION

Onsager [1] showed that, certain colloids solutions comprised highly asymmetrical particles (plates or rods) and they form anisotropic phases at remarkably low concentrations. Such theory exhibits limitations for the case when the hard rods have intermediate elongations; however, the predictions about the phase transition are accurate when the rods are infinitely large. An alternative to improving the quantitative predictions of Onsager´s theory is including higher-order virial coefficients [2-3]. It is important to note that when this consideration is done, the inclusion of a greater number of parameters causes a higher computational cost. One of the most successful approaches has been the scaling method proposed by Lee [4-5], in which Parson´s approach [6] is used to describe the pair distribution function for a fluid with a non-spherical hard-core. Also, this approach has been studied for other kind of hard-models [7-8].

On the other hand, it has been reported several models that consider the existence of Maier-Saupe´s attractive interactions [9]. Thus, considering such theory the Isotropic-Nematic (I-N) transition can be described by means attractive interactions of long-range dispersal. Despite the difference in the basic principles, Onsager´s and Maier-Saupe´s theories are alike. In both theories, Helmholtz´s free energy consists of a mixing entropy term, where molecules with different orientations are treated as different species, additionally a term of energy interaction is considered. Recent results have motivated the development of new theories which consider the properties of the Maier-Saupe´s anisotropic attractive interactions [10-11].

There are several studies that describe the I-N phase transition of the p-azoxianisol (PAA) using different theoretical models. In such studies, it was used the perturbation´s theory to first order type Barker-Henderson [12], developed by Williamson [11], using specifically the HERSWS model “Convex Peg”. A Convex Peg model comprises a hard uniaxial ellipsoidal (HER) core with Square Well (SW) spherical and incorporates the Ponce and Renon´s approximation [13], in conjunction with the Parsons decoupling approximation [6]. For the case of PAA, Williamson reported a comparison among the theoretical prediction and some experimental values [11]. The theoretical values were obtained following the adjustment procedure proposed by Tjipto-Margo and Evans [10] for two cores of rigid uniaxial ellipsoids 3:1. In such study, the molecular volume of PAA was fixed at 230 Å^3, which corresponds to a spheroid, and then fitting ε (depth square well potential) to reproduce the I-N transition temperature to 1 atm. The results obtained by Williamson, indicate that the adjustment procedure Tjipto-Margo and Evans [10] is ineffective, because the theoretical predictions do not compare favorably with experimental results. In this context, Martinez-Richa et al. [14] used the perturbation´s theory developed by Williamson to analyze the experimental behavior for PAA at 1 atm. The main difference in the original work of Williamson [11] and Martinez-Richa et al. [14], was that the size and volume of the PAA molecule were calculated using the parameters of the principal axis *a* of the ellipsoid semi axis of the Ellipsoid of revolution *b* and c, for the case uniaxial (*b* = *c*), It is important to mention that these parameters were previously reported by Garcia-Sanchez et al. [15]. Martinez-Richa et al. obtained that the molecular volume was approximately 150 Å^3. The results obtained by Martinez-Richa et al. in the case of two rigid uniaxial ellipsoids cores of 3.5:1 (where a=7.6 Å^3 and b=c=2.17 Å, then a/b=3.5:b/b=1), were better than those obtained by Williamson [11], however, in such work it was no possible to get a quantitative prediction comparable with an experimental behavior.

In another study [15], it was proposed a perturbation theory to second order in conjunction with the approach of Parsons´s [6] and the approximation of long-range by Ponce and Renon´s [13] to analyze the behavior of the I-N phase transition for PAA at 1 atm. In that study, the PAA structure was obtained performing a geometry optimization at PM3 level. To determine the volume of the molecule, the minimal energy structure of PAA was enclosed in an ellipsoid of revolution, and then the values *a* and *b* for uniaxial case were measured [15]. It was found that $a/b \approx 3.5$ and the molecular volume as 70.7 Å^3. Comprising the theoretical predictions for the reason 3.5:1 obtained by García-Sánchez *et al*. [15] with the obtained for Williamson [11] and Martínez-Richa *et al*. [14] with the experimental behaviour, one can conclude that the results obtained by García-Sánchez *et al*. [15] showed the best prediction. Analyzing the previous results, it is possible to observe that the molecular volume value is essential in the prediction of the pressure-temperature behavior and in the quality of the results obtained.

