Determination of the Temperature Dependence of the Limiting Activity Coefficients and Henry's Law Constants for MTBE in Water

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Large scale production of methyl tert-butyl ether (MTBE) and its worldwide use as an oxygenated fuel additive and octane number booster has resulted in the contamination of numerous industrial sites and groundwater resources and has become a severe environmental problem. To model the environmental transport and fate of MTBE, and to design efficient remediation procedures, data on the air-water partitioning of this volatile contaminant are needed. Although some measurements of the air-water partitioning of MTBE have been presented in the literature, their mutual agreement is not fully satisfactory, and new reliable determinations are thus necessary. In order to improve the situation, in this work, we report new accurate measurements of infinite dilution activity coefficients covering an extended range of environmental temperatures (273 to 333 K) for MTBE in water. Our results, obtained by several experimental techniques (Inert Gas Stripping, Exponential saturator, Headspace analysis with SPME sampling, and Phase Ratio Variation), show good mutual agreement supporting their credibility. In addition, employing our recently refined flow microcalorimetric setup, we carried out meticulous measurements of dissolution enthalpies at infinite dilution in the range 283 to 318 K. The observed highly exothermic dissolution enthalpies were found to be fully consistent with the observed steep rise of infinite dilution activity coefficients with temperature in the given temperature range, and the derived large positive dissolution heat capacity is well comparable to those exhibited by similar semihydrophobic aqueous solutes. The results for infinite dilution activity coefficients and dissolution enthalpies obtained here and the values of infinite dilution activity coefficients from the literature were simultaneously correlated to a suitable fitting equation, with individual data points weighted according to their probable uncertainties. Based on this correlation, recommended temperature dependences of infinite dilution activity coefficients, Henry's law constant, or the air-water partition coefficient of MTBE, values reliable in the range from the melting to the normal boiling point of water were established.