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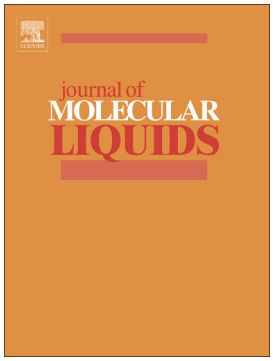

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Kathleen A. House, J.E. House

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THERMODYNAMICS OF DISSOLUTION OF UREA IN WATER, ALCOHOLS, AND THEIR MIXTURES

Kathleen A. House and J. E. House*, Department of Chemistry, Illinois Wesleyan University, Bloomington, IL 61701 jhouse@iwu.edu

Key words: Urea; dissolution; thermodynamics; solvation; aggregation; mixed solvents

ABSTRACT

A study has been carried out by making use of published data for the solubility of urea to evaluate the thermodynamic quantities associated with the dissolution of urea in water, alcohols, and mixture of these solvents. The ΔG values show an increase with the nature of the solvent in the order water, −1.75; methanol, +2.46; ethanol, +5.74; and 2-propanol, +7.26 kJ mol^{-1}, respectively. For mixtures containing 33.3, 50, or 66.7% water, there is little difference in the thermodynamic parameters regardless of the identity of the alcohol or the composition of the mixture. In the case of the pure alcohols, values for ΔS and ΔG show that dissolution is most favorable in methanol and least favorable in 2-propanol. For mixtures containing methanol/ethanol, ethanol/2-propanol, and methanol/2-propanol, the solubility data show that the mixture containing ethanol and 2-propanol is the least favorable to dissolution of urea whereas that containing methanol and 2-propanol is most favorable on the basis of values for ΔS and ΔG. These trends in thermodynamic properties are considered with regard to the nature of the solute-solvent interaction, the expected degree of aggregation of urea in the solvents, and the characteristics of the solvents.

1. Introduction

The importance of urea in commerce is indicated by the fact that annual production is approaching 200 million tons. The majority of urea is utilized as a fertilizer, but other uses include the manufacture of resins and in the production of products for use in dermatology. Urea has numerous other uses in biochemical and medical applications such as the denaturation of proteins. As a result of its wide ranging applications, the solution behavior of urea in both aqueous and nonaqueous solvents has been the subject of considerable practical importance. Accordingly, the results of numerous experimental and theoretical studies on such solutions have been reported [1-6]. Moreover, because it has very low toxicity and is environmentally safe, urea has been used as the basis for laboratory experiments in chemical education involving measurements of enthalpy of dissolution [7,8]. Urea has a dipole moment of 4.20 D in water and 6.25 D in a mixture containing 20 weight percent water/acetone [9]. As a result, one of the interesting aspects of urea is the fact that it forms molecular aggregates in solution [10-12]. The urea molecule has unshared pairs of electrons on both nitrogen atoms as well as on the oxygen atom of the carbonyl group. As a result, there are multiple possible sites by means of which urea can form hydrogen bonds to other urea molecules or to solvent molecules. Therefore, association of urea itself is possible with the greatest extent of association expected to occur in solvents that consist of larger, less polar molecules or in those that do not form strong hydrogen bonds.

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