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Publisher *Taylor & Francis*

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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Johri, M. , Johri, G. K. and Roberts, J. A.(1991) 'Determination of Effective Potentials for Non-polar Liquids Using the Continuum Dielectric Model', *Physics and Chemistry of Liquids*, 24: 1, 71 — 77

To link to this Article: DOI: 10.1080/00319109108030650

URL: <http://dx.doi.org/10.1080/00319109108030650>

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DETERMINATION OF EFFECTIVE POTENTIALS FOR NON-POLAR LIQUIDS USING THE CONTINUUM DIELECTRIC MODEL*

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(Received 8 April 1991)

The "effective potential" for each system, nitrogen, argon, krypton, xenon, methane, benzene, carbon tetrachloride, carbon disulfide, *n*-hexane and cyclohexane was calculated by using the Clausius-Mossotti, Onsager and Kirkwood reaction fields with Lennard-Jones and Kihara potential parameters assumed. It was found that the Kirkwood reaction field with an assumed Kihara potential is a useful technique to study interactions arising due to physical association and chemical bonding.

KEY WORDS: Reaction field, polarizability.

1 INTRODUCTION

Physical association and chemical bonding can be understood through the study of the effective potential of a given system. It is convenient to work with a pair-wise potential to simplify the understanding of the statistical mechanics of liquids and solutions. Hirshfelder¹ has described intermolecular forces in liquids and has described reaction field techniques. The Lennard Jones (LJ) and the Kihara (K) potentials may be considered when the effective potential of interaction is calculated. A knowledge of the distribution function, the reaction field, the shape of the molecular cavity, a dimensionless parameter and the nature of the interaction are required to make the required calculation. In addition, the molecular parameters, dipole moment, the ionization potential, the polarizability, etc., must be known. Such calculations are simpler for non-polar molecules than for others. Therefore, we have chosen the molecules nitrogen, argon, krypton, xenon, methane, benzene, carbon tetrachloride, carbon disulfide, *n*-hexane and cyclohexane since they have almost spherical molecular cavity geometry.

The effective potential for each system was calculated using the Clausius-Mossotti, the Onsager and the Kirkwood reaction field with the Lennard-Jones and the Kihara potentials assumed. The theoretical approach used¹ required some modification to apply to the spherical molecular geometry assumed for the systems studied.

* This work was supported in part by grant B-0842 from the Robert A. Welch Foundation, Houston, Texas.

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2 THEORY

For non-polar interactions and almost spherical molecular cavities, the main part of the effective potential in liquids is given approximately by¹ the following equation:

$$V^{\text{eff}}(R, d) \approx V(R) + (\Delta/n_{\text{in}})[C/(R-l)]DL, \quad (1)$$

where R is the separation between two molecules of the liquid of density d . The quantities Δ and L are given by Hirschfelder¹, n is the index of refraction of the medium, and D is defined later. The term C is the dispersion coefficient of the Kihara (K) potential given by:

$$V^K(\rho) = C[\sigma^6/\rho^{12} - 1/\rho^6], \quad (2)$$

where σ is a potential parameter and ρ is measure of the range over which the interaction holds. The K-potential given in Eq. (2) takes into consideration the size and shape of the molecule under consideration by assuming a core parameter of size l . The shortest distance of separation between two molecules of the liquid is given by ρ^0 for a fixed orientation and a separation distance of R between molecular centers. the quantities ρ^0 , C and σ are related by the equations:

$$\rho^0 = (2)^{1/6}\sigma \quad (3)$$

$$C = 4\epsilon\sigma^6 \approx (3/4)I\alpha^2, \quad (4)$$

where I is the ionization potential, α the polarizability and ϵ is the depth of the potential minimum. Two conditions for l hold. For the Lennard-Jones potential, $l = 0$, whereas, for the Kihara potential $l \neq 0$ since there is an interaction between the peripheral atoms even when the center-to-center R^6 effect is weak. The Lennard-Jones potential can be expressed as:

$$R^0(LJ) = \rho^0 + l. \quad (5)$$

Hirshfelder has given values of Δ and L as¹:

$$\Delta = [I_a(I_b + I_{b'} + I_a)]/\{(I_a + I_b)(I_{b'} + I_a)\} \quad (6)$$

and

$$L = \langle \sum_a \{(R_{bb'} - l_{bb'})^3 R_a^3 [1 + 3 \cos(\theta_b) \cos(\theta_{b'}) \cos(\theta_a)]\} / [(R_{ba} - l_{ba})^3 (R_{b'a} - l_{b'a})^3] \rangle_a, \quad (7)$$

where I_a is the ionization potential of the solvent molecule a , I_b and $I_{b'}$ that for the solute molecules b and b' , respectively. The angle θ_i is the angle whose vertex is on molecule i . In the continuum dielectric model, we have assumed the product between

L and Δ to be 1.5. i.e.,

$$L\Delta \equiv 1.5. \quad (8)$$

This approximation, Eq. (8), avoids computational difficulty and eliminates the requirement that L be calculated. We have assumed the validity of Eq. (8) for solute-solute interaction or for pure liquid where $b = b' = a$ holds. It is also assumed that $R \geq 3r_0$, where r_0 is the radius of the molecule. An exact solution of Eq. (7) for L can be obtained by a computer simulation technique.

