COMPARATIVE STUDY OF SURFACE TENSIONS OF AIR-AQUEOUS LAURYL ALCOHOL AND OF BENZENE-WATER INTERFACES WITH 1:1 SALTS

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Abstract. Surface tensions (γ, mN/m) for 25 to 0.05 mmol/kg aqueous Lauryl Alcohol (LA) and interfacial tension (IFT, mN/m) of benzene and water interfaces with 1.0, 0.5 and 0.1 mol/kg KF, KCl, KBr and KI halide salts are reported. The LA decreased surface tension of water by 57% with micelle formation at 5 mmol/kg with 29 mN/m, denoted as critical micelle concentration (CMC) and critical micelle surface tension (CMST), respectively. The KCl, KBr, KF and KI increased surface tensions by 5.2%, 4.0%, 3.1% and 3.0% respectively and with 51% decrease from air-water to benzene-water interfaces. The KI, KF, KCl and KBr salts decreased IFT of air-water by 63%, 61%, 61% and 56% with stronger ion-water interaction than those of the water itself. A decrease in surface tension with benzene depicted interacting activity of π-conjugation. The 57% decrease in surface tension with LA inferred stronger adherence to, to air-water interface. High quality air was used for generating pressure gradient in Survismeter operation for surface tensions and IFT.

Keywords: Survismeter, lauryl alcohol, interface, surface tension, π-conjugation

Introduction

Surface and interfacial tensions are industrially useful for analysis of materials for use in pesticides, insecticides, fumigation, colloids, syrups, sol gel, inks, capillary action and cosmetics to characterize resultant mixtures for better use. Chemical potential $\mu = \mu_{id}^{0} + 2.303\ RT \log x_i$, defines activity of components. The μ_{id}^{0} denotes chemical potential of ideal mixture where no mixing occurs and each component indi-

vidually have mole fractions equal one, with $\mu = \mu_{id}^{0}$ because log 1 = 0. Chosen individual components were mixed and had mole fractions less than one where a value of log x_i is less than zero that inferred solute-solvent interactions. Thus, our systems deviated from ideal behavior and tend to develop useful mixtures with wider chemical uses. Hence the effective solute-solvent interactions are authentic indicators for analysis of industrial quality of several products syrups, sol-gels, medicinal tablets, useful mixtures like coolants, dry-cleaning, atomizing mixtures like pesticides, spraying agents. Practically, very rare mixtures behave as ideal system, though sometimes the mixtures like previous one are useful. In general, the mixtures are designed to obtain required physicochemical properties to facilitate industrial or academic uses in certain processes. For example, dipole moment, chemical potential, entropy, enthalpy but viscosity and surface tensions are most sensitive parameters for various uses like dynamic light scattering analysis of micelles. Especially, the surface tension control is most helpful for atomizing of pesticides Aldrin, dieldrin etc for agricultural uses and insecticides phosphine, 1,3-dichloropropene, chloropicrin, methyl isocyanate, hydrogen cyanide, sulfuryl fluoride, formaldehyde, iodoform to be used as fumigation. The above mixtures as insecticides and pesticides do require certain level of surface tension for carrying out successful and economic process. Otherwise their large amounts go wastes, so for mists or micro globules the surface integrity is needed. Since our systems offered systematic study of surface and interfacial tensions to infer structural changes and are significant to depict homogenizations of the mixtures. The surface tensions of both LA and electrolytes are noted with opposite interactions. The LA decreased the surface tensions of its aqueous mixtures 0.05 to 5 mmol/kg however from 5 to 25 mmol/kg, the surface tensions were almost constant. The salts increased the surface tensions with their concentrations which is a fundamental difference in behavior of the salts as electrolytes and the surfactants as non-electrolytes on surface properties. The LA with dodecyl alkyl chain and hydroxyl (-OH) functional group, acts as surfactant and is preferably adsorbed at air-water interface. The salts deplete from surface due to attractive interactions in the bulk water. Similarly the LA showed a distinctive concentration dependence on surface tension with critical change at 5 mmol/kg. The surface tension for 5 mmol/kg is 29 mN/m and is noted as CMST, this value for similar other alcohols is 35 mN/m. Thus, the surface and interfacial tensions ensure quality of pesticides, sprayings, disinfectants, cosmetics etc. by lowering cohesive forces of their mixtures. Also solid-liquid interface are of use due to utilization of surfaces for cooking, electrochemistry and electroplating. For example, liquid-liquid interfaces (LLI) are used for fat removal from a milk sample as low density fat comes up?to a milk surface. Similarly, the LLI are indispensable from extraction and separation processes in industries oil and petroleum recovery, extraction of natural products from plants or animal extracts, chromatography, HPLC, sedimentation and phase transfer systems. The LLI constitutes a major part of interface chemistry [1, 2] to assist

