The Structure of Hydroxylamine – Water Mixtures

Results of Monte Carlo Simulations

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Z. Naturforsch. **50a,** 263–273 (1995); received September 24, 1994

Dedicated to Prof. H. Ohtaki on the Occasion of his 60th Birthday

Monte Carlo simulations have been carried our for 5, 25, 50, and 75 weight% aqueous solutions of hydroxylamine. Changes in the microstructure of the solutions have been evaluated by means of radial and angular distribution functions, coordination number distributions and pair energy analysis. The structure of liquid hydroxylamine is strongly altered by even small amounts of water, whereas water clusters similar to the pure water are maintained up to higher NH_2OH concentrations. The structural entities in the mixtures are determined by hydrogen bonding and electrostatic arrangement of ligands.

Introduction

Solvent mixtues are of great interest not only because of their practical applications in mediating and influencing chemical processes, but also from a theoretical viewpoint. Solvent–solvent interactions, especially in the case of species with hydrogen bond formation capacity, and the microstructures determining the properties of such mixtures are of equal interest as are the solvating properties of such mixtures for electrolytes. Monte Carlo and molecular dynamics simulation techniques have become a most valuable tool for such investigations, equivalent or even sometimes superior to experimental techniques.

Whereas water has ben studied extensively by experimental and theoretical methods [1–7], theoretical studies still prevail for the rather unstable pure hydroxylamine [8–12]. With regard to the most interesting properties of hydroxylamine – chemically situated between water and ammonia and providing 2 different hydrogen bonding sites as well as 2 potential coordination sites for cation binding – a systematic investigation of mixtures of water and hydroxylamine seemed of particular interest. So far, theoretical studies have been reported for hydrogen bonded pairs of both species in the gas phase [13, 14], and recently a potential function for the H_2O/NH_2OH energy surface has been presented [15], which also forms the basis for our further investigations of the condensed system by means of simulation techniques.

In order to obtain information about the microstructure of hydroxylamine/water mixtures, Monte Carlo simulations have been carried out for mixtures with the mole fraction of NH_2OH varying from 0.025 to 0.625. The results have been analyzed in terms of radial and angular distribution functions (RDF, ADF), coordination number distributions and H-bonding features.

Method

1. Intermolecular Potentials

For water–water interactions, the CF2 potential [3] has been used, and the potential of Michopoulos, Botschwina and Rode [8] was employed for the evaluation of hydroxylamine–hydroxylamine pair energies. For water–hydroxylamine, our recently constructed potential containing the Coloumb-, r^{-3}-, r^{-6}-, r^{-9}-terms and one exponential term [15], was utilized. All these pair potentials are based on *ab initio* calculated energy surfaces not including electron correlation and 3-body effects. Further, all simulations were performed with rigid molecules. The possible errors caused by these simplifications have been investigated in previous studies [8, 15] and were found to be well tolerable while aiming mainly at structural data.

Reprint requests to Prof. B. M. Rode.

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Table 1. Simulation details.

Simulation	NH_2OH	H_2O	$\%_{weight}$	X_{NH_2OH}	mol l^{-1}	Density ($g\,cm^{-3}$)	Box length (Å)
1	5	195	4.457	0.025	1.37	1.0068	18.2380
2	31	169	25.024	0.155	8.02	1.0533	18.5800
3	71	129	50.036	0.355	16.88	1.1099	19.1163
4	125	75	75.202	0.625	26.61	1.1662	19.8341

2. Simulations

Aqueous solutions containing 4.5, 25, 50 and 75 weight% NH_2OH were simulated in the canonical NVT ensemble, and this series of increasing concentration will be referred to as simulations, 1, 2, 3 and 4 throughout this work.

The appropriate elementary box lengths were evaluated from the interpolated densities [17] of the liquid systems at 20 °C. The basic data for all simulations are given in Table 1. Simulations were carried out with Metropolis algorithm [18] and periodic boundary conditions with minimal image convention [19]. A cut-off of half the box length was applied to exponential terms. The long-range forces were handled by means of Ewald summation, using $\varepsilon = \infty$ for the surrounding medium, since this has proven to be a valid choice in simulations for pure hydroxylamine [12].

Starting configurations were generated randomly, equilibration needed between 4 and 9 million configurations and a further 2 million configurations were used for sampling. The ratio of accepted to rejected configurations was adjusted to 0.5 by continuous adjustment of maximum shift and turn parameters.

All simulations were carried out with the program MC92 [20] on IBM RISC workstations (550 and 375). The total amount of computer time needed for one simulation varied between 100 and 260 hours.

Results and Discussion

1. General

Structural data have been evaluated with the help of radial and angular distribution functions (RDF/ADF), coordination number distributions and an analysis of hydrogen bonding in the mixed systems. Unfortunately, X-ray or neutron scattering data, which would allow a direct comparison of RDFs, are not available yet, but the general success of simulation methods in supplying reliable structures of similar systems as water and ammonia in the liquid state supports the validity of the structural data reported in this work.

It seemed reasonable to present these data focusing on either NH_2OH or H_2O as central molecule, investigating the solvation structure around each species, and to discuss the influence of the other species on this structure in comparison with the pure solvents.

2. Hydroxylamine Solvation

Due to the presence of 2 functional groups and the size of the NH_2OH molecule, hydroxylamine forms a relatively large solvation shell, consisting of about 13 molecules within a radius of almost 5 Å in the pure liquid state [12]. This solvation shell can be roughly divided into two subshells, one centered around the OH group, the other around the NH_2 group. Hydrogen bonding accounts only for a minor number of the coordinated molecules, most of them are arranged according to electrostatic interactions. The number of solvating species in the first shell remains rather constant up to a mole fraction of 0.85 for water, although the majority of NH_2OH molecules are replaced by water (cf. Table 2). Only when virtually no hydroxylamine is available ($x_{NH_2OH} = 0.025$), a pure hydration shell consisting of 16 water molecules is formed.

