An Interpretation of the Excess Molar Thermal Expansion of Binary Systems Formed by 1-Alkanols with 1-Alkenes in Terms of an Equation of State with Association

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The results of the excess molar thermal expansion A_p^E at 25 ºC calculated from the excess molar volume, V^E, at 15, 25, and 35 ºC for binary mixtures formed by 1-hexanol with 1-hexene, 1-octene, and 1-decene are reported. The volumetric properties change from positive over the whole concentration range for the 1-decene system to negative, except at high dilutions of alkanol, for the 1-hexene system.

These properties are described and interpreted in terms of the Treszczanowicz and Benson model adapted for mixtures of a self-associated component and an active solvent. The model contains the Flory equation of state combined with the association model proposed by Treszczanowicz and Kehiaian. Three association parameters: enthalpy, entropy and volume of the H-bond formation for 1-alkanols are taken from the previous estimations for mixtures formed of 1-alkanols with n-alkanes. The OH - pi interactions and residual non-specific interactions are taken into account by means of the Kehiaian-Guggenheim group contribution method. The model correctly predicts the size and shape of V^E and A_p^E as well as the partial molar properties of components, including the position of extremes and sign-inversion points. These properties are interpreted as a result of the mutual compensation effect of alkanol self-association, free volume, OH - pi interactions and residual contributions due to the disruption structure of the pure liquids. These results are compared with those for 1-alkanol n-alkane systems as well as those for the ERAS model, including prediction of the excess enthalpy and excess molar isobaric heat capacity.