

# Liquid-Liquid Equilibria from a More General Point of View: Mixtures of Alkanes with Ethanol or Acetonitrile

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In order to gain more insight into liquid-liquid phase behavior, we have performed a systematic study of the liquid-liquid phase behavior of mixtures of *n*-alkanes with the molecular solvents ethanol or acetonitrile. The main objective was to identify systematic trends of the phase behavior. Ethanol as a polar molecule with a dipole moment comparable to water is able to form hydrogen bonds. Acetonitrile exhibits a high dipole moment and shows partial miscibility with a couple of common molecular liquids, typically connected with the appearance of upper critical points. Acetonitrile allows for the study of molecular interactions influenced by a dipole moment without the appearance of hydrogen bonds. The present work contributes to the open discussion of whether acetonitrile-alkane mixtures might be suitable as reference systems for the verification of experimental procedures for the determination of liquid-liquid phase equilibria.

Therefore, by a gradual variation of chain lengths of one component of the investigated systems, small changes of the molecular interactions are achieved resulting in characteristic shifts of the phase behavior. The critical solution temperature, the critical composition and the parameters characterizing the shape of the phase diagram are determined by a numerical analysis of the phase diagrams presuming Ising criticality and a nonlinear diameter. Notably, this method also enables accurate predictions of the critical solution point on the basis of data at noncritical composition.

The systems studied so far show limited miscibility with upper critical solution temperatures (UCSTs), and show variations from an asymmetric shape to an almost symmetrical one. The UCST decreases with decreasing length of the alkyl chains of the alkane. Both classes of systems show the same universal critical behavior. The variations of the parameters are mainly determined by the size of the alkyl chains. A simple determination of the free enthalpies on the basis of a Flory-Huggins-like approach allows for a description and partial prediction of UCSTs of the different systems.