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Evaporation of polar and nonpolar liquids from silica gels and fumed silica

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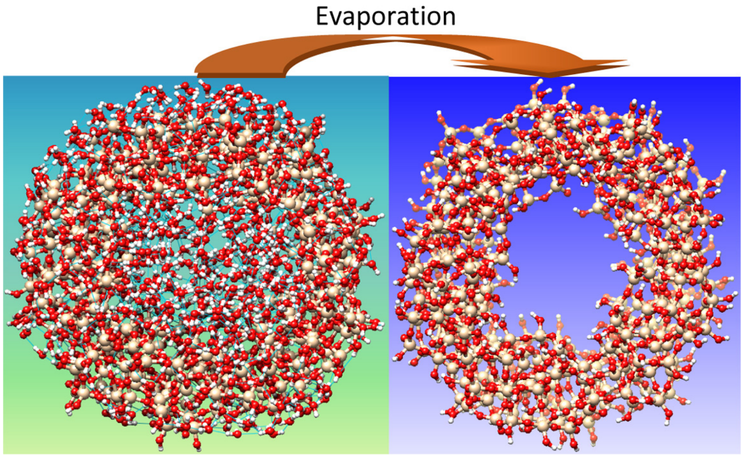
HIGHLIGHTS

- Significance of confined space effects upon evaporation of liquids from depth of silica pores.
- Intermolecular interactions *vs.* interactions of molecules with pore walls: which are stronger?
- Effects of intermolecular bond type and polarity of molecules on evaporation rate.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermogravimetry data on evaporation of polar water, acetone and 1-butanol and nonpolar benzene, *n*-hexane and carbon tetrachloride liquids from mesoporous silica gels Si-40 and Si-100 are analysed using theoretical computation of the evaporation/condensation coefficients and evaporation rate and time. The processes on silica gels Si-40, Si-60, and Si-100 are compared to the evaporation of nanodroplets in the gas phase and evaporation of water, 1-butanol, and *n*-hexane from fumed silica A-300 at room temperature. The evaporation rate $k(T)$ depends strongly on the characteristics of adsorbates (molecular weight, intermolecular bond type and strength, surface tension, boiling, T_b and critical, T_c temperatures) and adsorbents (surface structure, porosity characteristics), and it is exponential function of temperature. Different sequence order of the values of T_b and T_c for water and butanol lead to intersection of curves of evaporation rate (or time) *vs.* temperature between T_b and T_c. For other liquids, the curve position over the used temperature range correlates to the value of T_b; however, the gap between curves is not constant *vs. T*. Described approach can be useful to analyse experimental data on evaporation of pore-confined adsorbates, as well as free droplets of various liquids.

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1. Introduction

Evaporation of liquids and condensation of vapours or gases *vs.* temperature are important phenomena occurring in nature, agriculture, industry, and medicine [1–6]. These processes are affected by a type of liquid or vapour/gas, structure of liquids, surroundings (free bulk, droplets or pore-confined liquids, characteristics of adsorbents), presence of solutes (co-adsorbates), gas and liquid flow parameters, pressure, and exponentially on temperature as activated ones. Confined space effects lead to deceleration of evaporation, especially from long and narrow pores, despite changes in the surface tension (as well as some other characteristics such as density, critical temperature, *etc.*) of liquids located in pores. The stronger the intermolecular interactions between molecules of a liquid and solutes or between them and active surface sites of pore walls, the slower is the evaporation, especially from the depth of narrow pores [2–17]. These effects can enhance condensation of vapours or gases upon adsorption in porous media [14]. Adsorbates can form layers [18], *e.g.* upon adsorption of plane molecules (*e.g.* benzene) in slit-shaped pores of activated carbons, exfoliated graphite, clays, *etc.*, that lead to changes in their properties in comparison with bulk liquids free of layered structures. Free bulk and bound waters form clustered structures, which depend on confined space effects [8]. The properties of liquids (surface tension, boiling and critical temperatures, density, diffusivity, mobility, *etc.*) in strongly confined space can significantly differ from those of bulk liquids [8,19,20]. These effects become stronger in narrower pores depending on the pore wall nature and shape. However, in mesopores at radius $R_p > 10t$ (where t is the adsorbate monolayer thickness), the mentioned above changes can be relatively small [8,20].