Table 2. Structure solution characteristics around NH_2OH. Ligands distribution around hydroxylamine molecules.

Simulation	Coordination number	Ligand	
		H_2O	NH_2OH
1	15.9	15.9	–
2	13.3	12.2	1.1
3	12.7	9.1	3.5
4	12.8	4.7	8.1

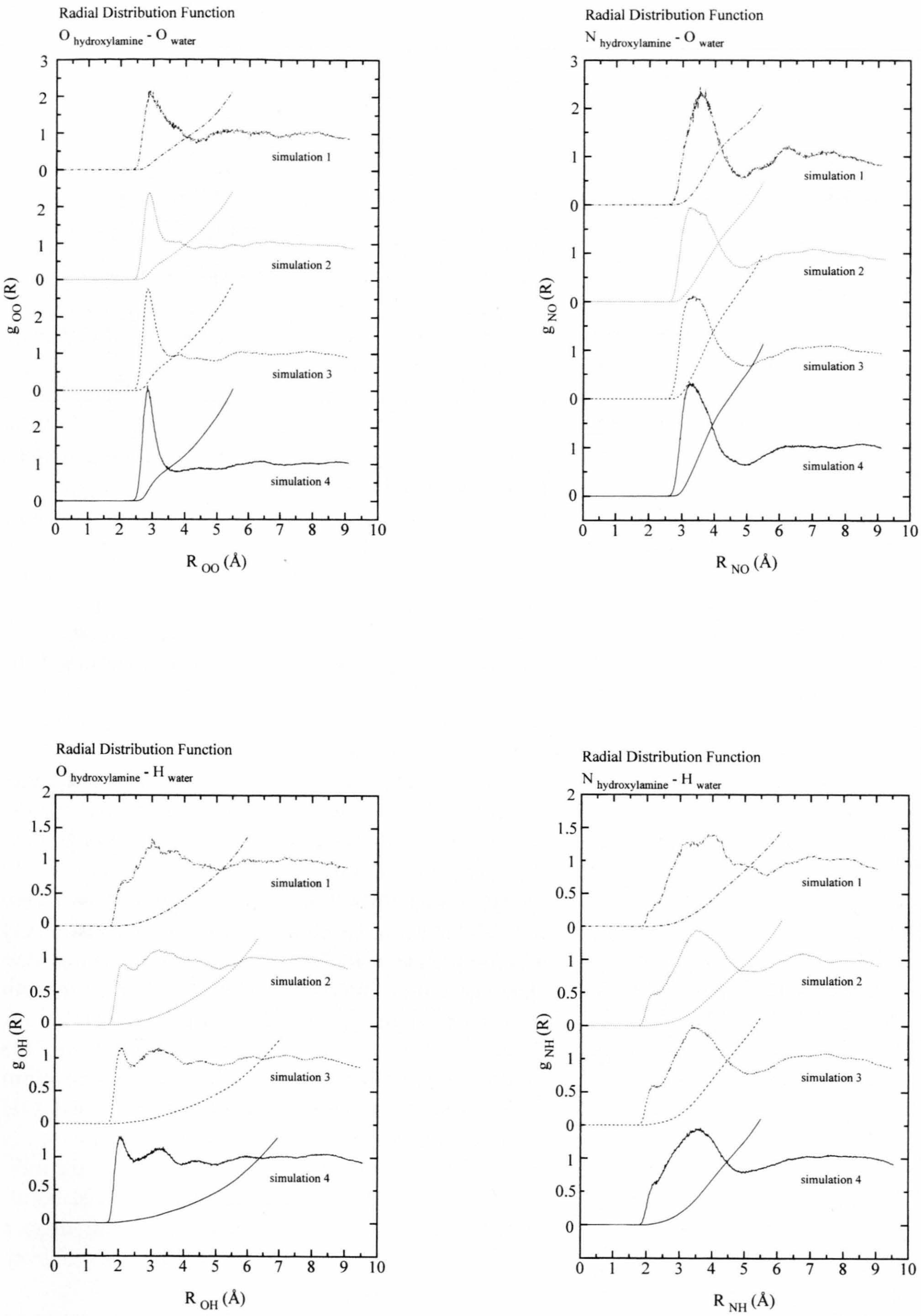

Fig. 1. Most important radial distribution functions and scaled running integration numbers (scale factor specified in the upper box) for Hydroxylamine–Water interactions.
a) pair O_h-O_w, —·— $n_{H_2O}/10$; ····· $n_{H_2O}/7$; ---- $n_{H_2O}/4$; —— $n_{H_2O}/2$.
b) pair O_h-O_w, —·— $n_{H_2O}/40$; ····· $n_{H_2O}/40$; ---- $n_{H_2O}/40$; —— $n_{H_2O}/20$.
c) pair N_h-O_w, —·— $n_{H_2O}/10$; ····· $n_{H_2O}/7$; ---- $n_{H_2O}/4$; —— $n_{H_2O}/2$.
d) pair N_h-H_w, —·— $n_{H_2O}/40$; ····· $n_{H_2O}/30$; ---- $n_{H_2O}/15$; —— $n_{H_2O}/8$.
Complete set of RDFs can be ordered from the editor. Subscripts h and w refer to hydroxylamine and water respectively.

