The Effect of Molecular Shape on the Volumic Behaviour of Liquid Mixtures: Silicons in Heptane

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In order to ascertain the different packing in the solvent and the different solute-solvent interaction and dependance on differently shaped molecules, we have undertaken a research on the thermodynamic properties (volume, enthalpy and Gibbs energy) of linear, branched and cyclic molecules in inert solvents [1,2]. In this paper we report excess volumes and partial molar volumes for mixtures of heptane with the following dimethylsiloxanes: hexamethyldisiloxane (dimer), octamethyltrisiloxane (trimer), decamethyltetrasiloxane (tetramer), dodecamethylpentasiloxane (pentamer), polydimethylsiloxane (M=2000), octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane. Silicons alone or in combination with partially fluorinate alkanes have been used as intramolecular tamponade in vitreoretinal surgery [3]. The excess volumes of mixing have been determined at 298.15 K using a vibrating tube densimeter. The excess volume for heptane + dimer and + trimer were found negative and nearly zero, respectively. All the other excess volumes were positive and increasing with chain lengthening of the dimethylsiloxane. The partial molar volumes of both components at infinite dilution have been obtained from excess volume data and from molar volumes of pure liquids. The partial molar volumes of different solutes have been compared using the van der Waals volume as molecular descriptor. The partial molar volume of silicones in heptane increase linearly with size, the mean increment being 76.5 cubic centimeter per mole for the -$OSi(CH_3)_2$- repeating unit. The silicons show partial molar volumes larger than n-alkanes in heptane, mostly due to their bulky shape of branched molecules, which need a large space to be accommodated in the solvent structure (looser packing). On the contrary, cyclic siloxanes have shown lower partial molar volume than linear siloxanes. This volume decrement is to be attributed to the compact shape of ring molecules which are better packed in the solvent (closer packing).

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[3] L. Lepori, E. Matteoli, A. Spanedda, F. Genovesi, S. Rizzo. Graefes Arch. Clin. Exp. Ophtalmol., 244, 79 (2006).