Molecular Interactions in Heptane + Amine Mixtures Studied Through Excess and Solvation Enthalpies

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In the frame of our studies on the excess thermodynamic properties (G, H ,V ,Cp) of mixtures containing organic compounds, [1] we have started a similar investigation on hepthane + amine mixtures [2]. We report here excess enthalpies for hepthane + secondary, tertiary, and cyclic amines (diethyl, dipropyl, dibutyl, triethyl, tripropyl, tributyl, cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl, trimethyleneimine, pyrrolidine, piperidine, hexamethyleneimine, heptamethyleneimine). A newly designed calorimetric technique and calculation procedure have been used to obtain excess enthalpies, HE, from heats of solution [3]. Accurate partial molar enthalpies at infinite dilution, H^{inf}, have been also obtained. All mixtures are endothermic, HE > 0, and the heat effects decrease with increasing amine size, indicating that the strong attraction between amine groups is broken during the mixing process with heptane. The enthalpies of solvation H^{solv} associated with the process ideal gas dilute solution have been obtained from H^{inf} and the known enthalpies of vaporization. Solute-solvent interaction have been examined by describing the H^{solv} with an additive scheme of surface interactions and by applying the Scaled Particle Theory. It is found that NH_2 and NH groups interact with heptane more strongly that the hydrocarbon groups CH_3, CH_2, CH. The chain lengthening causes the same decrease of H^{solv} for both amines and hydrocarbons in heptane. Cyclization produces a more negative H^{solv} and hence a stronger interaction with the solvent. On the contrary, branching causes a less negative H^{solv} and a weaker interaction with heptane molecules.

[1] C. Duce, M.R. Tinè, L. Lepori, E. Matteoli, Fluid Phase Equilibria 269 (2008) 59-68.
[2] E. Matteoli, L. Lepori, A. Spanedda. Fluid Phase Equilibria 212 (2003) 41-52.
[3] E. Matteoli, L. Lepori, Fluid Phase Equilibria 174 (2000) 115-131.