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The interaction of xenon with *n*-alkane solvents. Comparison between different cavity models

Joaquim J. Moura Ramos [a] and Raquel M.C. Gonçalves [b]

[a] *Centro de Química Física Molecular INIC, Complexo I, IST, Av Rovisco Pais, 1096 Lisboa Codex (Portugal)*
[b] *CECUL (INIC), FCL, Calçada Bento da Rocha Cabral, 14, 1200 Lisboa (Portugal)*

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Abstract

A recently proposed model for calculating the energetics of cavity formation in liquids is used to study the interaction of rare gases in *n*-alkane solvents. It is observed that the energy and the entropy of interaction of a given solute with different *n*-alkane solvents are very similar and show a monotonic variation with the *n*-alkane carbon number. This behaviour, which is not observed when other methods are used to calculate the energetics of cavity formation, reinforces the idea of the similarity of the contact energies of the different *n*-alkane molecules

INTRODUCTION

The solubility of xenon in organic liquids, and particularly in *n*-alkanes, was extensively studied by Pollack and coworkers [1–3]. The choice of xenon as a prototype solute gas was justified by the different applications of this rare gas. Xenon is highly soluble in lipids and fats, and this property correlates with its potency for general anaesthesia. It seems that the rare gas concentrates in liquids of cell membranes in the central nervous system, but the preferential interaction sites are not well known. In this context it is important to study the interaction of xenon with different media. Xenon is also used in nuclear medicine, in deep-sea diving and in nuclear reactor safety.

More recently, Park et al. [4] used the experimental data obtained by Pollack and Himm [1] for xenon/*n*-alkane systems in order to examine the different models proposed in the literature to estimate the energetics of cavity formation in liquids. The choice of the Xe/*n*-alkane systems is a good choice because Pollack's experimental data are very accurate, not only for the Gibbs energy but also for the enthalpy and the entropy of the solution process. Furthermore, the intermolecular interactions in such systems are weak, short range van der Waals interactions which can be well described by a Lennard-Jones potential, and xenon and the other rare gases are chem-

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ically inert and spherical solutes. The fact that the solute is hard and spherical, with no strong directional interactions with the solvent, defines good conditions for the use of the scaled particle theory (SPT) in the study of these systems [5]. However, the Xe/*n*-alkane systems are somewhat inconvenient to test the cavity models. The most important drawback is that there is a strong asymmetry in the molecular size and shape between the solute and the solvent. Since the solute size is very small compared with that of the solvent, the application of different models to calculate the energetics of cavity formation may lead to unreasonable results. The *n*-alkane molecules in the liquid state present a very strong shape anisotropy, and one may doubt whether it is possible to describe such molecules by a hard sphere diameter. Moreover, the results obtained by the SPT are strongly dependent on the solvent hard sphere diameter, as has been frequently emphasised [5,6]. For the model based on the microscopic surface tension concept [7] it is difficult to quantify the dependence of the surface tension, at the surface of those small cavities, on cavity curvature (this problem will be discussed later).

In a recent paper [8] we proposed a new model for calculating the energetics of cavity formation in liquids. The new model considers the cavitation process as work done against the surface forces of the solvent, as was the case for the Sinanoglu model [7,9] (also called the SRMR method). Nevertheless it differs from this approach in the description of the reference cavity formation process. The reference cavity is that which has the same volume and shape as the space occupied by a single molecule in the pure liquid, and its energetics can be calculated using [8]

$$E_{c0} \approx H_{c0} = 5.365(1+\omega)RT_c \tag{1}$$

$$S_{c0} = -5.365\omega R \tag{2}$$

$$A_{c0} \approx G_{c0} = 5.365R[T_c + \omega(T_c + T)] \tag{3}$$

where ω is the Pitzer acentric factor and T_c is the critical temperature. In addition, through this model we are able to calculate the energetics of any cavity by carefully taking into account the relative shape of the solute and the solvent molecules [6,8,10]. In the present paper we wish to apply the new model to the study of the interactions between xenon (and other rare gas solutes) and *n*-alkane solvents. Our conclusions will be compared with those obtained by the SPT and by the Sinanoglu method, and we will show that our model enables a most satisfactory description of the interactions.