2.1 *Hydroxylamine Coordination to Water*

The RDFs relevant for this structural feature and the change of coordination with increasing hydroxylamine concentration are given in Fig. 1 and Table 3. Whereas the N_h-O_w RDF (Fig. 1c) shows no recognizable details of structure, the O_h-O_w RDF (Fig. 1a) allows 3 zones to be distinguished: the first peak (2.85 to 3.00 Å, according to concentration) represents water molecules interacting with O of hydroxylamine mainly through H-bonds, followed by a not very well separated zone from 3.5 to 4 Å, representing water molecules H-bonded to the NH_2 group. At low water concentrations this intermediate peak disappears, indicating the relative weakness of such H bonds. The area discernible between 4 and 5 Å finally contains the water molecules coordinated in the first shell mainly electrostatically.

Table 3. Detailed radial distribution functions characteristics for H_2O around NH_2OH.

RDF	Peak 1*	n_{p1}[a]	Max 1	Min 1	n_1	Min 2	n_2
a) Simulation 1:							
N–O	–	–	3.35	3.85	8	5.05	17.5
O–O	–	–	3.00	3.90	8	5.00	16
H–H[b]	2.30	0.5	3.90	5.70	47	–	–
O–H[b]	2.10	1	3.00	5.00	32	–	–
H_N–O[c]	2.40	1.8	3.75	5.00	17.5	–	–
H_O–O	2.15	1	3.20	4.60	11.5	–	–
CM–CM	–	–	3.28	4.89	16	6.98	46
b) Simulation 2:							
N–O	–	–	3.25	5.00	13.5	–	–
O–O	–	–	2.90	4.30	8.40	–	–
N–H[b]	2.20	0.3	3.47	5.30	32.1	–	–
O–H[b]	2.15	1.5	3.20	5.10	27.5	–	–
H_N–O[c]	(2.25)	(0.5)	3.45	5.27	16.1	–	–
H_O–O	2.15	1.1	3.33	4.15	7.25	–	–
CM–CM	–	–	3.25	4.83	12.25	–	–
c) Simulation 3:							
N–O	–	–	3.32	5.11	10.2	–	–
O–O	–	–	2.85	5.00	8.90	–	–
N–H[b]	(2.1)	0.4	3.37	5.06	20.1	–	–
O–H[b]	2.08	1.0	3.23	(4.1)		5.09	19.1
H_N–O[c]	(2.2)	0.3	3.50	5.10	10.5	–	–
H_O–O	2.05[1]	1.0	3.40	4.07	4.85	–	–
CM–CM	–	–	3.24	4.93	9.1	7.4	31
b) Simulation 4:							
N–O	–	–	3.24	4.94	4.95	–	–
O–O	–	–	2.85	3.76	2.11	–	–
N–H[b]	(2.1)	(0.2)	3.64	5.04	10.3	–	–
O–H[b]	2.07[1]	0.8	3.37	3.96	4.7	4.86	8.57
H_N–O[c]	(2.3)	(0.4)	3.43	5.13	5.6	–	–
H_O–O	2.07[1]	0.7	3.27	4.20	2.5	–	–
CM–CM	–	–	3.19	4.90	4.7	7.63	17.5

[1] Main peak

CM refers to the molecule Center of Mass

* These data correspond either to a split-off peak or a shoulder.

[a] The first integration number n_{p1} corresponds to integration values for peak 1 and represents direct hydrogen bonding interactions, except in water–water interaction where this interaction is represented by the main peak. Second and third integration numbers, n_1 and n_2, reflect integration values up to first (m_1) and second minimum (m_2). The position of the main maximum is given as M_1.

[b] In the integration process both water hydrogens are taken into account.

[c] In the integration process both amino-hydrogens are taken into account.

Table 4. Structure solution characteristics around NH_2OH.

Percentual amount of	Simulation 1	Simulation 2	Simulation 3	Simulation 4
a) Water molecules distribution around hydroxylamine:				
H_2O around O	41.86	41.11	41.82	40.49
H_2O around N	46.38	44.72	46.92	48.09
H_2O in N–O zone	11.75	14.17	11.27	11.43
b) Hydrogen bonds NH_2OH-H_2O distribution:				
Hydrogen bonded H_2O in first shell	22.20	35.37	42.58	53.46
H. bonds pro. NH_2OH	3.52	4.31	3.87	2.473
Bond type $N-H_{water}$	15.37	10.93	10.67	8.46
Bond type $O-H_{water}$	21.66	32.68	32.87	30.86
Bond type H_N-O_{water}	29.90	19.96	30.01	31.95
Bond type H_O-O_{water}	33.07	36.43	26.45	28.74

A more detailed analysis of the simulations' history files (cf. Table 4a) reveals that a rather constant 48% of solvating water surrounds the amino group, 42% the OH group, about 11–14% of these waters could be attributed to a "joint" N–O region. The larger number or waters around the amino group is merely a consequence of its larger volume and coordination capacity, but not related to strength of interaction. An analysis of hydrogen bonding is given in Table 4b. With increasing hydroxylamine concentration, the number of H-bonded water ligands increases continuously, although the number of H bonds per NH_2OH runs through a maximum in simulation 2. Apparently a mole fraction of 0.155 provides the most ideal condition for hydrogen bonding. The majority of H bonds involves the OH group of hydroxylamine, hydrogen bonding of the NH_2 group preferentially occurs from H_N to O of water.

2.2 *Hydroxylamine–Hydroxylamine Coordination*

Table 5 gives the details, including average coordination numbers, of the hydroxylamine–hydroxyl-

Table 5. Detailed radial distribution functions characteristics for NH_2OH around NH_2OH.