nanotechnological uses. AMF (atomic force microscopy), polar metric microscopy, dynamic light scattering/static light scatter, refractive index or absorption etc. evaluates the surfaces. The interfaces are useful for analysis of dynamics [3-7] of mixtures of immiscible solvents with different dipole moments. A study of such mixtures ensures quality of electroplating, coating, solvents extraction and phase transfer catalysis. Since instrumentations for LLI are delicate, highly sensitive and cost intensive, this is a difficult hurdle for interface studies in colloidal and dispersive solutions. Thus, common, accurate and economic device is required and hence the Survismeter, a low cost and authentic instrument. It was used for present study. It is cost effective and potential device for interface chemistry [8-12]. The ultra microelectrode and scanning electrochemical microscopy for reactions at LLI are in use but are expensive and a mediocre researcher cannot afford them. In such situation the Survismeter is a best option for surface and interfacial tensions. However, parallel measurements of few systems were made with Face Automatic Surface Tensionmeter, CBVP-Z, Kyowa Interface Science Co. Ltd. Kyoto University, Japan. A striking agreement in results was noted with both the methods.

Material and methods

The 25 mmol/kg stock solution of the LA was prepared with Millipore water and was diluted for subsequent solutions w/w. The 1.0, 0.5 and 0.1 mol/kg aqueous salts solutions were prepared, w/w. The LA, salts and benzene (Wako, Japanese) were used as received. The Survismeter (Calibration no. 06070582/1.01/C-0395, NPL, Govt. of India) was mounted vertically in thermostat at a fairly temperature control. It worked on R_3 = Reduce-Reuse-Recycle, principle, with 95% resource saving without escape of volatile or inflammable liquids [13]. No direct atmospheric air was used for lifting a sample from reservoir bulb to operational bulb. A filter unit was used for air quality. The detailed procedure for surface tension and interfacial tension is reported elsewhere [13]. In usual methods, a heavily polluted atmospheric air is used for creating a pressure gradient inside the operational bulbs of the equipments [13]. To avoid a touch of samples with contaminated air with pollutants SO_x, CO_x, NO_x (x = 1, 2, 3), HCl, H_2O vapors, volatile organic compounds (VOC) and polychlorinated biphenyls (PCB), a air filter fitted Survismeter was used. It allowed only a purified air for creating pressure gradients inside operational bulbs. The samples to be used for measurements are highly precious and no polluted air must touch them during study. A filter unit [13] worked on cone and socket arrangements. The cone gets fitted in a socket of the Survismeter, and a middle part of the filter unit contains gauze embedded with anhydrous $CaCl_2$ to absorb the water vapor of the air being entered. The fine scrubbers were also fitted along with fine gauze to detain suspended particulate matter and dust particles. Almost all chemical impurities were detained and purified air was allowed to pass into a liquid to move to operational unit for surface and viscosity study.

Result

The surface and interfacial tensions were calculated with usual equations [3,5] and regression coefficients are plotted in Figs. 1 and 2 where with the concentrations of the LA, the surface tensions decreased from value 71.18 mN/m for water at a very high rate till concentration of the 5 mmol/kg is reached.

Discussion

The surface tension of the LA at around 5 mmol/kg, the curve is leveled off and is become independent of concentration (Fig.1), and the point illustrated the CMC, with almost zero rate of change of surface tension with increases in concentration. A limiting value of the surface tension above the CMC is around 29 mN/m which is independent of concentration. Above CMC the air-water interface is saturation of the LA accumulation in the surface monolayer. Thus at CMC point, the chemical potential also becomes saturated which further segregated the LA at air-water interface to induce micellization. Along a constant curve of surface tension with an increase in the concentrations, the cohesive forces also remained constants.