THE THERMODYNAMICS OF SOLUTION AND THE CHOICE OF THE STANDARD STATE

The experimental data obtained by Pollack and Himm [1] are presented on the mole fraction scale. The standard state for the solute vapour phase is the pure ideal gas at a pressure of 1 atm and at the experimental temperature. The definition of the standard state of the liquid phase is based on the so-called asymmetric convention (the activity coefficient $\gamma_i \to 1$ when $x_i \to 0$). The standard state which corresponds to this convention is simply a hypothetical one obtained by extrapolating Henry's law up to the pure solute. So, this standard state would correspond to a hypothetical pure solute in which the environment of each molecule would be the same as that at infinite dilution. The thermodynamic process corresponding to the quantities given by Pollack is

$$\text{Xe ideal gas at } p = 1 \text{ atm} \xrightarrow{X_s(x)} \text{Xe in solution in the hypothetical state} \tag{4}$$

where $X_s(x)$ represents the thermodynamic parameter associated with the process expressed on the molar fraction scale. In order to use these data to check both cavity models we need to convert them into the molar concentration scaled quantities (c). The thermodynamic dissolution properties $X_s(c)$ refer to the following process

$$\text{Xe ideal gas at } \rho_s^g \xrightarrow{X_s(c)} \text{Xe in solution at } \rho_s^l \tag{5}$$

where ρ_s^g and ρ_s^l are the number densities (or molar concentrations) of the solute in the gas and in the solution respectively and $\rho_s^g = \rho_s^l = p_s/RT$, where p_s is the partial pressure of the solute in the gas. The aim of the present work is to study the interactions between the solute and the solvent, or the solvation of the solute. As emphasised by Ben-Naim [11], the traditional standard thermodynamic quantities of transfer are inadequate measures of the solvation phenomenon. The solvation process of a solute molecule in a solvent is defined as the process of transferring the solute molecule from a fixed position in an ideal gas phase into a fixed position in the liquid solvent, and the solvation thermodynamic quantities X_s^* can be derived from the conventional standard thermodynamic quantities of solution using the following equations

$$G_s^* = G_s(x) - RT \ln(RT/V) \tag{6}$$

$$S_s^* = S_s(x) + R \ln(RT/V) - RT\alpha + R \tag{7}$$

$$H_s^* = H_s(x) - RT^2\alpha + RT \tag{8}$$

In these eqns. V and α are respectively, the molar volume and the isobaric thermal expansion coefficient of the solvent. We point out here that the quantity RT/V must be expressed in atmospheres if we consider as the standard state of the gas phase that at which the partial pressure of the solute is $p_s = 1$ atm.

In this work we thus prefer to use the solvation thermodynamic quantities X_s^*, instead of the dissolution quantities based on the molar concentration scale $X_s(c)$. Table 1 shows these solvation quantities for xenon in n-alkanes.

TABLE 1

Solvation Helmholtz energy A_s^*, solvation energy E_s^* and solvation entropy S_s^* for xenon in n-alkanes at 298.15 K [a]

Solvent	A_s^* (kJ mol^{-1})	E_s^* (kJ mol^{-1})	S_s^* (J K^{-1} mol^{-1})
n-Pentane	−6.45	−12.94	−21.8
n-Hexane	−6 31	−12.29	−20 2
n-Heptane	−6 09	−11.03	−16.6
n-Octane	−5 92	−11 02	−17.1
n-Nonane	−5.79	−10.74	−16.6
n-Decane	−5.66	−10.61	−16.6
n-Undecane	−5 54	−10.42	−16.4
n-Dodecane	−5.45	−10.24	−16.1
n-Tridecane	−5 32	−10.23	−16.5
n-Tetradecane	−5.26	−10.05	−16 1
n-Pentadecane	−5 17	−10.01	−16.2
n-Hexadecane	−5.07	−9.79	−15 7

[a] These values have been obtained from the corresponding values in the mole fraction scale given in ref 1.

The gas phase term RT has been subtracted from G_s^* and H_s^* in order to obtain the Helmholtz energy A_s^* and the energy E_s^*. Table 2 shows the same type of data for different rare gases in n-hexane, n-decane and n-tetradecane.