RDF	Shoulder	Max.	Min.	Integration number[a]	
a) Simulation 2:					
O–O		4.05	5.0	2.6	–
N–N	3.1/3.65	4.35	5.0	2	(0.1/0.4)
N–O	–	3.05	4.0	0.9	–
H_O–O	(2.75)	4.20	4.65	2	(0.08)
H_O–N	2.6	3.45	4.55	1.6	(0.05)
H_N–O	(3.6)	4.50	4.9	1.9	(0.5)
H_N–N	–	3.5/5.0	5.8	3.4	–
CM–CM	3.43/3.55	3.98	4.28	1.2	(0.15/0.23)
b) Simulation 3:					
O–O	3.75[1]	4.2	5.5	6.8	(1.4)
N–N	–	4.3	5.0	4.7	–
N–O	–	3.1	4.27/4.97	2.6/4.45	–
H_O–O	2.4	4.7	5.5	7	(0.1)
H_O–N	2.65	3.6	4.35	3	(0.14)
H_N–O	–	3.65	4.4	2.9	–
H_N–N	–	4.4	5.4	6	–
CM–CM	–	3.79	4.59	3.6	–
c) Simulation 4:					
O–O	3.9	4.2	5.6	11.5	(3.1)
N–N	–	3.8	5.0	7.8	–
N–O	–	3.05	4.3/4.9	4.7/7.1	–
H_O–O	2.37	3.43	3.8	3	(0.4)
H_O–N	2.66	3.5	4.5	5.7	–
H_N–O	–	3.6	4.6	5.7	–
H_N–N	–	3.65/4.5	4.1/5.3	3.6/9.3	–
CM–CM	–	3.82	5.0	8.1	–
d) Pure hydroxylamine simulation [12]:					
O–O	3.8	4.1	5.3	13	(4)
N–N	–	3.6	5.3	13	–
N–O	–	3.1	5.3	13	–
H_O–O	2.2	3.0	3.8	4	(1.5)
H_O–N	2.4	3.5	4.6	8	(2.5)
H_N–O	–	3.5	4.9	10	–
H_N–N	–	3.8	5.3	13	–

[a] Numbers in parentheses are integration numbers up to shoulder's position.

[1] Main peak.

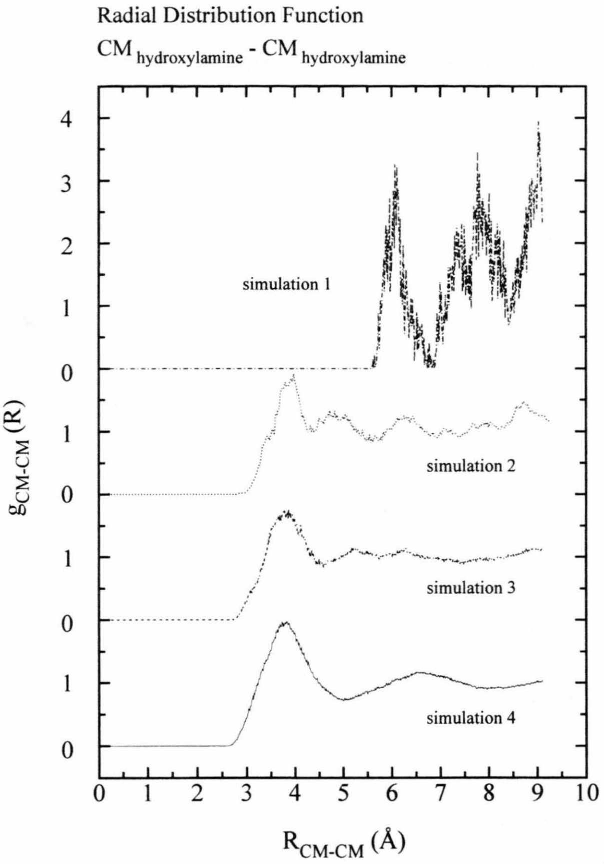

Fig. 2. Hydroxylamine–Hydroxylamine center of mass radial distribution functions. Complete set of RDFs can be ordered from the editor.

amine radial distribution functions. The increasing build-up of the entities making up the structure of liquid hydroxylamine [12, 21] can be recognized well, and for 50 and 75% NH_2OH content RDFs become very similar to those of the pure liquid, especially concerning the appearance of a distinct peak in the $O_h - H_{O-h}$ RDF, related to the most stable hydrogen bonding between two hydroxylamine molecules. However, Table 6 shows very clearly that the full H-bond framework of liquid hydroxylamine is not established by far even when 75% of the solution consist of NH_2OH: although the average number of close neighbouring NH_2OH molecules is already 3, only an average of 0.4 of them is truly H-bonded. This result indicates that even smaller amounts of water efficiently destroy the weak H-bond network of liquid hydroxylamine (or, vice versa, form more stable substructures involving stronger H-bonds to water, which can thus be supposed to be the reason for the higher chemical stability of aqueous hydroxylamine solutions compared to the pure liquid).

The coordination number distributions presented in Fig. 4 illustrate the composition of the first solvation shell of water and hydroxylamine molecules, respectively, as a function of varying solvent concentration. Changes in the surrounding of a NH_2OH molecule are quite dramatic and observable over the whole concentration range, whereas a significant change in surrounding of water molecules occurs only when considerably more than 25% of the mixture consits of hydroxylamine. The fact that the average