Derivation of the expression for D

The dependence of the polarization p on the electric field strength E is given² by the following expression:

$$p = (\varepsilon - 1)E/4\pi, \quad (9)$$

where ε is called the dielectric constant. The induced polarization p_α is then given by;

$$p_\alpha = \sum_k N_k \alpha_k (E_i)_k, \quad (10)$$

where N is the number of particles per cm^3 , α is the scalar polarizability of any particle and E_i is the average field strength acting upon that particle. The calculation of E_i is a central problem in the theory of electric polarization. We have adopted a continuum approach in which the given molecule interacts with its environment producing a field of strength E_i . If the system is composed of non-polar species, Eqs (9) and (10) become equal and

$$(\varepsilon - 1)E/4\pi = \sum_k N_k \alpha_k (E_i)_k. \quad (11)$$

The Lorentz equation for the internal field and Maxwell field for a spherical molecular cavity is

$$E_i = [(\varepsilon + 2)/3]E. \quad (12)$$

Thus, from Eqs (11) and (12) we get

$$(\varepsilon - 1)/(\varepsilon + 2) = (4\pi/3)\sum_k N_k \alpha_k. \quad (13)$$

This is the "Clausius–Mossotti" relation with n (the index of refraction) $\equiv \varepsilon^2$.

$$D = (n^2 - 1)/(n^2 + 2) = (4\pi/3)N\alpha. \quad (14)$$

In this derivation the Lorentz field, Eq. (2), was used for both the internal and the external directing field. Onsager⁴ showed, however, that this is not permissible because of the manner in which the Lorentz field arises. For non-polar liquids the internal field can be considered as the sum of two parts; one the cavity field and the other the reaction field of the dipole induced in the molecule.

In order to calculate the directing field E_d , the polarizability of the molecule must be considered. The field E_d produces a dipole $\propto E_d$ and a reaction field $f \propto E_d^2$. Thus E_d is given by

$$E_d = 3n^2 E [1/(1 - f\alpha)] / (2n^2 + 1) \quad (15)$$

with

$$f = 2(n^2 - 1)/a^3(2n^2 + 1). \quad (16)$$

Therefore,

$$D = 1 - f\alpha = 1 - 2(n^2 - 1)/(2n^2 + 1), \quad (17)$$

with $\alpha \equiv a^3$ and it is assumed that the particles are spherical with no specific interaction between particles.

Kirkwood⁵ generalized Onsager's treatment for the case of specific molecular interactions. The method consists of taking a region with N molecules which are treated explicitly and $N - N$ molecules assumed to comprise the continuum. The approximations can be adjusted by changing the value of N . Kirkwood introduced

Table 1 Interaction potentials in non-polar liquids with a comparison of Leonard-Jones and Kihara potentials.

System	Clausius-Mossotti reaction field $V^K(\rho^0)$ (erg-cm ⁵) (10 ⁵²)		Onsager reaction field $V^K(\rho^0)$ (erg-cm ⁵) (10 ⁵²)		Kirkwood reaction field $V_K(\rho^0)$ (erg-cm ⁵) (10 ⁵²)		$V^{LJ}/V^K(\rho^0)$ ($\times 100$)
	D		D		D		
Nitrogen	0.131	3.07	0.676	15.872	0.933	21.909	85.25
Argon	0.148	3.159	0.741	15.814	0.962	20.530	86.01
Krypton	0.180	7.030	0.695	27.147	0.692	36.912	86.01
Xenon	0.227	19.488	0.630	54.085	0.917	78.723	84.39
Methane	0.181	7.377	0.692	28.205	0.945	38.517	90.09
Benzene	0.292	145.789	0.548	273.604	0.867	432.871	63.12
Carbon tetrachloride	0.273	183.015	0.572	369.911	0.884	571.678	59.69
Carbon disulfide	0.354	122.992	0.477	165.727	0.814	282.811	74.19
<i>n</i> -hexane	0.234	171.370	0.621	454.791	0.913	668.638	55.52
Cyclohexane	0.256	146.868	0.593	340.207	0.913	523.793	59.12

a factor “g”-the Kirkwood factor which when set equal to 1 gives the result of Onsager. Kirkwood neglected translational fluctuations as had been done in the derivation of the Clausius–Mossotti equation. Buckingham³ derived an expression for D from Kirkwood’s concept of the reaction field as given below:

$$D = 9n^2/[(2n^2 + 1)(n^2 + 2)] \quad (18)$$

which differs from Onsager’s expression for D by a factor of $3n^2/(n^2 + 1)$ and which arises when short-range forces are included. Equation (1) can now be used to calculate the interaction potential $V = V^{\text{eff}}(R, d) - V(R)$ for the solute-solute interaction ($n_{\text{int}} \equiv 1$). i.e.,

$$V = (9/8)I\alpha^2D/\rho^0. \quad (19)$$

In Eq. (19), the reaction field term is defined as $1/D^2$ for a spherical cavity with a shape factor of $1/3$ when SI units are employed.

