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AN INTERACTION POTENTIAL FOR THE Cu^{o}-H_2O SYSTEM. APPLICATION TO A MONTE CARLO SIMULATION (*)

A two-body analytic potential for the interaction of the Cu^{o} atom with the H_2O molecule has been determined by fitting to quantum energies of the monohydrate Cu^{o}–H_2O. These, in turn, were computed by an ab initio method with effective core potentials for a set of 146 points in the Cu^{o}–H_2O potential energy surface. In addition, the quality of the fit and the results obtained by applying this new interaction potential in a Monte Carlo simulation are examined.

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1. INTRODUCTION

There is a continued interest in the studies of ionic aqueous solutions of transition metals. This interest derives from the fact that transition metals participate in many redox reactions in solution and the rates of such reactions are much influenced by the characteristics of their solvation shells.

Our final goal is the theoretical study of the solvent effects in the $2Cu^{+}$ (aq.) $\rightarrow$ Cu^{o} (aq.) + Cu^{2+} (aq.) exchange reaction, using the Monte Carlo's method [1]. To begin with, we intend to simulate the aqueous solutions of the reagents and products of that reaction.

The application of Monte Carlo's method to these cases requires, however, the knowledge of the interaction potentials for the pairs water-water and water-metallic species. As to the potential of the H_2O–H_2O pair, the analytical potential of Clementi et al [2] will be used, a potential which has been demonstrated to gove a good description of water in condensed state [3].

In what concerns the interaction potentials of the copper species, reasonable results have already been attained for the Cu^{+}–H_2O system [4], with an heuristic procedure that uses, for the representation of this system's potential, an analytical function with adjustable parameters. These parameters were determined by fitting the chosen function to energy interaction values of the Cu^{+} monohydrate, evaluated according to pseudo-potentials method of Barthelat et al [5]. The analytical function used was an expansion in the inverse powers of the internuclear distances.

The focus of the present work is the construction of an interaction potential for the Cu^{o}–H_2O system, using the same kind of procedure and a similar analytical function. In fact, to perform the statistical study of the above referred exchange reaction, suitable interaction potentials for all the intervenient copper species are necessary.

In the next section, we will present the form of this analytical function applied herein to

the Cu^o–H_2O system and, describe the main details of the interaction energy calculations, which were performed within the quantum model of Barthelat et al. Moreover, the results of these energy calculations are compared with the ones previously obtained for the Cu^+–H_2O system. The quality of the two fits is also compared. In section 3, the new Cu^o–H_2O interaction potential is used in a Monte Carlo simulation of a Cu^o aqueous dilute solution, in order to investigate the changes in the liquid structure of water produced by the Cu^o atom. The results obtained in the simulation at 298K of the $[Cu^o(H_2O)_{100}]$ system are collected and analysed.

2. CONSTRUCTION OF THE Cu^o–H_2O INTERACTION POTENTIAL

The form of the analytical function to use, was selected by our previous studies of Cu^+ hydrates [4] and also from other studies of transition metal systems, namely the Fe^{2+}–H_2O, the Fe^+–H_2O and the Fe^o–H_2O systems [6]. As we have mentioned above, it is written as a combination of inverse powers of the several internuclear distances with the following structure:

$$V[Cu^o\text{–}H_2O] = c_1\,[1/r_a^{\,2} - 1/2(1/r_b^{\,2} + 1/r_c^{\,2})] + c_2\,[1/r_a^{\,3} - 1/2(1/r_b^{\,3} + 1/r_c^{\,3})] + c_3/r_a^{\,4} + c_4\,(1/r_b^{\,4} + 1/r_c^{\,4}) + c_5/r_a^{\,5} + c_6\,(1/r_b^{\,5} + 1/r_c^{\,5}) + c_7/r_a^{\,6} + c_8\,(1/r_b^{\,6} + 1/r_c^{\,6}) + c_9/r_a^{\,12} + c_{10}\,(1/r_b^{\,12} + 1/r_c^{\,12}) \quad [1]$$

where r_a, r_b and r_c are the Cu^o-oxygen and Cu^o-hydrogens internuclear distances and c_i (i=1,2,..., 10) the adjustable parameters. It should be noted that the energy $V[Cu^o\text{–}H_2O]$, in eq. 1, is obtained in hartrees when the distances r_a, r_b and r_c are in bohrs. It is also important to stress that $V[Cu^o\text{–}H_2O]$ does not contain Coulombic terms as there are no electrostatic Coulomb interactions on the Cu^o–H_2O system. No exponential terms have been included in that potential just to simplify its later utilization on Monte Carlo's simulations.

