

DESCRIPTION OF INFINITE DILUTION THERMODYNAMIC PROPERTIES OF SOLUTES IN BINARY FLUID MIXTURES, INCLUDING THE NEAR-CRITICAL REGION

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Abstract— The description of the thermodynamic behaviour of dilute binary solutions over wide ranges of solvent density requires a different approach to that normally applied for liquid solvents near their triple point. The abnormal behaviour of the partial molar quantities of the solute in the near-critical region of the solvent hampers the use of the same treatment, thus an alternative procedure must be devised. It is shown that a successful procedure may be developed on the basis of the Krichevskii function, $(\partial p/\partial x)_{T,V}^{\infty}$, a well behaved thermodynamic quantity. We have used it to describe the distribution of CO₂ between water and steam and the heat capacity of the solute in water over a wide density range. We also present the description of the system B(OH)₃-H₂O and calculate its heat capacity. The results of the predictions are compared to experimental values.

Keywords— Krichevskii function, thermodynamic properties, supercritical solutions, solvation.

I. INTRODUCTION

The behaviour of solutes at infinite dilution is a consequence of solvation phenomena, either equilibrium or dynamic, upon the solute molecule. Solvation under equilibrium conditions is characterized by the standard thermodynamic properties of the solutes at infinite dilution which refer to the Henry activity scale. Consequently there is great interest on being able to characterize in detail the behaviour of solutes at infinite dilution with the ultimate goal of having a general descriptive tool for the solute's standard thermodynamic properties. The description should be valid even

in the particularly difficult region of near-criticality where moderate changes in temperature and pressure cause appreciable density variations. From the scientific point of view, supercritical near-critical fluids are the best solvent systems to explore the effect on intermolecular interactions of the solvent number density, a variable which is known to be of paramount importance in characterizing solvation phenomena. Moreover, practically all the industrial processes making use of supercritical fluids operate in the near-critical region because the large compressibility of the solvent in that thermodynamic region facilitates the alteration of the solvent density, which in turn affects the solvent's capacity to solvate different species.

Considering the increasingly large number of chemical processes that rely on the use of supercritical fluids, the possibility of describing the behaviour of these (dilute) solutions in the vicinity of the solvent's critical point is of great practical importance. Many of these chemical processes are optimized by fine tuning the intermolecular interactions present in the fluid, accomplished with a careful adjustment of the thermodynamic variables and/or by addition of adequate co-solvents. This fine tuning requires a good knowledge of the intermolecular interactions which prevail in the solution. In order to understand at a molecular level the processes that occur in such an important thermodynamic region it is essential to separate the long-range effect due to the high solvent susceptibility (*i. e.* compressibility), from the short-range intermolecular interactions (Fernández-Prini and Japas, 1994).

To describe the general behaviour of a dilute binary solution including the near-critical region, it is necessary to avoid the well known difficulties generated by the anomalous behaviour of many thermodynamic properties (response functions) when the solvent is in