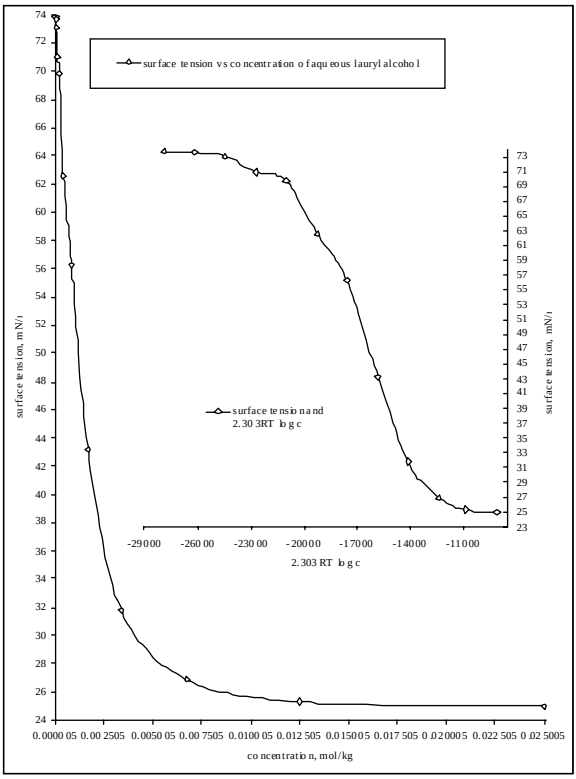

Fig. 1. Surface tension of LA with water and application of Gibbs Isotherm for surface excess concentration function (Γ').

Gibbs adsorption equation

A partitioning of LA is considered at interface and established a relation between the surface tension and concentration. An excess concentration of the LA is considered at air-water interface with a finite layer of thickness that influenced the dipolar interactions of the water. The LA could not effectively disrupt the water structure and from the bulk, it is repelled out to air-water interface. In comparison to its concentration in bulk of the water, a considerably larger amount is accumulated at the interface. It could be notified that LA and similar other molecules could establish stronger interaction with dipolar water and make an easy access to move to the interface. The columbic forces of the water due to its $(q^{+}.q^{-})/r^{2}$ relations have higher cohesive forces and do not allow LA molecules to get fitted in very strong long range arrangements of the molecular forces of the water. Thus the LA has excess concentrations on the surface and is denoted as $(\acute{\Gamma})$ in the equation:

$$\gamma = -2.303\, RT\, (\acute{\Gamma})\, \log\, (c)$$

The R is gas constant, 8.314 J $mol^{-1}K^{-1}$. The surface tensions γ are plotted in Fig.1 and a sigmoid curve is noted. The Fig. 1 demonstrates a relation in variation of surface tensions with an adsorbed concentration of the alcohol at water surface and micellization in the bulk. It might also be a strong possibility of concentration independence of surface tension above the CMC which is caused because the surface excess is saturated due to formation of a complete monolayer at the CMC point. Above the CMC, the LA molecules are unable to be adsorbed at air-water interface and get accumulated to form micelles in the bulk phase. Further the LA in dilute solution behaved an ideal gas. A comparison of a behavior of the LA with those of the salts systems, a much difference is seen, in fact, there is no match because of totally opposite behavior of the systems. The salts disrupted the dipolar structure of the water and get dissolved in the bulk while the LA is not able to disrupt the dipolar forces and is repelled out to the surface. However when the air-water interface is made saturated with LA concentrations then its accumulation formed the micelle. The salts developed the stronger interaction in the bulk phase but when they are in contact of benzene and water phases where both the phases are thermodynamically most active [6]. Because of their different dipole moments and electronic structures where the salts get dissociated in water phase but the benzene does do so however its pi-conjugation responds to ionic states of the salts. The benzene developed mild hydrophobic interactions with the water and led a mutual mixing which is also controlled by the hydrophilic interactions of the salts [7].