In other work, our group used the perturbation theory developed by us [15] for studying the experimental pressure-temperature behaviour of PAA at 1 atm in an I-N transition phase [16]. We proposed to calculate the isolated molecule volume by using density functional theory and Isodensity Polarized Continuous Model (IPCM); the results indicated that the molecular volume for PAA was 70.6 Å^3. A comparison of the results found by García-Sánchez *et al*. [15-16] indicates that the best theoretical prediction of the PAA experimental behavior was obtained when a DFT theory and IPCM model was employed [16]. Additionally, in that work it was found that $a/b \approx 3.643$. Thus, we performed theoretical calculations for the ratio 3.6:1 and 3.7:1. Albeit, the effect of *a/b* ratio was analyzed, it was found that, for the case $a/b = \lambda = 3$, the theoretical prediction overestimates the experimental behavior pressure versus temperature for the PAA, while for $a/b = \lambda = 3.5$ is the best theoretical prediction of the experimental behavior until now. On the other hand, García-Sánchez *et al* [17] used the perturbation theory developed by García-Sánchez *et al* [15], and they reported a study on the effect of the potential range in the experimental behavior pressure versus temperature for the PAA.

In other context, González-Cabrera *et al* [18] used different convex peg models, and they found that the convex peg model HERSW predict quantitatively the experimental pressure-temperature behavior for the isotropic-nematic phase transition. In this work, we used the HERSW Convex Peg Model [18] to analyze the pressure-temperature behavior in the I-N phase transition of PAA at 1 atm. Additionally, we calculated the molecular volume of PAA using the semiempirical methods PM3 [19] and PM6 [20] and Density Functional Theory (DFT) [21] at B3LYP/6-311++G level. The reason for testing these levels of theories is to be able to assess whether it is critical or not to include all-electron effects (PM3 and PM6 methods versus DFT theory), and the effect of the correlation energy (DFT theory vs. PM3 and PM6 methods). Also, we analyzed the effect of the molecular interaction by calculating the molecular volume from the system $(PAA)_5$ (Figure 1). In this system, the molecular volume was calculated using an isosurface electronic density with the values of 0.08 and 0.002 e/u.a.[3]. The individual PAA molecular volume was calculated through the ratio (total volume of $(PAA)_5$)/(number of PAA molecules).The volume so calculated was used into the perturbation theory for studying the experimental behaviour of PAA.

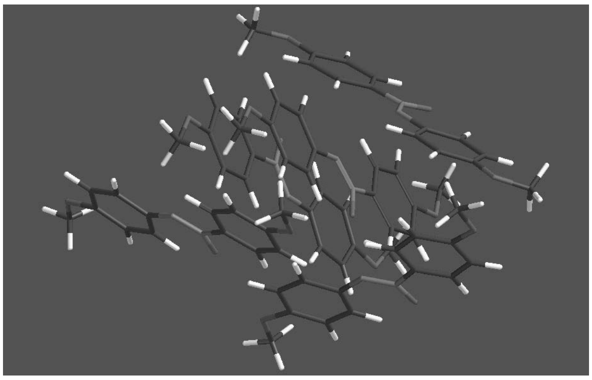

Figure 1 *Five Molecules of p–azoxi-anisol interacting with them.*

MATERIALS AND METHODS

If one considers a system of *N* molecules in a volume *V* at a temperature *T*, density (ρ) is defined as ***N*** / *V*. The center of the mass coordinates in a molecule *i* can be written as $\mathbf{r}_i$ and the orientational coordinates as Ω_i. The normalization condition for an orientation of a set of coordinates is given by:

$$\int d\Omega_i = 1 \qquad (1)$$

In the case of a linear molecule $d\Omega_i$ may be written as $d\cos\theta\ d\phi/4\pi$, where θ is the polar angle of the molecular axis and ϕ the azimuthal angle. The full set of translational and orientational coordinates is written as $d\mathbf{i} = d\mathbf{r}_i\, d\Omega_i$.

