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# Theoretical Study of Styrene (Methanol)$_n$ Clusters, $n = 1-9$. Comparison with Methanol Clusters

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The structures, energetics, and growth pattern of styrene (methanol)$_n$ clusters, (SM$_n$), with $n = 2-9$ are investigated using a search technique that employs Monte Carlo procedures. A 6−12−1 all-atom potential was developed that accurately reproduces the heat of vaporization, heat capacity, and density of liquid styrene. This potential, in conjunction with the OPLS potential for methanol, yields results strongly correlated with the experimental observations from our R2PI study of the SM$_n$ clusters. The progressive addition of methanol molecules to styrene leads to the formation of stable methanol clusters similar to those formed in the absence of styrene, with the exception of the SM$_3$ cluster where the lowest energy structure incorporates the methanol trimer as a hydrogen-bonded chain, rather than as the more stable cyclic structure of M$_3$. For the SM$_n$ clusters with $n = 4-9$, cyclic and branched cyclic methanol structures are found. In the clusters containing 5, 7, and 9 methanol molecules, the methanol subclusters are present on both sides of the plane of the styrene. The nonadditivity and size specificity of observed spectral shifts are explained through the use of a series of compact and expanded structures, with the interaction energy calculated between the styrene and the methanol subcluster (M$_n$). The results indicate that the spectral shifts correlate with the interaction energies between styrene and M$_n$ within the SM$_n$ clusters. The modeled cluster structures and simple energetic arguments provide a reasonably compelling picture of the spectral shifts associated with hydrogen bonding interaction among methanol molecules and between styrene and the methanol subclusters.