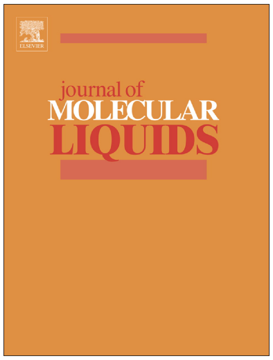

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Tomaž Mohorič, Urban Bren

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How does microwave irradiation affect aqueous solutions of polar solutes?

Tomaž Mohorič[1] and Urban Bren[2,3]*
[1] Faculty of Chemistry and Chemical Technology,
University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia
[2] National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia and
[3] Faculty of Chemistry and Chemical Technology,
University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia
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We employed an empirical molecular mechanical model and non–equilibrium molecular dynamics simulations to investigate the structure of aqueous solutions of some prototypical polar compounds upon microwave heating. Microwave irradiation has been taken into account implicitly by performing simulations at a rotational temperature exceeding the translational one ($T_{\mathrm{r}} > T_{\mathrm{t}}$). We studied aqueous solutions of 5 polar compounds (acetone, acetaldehyde, dimethylether, methanol, and acetonitrile), which have been recently classified as hydroneutral or hydrophilic, depending on their hydration number determined experimentally via dielectric spectroscopy. We have shown that the two groups of polar compounds could indeed be distinguished also based on the changes in their hydration upon a T_{r} increase. Moreover, we have clearly demonstrated the crucial effects of mass and charge distribution in a solute molecule on its hydration properties under the studied non–equilibrium microwave conditions.

I. INTRODUCTION

On the contrary to the usual classification of polar compounds as hydrophilic, it has been recently shown that the term "hydrophilic" may not be appropriate for some polar groups [1–6]. Hydration numbers of various polar solutes in aqueous solutions were determined using dielectric spectroscopy and polar groups were classified as either hydrophilic or hydroneutral [1, 2]. It should, however, be noted that the term "hydration number" is not uniquely defined and its physical meaning does somewhat depend on the experimental technique employed [7]. Even though different methods provide different hydration numbers for the same substance, they still preserve the order in a molecular series [8], hence reflecting substance's hydrophilicity. In dielectric spectroscopy studies hydration number represents the number of "irrotationally" (tightly) bound water molecules [1, 2, 7]. While ether, hydroxyl, and amide groups turned out to be well hydrated with hydration numbers between 4 and 6, other investigated groups like ester, carbonyl, and nitrile were classified as hydroneutral with hydration numbers close to 0, indicating a weak interaction with water and consequently an almost free rotation of solute molecules in aqueous solutions [1, 2]. Higher hydration numbers designate stronger solute–water interactions, which are primarily due to hydrogen–bonding. The main conclusion of these studies is that aqueous solubility is not determined solely by solute's dipole moment, but to a large extent also by solute's pK_{a} value [1, 2].

The distinction between hydrophilic and hydroneutral compounds provided a starting point to examine the non–equilibrium microwave effects on their aqueous solutions. Under the influence of microwaves, water molecules tend to align their dipole moments with the alternating external field, thereby enhancing the rotational portion of their kinetic energy [9–11]. Upon continuous microwave irradiation the excess rotational energy cannot fully dissipate into translations or vibrations and builds up in the form of faster rotations. The net effect results in the formation of "rotationally excited" water molecules, which can be described by a non-equilibrium state with higher rotational temperature than the one governing translational and vibrational degrees of freedom. Note that the term "temperature" usually refers to the equilibrium temperature, hence a state where the rotational temperature exceeds the translational one represents the non–equilibrium effect of microwaves.

In the scientific literature one can find a number of papers in which the effects of microwaves are examined by non-equilibrium molecular dynamics with an explicitly included electric field of microwaves. Such simulations have been successfully applied to study liquid water [12, 13], aqueous solutions of salt [13–15], proteins [16–18], ionic liquids [19], and various other systems [20, 21]. We have proposed an alternative approach [22–24] in which the rotational and translational degrees of freedom are controlled by separate thermostats. In this way we are able to keep the rotational temperature (T_{rot}) higher than the translational one (T_{trs}). This non–equilibrium situation serves to simulate the effects caused by the microwave irradiation.

Auerbach and coworkers [25–27] indeed provided convincing simulation and experimental evidence that in microwave irradiated systems the rotational temperature may substantially exceed the translational one. Using quasielastic neutron scattering measurements on zeolite–guest systems under microwave irradiation they: (i) demonstrated the selective heating of methanol in silicalite and little to no heating of benzene in silicalite;

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* Author to whom correspondence should be addressed. Electronic mail:; urban.bren@um.si