



## Surface tension study of concentration dependent cluster breaking in acetone-alcohol systems

Jonathan Lalnunsiam\* and V. Madhurima

*Department of Physics, Mizoram University, Aizawl 796 004, India*

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### ABSTRACT

Alcohols are well-known for the formation of clusters due to hydrogen bonds. When a second molecular species such as acetone is added to an alcohol system, the hydrogen bonds are broken leading to a destruction of the molecular clusters. In this paper we report the findings of surface tension study over the entire concentration region of acetone and six alcohol systems over the entire concentration range. The alcohols chosen were methanol, ethanol, isopropanol, butanol, hexanol and octanol. Surface tension was measured using the pendent drop method. Our study showed a specific molecular interaction near the 1:1 concentration of lower alcohols and acetone whereas the higher alcohols did not exhibit the same.

**Key words:** Surface tension; hydrogen bond; alcohols; acetone.

### INTRODUCTION

Alcohols are marked by their ability to form hydrogen bonded clusters.<sup>1,2</sup> The addition of a second molecular species, whether hydrogen-bonded or not, will change the intermolecular interactions in the alcohol system, especially by breaking of the hydrogen-bonded clusters. Since hydrogen bonds have a small bond-energy (usually taken to be between 5-30 kcal/mol) they are broken by thermal energy<sup>3</sup> at room temperature. Hydrogen bonds are usually studied in the gaseous cluster form rather than in solvent because of sol-

vent effects<sup>4</sup> but such effects are important and hence there are many studies of hydrogen bonds in solvents.<sup>5</sup> Dielectric and calorimetric studies of clusters in alcohols in carbon-tetrachloride were attributed to homogeneous associations of the alcohol.<sup>6</sup> For methanol in p-dioxane the chain-like clusters were seen to form the networks and not cyclic structures.<sup>7</sup>

The surface tension of hydrogen bonded liquids is usually higher than non-hydrogen bonded liquids. This is because more energy has to be supplied to break the hydrogen bonds and resulting in more cohesion between the molecules. Surface tension of alcohols has been studied previously. Marangoni instability caused auto-oscillations in the surface tension of higher alcohols at the air-water interface were observed.<sup>8</sup> Surface tension of alco-

*Corresponding author:* Lalnunsiam\*

Phone: +91-9862306780

Fax : 0389-2330522

E-mail: [jsailo.sailo@gmail.com](mailto:jsailo.sailo@gmail.com)

hol-water systems was measured using a tensiometer and reported between 20-50°C.<sup>9</sup> Semi-empirical theories such as gradient theory of inhomogeneous fluids were found to be inadequate to describe the surface tension of alcohol binary systems.<sup>10</sup> Water-ethanol binary system showed a maximum refractive index for 0.667 mole fraction.<sup>11</sup>

In this paper the findings of surface tension studies over the entire concentration range of acetone-alcohol binary systems are reported. The alcohols studied were methanol, ethanol, isopropanol, butanol, hexanol and octanol. The choice of alcohols was to enable the study of influence of side-chain length on the intermolecular interactions.

## MATERIALS AND METHODS

The surface tension measurements were performed using Rame-Hart contact angle Goniometer. It consists of volume controlled syringe where the sample liquid whose contact angle is to be measured is inserted, CCD camera which capture live drop image and advanced drop image software for processing of data. This software is programmed to measure the surface tension of the sample liquid. The experiment was conducted at 27°C and the surface tension was determined using the pendant drop method. In this method the droplet of liquid formed at the tip of the syringe needle before it falls due to gravity. An image of this drop is captured by the camera and analyzed by the proprietary 'Advanced Drop Image Software' of Rame-Hart Contact Angle Goniometer.

### Chemicals

The choice of chemicals is based on the formation of hydrogen bond C=O--H in alcohol-acetone system which is a prototype of hydrogen bond seen in biomolecules. This feature will help in bio-MEMS devices. All chemicals were of AR grade, procured commercially from Merck and were used after

distillation.

## RESULTS AND DISCUSSION

The surface tensions of the six binary liquids studied are shown in Figure 1. The error in the estimation of surface tension is  $\pm 0.5$  mJ/m<sup>2</sup>. A sharp dip in the value of surface tension is seen in the 0.5-0.6 mole fraction region of acetone and methanol, ethanol and isopropanol whereas the dip is at 0.8 mole fraction in butanol and no dip is seen in the hexanol and octanol binary systems.