From perturbation theory it has been shown that the Helmholtz free energy of a fluid interacting through a potential with both attractive and repulsive contributions can be written as

$$\frac{A}{NkT} = \frac{A_{ideal}}{NkT} + \frac{A_{\Omega}}{NkT} + \frac{A_{excess}}{NkT} + \frac{A_{attractive}}{NkT} \qquad (2)$$

Where *k* is the Boltzmann's constant, A_{ideal} is the ideal contribution to the free energy, A_{Ω} is a contribution to the free energy for entropy loss due to the orientational order, A_{excess} is the free energy of the reference fluid and $A_{attractive}$ is the attractive contribution of the free energy. The ideal contribution or kinetic contribution is given by

$$\frac{A_{ideal}}{NkT} = \ln\left(\rho\Delta^3\right) - 1 \qquad (3)$$

In this expression Δ is the Broglie's mean thermal wavelength. The orientational term of free energy is given by the Onsager's expression

$$\frac{A_{\Omega}}{NkT} = \int f(\Omega)\ln\left[f(\Omega)\right]\ d\Omega \qquad (4)$$

Where *f (Ω)* is the single particle orientational distribution function for a solid angle *Ω*, that satisfies the normalization condition

$$\int f(\Omega)\ \ d\Omega = 1 \qquad (5)$$

The hard core or excess free energy is given by the following expression [4, 6-7]

$$\frac{A_{excess}}{NkT} = \Psi\,\frac{A_{HS}}{NkT} \qquad (6)$$

In this expression

$$\Psi = \frac{\langle V_{ex}^{HC}\left(\Omega_1,\Omega_2\right)\rangle}{8V_0} \qquad (7)$$

and

$$\frac{A_{HS}}{NkT} = \left[\frac{4\eta - 3\eta^2}{\left(1-\eta\right)^2}\right] \qquad (8)$$

In last equations, V_0 is the hard core volume, $\eta=\rho v_0$ is the packing fraction, $<V_{ex}^{HC}(\Omega_1,\Omega_2)>$ is the volume excluded to one convex hard core particle with orientation given by Ω_2 due to the presence of another convex hard core particle oriented along Ω_1, the pointed brackets represent a weighted average over the molecular orientations and finally, the expression (8) is the Carnahan-Starling´s equation state [22]. For sake of clarity, we described the attractive contribution for a set of potential's family in next sections.

THE HERSW POTENTIAL FAMILY

In this section we consider a potentials family which comprise a hard uniaxial ellipsoidal (HER) surrounded by a SW which is close to the edge of the hard core at the end of its major axis.

Into the Van der Waals approach of Tjipto-Margo and Evans, the attractive contribution to the free energy is given by

$$\frac{A_{attractive}}{NkT} = -\frac{\rho}{2V}\int\left[e^{\left(\frac{-U_{at}}{kT}\right)} - 1\right]\quad f\left(\Omega_1\right)f\left(\Omega_2\right)d\Omega_1 d\Omega_2$$

(9)

$$U\left(r_{12},\Omega_1,\Omega_2\right) = \begin{cases} \infty & \sigma\left(r_{12},\Omega_1,\Omega_2\right) < \sigma_{HC}\left(r_{12},\Omega_1,\Omega_2\right) \\ -\varepsilon & \sigma_{HC}\left(r_{12},\Omega_1,\Omega_2\right) \le \sigma\left(r_{12},\Omega_1,\Omega_2\right) \le \sigma_{\lambda}\left(r_{12},\Omega_1,\Omega_2\right) \\ 0 & \sigma\left(r_{12},\Omega_1,\Omega_2\right) > \sigma_{\lambda}\left(r_{12},\Omega_1,\Omega_2\right) \end{cases}$$

(10)