APPLICATION OF THE CAVITY MODELS: THE INTERACTION ENERGIES OF RARE GASES WITH *N*-ALKANES

The thermodynamic parameters X_s^* associated with the process (5) can be described as a sum of two terms: the cavity term and the interaction term

$$X_s^* = X_{cav} + X_{int} \tag{9}$$

It emerges that the solute–solvent interaction can be estimated from the experimental X_s value and the calculation of X_{cav} using an appropriate cavity model

$$X_{int} = X_s^* - X_{cav} \tag{10}$$

To calculate X_{cav} we will consider three models: the method we recently proposed [8], based on eqns. (1), (2) and (3), the scaled particle theory developed by Pierotti [13–15] and the Sinanoglu model [7]. According to this last model the energetics of the reference cavity are calculated by the following equations

$$E_{c0} \approx H_{c0} = H_v \tag{11}$$

$$A_{c0} \approx G_{c0} = -RT \ln p + RT \ln(V_g/V_0) \tag{12}$$

TABLE 2

Solvation Helmholtz energy A_s^*, solvation energy E_s^* and solvation entropy S_s^*, for different rare gases in *n*-hexane, *n*-decane and *n*-tetradecane at 298.15 K [a]

	n-Hexane			*n*-Decane			*n*-Tetradecane		
	A_s^* (kJ mol^{-1})	E_s^* (kJ mol^{-1})	S_s^* (J K^{-1} mol^{-1})	A_s^* (kJ mol^{-1})	E_s^* (kJ mol^{-1})	S_s^* (J K^{-1} mol^{-1})	A_s^* (kJ mol^{-1})	E_s^* (kJ mol^{-1})	S_s^* (J K^{-1} mol^{-1})
He	5.02	7.00	6.7	6.30	6.97	2.3	7.09	5.21	−6.3
Ne	4.16	4.61	1.5	5.29	5.64	1.2	6.10	5.20	−3.1
Ar	−0.60	−3.73	−10.5	0.40	−2.25	−8.9	0.97	−2.15	−10.5
Kr	−3.12	−6.76	−8.8	−2.22	−5.65	−11.5	−1.77	−6.00	−14.2
Xe	−6.31	−12.29	−20.2	−5.66	−10.61	−16.6	−5.26	−10.05	−16.1

[a] The solution properties in the mole fraction scale were taken from refs. 1 and 12.

where H_v is the solvent vaporisation enthalpy at 25 °C, p its saturated vapour pressure at 25 °C (in atmospheres), V_0 its molar volume at 25 °C and V_g the molar volume of an ideal gas at 25 °C and 1 atm. Many authors [5,6] have pointed out some limitations of the SPT: the strong dependence of the results on the hard sphere diameter values of the solvent, the impossibility of taking into account the molecular shape of the solute, and its non-applicability to systems where strong and directional interactions occur. Pullman and coworkers [16] tried to improve Pierotti's version of the SPT, describing the solute as an ensemble of intersecting spheres. This modification enables account to be taken of the molecular shape of the solute and probably allows the description of some orientational correlations between the solute and the surrounding solvent. Nevertheless, in the rare gases/*n*-alkane solutions the solute is hard and spherical, so that the original Pierotti version of the SPT can be used to describe those systems.

To calculate the cavity term according to our new model, eqns. (1), (2) and (3) are used with respect to the energy, the entropy and the Helmholtz energy of the reference cavity. Now we need to describe the relative shape and curvature of the solute cavity and of the reference cavity. The rare gases are spherical and the reference cavities in *n*-alkanes are cylindrical with radius 3.5 Å, [6]. The molar volume of xenon is 42.6 cm^3 mol^{-1} if calculated from the density at the normal boiling point. If we consider $V = 4\pi r^3 N_A/3$, where N_A is Avogadro's constant, we obtain for the radius of the Xe cavity $r = 2.56$ Å. This radius is smaller than those for small organic molecules like acetone, *n*-pentane or neopentane, and is also smaller than the radius of 3.5 Å we suggested [6] for the cylindrical cavities occupied by the *n*-alkane molecules in the liquid state. This situation is even more pronounced for other rare gases. Under the circumstances, it therefore seems acceptable to consider that, when a small solute is dissolved in a solvent whose molecular curvature is higher than the molecular curvature of the solute, the cavity occupied by the solute in solution will have a curvature which is imposed by the solvent molecular curvature. We thus propose to describe the solutions of rare gases at infinite dilution in *n*-alkanes considering that the solvent is cylindrical and that the solute cavity is spherical and has the same curvature as the reference cavity. Then the thermodynamic parameters associated with the cavity of rare gases in *n*-alkanes X_c can be evaluated from those of the reference cavity X_{c0} by the equation