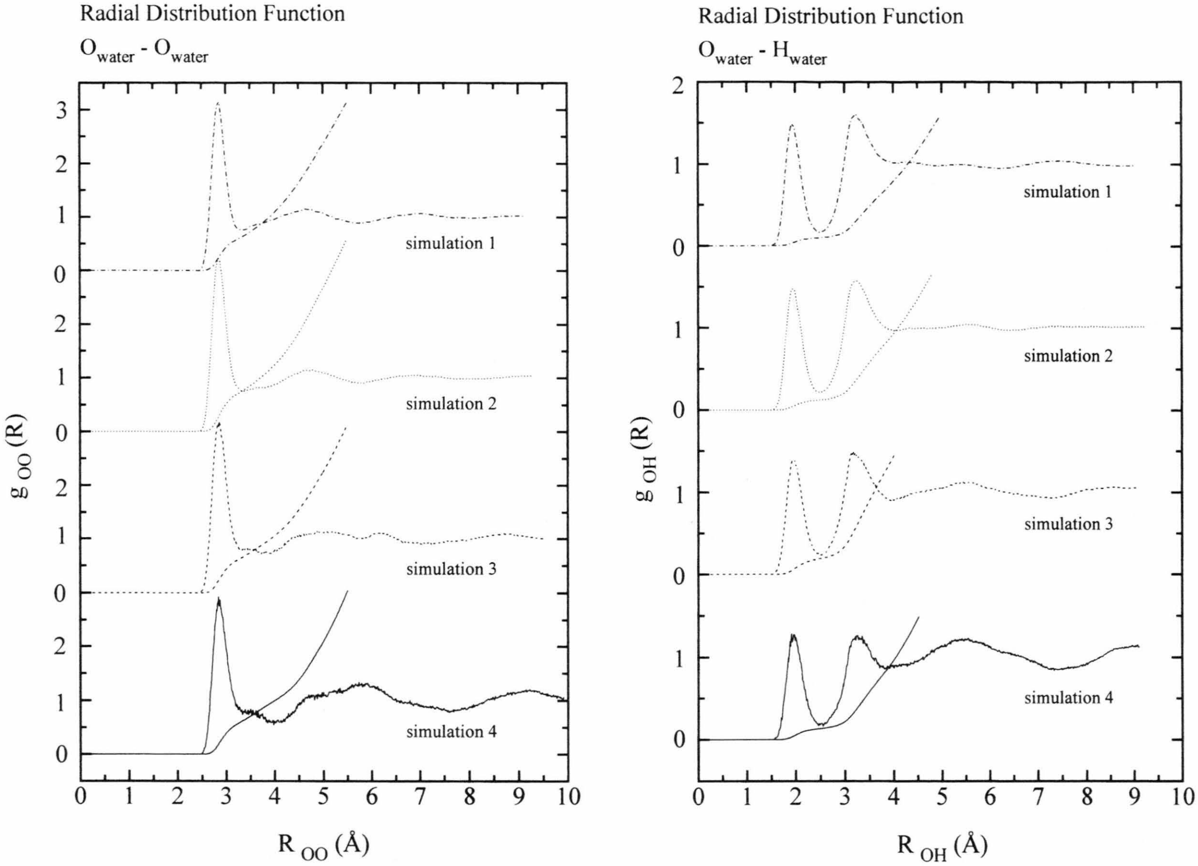

Fig. 3. Most important radial distribution function and scaled running integration numbers for Water–Water interactions.
a) pair O_w–O_w; -·-· $n_{H_2O}/7$; ····· $n_{H_2O}/5$; ---- $n_{H_2O}/4$; —— $n_{H_2O}/2$.
b) pair O_w–O_w, -·-· $n_{H_2O}/10$; ····· $n_{H_2O}/7$; ---- $n_{H_2O}/3$; —— $n_{H_2O}/2$.

coordination number for 75% NH_2OH solution varies from 4 to 13, with average 8.1 compared to 13 for the pure liquid, confirms once more the previous statement that small amounts of water lead to a pronounced change in the structural entities prevalent in liquid hydroxylamine.

Table 6. Hydroxylamine molecules structure around hydroxylamine. Hydrogen bonds NH_2OH–NH_2OH distribution. MBR: pure hydroxylamine solution [12].

Simulation	NH_2OH	Close neighbours	Hydrogen bonds type	
			(–OH)	(–NH_2)
1	–	–	–	–
2	2.8	0.3	0.13	0
3	5.7	1.4	0.24	0
4	9.3	3.1	0.4	0
MBR	13	4	4	0

The molecular orientations of molecules in the first solvation shell can be extracted from the ADFs for the angle defined in Figs. 5a and c and displayed in Figs. 5b and d. Figure 5b shows the broad distributions around the two functional groups of hydroxylamine, corresponding to rather weak orientational forces, Figure 5d illustrates these distributions in more detail. At the amino site ($\varphi = 45°$) the O atoms of water are located slightly outside the molecular symmetry plane σ_V ($\theta = -30°/30°$). Such arrangements correspond to 3 of the most stable adduct configurations resulting from *ab initio* calculations [15], which should also be of importance in the liquid state. The second zone compressed between $\varphi = 240°$ and 300° describes the surrounding of the OH group of hydroxylamine. In this zone, the location of ADF maxima does not show the continuous change observed for the NH_2 region.

