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TEMPERATURE ENHANCEMENT OF WATER–OLIGOMER POPULATIONS IN SATURATED AQUEOUS VAPOUR

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ABSTRACT

Gas-phase water is treated as an equilibrium mixture of the clusters $(H_2O)_i(g)$, their stability being described by equilibrium constants of the cluster formation, derived from available theoretical information (RRHO MCY–B/EPEN model). The cluster populations under the condition of vapour saturation are evaluated and their increase with temperature is shown. Differences in results, caused by the use of either the total pressure or the total density of the saturated steam as input information for the cluster model, are discussed.

INTRODUCTION

The cluster (or supermolecule) approach has been a subject of interest for some time as a model of real gas or liquid phases (see, e.g., refs. 1–5), particularly when water is concerned. Water clusters, $(H_2O)_i(g)$, have frequently been studied theoretically (e.g., refs. 6–16) including the theoretical evaluation of the thermodynamics of their formation [17–32], i.e., of the reactions:

$$i H_2O(g) \rightleftharpoons (H_2O)_i(g) \tag{1}$$

In the theoretical description of water dimer thermodynamics, the powerful ab initio SCF CI MCY pair interaction potential ** [6] played a crucial role. However, it has recently been proved [31] that values from the MCY–B modification [10] of the potential (in conjunction with the rigid-rotor and harmonic-oscillator (RRHO) partition functions) are, of all the theoretical

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** Quite recently, the MCY potential was extended to include the intramolecular force field from advanced ab initio calculations, yielding flexible MCYL potential (see ref. 7).
For our purposes the MCY–B pair interaction potential [10] was supplied with a harmonic intramolecular part [17] based on experimental force constants of the free water molecule, thus a flexible form of the potential was actually used.

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evaluations, in closest agreement with the available observed information on the standard Gibbs energy of water dimerization. With higher water clusters the situation is less favourable; the most comprehensive theoretical data available on their thermodynamics are based [22] on the EPEN potential (dimers to pentamers). An interesting feature of the data [22] was pointed out recently [32], viz. the practically constant value of the increment δG_T^0 in the standard Gibbs energy term corresponding to the increase of the cluster order by one, and, moreover, a linear dependency of the increment itself on temperature. The increment δG_T^0 is introduced as:

$$\delta G_T^0 = \Delta G_{T,i+1}^0 - \Delta G_{T,i}^0$$

with $\Delta G_{T,\,i+1}^0$ and $\Delta G_{T,\,i}^0$ denoting the standard Gibbs energy change on association of $i + 1$ and i molecules of water (expressed in the kcal mol^{-1}; 1 kcal = 4.184 kJ), respectively. The following extrapolation formula can be deduced from the data of ref. 22 (maintaining the choice [22] of the standard state, i.e., an ideal gas phase at 1 atm = 101325 Pa pressure):

$$\delta G_T^0 = -7.5330 + 0.029337T$$

where T is the absolute temperature in K. The following holds for the series of deuterated clusters $(D_2O)_i(g)$:

$$\delta G_T^0(D) = -7.9965 + 0.029899T$$

This led to the suggestion of a simple extrapolation formula for the values of the subsequent equilibrium constants * of reactions (1):

$$z = \frac{K_{p,i+1}}{K_{p,i}} \qquad (i > 1) \tag{2}$$

where

$$z = \exp[-\delta G_T^0/(RT)] \tag{3}$$

and R and T denote the gas constant and absolute temperature, respectively. In order to improve the prediction abilities of the procedure according to eqn. (2), the EPEN values of the increment are combined [32] with the MCY-B $K_{p,2}$ terms [31] to form the RRHO MCY-B/EPEN model of gas-phase water clusters.

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* The equilibrium constant of formation (1) of the cluster $(H_2O)_i(g)$ is defined as:

$$K_{p,i} = p_i/p_1^i,$$

where p_i and p_1 denote the partial pressures of the i-th cluster and of the monomer, respectively (formally, $K_{p,1} = 1$), fulfilling the familiar relation to the standard Gibbs energy change connected with the association:

$$K_{p,i} = \exp(-\Delta G_{T,i}^0/(RT))$$

(As standard state throughout this paper an ideal gas at 1 atm = 101325 Pa pressure was chosen.)

Recent progress in the theoretical description of water cluster thermodynamics creates a reliable basis for evaluating cluster populations at various temperatures and pressures. From the physico-chemical point of view, populations under saturated vapour pressures are particularly interesting, their evaluation being the aim of this article.