$$X_c = X_{c0}^{*} V^{2/3}/(0.140 V_0 + 11.3509) \qquad (13)$$

where V and V_0 are, respectively, the molar volume of solute and solvent [6,10]. This seems to be the most realistic picture of the studied systems, and the results we will present confirm this idea. According to the Sinanoglu model, the curvature of the solute cavity is taken as being dependent on the solute/solvent molecular volume ratio [7], and in this case X_c can be obtained from X_{c0} using the following equations

$$E_c = 40.84\sigma_0 A\left(V^{2/3} - V_0^{2/3}\right) + E_{c0} \tag{14}$$

$$A_c = 40.84\sigma_0\left(V^{2/3} - V_0^{2/3}\right) + A_{c0} \tag{15}$$

TABLE 3

Energies and entropy of cavity formation for the xenon solute in *n*-alkane solvents. The first line corresponds to values calculated by our model [eqns. (1), (2), (3) and (13)], the second line to those obtained from SPT, and the third line to those obtained by the Sinanoglu model [eqns (14) and (15)]

Solvent	A_{cav} (kJ mol^{-1})	E_{cav} (kJ mol^{-1})	S_{cav} (J K^{-1} mol^{-1})
n-Pentane	13.13	11.64	−5.0
	14.96	17.16	7.4
	6.93	5.57	−4.6
n-Hexane	13.76	12.12	−5.5
	15.55	16.70	3.9
	7.01	5.91	−3.7
n-Heptane	14.25	12.47	−6.0
	16.38	16.91	1.8
	6.99	6.89	−3.6
n-Octane	14.61	12.71	−6.4
	16.81	16.76	−0.2
	7.09	7.75	2.2
n-Nonane	14.88	12.89	−6.7
	17.56	16.99	−1.9
	7.12	8.37	4.2
n-Decane	15.04	12.99	−6.9
	17.80	17.36	−1.5
	7.30	9.45	7.3
n-Undecane	15.25	13.12	−7.2
	18.77	18.90	0.4
	7.33	11.10	12.6
n-Dodecane	15.26	13.09	−7.3
	19.00	18.36	−2.1
	7.74	11.91	14.0
n-Tridecane	15.34	13.13	−7.4
	19.31	18.86	−1.5
	–	13.55	–
n-Tetradecane	15.61	13.30	−7.8
	19.37	18.84	−1.8
	–	14.31	–
n-Pentadecane	15.44	13.15	−7.7
	19.38	18.73	−2.2
	–	15.83	–
n-Hexadecane	15.42	13.11	−7.7
	19.12	18.48	−2.1
	–	17.33	–

where σ_0 is the surface tension of the solvent at 25 °C and A is given by

$$A = 1 - T\left(\frac{1}{\sigma_0}\frac{\mathrm{d}\sigma_0}{\mathrm{d}T} + \frac{2}{3}\alpha_0\right) \tag{16}$$

where α_0 is the isobaric thermal expansion coefficient of the solvent. The factor 40.84 contains constants and unit conversion factors which enable X_c

TABLE 4

Xenon/*n*-alkane interaction energies and entropy. The cavity terms were calculated by our model (first-line), the SPT (second line), and the Sinanoglu model (third line)

Solvent	A_{int} (kJ mol^{-1})	E_{int} (kJ mol^{-1})	S_{int} (J K^{-1} mol^{-1})
n-Pentane	−19.68	−24.58	−16.8
	−21.41	−30.10	−29.2
	−13.38	−18.51	−17.2
n-Hexane	−20.07	−24.41	−14.7
	−21.86	−28.99	−24.1
	−13.32	−18.20	−16.5
n-Heptane	−20.35	−23.50	−10.6
	−22.47	−27.94	−18.4
	−13.08	−17.92	−13.0
n-Octane	−20.54	−23.73	−10.8
	−22.73	−27.78	−16.9
	−13.01	−18.77	−19.3
n-Nonane	−20.67	−23.63	−10.0
	−23.35	−27.73	−14.7
	−12.91	−19.11	−20.8
n-Decane	−20.70	−23.60	−9.7
	−23.48	−27.97	−15.1
	−12.96	−20.06	−23.9
n-Undecane	−20.79	−23.54	−9.2
	−24.32	−29.32	−16.8
	−12.87	−21.52	−29.0
n-Dodecane	−20.69	−23.33	−8.9
	−24.45	−28.60	−14.0
	−13.19	−22.15	−30.1
n-Tridecane	−20.66	−23.36	−9.0
	−24.63	−29.09	−15.0
	–	−23.78	–
n-Tetradecane	−20.87	−23.35	−8.3
	−24.63	−28.89	−14.3
	–	−24.36	–
n-Pentadecane	−20.61	−23.16	−8.5
	−24.55	−28.74	−14.0
	–	−25.84	–
n-Hexadecane	−20.48	−22.99	−8.0
	−24.19	−28.27	−13.6
	–	−27.12	–