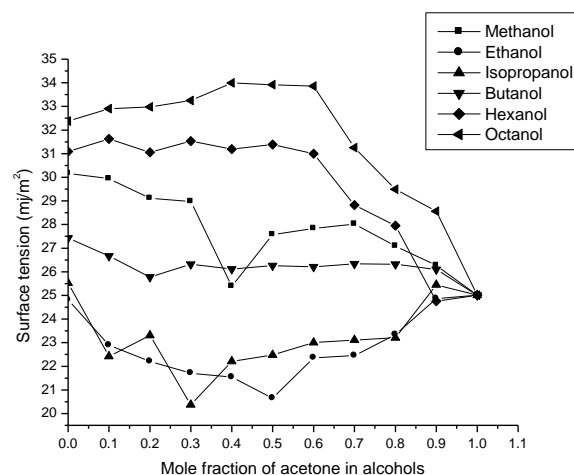


Figure 1. Variation of surface tension of acetone-alcohols binary mixture.

These results can be understood from the hydrogen bond cluster breaking phenomenon. Lower alcohols form extensive hydrogen bonding compared to higher alcohols. As the chain length of the alcohols increases two effects reduce the hydrogen bonding capability of the alcohol. The first is the higher electronegativity of the lower alcohol oxygen compared to higher alcohols and the second is the steric effect of the larger alkyl chain of higher alcohols.

On addition of acetone to methanol, for small concentrations of acetone, the methanol

clusters are broken causing a decrease in the surface tension. At the 1:1 ratio of acetone and methanol the sharp decrease in the surface tension corresponds to the formation of a ring-like conformer of the two species<sup>12</sup> and shown in Figure 2. Since all the active sites of acetone and methanol are participating in hydrogen bonds, the system behaves in effect like a non hydrogen bonded liquid, with very low surface tension. On the addition of more acetone to the system the surface tension tends towards that of the major component, i.e. acetone. The same effect is seen in acetone-ethanol and acetone- isopropanol systems. The minor variation at the 0.6 mole fraction is with the experimental error limits.

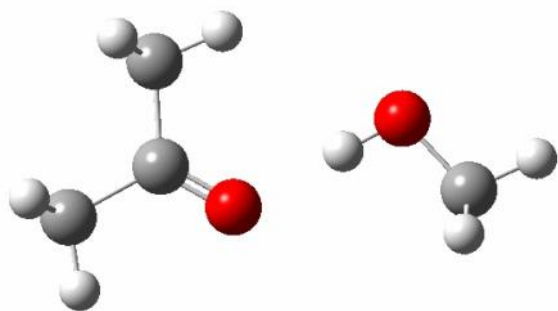


Figure 2. Conformation of 1:1 acetone-methanol binary mixture.

As the chain length increases in the case of butanol, the initial breaking of the clusters is seen but there is no subsequent dip in surface tension at the mid-concentration region. As the alkyl chain length increases the second effect, namely the steric hindrance offered by the side chain begins to dominate with the alkyl chain moving away from the main site of hydrogen bond interaction, as shown in Figure 3 for acetone-hexanol. The surface tension of alcohols decreases modestly with chain length.

In the case of acetone-hexanol and acetone-octanol the hydrogen bonding in the pure alcohols is not strong enough to cause clusters. The addition of acetone in small quanti-

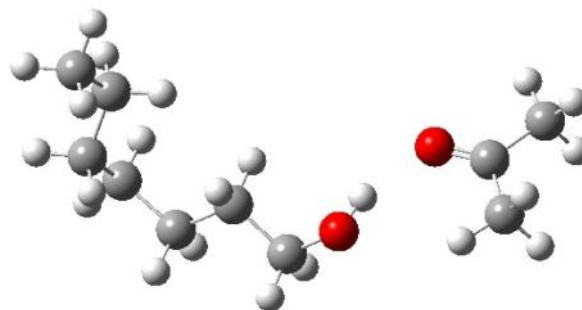


Figure 3. Conformation of 1:1 acetone-hexanol binary mixture.

ties has no effect on the structure of alcohol, as seen from the surface tension value. On the addition of a large quantity of acetone to alcohol, about 70% mole fraction, the surface tension of the binary liquid begins to lower and reaches the value of acetone for 100% acetone. In the two large chain alcohol systems there is no dramatic influence of addition of acetone to alcohols.

## CONCLUSIONS

Surface tensions of six binary systems of acetone-alcohol are reported in this paper. The addition of acetone to alcohols is seen to break the alcohol clusters when the size of alcohol molecule is small. The influence of addition of acetone to large chain alcohols is minimal and there is no evidence of cluster breaking in these systems as seen from the surface tension studies.

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