Where ε is the square-well depth, λ is the square-well range, $\sigma(r_{12},\Omega_1,\Omega_2)$ is the closest approach of the center of mass of two molecules, $\sigma_{HC}(r_{12},\Omega_1,\Omega_2)$ y $\sigma_{\lambda}(r_{12},\Omega_1,\Omega_2)$ are the closest approach of the centre of mass of two molecules of Hard Core and attractive of two molecules, respectively. Using this potential for evaluating the expression (9), we have

$$\frac{A_{attractive}}{NkT} = -\frac{\rho}{2}\left[e^{\frac{1}{T^*}} - 1\right]\iint f\left(\Omega_1\right)d\Omega_1 f\left(\Omega_2\right)d\Omega_2\quad \left[V_{ex}^{\lambda}\left(\Omega_1,\Omega_2\right) - V_{ex}^{HC}\left(\Omega_1,\Omega_2\right)\right]$$

(11)

or

$$\frac{A_{attractive}}{NkT} = -\frac{\rho}{2}\left[e^{\frac{1}{T^*}} - 1\right]\left[\langle V_{ex}^{\lambda}\left(\Omega_1,\Omega_2\right)\rangle - \langle V_{ex}^{HC}\left(\Omega_1,\Omega_2\right)\rangle\right] \qquad (12)$$

Where $T^* = kT/\varepsilon$ is the reduced temperature and $\langle V_{ex}^{\lambda}(\Omega_1,\Omega_2)\rangle$ is the volume excluded to one attractive core due to the presence of relative orientations of two attractive cores.

In general, the excluded volume of two uniaxial ellipsoids with arbitrary orientations Ω_1 and Ω_2 can be written as

$$V_{ex}^{ellipsoid}(\Omega_1,\Omega_2) = \frac{4}{3}\pi\frac{a}{b}\sigma^3\sum_{n=0}^{\infty}\alpha_{2n}P_{2n}(\Omega_1\cdot\Omega_2) \quad (13)$$

Where *a/b* is the ratio of the semi-major axis and the semi-minor axis, which describes the anisotropy of an ellipsoid, σ is the minor axis and $P_{2n}(\Omega_1 \cdot \Omega_2)$ is the 2nth Legendre polynomial of $\Omega_1 \cdot \Omega_2$. In the case of the HERSW family the necessary volume functions for expression (11) are

$$V_{ex}^{\lambda}(\Omega_1,\Omega_2) = 8V_0\frac{b_\lambda^2}{b^2}\sum_{n=0}^{\infty}\alpha_{2n}P_{2n}(\Omega_1\cdot\Omega_2) \quad (14)$$

and

$$V_{ex}^{HC}(\Omega_1,\Omega_2) = 8V_0\sum_{n=0}^{\infty}a_{2n}P_{2n}(\Omega_1\cdot\Omega_2) \quad (15)$$

Where b_λ is the semi-minor axis of the ellipsoidal shaped SW range.

Additionally, the expression (12) can be expressed by

$$\frac{A_{attractive}}{NkT} = -\frac{\rho}{2}\left[e^{\frac{1}{T^*}}-1\right]\left[\frac{\langle V_{ex}^{\lambda}(\Omega_1,\Omega_2)\rangle}{\langle V_{ex}^{HC}(\Omega_1,\Omega_2)\rangle}-1\right]\langle V_{ex}^{HC}(\Omega_1,\Omega_2)\rangle \quad (16)$$

In this work, we proposed that

$$\frac{\langle V_{ex}^{\lambda}(\Omega_1,\Omega_2)\rangle}{\langle V_{ex}^{HC}(\Omega_1,\Omega_2)\rangle} = \frac{V_0^{attractive}}{V_0^{HC}} = \left(\frac{b_\lambda}{b}\right)^2 \quad (17)$$

ISOTROPIC-NEMATIC PHASE TRANSITION

In general, to evaluate the free energy, the functional must be minimized with respect to $f(\Omega)$. In the isotropic phase calculations are simple because $f(\Omega)$ is uniform and takes the value 1 according to the normalizing condition (1). Substituting this into the full expression for the free energy, the necessary integrals can be evaluated and a closed expression for the isotropic free energy is obtained. The reduced pressure and chemical potential can be calculated by using the usual thermodynamic relationship, given by

$$\frac{PV_0}{kT} = \eta\left(1+\eta\frac{\partial\left(A-A^{ideal}\right)}{\partial\eta}\right) \quad (18)$$

and

$$\frac{\mu}{kT} = \ln(\eta) + \frac{\left(A-A^{ideal}\right)}{NkT} + \eta\left[\frac{\partial\left(A-A^{ideal}\right)}{\partial\eta}\right] \quad (19)$$