TABLE 5

The energy of interaction (kJ mol^{-1}) between the rare gases and solvents *n*-hexane, *n*-dodecane and *n*-tetradecane. The cavity terms were calculated by our model (first line), the SPT (second line) and the Sinanoglu model (third line)

	n-Hexane	*n*-Decane	*n*-Tetradecane
Helium	1.83	1.42	−0.47
	−1.43	−1.75	−4.21
	13.57	10.71	4.42
Neon	−1.84	−1.27	−1.88
	−4.53	−3.82	−5.02
	8.88	6.95	1.93
Argon	−12.99	−12.17	−12.31
	−16.12	−15.11	−16.08
	−4.50	−6.26	−10.88
Krypton	−17.28	−16.91	−17.53
	−20.32	−19.72	−21.25
	−9.77	−12.04	−17.17
Xenon	−24.41	−23.60	−23.35
	−28.99	−27.97	−28.89
	−18.20	−20.06	−24.36

TABLE 6

(6–12) Lennard-Jones force parameters ε_{LJ} for rare gases and *n*-alkanes and saturated vapour pressure p for *n*-alkanes at 25 °C

	ε_{LJ} (k/K)		p (atm)
Helium	6.03 [a]		
Neon	32.0 [b]		
Argon	113.5 [b]		
Krypton	178.0 [b]		
Xenon	230.2 [b]		
n-Pentane	292.7 [c]	326.5 [d]	0.67434
n-Hexane	299.7 [c]	341.8 [d]	0.19908
n-Heptane	299.8 [c]	351.7 [d]	0.06013
n-Octane	298.9 [c]	357.7 [d]	0.01842
n-Nonane	297.4 [c]	361.4 [d]	5.6579×10^{-3}
n-Decane		363.2 [d]	1.71053×10^{-3}
n-Undecane		362.4 [d]	5.49342×10^{-4}
n-Dodecane		361.5 [d]	1.5789×10^{-4}
n-Tridecane		357.9 [d]	–
n-Tetradecane		347.8 [d]	–
n-Pentadecane		346.6 [d]	–
n-Hexadecane		342.2 [d]	–

[a] From ref. 19.

[b] From ref. 20.

[c] From ref. 21.

[d] Values predicted by the method of L.S. Tee, S. Gotoh and W.E. Stewart (TGS), see ref. 20 for a discussion of the different methods for predicting the Lennard-Jones force constants.

TABLE 7

Hard sphere diameters σ and molar volumes V for rare gases

	σ (Å) [a]	V (cm^3 mol^{-1}) [b]
Helium	2.63	12
Neon	2.78	16.7
Argon	3.40	28.7
Krypton	3.60	34.7
Xenon	4.10	43.0

[a] From ref. 4

[b] Molar volumes obtained from the density at the normal boiling point.

to be obtained in J mol^{-1} if V is expressed in cm^3 mol^{-1} and σ_0 in dyn cm^{-1}.

In Table 3 we present the values of the Helmholtz energy of cavity formation, A_{cav}, the energy of cavity formation, E_{cav}, and the entropy of cavity formation, S_{cav}, for xenon as solute in *n*-alkane solvents calculated by our model [eqns. (1), (2), (3) and (13)], by the SPT model and by the Sinanoglu model [eqns. (14) and (15)]. The physical properties of *n*-alkanes were taken from ref. 6 except the saturated vapour pressures, which are presented in Table 6. Table 4 shows the values of the xenon–solvent interaction energies and entropy obtained from eqn. (10) and using the three cavity models. Table 5 shows the interaction energy E_{int} between the different rare gases and the solvents *n*-hexane, *n*-decane and *n*-tetradecane. Table 7 shows the hard sphere diameters, σ, and the molar volumes V of the rare gases used in the calculations.