The parameters c_i in the above equation were obtained by fitting the $V[Cu^o\text{–}H_2O]$ to the interaction energies of the Cu^o–H_2O system, related to eleven orientations of the H_2O molecule around the Cu^o atom. In this way, five planar and six non-planar configurations have been considered. The five planar ones differ in the values of angle α, as presented in Figure 1. The six non-planar configurations are constructed, from a configuration in which the H_2O molecule is in a plane perpendicular to the plane containing the Cu^o atom, by successive rotations by angles β and γ, defined as shown in Figure 2. In all these orientations, the interaction energies, $E[Cu^o\text{–}H_2O]$, where computed for several Cu^o–O distances, with the water molecule fixed at its equilibrium geometry, i.e., with r_{OH} = 0.9572 Å and $\sphericalangle HOH = 104.5^o$ [7].

As we have already mentioned, the energies $E[Cu^o\text{–}H_2O]$ were attained by means of the pseudo-potentials method of Barthelat and coworkers [5]. The appeal to this method can be justified by the obvious difficulties that an all-electron calculation of the $E[Cu^o\text{–}H_2O]$ energy points, on the above-considered orientations, would bring about. Program PSHONDO [8] was used on such calculations and we employed the pseudo-potentials parameters of Cu^o and O atoms, together with the double-zeta valency basis set of the atoms Cu^o (3d and 4s functions), O (2s and 2p functions) and H (1s function), which were suggested by the authors of this method [5].

In Figs. 1 and 2, the calculated Cu^o–H_2O interaction energies, in a total of 146 points, are plotted, respectively, for the planar and non-planar configurations as functions of the internuclear distance Cu^o–O. From these figures it can be seen that all the Cu^o–H_2O studied configurations have a pronounced repulsive character, with the exception of the $\alpha=0^o$ planar configuration. For this configuration, an energy minimum of –1.22 kJ mol^{-1} was found at a Cu^o–O distance of 2.80 Å. This

binding energy was interpreted by those authors as the result of important water dipole-metal dipole induced attractions. However, the binding between H_2O and the Cu^o seems to be rather weak and, therefore, we don't expect to find a stable $[Cu^o(H_2O)_n]$ complex in solution at room temperature. It is worth noting that for the Cu^+ ion, a stable $[Cu^+(H_2O)_6]$ complex appears appears to exist in solution at 298 K [4] but, in this case, a much larger binding energy (–166.35 kJ mol^{-1}) at a much shorter copper-oxygen distance (2.05 Å) was obtained for the $\alpha = 0^o$ configuration.

The fitting of the $V[Cu^o–H_2O]$ function of equation (1) to these $Cu^o–H_2O$ calculated energies was made by a least-squares procedure giving the following statistical parameters:

$\mathbf{d} = 4.31$ kJ mol^{-1} and $\mathbf{s} = 7.90$ kJ mol^{-1}

in which **d** stands for the average of absolute deviations and **s** for the average of square deviations. In fact, these parameters were improved in relation to the ones achieved on the $Cu^+–H_2O$ fitting [4].

A list of the resulting c_i parameters for the $V[Cu^o–H_2O]$ potential is specified in Table I.

Table 1

Parameters of $V[Cu^o—H_2O]$ determined in the adjustment of the $E[Cu^o—H_2O]$ quantum energy points

Parameter	Adjusted value
c_1	–0.33372
c_2	+7.81396
c_3	–50.73922
c_4	–6.20687
c_5	+44.73850
c_6	+70.92578
c_7	–207.98939
c_8	+123.98845
c_9	–13571.56457
c_{10}	+1522.24804

The goodness of the present fitting can be judged with the above mentioned statistical parameters and, also, through examination of Figs. 1, 2 and 3.