EQUILIBRIUM CLUSTER POPULATIONS

Formally, clusters of any order can be taken into account and, thus, the total pressure of gas-phase water can be considered in terms of the equilibrium cluster partial pressures, p_i, as:

$$P = \sum_{i=1}^{\infty} p_i \tag{4}$$

Introducing the mole fraction of the monomer in the equilibrium cluster mixture, x_1, the following master equation can be obtained:

$$P = \sum_{i=1}^{\infty} K_{p,i}(x_1 P)^i \tag{5}$$

Using the properties of geometrical series (2), eqn. (5) can be solved with respect to the variable x_1 in the following closed form:

$$x_1 = \left\{-1/z - P + \left[(1/z + P)^2 + 4P(K_{p,2}/z - 1)/z\right]^{1/2}\right\} \Big/ \left[2P(K_{p,2}/z - 1)\right] \tag{6}$$

If the value x_1 is available, the population of any cluster can be evaluated, e.g., in terms of its mole fraction x_i:

$$x_i = K_{p,i} x_1^i P^{i-1} \tag{7}$$

Up to now, two governing parameters have been considered: temperature, T, and total water-vapour pressure, P. However, in atmospheric observations for example, the total water density (mass per volume), C, is usually recorded [33] and, consequently, it can be useful to convert the master equation (5) from P to C representation. In the C representation an analogue of eqn. (4) reads

$$C = \sum_{i=1}^{\infty} c_i$$

where c_i denotes the concentration of the ith cluster. While eqn. (4) leads with the application of eqn. (2) to the summation of a geometrical series, q_i, the C representation leads to the summation of a series of iq_i members. This can finally be condensed into the following form:

$$C = \frac{M}{RT}(1 - x_1)\frac{z(x_1 - 1)^2 - x_1 K_{p,2}(x_1 - 2)}{x_1^2 K_{p,2}(x_1 K_{p,2} - x_1 z + z)} \tag{8}$$

where M denotes the monomer mass. Equation (8) represents a cubic equation for the unknown x_1.

DATA USED

The equilibrium constants $K_{p,i}$ were generated by eqn. (2). MCY–B $K_{p,2}$ values [31] were used to adjust the beginning of the series, and the EPEN z term was derived from the data of ref. 22. Although eqns. (6) and (8) are applicable to any values of P or C, in this paper only terms related to the saturated water vapour are considered, reported in ref. 4 for the temperature region between 0 °C and the critical temperature of water (i.e., 374.15 °C [4]), along with some of the information on saturated steam from ref. 34.

RESULTS AND DISCUSSION

The deconvolution of total pressure (eqn. 5) or total density (eqn. 8) of saturated steam leading to the cluster populations in terms of the mole fraction x_i is illustrated in Table 1 for the first five members of the series $(H_2O)_i(g)$. When only cluster populations larger than, e.g., 0.1% are defined as significant, only dimers and trimers are significantly populated under saturated steam conditions. In fact, there are two series of cluster populations: those originating from eqn. (5) (i.e., using the total pressure P as input information) and those originating from eqn. (8) (i.e., where the total density is the input). The results from both procedures are identical only if the individual clusters obey the perfect-gas equation of state (consequently, comparisons of the results of the two procedures at the same temperature can serve as a test of the ideal behaviour of a cluster). Clearly enough, the results of both approaches are very close to temperatures of ~ 500 K. However, at higher temperatures there are considerable differences; the cluster-population estimates based on the total density being substantially higher than those based on the total pressure (and, therefore, the monomer mole fraction obtained by the total-pressure approach is higher). The monomer mole fraction x_1 itself essentially decreases with temperature because of the binding condition

$$\sum_{i=1}^{\infty} x_i = 1$$

The ideal behaviour, i.e., the conformity of the triads T–p_i–c_i of the individual clusters (firstly of the monomers and of the smallest oligomers) with the perfect-gas equation of state, is a crucial question connected with the reliable application of the cluster model. This question is important not only for equivalency between the cluster populations from eqns. (5) and (8)

TABLE 1

Mole fractions, x_i (%), of water oligomers, $(H_2O)_i(g)$ ($i < 6$), in equilibrium saturated water vapour evaluated with total density [4] (*C*) or total pressure [4] (*P*) as input information