DISCUSSION

Inspection of Table 3 indicates that the E_{cav} values obtained from the Sinanoglu method are very different from those obtained by the present model and by the SPT, and show a different qualitative behaviour which is depicted in Fig. 1. In fact, according to our model (filled circles), the energy of the xenon cavity in the *n*-alkane series is nearly the same from *n*-pentane to *n*-hexadecane. A similar behaviour is observed for E_{cav} values calculated from SPT (open circles), although in a less clear way, as can be seen from Fig. 1. On the other hand, the Sinanoglu model (filled squares) leads to a completely different behaviour: the E_{cav} values grow strongly with the number of carbon atoms of the *n*-alkane. Since all the *n*-alkane molecules are composed of methyl and methylene groups, which are very similar from a thermodynamic point of view, we would expect that the energy required to create a given cavity in all these solvents would be nearly the same, and this is in agreement with the results obtained by our model, and to a certain extent with SPT, but conflicts with the results obtained by the Sinanoglu

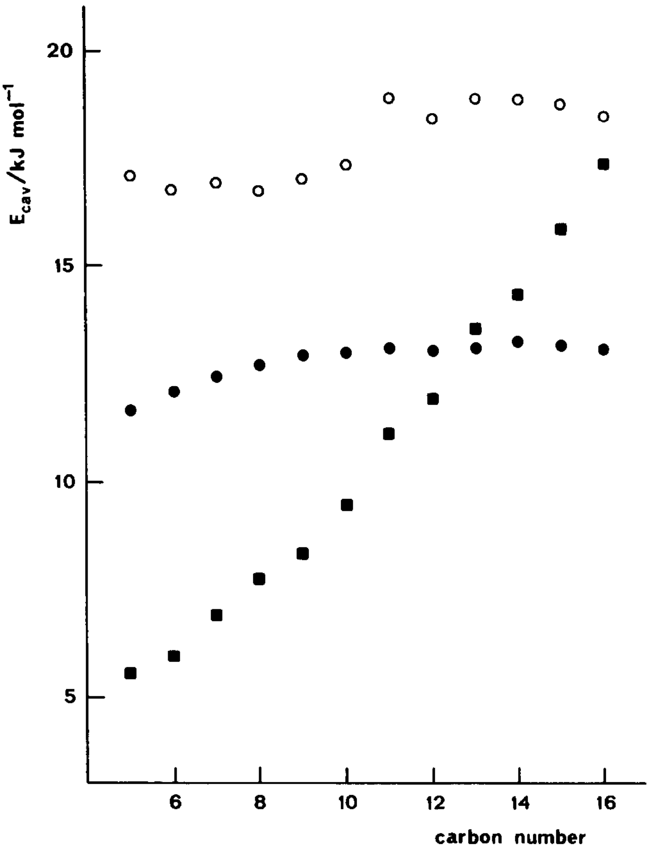

Fig. 1. Energy of cavity formation for xenon solute in *n*-alkane solvents as a function of the solvent carbon number. Filled circles correspond to our model, open circles to SPT and filled squares to the Sinanoglu model.

model. Different facts suggest that the contact energies between *n*-alkane molecules are similar and independent of the carbon atom number.

In previous papers [8,10] we pointed out that the interaction energy by unit of exposed surface area, defined by H_{c0}/S_0, where S_0 is the surface area of the reference cavity and $H_{c0} = E_{c0}$ is the energy of the reference cavity, has the same value for all *n*-alkane liquids. This fact reinforces the idea that the *n*-alkanes have the same contact energies. Moreover, as can be seen from Table 6, the (6–12) Lennard-Jones force parameters are almost the same for all *n*-alkanes, which strengthens our previous statement that the E_{cav} values should be similar in all these solvents. We should point out, on the other hand, that in extreme cases of very small solutes like helium and neon the Sinanoglu method leads to cavity energies which are negative. These results are meaningless from a physical point of view, and are a consequence of the difficulty of describing the limit of the surface tension for zero-sized (infinitely curved) cavities. At this point we are able to conclude that the