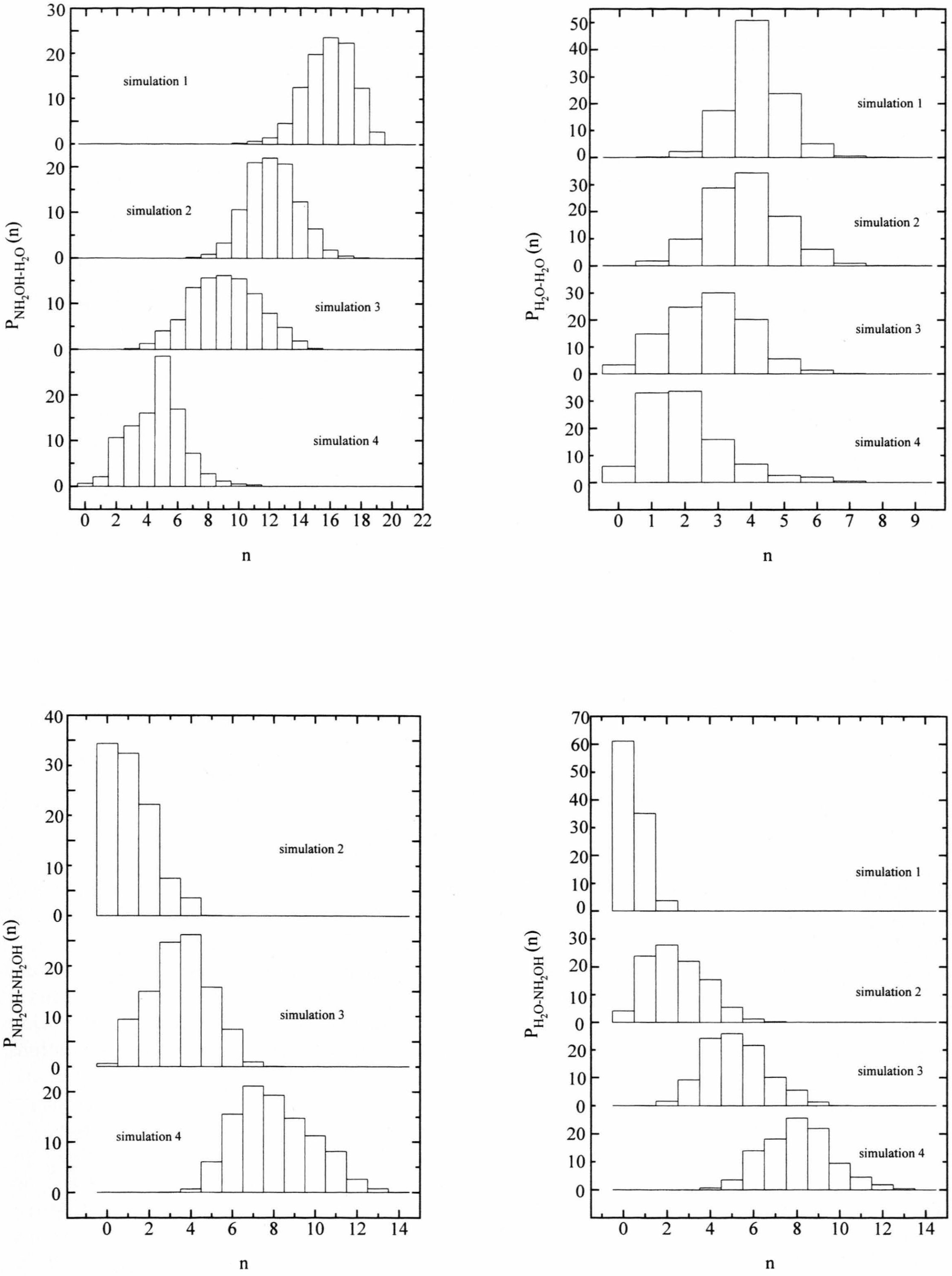

Fig. 4. Coordination number distribution. a) Hydroxylamine–Water interaction; b) Hydroxylamine–Hydroxylamine interaction; c) Water–Water interaction; d) Water–Hydroxylamine interaction.