T (K)	$i = 1$		$i = 2$		$i = 3$		$i = 4$		$i = 5$	
	C	*P*	*C*	*P*	*C*	*P*	*C*	*P*	*C*	*P*
273.15	99.94	99.94	6.210×10^{-2}	6.212×10^{-2}	1.543×10^{-4}	1.544×10^{-4}	3.834×10^{-7}	3.838×10^{-7}	9.527×10^{-10}	9.538×10^{-10}
298.15	99.82	99.82	0.1766	0.1767	7.096×10^{-4}	7.102×10^{-4}	2.851×10^{-6}	2.855×10^{-6}	1.146×10^{-8}	1.148×10^{-8}
323.15	99.58	99.58	0.4158	0.4165	2.425×10^{-3}	2.434×10^{-3}	1.414×10^{-5}	1.422×10^{-5}	8.246×10^{-8}	8.305×10^{-8}
373.15	98.44	98.44	1.543	1.542	1.520×10^{-2}	1.519×10^{-2}	1.498×10^{-4}	1.497×10^{-4}	1.477×10^{-6}	1.475×10^{-6}
423.15	96.02	96.04	3.926	3.908	5.362×10^{-2}	5.313×10^{-2}	7.323×10^{-4}	7.223×10^{-4}	1.000×10^{-5}	9.819×10^{-6}
473.15	92.06	92.20	7.808	7.671	0.1317	0.1269	2.221×10^{-3}	2.100×10^{-3}	3.745×10^{-5}	3.474×10^{-5}
523.15	86.49	87.15	13.24	12.61	0.2607	0.2346	5.132×10^{-3}	4.363×10^{-3}	1.010×10^{-4}	8.117×10^{-5}
573.15	79.14	81.31	20.39	18.32	0.4643	0.3650	1.058×10^{-2}	7.270×10^{-3}	2.408×10^{-4}	1.448×10^{-4}
623.15	68.58	75.01	30.53	24.47	0.8669	0.5091	2.462×10^{-2}	1.059×10^{-2}	6.989×10^{-4}	2.204×10^{-4}
647.30 [a]	53.69	71.80	44.20	27.60	2.010	0.5862	9.141×10^{-2}	1.245×10^{-2}	4.157×10^{-3}	2.644×10^{-4}

[a] Critical point of water [4].

TABLE 2

Comparison of observed saturated [4] water vapour pressures [a] (P_{obs}) with those evaluated [b] within the ideal-gas equilibrium cluster mixture (P_{cl})

T (K)	P_{id} [c]	P_{cl}	P_{obs}
273.15	0.0061090	0.0061052	0.006107
298.15	0.031703	0.031647	0.03166
323.15	0.12364	0.12312	0.12334
373.15	1.0295	1.0135	1.0132(5)
423.15	4.9760	4.7830	4.760
473.15	17.159	15.877	15.551
523.15	48.264	42.418	39.78
573.15	122.47	100.92	85.92
623.15	326.70	246.86	165.37
647.30 [d]	941.02	633.63	221.29

[a] All pressures are given in bar; 1 atm = 1.01325 bar = 101325 Pa.

[b] I.e., from the total density [4] of vapour.

[c] The pressure derived from treatment of the ideal gas phase as composed of monomeric units only.

[d] Critical point of water [4].

but also for the problem of substituting the partial pressures in defining the equation for equilibrium constants by activities. The results in Table 1 indicate that this question is not significant below a threshold of ~ 500 K. Another crucial question is the quality of the equilibrium constants, $K_{p,i}$, used. Although the MCY–B $K_{p,2}$ values [31] were derived in the RRHO approximation of partition functions, they were successfully tested with the

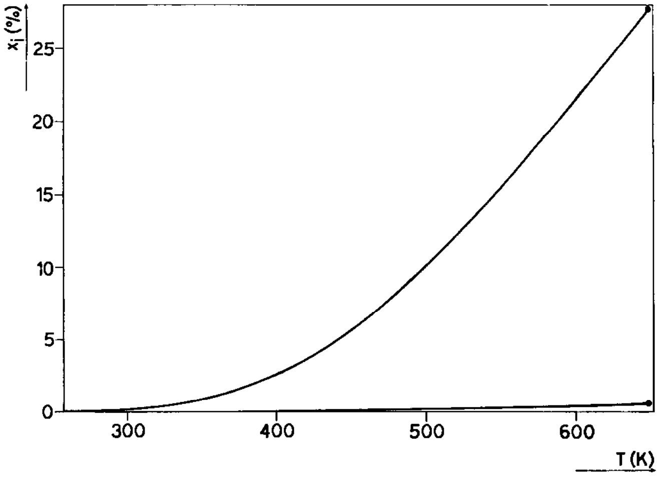

Fig. 1. Temperature dependence of the water dimer (upper curve) and trimer mole fractions, x_i, in saturated steam (evaluated from the total pressure [4], P).