Where *P* is the pressure and *μ* is the chemical potential. To evaluate the thermodynamic properties of the nematic phase we must minimize the free energy functional with respect to $f(\Omega)$; however, the procedure can be simplified employing symmetry properties of the nematic phase. In the nematic phase, the symmetry of hard cores is cylindrical and thus $f(\Omega)$ does not depend on the azimuthal angle ϕ and can be written as $f(\theta)$. In all the system considered in this work, the angular dependence of second virial coefficient is expressed using a Legendre's expansion in $(\Omega_1 \cdot \Omega_2)$. The explicit dependence on these Legendre's polynomials can be written employing the addition theorem:

$$P_n(\Omega_1\cdot\Omega_2) = P(\cos\theta_1)P(\cos\theta_2) + 2\sum_{m=1}^{n}\frac{(n-m)!}{(n+m)!}P_n^m(\cos\theta_1)P_n^m(\cos\theta_1)\cos m(\phi_1-\phi_2)$$

(20)

Since $f(\theta)$ does not depend on the azimuthal angle each term in the polynomial series can be integrated with respect to ϕ_1 and ϕ_2, which leaves to:

$$\iint P_n(\Omega_1\cdot\Omega_2)d\phi_1 d\phi_2 = 4\pi^2 P_n(\cos\theta_1)P_n(\cos\theta_2) \quad (21)$$

To perform a final minimization, in this work we adopt the trial function method suggested by Onsager [23].

$$f(\theta) = \frac{\alpha\cosh(\alpha\cos\theta)}{\sinh\alpha} \quad (22)$$

In this approach, the functional form *f (θ)* is assumed by choosing a function with one or more variable parameters. The necessary integrals can be evaluated and the free minimized with respect to the variable parameter η. Usually, in this process, a temperature is chosen and the free energy is minimized over a range of α. The minimized values for η are fitted to a polynomial in α and substituted back into the free energy for the Nematic phase expression. The pressure and chemical potential are then calculated from:

$$\frac{PV_0}{kT} = \eta\left(1+\eta\frac{\partial\left(A(\alpha)-A^{ideal}\right)}{\partial\eta}\right) \quad (23)$$

and

$$\frac{\mu}{kT} = \ln(\eta) + \sigma(\alpha) + \frac{\left(A(\alpha)-A^{ideal}\right)}{NkT} + \eta\left[\frac{\partial\left(A(\alpha)-A^{ideal}\right)}{\partial\eta}\right]$$

(24)

Where σ(α) is obtained by substituting the trial function into the expression (4) and integrating. The isotropic-nematic phase transition is then evaluated by ensuring for a fixing temperature that the chemical potential and pressure of each phase are the same.

MOLECULAR VOLUME

The molecular volume can be defined as the space region that is occupied by the molecule and such space can be related to the spatial distribution of minimal energy of nucleus and electrons in the molecule. The application of quantum theory to chemical systems allows the calculation of this molecular parameters [24] performing a geometry optimization [19]. In a previous works, our group has calculated the molecular volume of PAA considering different levels of theory and the influence of the solvent by mean of an isodensity PCM model [21]. In present work we analyzed the influence of molecular interactions caused by others PAA molecules on the individual molecular volume. We performed geometry optimizations of $(PAA)_5$ employing the PM3 and PM6 semiempirical methods [19-26]. Next, we optimized the $(PAA)_5$ molecule using B3LYP/6-311++G level and the IPCM model [21]. From last calculation we determine the volume value occupied by an isosurface density of 0.08 and 0.002 electrons/Å^3 and we related this to the molecular volumes of the hard and attractive cores for the molecule. All calculations were performed on a server with Intel Core 2 Duo processors