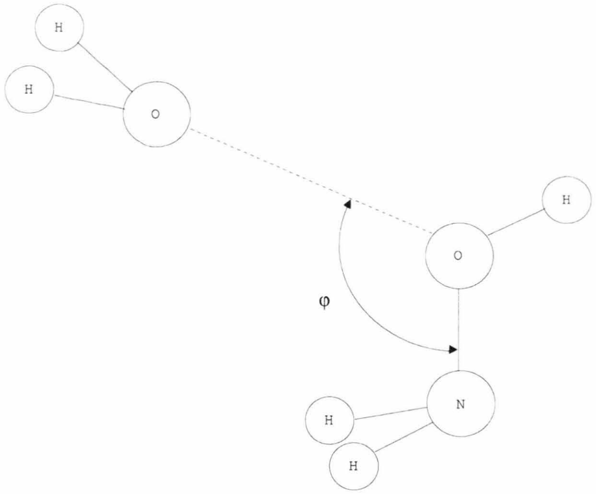

Fig. 5a

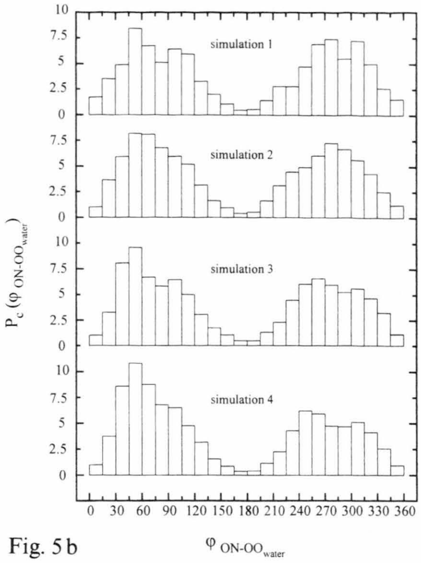

Fig. 5b

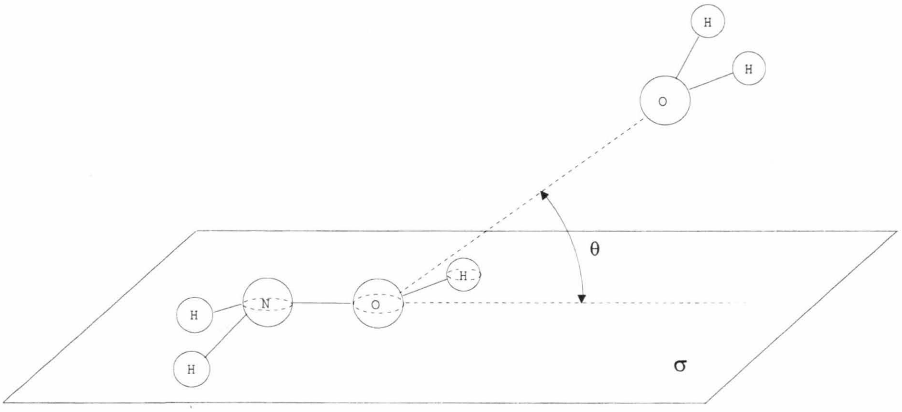

Fig. 5c

At very low hydroxylamine concentration (simulation 1) 2 maxima appear, only one of them is preserved at 0.155 mole fraction. At 0.355 mole fraction orientations are widespread, and at the highest concentration a new maximum is found at $\theta = 0°$ and $\varphi = 240°$ which corresponds to the stronger $OH_O..O$ hydrogen bonded orientation. This corresponds to successive break-away of water molecules surrounding this site, corresponding to the preference of other NH_2OH molecules to be associated with the OH group.

A more detailed analysis of molecular orientations, examining the angle between molecular dipole moments, showed that dipole alignment is not determining the optimal arrangement, also of non-H-bonded molecules in the first hydration sphere of hydroxylamine, but that the structure is rather a compromise between various attractive and repulsive interactions.

3. Water Solvation

The RDFs containing information relevant for the composition of the solvation shell centered around water molecules are depicted in Fig. 3, their characteristics and the average coordination numbers are collected in Table 7.

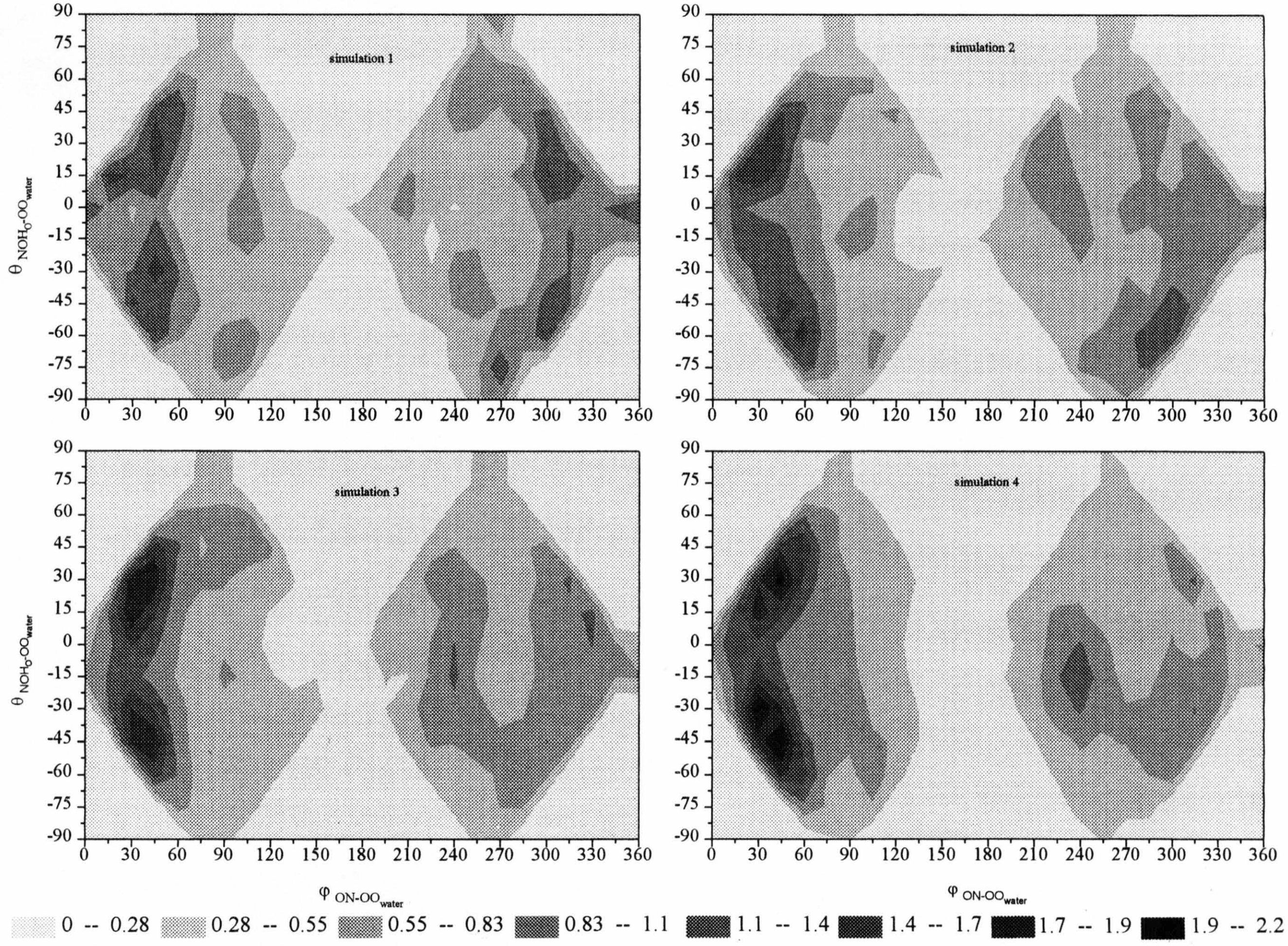

Fig. 5. First shell water ligand angular dimensionals around hydroxylamine. a) Definition angle φ; b) Angular distribution function for angle φ; c) Definition angle θ; d) NH_2OH-H_2O relative orientation probability density plot.