observed terms in the temperature region ~ 100–300 ° C. However, it should be stressed that the success [31] of the RRHO MCY–B evaluation of the $K_{p,2}$ terms does not imply that the MCY–B potential is preferable as a tool in other, physically different situations, particularly in liquid water studies (cf. refs. 10–12). Thus, the $K_{p,2}$ terms employed should be reliable over the whole region of saturated steam treated. Even though the precision of higher $K_{p,i}$ terms (i.e., $i > 2$) may be lower than that of the MCY–B $K_{p,2}$ values, it should not substantially influence the values of x_2. Similarly, the order of the largest clusters does not affect x_i values of the smallest ones. However, owing to assumption (2), a solution of the master equation (5), even in the

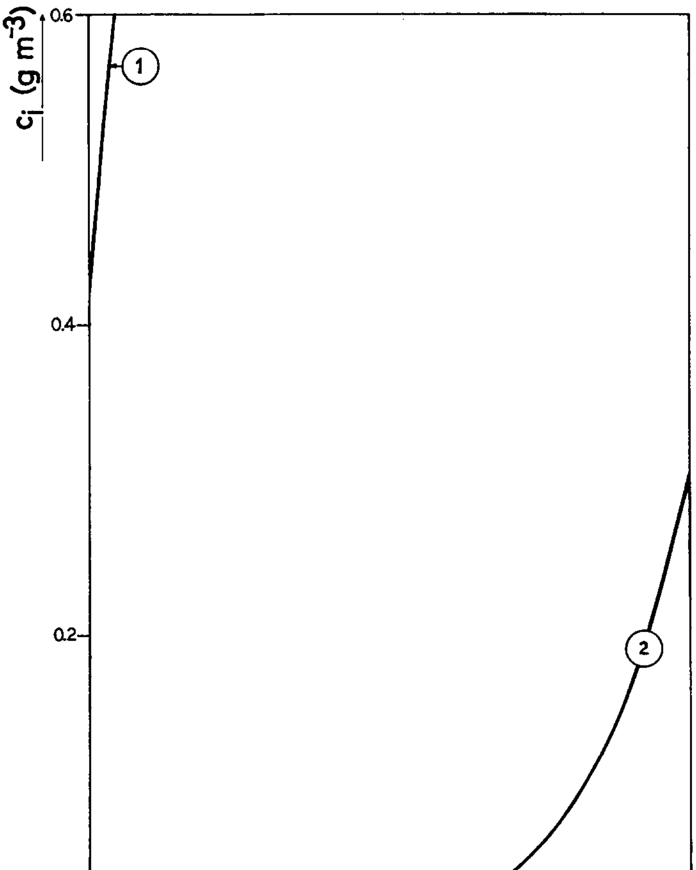

Fig. 2. Temperature dependence of concentrations c_i of the water monomers (1), dimers (2), and trimers (3) in saturated steam (evaluated from the total concentration [34], C).

analytical form (6) (which is otherwise impossible for a finite upper limit of the cluster dimensions).

Table 2 presents another quantization of the question of ideal behaviour of individual clusters by a comparison of the observed [4] saturated steam pressures, P_{obs}, with the total pressure of the equilibrium cluster mixture, P_{cl}, derived from the total-density input (eqn. 8). The pressure P_{id} is derived from the total density, simply supposing the presence of monomers and applying the perfect-gas equation of state. Again, below ~ 500 K the agreement between P_{obs} and P_{cl} is very good.

Temperature dependences of cluster populations result from competition between two types of governing parameters: the equilibrium constants $K_{p,i}$ decreasing with temperature and the pressure of saturated steam, P (or the density, C), increasing with temperature. This competition leads to a large increase of the cluster mole fractions x_i $(i > 1)$ with temperature, as visualized in Fig. 1 for the water dimer and trimer. While, for example, at the normal boiling point of water the dimer forms about 1.5 mol%, at the critical point of water it attains about 28 or 44% in the P input or C input treatments, respectively. The increase with temperature of the cluster populations is also maintained in terms of the c_i concentrations (Fig. 2), including the concentration of monomers, c_1.

Finally, it should be mentioned that the increase with temperature of water-cluster populations in the saturated steam found in this paper is to be considered as a general feature of real gas-phase systems. With other vapours the association equilibrium constants will generally be lower than that for steam. However, this fact can be compensated by a more pronounced increase of the saturated vapour pressure with temperature. Evaluations of cluster populations in saturated vapours can, inter alia, be helpful in the elucidation of temperature/pressure regions convenient for spectroscopic observations of the complexes.

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