3 RESULTS AND DISCUSSION

The interaction potential, Eq. (19), was derived from Eq. (1) with the approximation given in Eq. (8) for the continuum dielectric model and an assumed spherical cavity geometry. It was also assumed that a multiple of the ionization potential for a molecule (Δ) is equal to the ionization potential (I) in accordance with the approximation made by London⁶. This result can be obtained when the proportionality constant (μ) is set equal to 1 in the equation $\Delta = \mu I$. The constant of proportionality varies between 1 and 2, as pointed out by Pitzer⁶. The polarizability was taken from Ref. [1]. The parameter ρ^0 in Eq. (5) is the Kihara potential parameter⁸. The value of D for the Clausius–Mossotti², the Onsager⁴ and the Kirkwood⁵ reaction field was derived from Eqs. (14), (17) and (18), respectively.

The main part of the effective potential, the interaction potential, obtained from Eq. (19) for nitrogen, argon, krypton, xenon, methane, benzene, carbon tetrachloride, carbon disulfide, *n*-hexane and cyclohexane, along with the value of D , are given in Table 1. The various molecular parameters used in the calculations are given in Table 2.

The principal advantage in using Eq. (19) is that we do not need to consider exact calculations for the dimensionless parameters L in Eqs. (1) and (19) and Δ in Eq. (1) to obtain satisfactory results.

All of the systems considered are non-polar or weakly polar. Both carbon disulfide and, *n*-hexane have been reported by Mopsik⁹ to be slightly polar. (Dipole moments are slightly less than 0.3D.) Thus, the approximation in Eq. (8) is reasonable for the spherical molecular cavity model for non-polar molecules.

An examination of the results in Table 1 shows that interaction potentials can be ranked in the following order

$$V_{\text{Kirkwood}}^{\text{K}} > V_{\text{Onsager}}^{\text{K}} > V_{\text{Clausius–Mossotti}}^{\text{K}} \quad (20)$$

Table 2 Refractive index n , ionization potential I , polarizability α , the Kihara gas phase potential minimum ρ^0 and the quasi-spherical Kihara core diameter l .

System (temp. K)	n	I (eV)	α (\AA^3)	ρ^0 (\AA)	l (\AA)
Nitrogen (67)	1.31050	15.70	1.703	3.49	0.604
Argon (81)	1.23300	15.75	1.653	3.63	0.273
Krypton (112)	1.28800	13.99	2.450	3.87	0.292
Xenon (155)	1.37100	12.16	4.010	4.10	0.347
Methane (102)	1.29200	12.99	2.567	3.78	0.416
Benzene (300)	1.49635	9.25	10.390	3.60	2.103
Carbon tetrachloride (297)	1.47759	11.46	10.490	3.51	2.370
Carbon disulfide (291)	1.62704	10.08	8.440	3.72	1.294
<i>n</i> -hexane (271)	1.38460	10.40	11.810	3.57	2.860
Cyclohexane (296)	1.42470	9.50	10.990	3.60	2.489

and the LJ-potential gives smaller values of the interaction potential than does the Kihara potential. This difference arises due to a neglect of the core potential l in the LJ-potential. Use of the LJ-potential in the treatment of nitrogen, argon, krypton, xenon and methane gives 10 to 15% less interaction potential than that found when the K-potential is employed in the calculations. When the same procedure is employed for benzene, carbon tetrachloride, carbon disulfide, *n*-hexane and cyclohexane, the difference between the two approaches gives much larger differences.

The effect of considering a slightly polar or a non-spherical molecular cavity in the systems considered in this work should not alter the results more than a few percent. The approximations made should lead to results that are good to better than 10%.

It is worth noting that a reaction field introduced² when the Clausius–Mossotti equation is employed requires that higher order terms in the energy of interaction be included in the calculations. Also, the model does not take into consideration either long-range solute-solute interactions, which are effective in even in the dilute solution limit, or the short-range (complex) solute-solute interactions. Onsager's⁴ reaction field concept accounts for the local field correction and includes the long range solute-solute interactions in the liquid environment. The solute-solvent and the short range solute-solute interactions, however, were not considered. The approach of Kirkwood⁵ takes into consideration both long and short range interactions. Thus, the variations of the interaction potential given in Eq. (13) follows more closely

the trend predicted by Kirkwood's approach. His reaction field approach is convenient and seems to better predict interactions among molecules in the liquid environment, which may arise due to associative behavior or chemical bonding or both depending upon the nature of the molecules.

4 CONCLUSIONS

From the results of this investigation, it appears that the Kihara potential and the Kirkwood reaction field used in the calculation of the effective potential provide useful information about the interactions arising due to physical association of a system and/or the chemical bonding existing between molecules in solution.

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