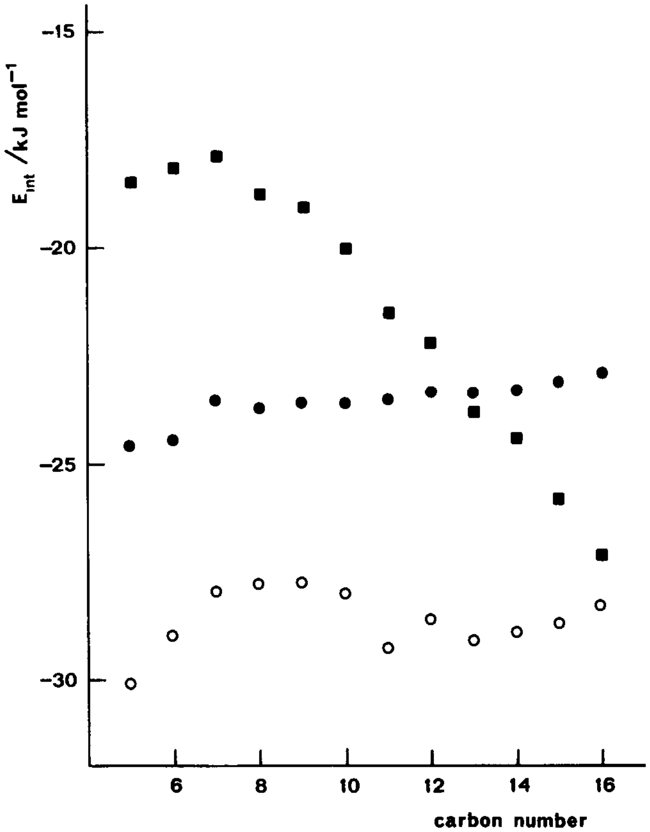

Fig 2. Solute–solvent interaction energy for xenon solute in n-alkane solvents as a function of the solvent carbon number. Filled circles correspond to our model, open circles to the SPT and filled squares to the Sinanoglu model

Sinanoglu model fails to describe the curvature dependence of the surface solute cavity in the rare gas/n-alkane systems. From Table 3 it can also be seen that the same qualitative difference between the Sinanoglu and the other two models is observed for S_{cav} (the values of n-alkanes higher than dodecane are not presented because saturated vapour pressures are not available).

The values of E_{int} presented in Table 4 and illustrated in Fig. 2 show the same difference between the three models for calculating the cavitation energetics. The values obtained from our model are nearly the same in all n-alkane solvents, the values obtained from SPT are not too far apart but show a slight variation with the solvent carbon number and those obtained by the Sinanoglu model show a strong variation with the size of the solvent molecule. Again if all the n-alkane molecules are composed of methyl and methylene groups, the contact energies of n-alkanes are similar, and we would expect the E_{int} values to be the same for the same solute in all those solvents. Otherwise stated, a given solute "sees the same landscape" in all *n*-alkane solvents. This idea is confirmed by several experimental facts. One of them is the fact that there is no *n*-alkane solvent effect on the π to π^* transition energies of a very large number of chromophores. This was shown by Brady and Carr [17], who carried out extensive experimental work on the solvatochromism in those transitions. For example, for *p*-nitroaniline, whose excited state is much more polar than the ground state, the transition energy does not change on going from *n*-heptane to *n*-hexadecane (31.0 cm^{-1}) and shows a very small change from *n*-pentane (31.45 cm^{-1}) to *n*-heptane (31.07 cm^{-1}). These results indicate that both states involved in the transition (which have quite a different polarity) are equally stabilised in the different *n*-alkanes. In other words, and using the previous picture, the ground state (as well as the Franck–Condon excited state) sees the same landscape in all *n*-alkanes, so that there is no observed solvent effect. Further experimental evidence comes from the fact that there is no apparent *n*-alkane solvent effect on the conformational equilibrium of *trans*-1,2-dibromocyclohexane [18]. This molecule exists in solution as a rapid equilibrium between two conformers of different polarity: the diaxial conformer, whose dipole moment is 1.20 D, and the diequatorial conformer, whose dipole moment is 3.30 D. It is thus a solvent dependent conformational equilibrium. In this case no Franck–Condon species is involved, the characteristic time for the conversion being long enough to allow the eventual reorganisation of the solvent in the cosphere of the solutes. Measurement of the dipole moment of *trans*-1,2-dibromocyclohexane in five *n*-alkane solvents from *n*-pentane to *n*-dodecane does not show any significant solvent influence on the position of the equilibrium.