Table 7. Detailed structure characteristics of H_2O around H_2O
a) Coordination number and hydrogen bonds

Simulation	H_2O ligands[a]	Hydrogen bonds[b]
1	4.2	4
2	3.9	3.4
3	2.7	2.4
4	2	1.1

b) Radial distribution functions characteristics for $O_{water}-O_{water}$

Simulation	Max 1	min$_a$	n_a	Min 1	n_1	Max 2	Min 2	n_2
1	2.82	–	–	3.35	4.2	4.65	5.73	24.5
2	2.85	–	–	3.38	3.90	4.80	5.75	20.5
3	2.86	3.32	2.1	3.92	4.01	5.05	5.77	14.6
4	2.84	3.34	1.25	3.98	1.97	5.9	–	–
CF2 pot.[c]	2.85	–	–	3.35	4.5	4.5	nvs	nvs
Pure H_2O[d]	2.83	–	–	3.53	4.5	4.25	5.6	nvs
Exp.[e]	2.85	–	–	3.45	nvs	4.53	5.6	nvs

c) Radial distribution functions characteristics for $O_{water}-H_{water}$

Simulation	Max 1	Min 1	n_1	Max 2	Min 2	n_2
1	1.94	2.5	1	3.21	4.0	8
2	1.93	2.48	0.85	3.22	4.0	6.5
3	1.94	2.5	0.6	3.18	3.95	4.2
4	1.96	2.53	0.27	3.24	3.8	1.6
CF2 pot.[c]	1.85	2.5	nvs	3.16	nvs	nvs
Pure H_2O[d]	1.90	2.55	nvs	3.35	4.85	nvs
Exp.[e]	1.92	2.45	nvs	3.28	nvs	nvs

d) Radial distribution functions characteristics for $CM_{water}-CM_{water}$

Simulation	Max 1	min$_a$	n_a	Min 1	n_1	Max 2	Min 2	n_2
1	2.85	–	–	3.28	4.2	4.61	5.8	25.4
2	2.85	–	–	3.35	3.84	4.82	5.8	21
3	2.84	3.33	2.6	3.88	3.91	4.96	5.78	14.7
4	2.85	3.26	1.14	4.04	2.03	5.72	7.62	17.2

[a] Integration up to $CM_{water}-CM_{water}$ first minimum position (Table 7d)
[b] Integration up to $O_{water}-H_{water}$ first minimum position (Table 7c)
[c] Ref. [16]. [d] Ref. [6]. [e] Ref. [1]. [f] Ref. [2].
nvs No value specified by the authors.
min$_a$ Close neighbour ligands minimum.
n_a Integration up to close neighbour ligands minimum.

The results show that – in contrast to the breakdown of the liquid hydroxylamine structure – structural entities of liquid water are preserved up to rather high concentrations of the foreign solvent. A reduction of the water–water coordination number of 4 is only recognized when 50% of the mixture already consists of hydroxylamine. The O_W-O_W RDF displays a small additional peak around 3.5 Å at this concentration, which becomes more pronounced in the 75% solution, indicating that some of the first shell water molecules are no longer coordinated any through H-bonds, but rather in electrostatically determined locations. The coordination number distributions of Fig. 4 illustrate the gradual changes in the first coordination sphere of water molecules quite well. Up to 25% hydroxylamine, only minor effects are observed, mainly consisting in additional coordination of some NH_2OH molecules, without changing the water–water coordination to a larger extent. At higher concentrations, the number of coordinated

NH_2OH increases rapidly, but even then the central water molecule retains some ligands of the same species. This tendency to form at least small water–water clusters even at high hydroxylamine concentrations can be ascribed to the stability of water–water H-bonds and the higher flexibility of the smaller water ligand in adapting to suitable H-bonded arrangements.

Pair energy distributions for water–water, water–hydroxylamine and hydroxylamine–hydroxylamine pairs in the solutions have also been evaluated. The most interesting feature accessible through these data is the rather constant water–water pair energy distribution up to 50% NH_2OH, whose average energy increases within that range only from −3.6 to −3.1 kcal/mole, displaying a constant separate band around −4.5 kcal/mole corresponding to "ideal" H-bond conditions. Within that gradient of concentration, the water–hydroxylamine pair interaction changes from −1.0 kcal/mole (5%) to −1.4 (50%). With 75% NH_2OH in the solution, water–water pair energy reduces to −2.6 kcal/mole (without discernible band), whereas the water–hydroxylamine pair energy remains constant at −1.4 kcal/mole. These results confirm the conclusions about the strong tendency of water to maintain its main structural entity upon addition of fairly large amounts of the foreign solvent.

Conclusions

Water–hydroxylamine mixtures are polar solvents whose structure is determined both by hydrogen bonding and electrostatic interactions. Hydrogen bonding is responsible for maintaining small water clusters up to relatively high hydroxylamine concentrations and is also playing a part in the coordination of water to NH_2OH molecules, especially in the OH region. Other coordinates are highly flexible and concentration dependent, apparently a compromise between dipole alignment and achievement of the optimal coordination number within spatial requirements and limits. Water, even in small amounts, leads to an overall more stabilized liquid structure and consequently the weak hydrogen bond network of pure hydroxylamine is sacrificed for this purpose.

Acknowledgement

This work was supported by the Bilateral Cultural Agreement between the Republic of Austria and the Kingdom of Spain and by the Austrian Science Foundation (Project 9078 MOB).

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