Table 2 *Comparison of experimental parameters of the I-N phase transition at 1 atm for PAA with the theoretical prediction.*

Work	*a:b:c*	σ_0	*1+L/D*	λ	a/b_λ	V_m [A^3]	$(T[K])_{1\ atm}$	η_N	<P_2>	<P_4>	$\Delta S/Nk$
Experiment (PAA) [28]							408.9	0.620	0.550	0.180	0.170
Linder et al. [31]		5				230	408.0	0.220			0.120
Kromhout et al. [32]		5				230	408.0	0.380	0.200		
Eldredge et al. [33]			2.5			230	434.0	0.510	0.970		6.500
			2.5			295	295.0	0.510	0.970		6.500
Baron et al. [34]			2.5			230	627.0	0.450			3.500
			2.5			295	208.0	0.550	0.930		3.250
Flapper et al. [30]			1.464			230	409.0	0.620	0.437		0.536
			1.380			230	409.0	0.621	0.452		0.567
Ypma et al. [35]			3.0				409.0	0.596	0.473		0.590
Cotter M. A. [36]			3.0			230	410.4	0.445	0.542		0.887
Williamson D. C. [11]	3:1:1			3.0		100	408.8	0.548	0.570	0.230	0.670
	3:1:1			3.0		230	409.0	0.548	0.570	0.230	0.670
Tjipto-Margo et al. [10]	3:1.4:1			3.0		230	406.0	0.523	0.400	0.110	0.230
	3:1.45:1			3.0		230	411.0	0.523	0.360	0.090	0.230
Martínez-Richa et al. [14]	3:1:1			3.0		150	409.0	0.562	0.630	0.220	0.800
García-Sánchez et al. [15]	3:1:1			3.0		230	409.0	0.562	0.630	0.220	0.800
	3.5:1:1			3.5		70	409.0	0.519	0.690	0.300	1.070
García-Sánchez et al. [16]	3.5:1:1			3.5		70.7	408.9	0.519	0.690	0.300	1.070
	3.6:1:1			3.6		70.7	408.9	0.511	0.706	0.319	1.124
	3.7:1:1			3.7		70.7	408.9	0.504	0.741	0.373	1.340
González-Cabrera et al [18]	3.5:1:1				1.75	70.7	408.9	0.499	0.972	0.910	2.705
	3.6:1:1				1.80	70.7	408.9	0.493	0.771	0.423	2.788
	3.7:1:1				1.85	70.7	408.9	0.492	0.782	0.443	2.869
In this Work	3.5:1:1				1.75	70.7	408.9	0.493	0.760	0.404	2.704
	3.5:1:1				1.75	70.75	408.9	0.493	0.760	0.404	2.704
	3.5:1:1				1.778	70.75	408.9	0.495	0.765	0.414	2.754
	3.5:1:1				1.928	70.90	408.9	0.504	0.775	0.432	2.969
	3.6:1:1				1.80	70.7	408.9	0.492	0.776	0.493	2.788
	3.6:1:1				1.80	70.75	408.9	0.492	0.776	0.493	2.788
	3.6:1:1				1.828	70.75	408.9	0.494	0.776	0.434	2.833
	3.6:1:1				1.938	70.90	408.9	0.504	0.787	0.453	3.056
	3.7:1:1				1.85	70.7	408.9	0.492	0.785	0.449	2.869
	3.7:1:1				1.85	70.75	408.9	0.492	0.785	0.449	2.869
	3.7:1:1				1.879	70.75	408.9	0.494	0.787	0.453	2.901
	3.7:1:1				2.038	70.90	408.9	0.506	0.777	0.434	3.149

Xenon (Linux Fedora 1 operating system, 2.8 GHz, 1 Gb RAM) and calculated with Q-chem ver. 3.0 [27]. In Table 1 are reported the molecular volumes values obtained from quantum calculations and IPCM methods for different hard attractive cores considering electron densities of 0.08 and 0.002 electrons/Å^3.