Experimental techniques based on evaporation (thermogravimetry (TG), temperature-programmed desorption (TPD) of adsorbates) [21–23] or condensation (used in recording of adsorption/desorption isotherms of gases or vapours) [24] give information on features of interactions between adsorbates and adsorbents depending on the nature of both ones, the texture and morphology of adsorbents [8]. Polarity, features of intermolecular interactions, molecular weight and size of adsorbates can strongly affect their temperature and interfacial behaviour [8,14]. The evaporation rate and evaporation/accommodation coefficients give important information for deep insight into the phenomena affected by confined space effects [1–6,14–17]. To elucidate features of these phenomena, a set of various compounds (nonpolar *n*-hexane, carbon tetrachloride, and benzene and polar water, 1-butanol, and acetone) were evaporated from silica gels Si-40 and Si-100 having narrower and broader pore size distributions (PSD), respectively. Thermodesorption of these liquids with increasing T or evaporation of them in air at a constant temperature from silicas, recording of low-temperature nitrogen adsorption–desorption isotherms analysed, and theoretical (DFT quantum chemical calculations and modelling) methods were used to elucidate the influence of a set of factors on evaporation: size and polarity of adsorbed molecules, conformerisation effects for *n*-hexane and 1-butanol, changes in confined space effects depending on pore size and length, location of adsorbates in pores (in depth or at entrance), and features of intermolecular interactions of adsorbates with a silica surface.

2. Materials and methods

2.1. Materials

Silica gels Si-40, Si-60, and Si-100 (Merck, bead fraction of 0.2–0.4 mm in diameter used for column chromatography) and fumed silica A-300 (pilot plant of the Chuiko Institute of Surface Chemistry, Kalush, Ukraine) were used in the experiments as well-characterised adsorbents [8,25,26]. Water, 1-butanol, acetone, benzene, *n*-hexane, and carbon tetrachloride were used as the wetting and evaporated liquids under varied conditions.

2.2. Characterisation methods

To study the textural characteristics of silicas, low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2405N adsorption analyser or a Quantachrome Autosorb adsorption analyser. The NLDFT method (equilibrium cylindrical pore model for silica, Quantachrome software) [27] was used to calculate the pore size distributions (PSD) of silica gels Si-40, Si-60, and Si-100. To characterise fumed silica, a complex model of pores with slit-shaped and cylindrical pores and voids between spherical particles (SCV) packed in random aggregates was applied with an integral adsorption equation solved using a self-consistent regularisation (SCR) [28].

Thermogravimetric (TG) experiments were carried out using a Derivatograph C (MOM, Hungary) apparatus with the quasi-isothermal program at a heating rate of 3 K/min (upon complete evaporation of adsorbates). To remove adsorbed water, the samples were heated before experiment at 180 °C in vacuum for several hours. Prior to experiment, silica gels were outgassed to facilitate the penetration of liquid adsorbate into pores in gel-like paste prepared with excess of adsorbate (up to 2.66 ml per gram of silica). The samples were placed in a conical platinum crucible [21]. For easy comparison of the TG results, the curves were normalised by subtraction of the silica weight and dividing by the initial weight of a liquid. Thermoporometry method [8,25,26] was used to calculate the PSD based on the water desorption *vs.* temperature.

Evaporation of water or 1-butanol (1 g per 0.3 g of silica) and hexane (0.1 g per 0.1 g of silica) was studied at a constant temperature (18 ± 1 °C) for silica gels (Si-40, Si-60, and Si-100) and fumed silica A-300 in comparison with evaporation of liquids without silica using an ABT 220-5 DM (Kern, Germany) analytical balances. Time of observation was 550.5 h, 689.3 h and 326 min for water, butanol (slow evaporation), and hexane (rapid evaporation), respectively. To reduce the errors caused by changes in environmental conditions, the evaporation of liquids from open glass vials (volume 10 cm^3) was carried out simultaneously for all silicas and a control sample without silica.

2.3. Computation methods

Quantum chemical (QC) calculations using density functional theory (DFT) method were carried out using a hybrid functional ωB97X-D [29–31] (labelled as wB97XD in Gaussian 09) and various basis sets (aug-cc-pVQZ, aug-cc-pVTZ, cc-pVTZ, and cc-pVDZ) with the Gaussian 09 program suit [29]. The solvation effects (molecule alone or in adsorbed state on a silica cluster in a medium with this compound or in the gas phase) were analysed using the solvation method SMD [32] implemented in Gaussian 09. To compute the Gibbs free energy of solvation (subscript s), $\Delta G_s = G_l - G_g$, where G_l and G_g are the Gibbs free energies of a molecule free or bound to silica cluster in the liquid (subscript l) and gas (g) media, respectively. The calculations were performed taking into account zero-point and thermal corrections to the Gibbs free energy in the gas phase and for solved molecules and silica clusters using the geometry optimised using HF/cc-pVDZ, ωB97X-D/cc-pVDZ, ωB97X-D/cc-pVTZ or ωB97X-D/aug-cc-pVQZ (last basis was used only for water). The solvation effects were analysed for the silica clusters with 8 and 22 tetrahedrons alone and with an adsorbed molecule (see the Supporting Information (SI) file). Note that functional ωB97X-D introduces empirical damped atom-pairwise