On the first two figures, the $Cu^o–H_2O$ quantum energies points are compared with the potential energy curves given by the $V[Cu^o–H_2O]$ function, for the two kinds of configurations analysed. In Fig. 3, the quantum energy points $E[Cu^o–H_2O]$ are plotted against those predicted by the $V[Cu^o–H_2O]$ function. The correlation between the two types of interaction energy values is rather good and, hence, we believe that this new $Cu^o–H_2O$ potential will be appropriate to use in the subsequent Monte Carlo simulations.

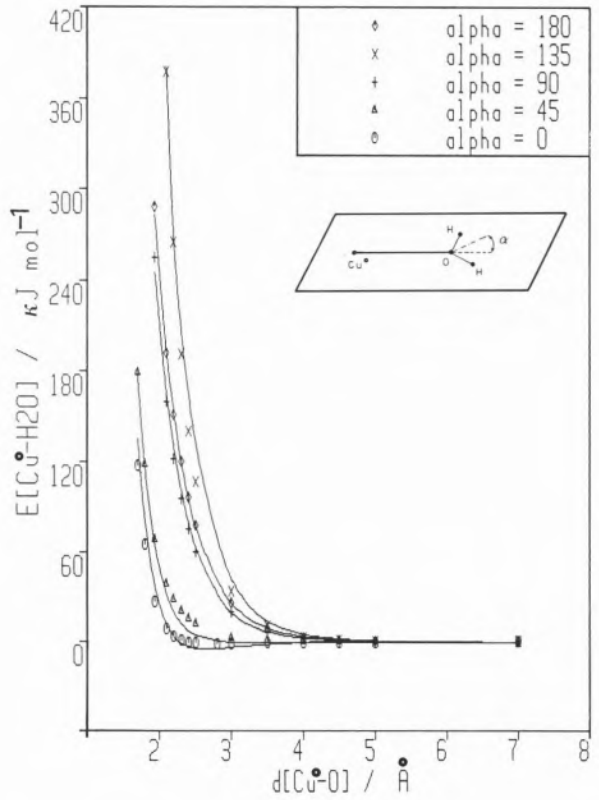

Figure 1

Potential energy curves for the $Cu^o—H_2O$ in the planar configurations depicted. The points were calculated by the pseudo-potential method described in the text. The solid lines correspond to the fitted potential $V[Cu^o—H_2O]$

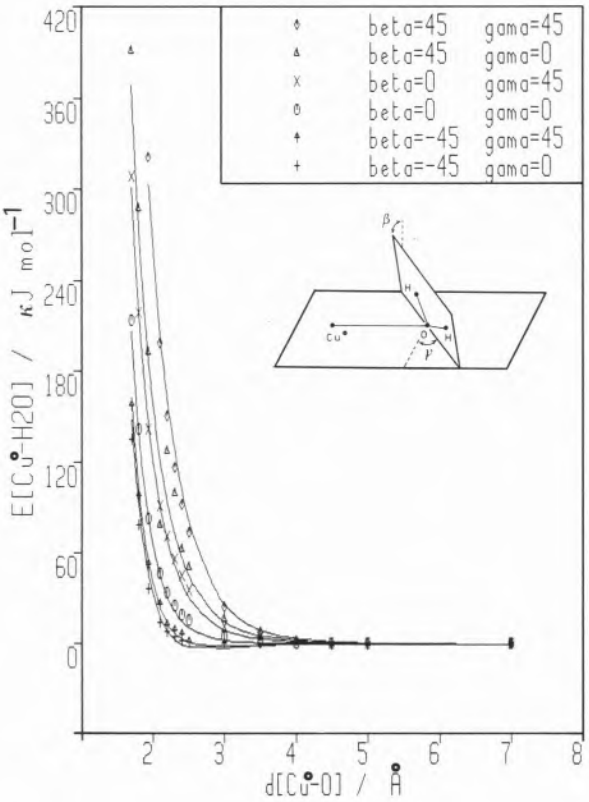

Figure 2

Potencial energy curves for the Cu^o—H_2O in the non-planar configurations depicted. The points were calculated by the pseudo-potential method described in the text. The solid lines correspond to the fitted potential V[Cu^o—H_2O]

