We studied the effects of various surfactants on the textural properties (BET surface area, pore size, and pore volume) of the silica aerogels prepared at an ambient pressure. A simple surface modification of silica gel prepared at an ambient pressure through hydrolysis and polycondensation of TEOS as a silica precursor was conducted using various structure directing agents. The treatment was found to induce a significant difference in the porosity of the silica aerogel. Highly porous silica aerogels with bimodal porous structures were prepared by modifying the surface of the silica wet-gel (alcogel) with trimethylchlorosilane (TMCS) in order to preserve its porosity. The samples were analyzed by small-angle X-ray scattering and nitrogen adsorption. In this work, a possible new type of highly porous hydrophobic silica aerogel with a bimodal porous structure is presented. A hydrophilic extremely porous (high surface area and large pore volume) silica aerogel was obtained by heating the as-synthesized hydrophobic silica aerogel at 400◦C for 1 h. There was a significant effect of structure directing agent on the textural properties, such as specific surface area, pore size distribution and cumulative pore volume of the silica aerogels.