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The effect of structural modifications on the solution and interfacial properties of straight and branched aliphatic alcohols: The role of hydrophobic effects

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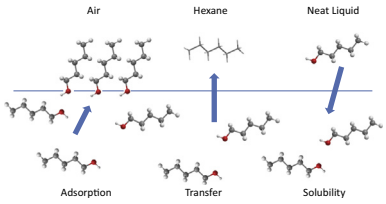
GRAPHICAL ABSTRACT



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ABSTRACT

The effect of structural modifications, such as branching of the hydrocarbon chain on the solution and interfacial properties of short-chain aliphatic alcohols has been investigated. Surface tension measurements have been used to study the adsorption of the alcohols at the aqueous solution/air interface from water/alcohol mixtures, and to determine the aqueous solubilities of the alcohols. The related process of the partitioning behaviour of the alcohols between two immiscible phases has also been studied. Standard free energies of adsorption at the aqueous solution/air interface, standard free energies of transfer between water and hexane, and standard free energies of solution were obtained for the alcohols. A linear "Traube" relationship, an elegant demonstration of the hydrophobic effect, was found to exist between the various free energies for the normal alcohols and the number of carbon atoms in the alcohol molecule. The free energies showed that structurally modified alcohols have less negative free energy of adsorption, transfer or solution compared to the normal alcohol with the same number of carbon atoms. We assign effective numbers of carbon atoms for each branched alcohol for each transfer process. The position of the hydroxyl group relative to the branched part of the molecule was found to be a factor which influences the hydrophobic contribution to the free energy of each transfer process.

An attempt has been made to ascertain whether there is a correlation between the molecular surface area, or the molecular volume, and the interfacial and solution thermodynamic properties of an alcohol in aqueous solution. The standard free energies of some of the branched alcohols have been found to be inconsistent with the values expected from the energetic of the adsorption and the water/hexane transfer processes. This is thought to reflect the different modes of association of the branched and normal alcohols in the liquid state as revealed by small and wide angle X-ray scattering which identifies correlation peaks attributable to intermolecular hydrogen bonding and interchain associations consistent with non-polar segmentation.

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1. Introduction

Normal alcohols are some of the most studied surfactants, and both normal and branched short-chain aliphatic alcohols have industrial applications as highly active and very selective flotation reagents in minerals processing [1], and as co-surfactants in microemulsion systems [2,3]. These low molecular weight alcohols are surface active and may be considered simple amphiphiles. They have been used as model surfactants for the investigation of the relationship between solution and interfacial properties [4–7] and historically investigations of simple alcohol-water solutions have played an important role in the study of surface activity [8–16] since it is well known that the carbon chain length can alter surface activity, viscosity, foaming and detergency [17]. The hydroxyl (alcohol) group is an important moiety in biologically relevant macromolecules, carbohydrates, alcohols and water that interacts strongly with its environment to affect function. The stability of bio-polymers in water may be attributed to the balance of the hydrophobic-hydrophilic in the hydration sphere. Thermodynamic properties such as surface tension is important for many industrial as well as biological process including enhanced oil recovery, the spraying of pesticides, and the stabilisation of lung surfactant [18]. There are many reviews where the interrelationship between chemical structure and its adsorption characteristics *viz* its adsorption activity, surface tension and liquid–vapour layer composition have been discussed [5,19].

Simple alcohols provide the possibility of studying the hydration sphere, structure and dynamics in these more complex molecules and hydrophobic interactions are often modelled from partitioning (octanol–water) or solubility data. The short chain alcohols have therefore been used to characterise hydrogen bonding and the intra-/intermolecular structure of the alcohols for a better understanding of hydrophobic effects since it is often assumed that thermodynamic parameters for such model systems will translate to more complex systems in biology [20]. The role of the hydrophobic effect has recently been expanded to include the properties and behaviour of the "hydrophobic patches" on biopolymers including proteins [17,21–25].