From Table 4 it can also be seen that the S_{int} values from our model and from SPT show a monotonic variation with the carbon number of the solvent.

From Table 5 we can observe an identical behaviour: the same rare gas has a similar interaction energy with different *n*-alkanes. Figure 3 shows the plot of the interaction energy of different rare gas solutes with the *n*-decane solvent as a function of the (6–12) Lennard-Jones force parameter ε_{LJ} of the solute. According to our model the interaction energy is a smooth function of ε_{LJ} (correlation coefficient 0.996) and the intercept is nearly zero. Similar conclusions are obtained from SPT even if the correlation coefficient is slightly smaller. On the other hand, the values obtained from the Sinanoglu model lead to an intercept which is very different from zero. This is again a meaningless result, which shows that this model is not appropriate to describe the intermolecular interactions in such systems. The same plot for other *n*-alkane solvents also leads to good correlation coefficients, to intercepts near zero (except for the Sinanoglu model) and, interestingly, to slopes which do not differ significantly from solvent to solvent. This is again an indication of the similarity of the contact energies of the solvents.

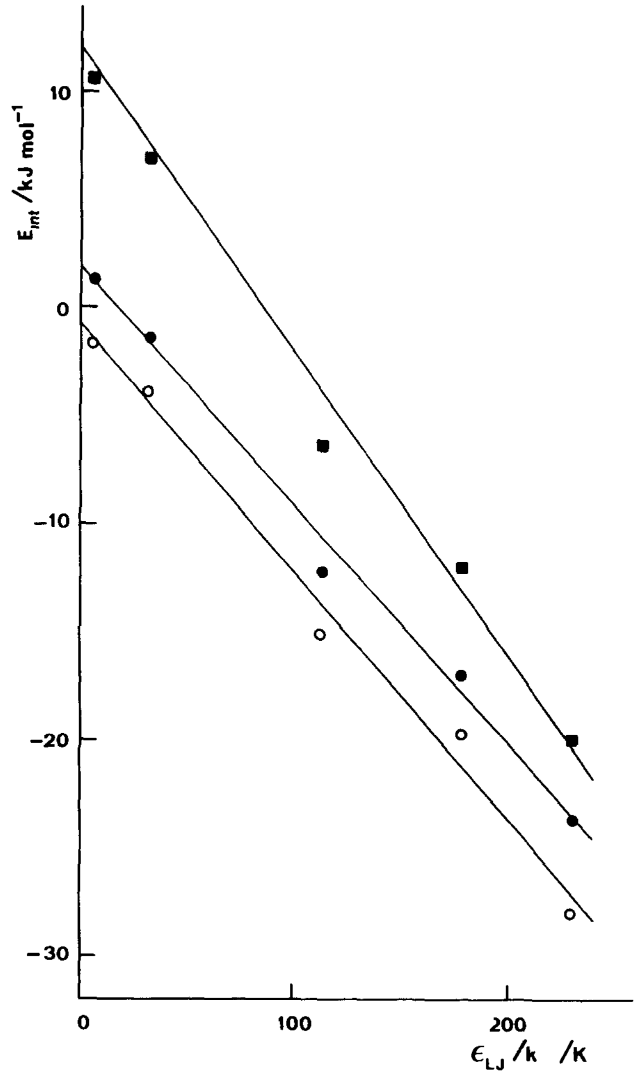

Fig. 3 Interaction energy of rare gases with n-decane as a function of the rare gas (6–12) Lennard-Jones force parameter. Filled circles correspond to our model, open circles to the SPT and filled squares to the Sinanoglu model.

CONCLUSIONS

As shown previously [9] interaction energies obtained from a cavity model provide a better understanding of chemical phenomena in solution than the overall solution properties or transfer properties. Park et al. [4] used this methodology to study the inert gas interactions with homologous n-alkane solvents, and concluded that the Pierotti implementation of the scaled particle theory leads to reasonable estimates of the cavity energetics. In the present paper we applied a new model for calculating the cavitation energetics in order to study the same systems, and we showed that the results obtained from this model seem to be more reasonable from a physico-chemical point of view. In previous work [6,8,10] we compared the different cavity models by applying them to other systems. We showed for example that, as pointed out by Pullmann and coworkers [16], the SPT presents some difficulties when polyatomic solutes are involved. We can conclude that the model we present here is, at the present moment, the most promising method to calculate the cavitation energetics.

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