Table 1. *Molecular volume obtained for $(PAA)_5$ from PM3, PM6 and B3LYP/6-311++G calculations.*

Optimized geometry methods	Molecular Volume 0.08 electrons/Å^3	Molecular Volume 0.002 electrons/Å^3
PM3	70.90	281.12
PM6	70.85	282.15
B3LYP/6-311++G	70.86	254.25

RESULTS AND DISCUSSION

The main objective in this work is analyzing the predictive capacity of the Convex Peg Model HERSW of pressure-temperature behavior in the Isotropic-Nematic phase transition for PAA at 1 atm. In general, we found that the phase diagram obtained in this work exhibits a Liquid (L) – Vapor (V) coexistence with a critical temperature T_c. Also there is an L-V-N triple point with a triple point temperature T_t. Under this point there is an N phase which coexists with the V phase. Note the triple point and the critical point of the N phase is coexisting with the L phase and above the critical point with a supercritical Isotropic fluid. Maybe the main limitation of this theory is that it is valid only for the Isotropic and Nematic fluids and it cannot predict phases with positional Smectic order (Sm), Crystalline (K), V-L-Sm or V-L-K triple points. Here, it is important to mention that as far as we know, the experimental phase diagram of PAA does not show these phases and triple points [28] which offers new possibilities to use perturbation theories for these kinds of studies [15, 29].

In Table 2, we compared the theoretical predictions for the PAA I-N phase transition at 1 atm, with the experimental data reported [28]. In this table <P_2> is the second rank order parameter, <P_4> is the four rank order parameter and $\Delta S/Nk$ is the entropy change. Observe that the all theories predict correctly the transition temperature. For the packing fraction, Flapper *et al* [30] by using an equation of state for hard sphere predicted adequately the properties considered in the Table 2. However, the others theories underestimate such properties even though the biaxial cores are used. It has been observed [10] that for systems formed by biaxial ellipsoids the I-N phase transition shifts to higher densities by increasing their biaxiality. Thus the opposite trend observed in Table 2 suggests the biaxial core theory overestimates the angular dependence on the attractive forces and then it induces a shift on the phase transition at lower densities. Biaxiality decreases the density jump in the I-N transition and reduces the orientational order in the nematic phase. These effects are predicted correctly by the biaxiality core theory when it is compared with the uniaxial models. Also, the entropy change in the phase transition is well represented by using a biaxial core, and the effect can be explained because the density, which jumps for the I-N phase transition, is smaller for these models. Also, it is important to mention that, in order to improve the prediction of the PAA isotropic-nematic behavior, several approximations have been proposed. Thus, most of them include higher order virial coefficients since the inclusion of these parameters causes a higher computational cost. Additionally, some terms in those theories employ fitting parameters without physical meaning. Additionally, an advantage of the Convex Peg model used in this work is related to the inclusion of molecular measurable parameters such as the molecular volume in the prediction. In where the terms employed to improve the prediction a have physical meaning.

Figure 2 shows a comparison between the HERSW model and experimental data [28], in the figure, the best prediction is obtained for the case, which considers the interaction between molecules, which a/b=3.5, V_0=70.86 Å^3 and a/b_λ=1.85. In this context, Figure 3 shows that for a/b=3.6, the best theoretical prediction was obtained when the model considers the volume (V_0=70.86 Å^3) and the parameter a/b_λ=1.9. Finally, in Figure 4 we can see the same result as in the previous cases, as in the case a/b=3.7, the model that better describes the transition is when the molecular interaction is considered, it is for V_0=70.86 Å^3 and a/b_λ=1.95. On the other hand, in Figure 5 a comparison of the theoretical model with experimental data is shown. In all cases the molecular volume employed was V_0=70.86 Å^3 and different values for a/b_λ. It is possible to observe that the best prediction is for a/b_λ=1.95.