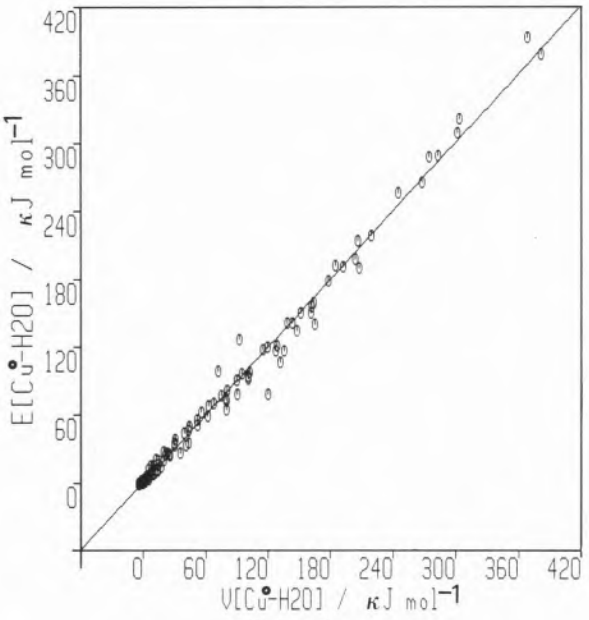

Figura 3

Comparison between calculated interaction energies of the Cu^o—H_2O system and those resulting from the fit to potential V[Cu^o—H_2O]

3. MONTE CARLO SIMULATION OF THE [$Cu^o(H_2O)_{100}$] SYSTEM

In this work, the simulation of the [$Cu^o(H_2O)_{100}$] system is the canonical (N,V,T) ensemble at T = 298 K has been done by Monte Carlo method [1], according to the Metropolis algorithm [10]. In this simulation, we used a cubic box with side lenghts of 15 Å in order to have a density of $\approx$ 1 g cm^{-3} for the 100 water molecules. Periodic boundary conditions have been introduced following the minimal image method. An initial configuration of the [$Cu^o(H_2O)_{100}$] system has been achieved from a cubic distribution of water molecules, by placing the Cu^o atom at the centre of the octahedron formed by the six nearest H_2O molecules. Statistical equilibration was attained after the simulation of 4000n configurations and, the simulation of another 4000n additional configurations was done afterwards.

In order to compute the energies of the configurations involved in the pair-potential approach, we used the following two-body potentials: the MCY potential [2] and the V[Cu^o–H_2O] potential just described.

With the purpose of discussing the energy features of the [$Cu^o(H_2O)_{100}$]system, we have determined the averages of the water-water and of the copper-water interaction energies per mol of water. An average water-water interaction energy of –37.17 kJ mol^{-1} was obtained and, this value is quite close to the corresponding value for pure water, which has been computed using a box of similar side lenghts [11]. This clearly indicates that the Cu^o atom is unable to modify the tetrahedral structure of water, at least in a significant way. The small value of –0.15 kJ mol^{-1} found for the averaged copper-water interaction energy also confirms the above assumption.

There is another interesting value that can be determined on this simulation, i.e. the orientation parameter of the H_2O molecules in the [$Cu^o(H_2O)_{100}$]. This parameter is defined as the average value of the cosine of the angle formed by the water molecule's dipolar moment

vector and the position vector of the respective oxygen atom, the origin of this position vector being fixed on the Cu^o atom. The magnitude of this orientation parameter can also be compared with the corresponding pure water value. We have found for the studied system an orientation parameter of –0.0010 which is almost null and analogous to that obtained (+0.0028) for pure water [11]. Again, this reflects that the water molecules are so hazardously oriented in the $[Cu^o(H_2O)_{100}]$ system as they are in pure water. The same conclusion can be reached by analysis of Figs. 4 and 5. where the copper-oxygen radial distribution function (RDF) and the running coordination number of Cu^o atom, N(R), have been reported.

It shoud be mentioned that this number N(R) has been taken as the average number of oxygen atoms within a sphere of radius R around the central Cu^o atom.