The hydrophobic effect is ubiquitous in nature and at the molecular level is responsible for diverse phenomena, ranging from those of biological relevance [20–26] such as the formation of cell membranes and protein folding; to industrial importance such as detergency and emulsions. However a detailed molecular understanding of how non-polar groups interact in water remains unclear. The process is entropically driven and the classical view of Frank and Evans [27] argues that this relates to structuring of the solvent (water) in the vicinity of the hydrophobic group. The low solubility of organic solvents in water leads to segregation and formation of a molecular interface. For amphiphilic molecules where the apolar hydrocarbon chain is tethered to a hydrophilic head group, de-mixing is frustrated and the amphiphile self-assembles to form micelles, as well as potentially other mesoscopic structures. The Gibbs free energy provides a measure of the thermodynamic potential of the system and may be expressed:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where ΔH° is the enthalpic contribution, $-T\Delta S^{\circ}$ is the entropic component and T is temperature. Historically, hydrophobic hydration shells were thought to resemble solid clathrate hydrates with solutes surrounded by polyhedral cages composed of tetrahedrally hydrogen-bonded water molecules. Upon addition of an apolar solute to water a "cavity" is produced that is accommodated through the re-orientation or displacement of the hydrogen bonding network. The extent to which this occurs is a function of the length scale and is dependent upon whether the hydrophobic molecules are individually hydrated or driven to self-assemble. For small hydrophobic species (*ca.* 0.3–0.5 nm), molecular reorientation permits water to accommodate the solute without sacrificing hydrogen bonds, although there is an entropic penalty. For large clusters of amphiphiles in water or larger hydrocarbons that necessarily create larger cavities (>1 nm), the hydrogen bonded network of bulk water is depleted, leading to an unfavourable enthalpy term. For large hydrophobic solutes, the formation of a "cavity" is associated with a significant interface like that between liquid and vapour [28–30].

Despite its importance in biology and chemistry, current understanding of the hydrophobic effect remains ill-defined and there is little experimental detail to support the original hypothesis of Frank and Evans [27]. As the short chained alcohols are the simplest amphiphilic molecules, understanding thermodynamic properties such as their aqueous solubility, free energy and partition coefficients is essential to the understanding of phenomena such as solution behaviour, interfacial properties and hydrophobic interactions. In the current work a systematic study of some short chained alcohols with carbon chain lengths of five to seven carbon atoms and their structural modifications is investigated. The alcohols are shown in schematic form in Fig. S1 and were selected such that the effect of successive additions of a methylene group ($-CH_2-$) to either the linear backbone or as a side chain (branching) may be investigated. Whilst there has been considerable work on the normal alcohols, there has been little work done on the simple branched alcohols other than the work of Eastoe et al. [31,32]. For each of these alcohols the standard free energies of adsorption at the liquid–vapour interface (ΔG^0_{ads}), standard free energies of transfer (ΔG^0_{trans}) between water-hexane and standard free energies of solution (ΔG^0_{sol}) are determined. These techniques however, do not provide detailed understanding of the molecular ordering at the interface as they lack the sensitivity to discriminate submonolayer structure. Small- and wide-angle X-ray scattering (SAXS–WAXS) has been used to investigate the mesostructure consisting of segregated polar and nonpolar domains, and the hydrogen bonding within these liquid alcohols.

2. Experimental section

Materials were supplied by Tokyo Kasei Kogyo Co and were at least 98% purity. Surface tension measurements were performed using the du Nouy ring detachment method at 20.0 ± 0.5 °C. A Mettler AK 160 analytical balance was used to obtain the apparent mass that was converted to surface tension using the empirical formula of Zuidema and Walters [33]. The aqueous solubilities of the saturated solutions of the alcohols were extrapolated from the surface tension versus logarithm of the concentration curve. The partition coefficient of the alcohol in hexane was measured at 20.0 ± 0.5 °C at concentrations of 8×10^{-3} to 5.0×10^{-2} mol dm^{-3} [34] (Table S1a). The partition co-efficient of the alcohols are defined by (concentration in the aqueous phase)/concentration in the hexane phase). The aqueous alcohols were placed in a separating funnel and an equal volume of hexane was added before vigorously agitation. The phases were left to separate for 2–3 h before the concentration of the alcohols in hexane were determined by gas chromatography calibrated using an internal standard with a calibration curve for each of the alcohols. A Varian model 3700 dual column temperature programmable gas chromatograph was used with 40 cm, ¼ inch O.D stainless steel column packed with 5% OV-101 Gas Chrom G-HP, 100–200 mesh stationary phase. A Hewlett Packard HP 3000 reporting integrator was used to record the gas chromatogram. The flame ionisation detector (FID) was operated at 250 °C while the injection port was held constant at 200 °C. The oven temperature was held at 40 °C then increased to

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