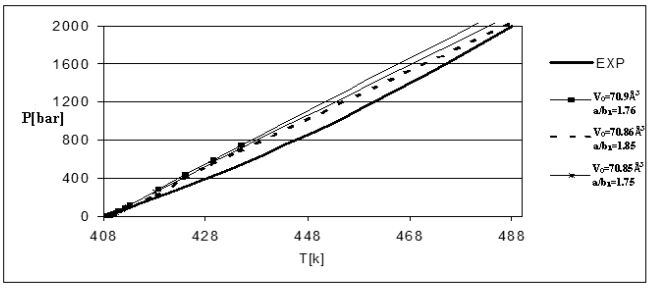

Figure 2 *Comparison between theoretical prediction HERSW model (with a/b=3.5 and different values for a/ b_λ) and experimental data of pressure-temperature behavior in the I-N phase transition at 1 atm of PAA [28].*

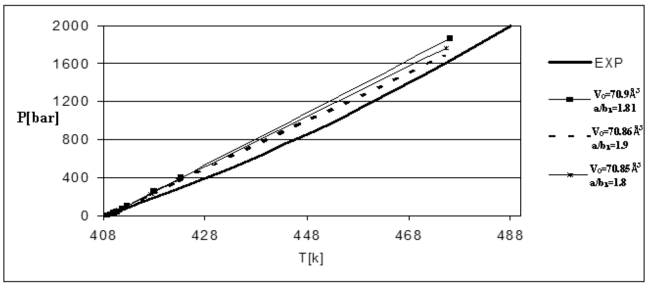

Figure 3 *Comparison between theoretical prediction of HERSW model (with a/b=3.6 and different value for a/ b_λ) and experimental data of pressure-temperature behavior in the I-N phase transition at 1 atm of PAA [28].*

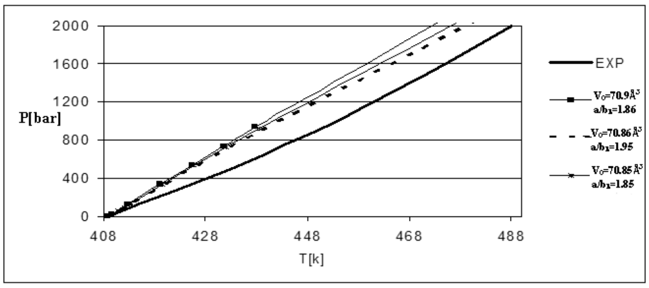

Figure 4 *Comparison between theoretical prediction HERSW model (with a/b=3.7 and different value for a/ b_λ) and experimental data of pressure-temperature behavior in the I-N phase transition at 1 atm of PAA [28].*

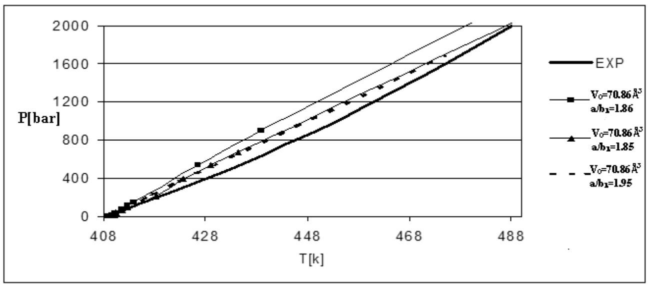

Figure 5 *Comparison between theoretical prediction HERSW model (with V_0=70.9 Å^3 and different values for a/ b_λ) and experimental data of pressure-temperature behavior in the I-N phase transition at 1 atm of PAA [28].*

CONCLUSION

In this work, we used the PAA molecular volume value obtained using PM3, PM6, DFT calculations and considering the molecular interaction among PAA molecules [28]. We found the best prediction for experimental data appears when the effect of the molecular interaction is considered into the volume calculation. Specifically for a/b=3.7, V_0=70.86 Å^3 and a/b_λ=1.95 the best prediction was obtained. As to future directions, we confine ourselves below to isolating a few specific topics on particular materials considered above. Thus we single out:

1. To incorporate in Helmholtz´s free energy terms a contribution due to the flexibility. Although for the case of the PAA is quite small, for other liquid crystal this contribution is significant.
2. To use the HERSW model biaxial cores.
3. To study other molecules like PAP, 5CB, MBBA and EBBA by mean of the HERSW model and the molecular volume value obtained from PM3, PM6 and DFT calculations considering the interaction with neighbor molecules.

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