Mixtures of 1,1,2,2-Tetrachloroethane + Aromatic Hydrocarbons: Excess and Solvation Thermodynamic Functions

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In the frame of our studies on thermodynamics of solutions, we have undertaken the investigation of mixtures of 1,1,2,2-tetrachloroethane (TCE) with other organic compounds. The aim is the characterisation of the interaction between the chlorine atoms and different functional groups. TCE is used as non-flammable solvent for fats, oils, waxes, resins, cellulose acetate, rubber, phosphorus and sulfur and in the manufacture of paint, varnish and rust remover. The following binary mixtures have been studied: TCE + benzene, + toluene, + ethyl-, + n-propyl-, + iso-butyl-, + n-butyl-, + sec-butyl-, + tert-butyl-benzene, + heptane, + cyclohexane. VLE have been measured by head-space gas-chromatographic analysis of the vapour phase equilibrated with the liquid mixture. From these x-y data, activity coefficients and excess Gibbs energies G^E have been obtained by a least-squares adjustment to selected G^E equations. Excess enthalpies H^E and enthalpies of solutions have been determined by means of a flow calorimeter (TAM, LKB, Sweden). Excess volumes V^E and limiting partial molar volumes $\overline{V}^\circ$ have been obtained from density measurements carried out by means of the vibrating tube technique. From activity coefficients and enthalpies of solution at infinite dilution, the solvation functions ΔX° (X=G,H) for the transfer process from an ideal gas to dilute solution have been calculated using vapour pressures [1] and heats of vaporisation [2] of pure liquids.All mixtures with aromatic compounds show negative G^E, H^E and V^E, whose magnitude decreases on going from toluene to butyl-benzene. ΔG°, ΔH° and $\overline{V}^\circ$ of different solutes (aromatic, aliphatic, cyclic and branched hydrocarbons) have been compared using van der Waals surface area volume as molecular descriptor. This comparison suggests that aromatic hydrocarbons interact with TCE more strongly than alkanes and cyclohexane. This is due to the strong interaction between the TCE Cl atoms and aromatic π-electrons and, to a lesser extent, to the compact shape of the benzene ring which better packs in the solvent than linear aliphatic hydrocarbons (closer packing). Branching produces an appreciable volume increase mostly due to the bulky shape of branched alkyl portions, which need more space to be accommodated in the solvent structure. This looser packing causes a weaker interaction with TCE and, consequently, less negative ΔH° and ΔG° of branched alkyl-benzenes with respect to n-alkyl benzenes.

[1] T. Boublik, V. Fried, and E. Hala, *The vapour pressures of pure substances*, Elsevier, Amsterdam (1973).
[2] V. Majer, V. Svoboda, *Enthalpies of vaporization of organic compounds*, Blackwell, Oxford (1985).