Excess and Solvation Enthalpies of Perfluoroalkane + Alkane Mixtures

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As part of a research project dealt with in our laboratories involving the themodynamics of mixtures, we have undertaken the investigation of the thermodynamic properties (G^E, H^E, V^E) of mixtures of fluorocarbons with organic compounds. The aim is the characterization of the interactions between the fluorine atom and different functional groups. In this work, the effect of temperature, branching, and cyclization on excess and solvation enthalpies is examined. The following binary mixtures have been studied: hexane + C_nF_{2n+2} (n = 5-8), and C_6F_{14} + C_nH_{2n+2} (n = 5-8), + 2-methylheptane, and + cyclohexane. A newly designed calorimetric technique and calculation procedure [1] has been used to obtain partial molar enthalpies and excess enthalpies, H^E's, where a TAM heat-flow calorimeter equipped with a titration cell has been employed. This procedure was demonstrated capable to successfully replace the mix-flow technique, and to obtain accurate enthalpies of solution at infinite dilution in addition to H^E. Results show that the enthalpies of solution have very large positive values, which increase with increasing size of dilute component and with decreasing temperature. These enthalpy effects are the largest ever observed for mixtures of non-polar compounds.

The enthalpies of solvation, $\Delta H°$, in hexane and perfluorohexane were obtained from the known heats of vaporization and the enthalpies of solution at infinite dilution. The plot of $\Delta H°$ vs the van der Waals surface area of the solute molecules shows that alkanes and perfluoroalkanes have similar $\Delta H°$ in perfluorohexane, while in hexane as solvent perfluoroalkanes have sensibly less negative values than alkanes, the difference in $\Delta H°$ being about 30 kJ mol^{-1}. Cycloexane exhibits a more negative $\Delta H°$ than linear alkanes in both solvents, the cyclization producing a $\Delta H°$ change larger in hexane than in perfluorohexane. 2-Methylheptane shows a less negative $\Delta H°$ than octane in both solvents. Branching causes a $\Delta H°$ change larger in hexane than in perfluorohexane. These comparisons, together with the comparison of $\Delta G°$, vapor pressures and volumes of pure liquids, suggest that perfluorocarbons are very inert molecules that interact weakly with themselves as well as with hydrocarbons. The virial coefficients of pure gases and mixtures indicate that perfluorocarbons interact feebly both with themselves and with hydrocarbons also in the gaseous state [2].

[1] E. Matteoli, and L. Lepori, *Fluid Phase Equilibria.* **174**, 115-131 (2000).
[2] L. Lepori, E. Matteoli, A. Spanedda, *The 18th IUPAC International Conference on Chemical Thermodynamics*, August 17-21, 2004, Beijing, China. Oral Communication 06-O-13, p.296.