From Fig. 4, we can observe that in the copper oxygen RDF funcion no significant distinct peaks are found. On the contrary, this distribuition is very uniform along all the

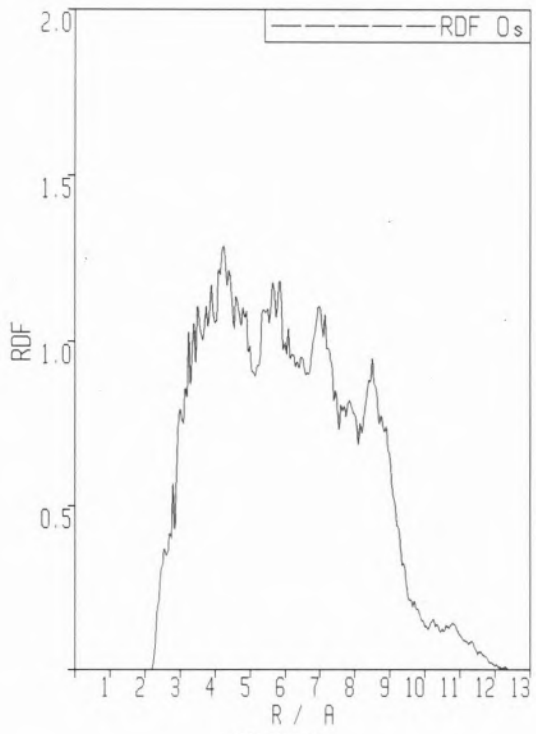

Figure 4

Radial ion-oxygen distribution function for the $[Cu^o(H_2O)_{100}]$ system at T=298K

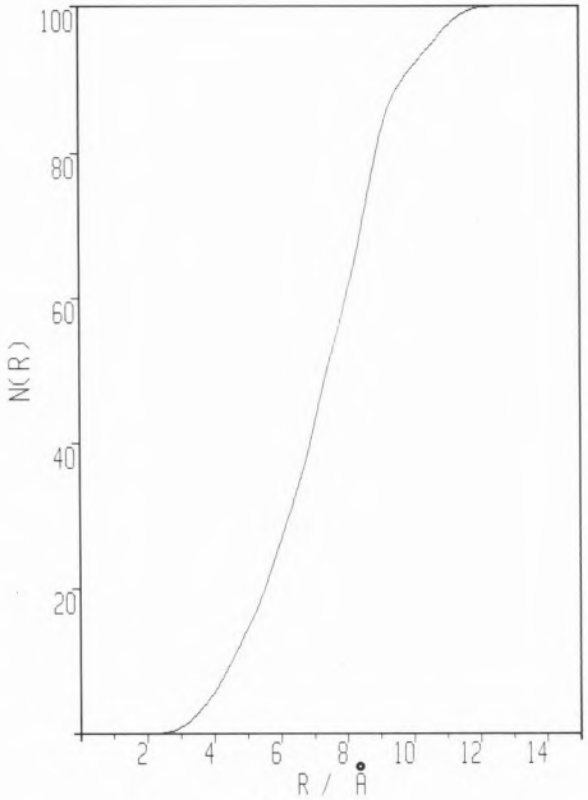

Figure 5

Running coordination number for the $[Cu^o(H_2O)_{100}]$ system at T=298K

Cu^o–O distances. In the same say, no plateau can be viewed on the N(R) curve of Fig. 5.

All these trends can be explained by the feeble copper-water interaction energy, especially if this interaction energy value is compared with the one of –24.55 kJ mol^{-1} that has been achieved for the water-water interaction, employing the MCY potential [12].

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RESUMO

Um potencial de interacção para o sistema Cu°—H_2O. Sua aplicação numa simulação de Monte Carlo.

Um potencial analítico para a interacção, a dois corpos, entre o átomo de Cu° e a molécula de H_2O foi determinado por ajuste das energias quânticas do monohidrato Cu°—H_2O. Estas energias foram por sua vez calculadas, recorrendo a um método ab initio com potenciais efectivos de cerne, para um conjunto de 146 pontos da superfície de energia potencial do sistema Cu°—H_2O. Além disso, são ainda examinados a qualidade do ajuste feito e os resultados obtidos na aplicação deste novo potencial de interacção a uma simulação de Monte Carlo.