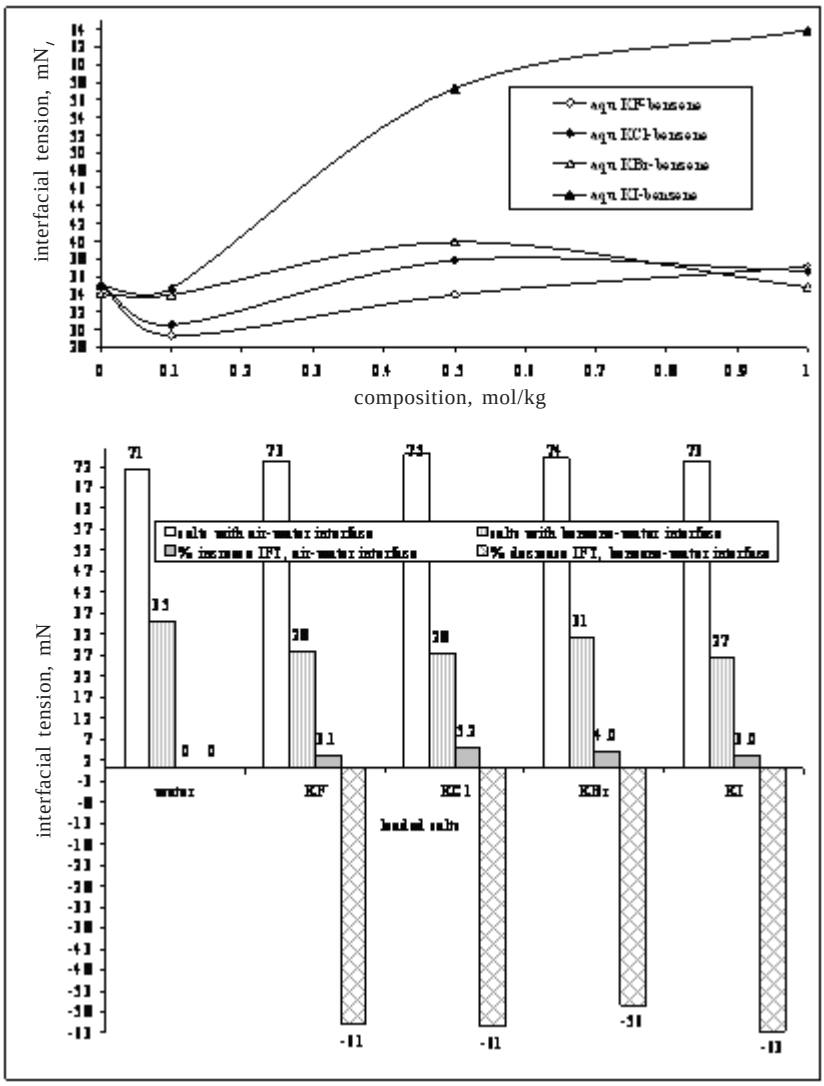

Fig. 2. Surface and interfacial tensions of air-water and benzene-water interfaces with salts

Salt systems

From air-water to the benzene-water systems, a decrease in the surface tension is by 51% which inferred the benzene interaction with the hydrogen bonding of water (Fig. 2). A residual or van der Waals forces of the water are influenced by the pi-conjugation of benzene with a result of the 51% decrease in the surface tensions. The water with 71.18 mN/m is noted as 100% hydrogen bonded but the salts decreased

the surface tension due to stronger ionic bond by disrupting hydrogen bonded water with weaker cohesive forces. The pi-conjugation further weakened the cohesive forces of the water and the weaker cohesive forces led higher wetting of benzene and the water mutually with development adhesive forces between the benzene and the water interfaces. As the stronger is the cohesive forces weaker would be the adhesive forces between two adjacent interfaces.

In this context, the K^+ effectively weakened the cohesive forces and the Br^- has slightly weakened for breaking the cohesive forces due to its larger size. The salts disrupted the water structure and produced the water monomers with higher residual forces to interact with the pi-conjugation poles of the benzene with weaker interfacial tension. Since the I^- is lager sized ion with induced dipoles probably disrupted the water and also interact with pi-conjugation. The I^- with higher ionic charge as compared to charge of the pi-conjugation poles, avoids direct ion-benzene interaction. With KI, the ionic sizes of K^+ and I^- are very different so its dissociation occurs quickly as compared to the KCl where the K^+ and Cl^- have similar sizes. A dissociation of KCl into K^+ and Cl^- ions is probably less energy consuming. Thus a sharing of charges in case of dissimilar ions needs some additional ionic distribution. It seems applicable with KCl interfaces with 61% decrease as compared to 63% of the KI but the KCl remains more affective as compared to the KF and KBr. The KF showed 61% decrease which is slightly lower than that of the KCl (Fig. 2). Perhaps size disparity of the K^+ and F^- caused this difference in IFT values. The F^- with 2s2p suborbital is tightly bond by nuclear force and is not able to dissociate as the KCl does dissociate. So a decrease is in IFT is lower than of the KCl. However as compared to the KBr this value is higher by -56%. The KBr again has sized disparity however like I^- it does not develop induced dipoles potential. The KBr mildly weakened cohesive forces of water and KI caused the stronger effect on IFT may be due to induced potential and KBr is weaker. This study constitutes a dipolar biphasic interaction model (DBIM), a highly useful for developing interfaces of designed IFT values for phase transition or transfer catalysis. The 51% decrease in surface tension of water with benzene interface inferred benzene interaction with water or vice versa. Buoyancy could be a reason but variations in surface tensions of the salts solutions are noted where buoyancy is considered constant. The decrease in interfacial tensions is attributed to ionic influence on benzene-water interface interactions. The DBIM is diffe-rent than the interaction models which illustrate interactions inside bulk phase of liquids.

Industrial applications

Aqueous mixtures of the lauryl alcohol and salts constitute industrial products of daily use like cosmetics, lotions, sprayants, drugs, insecticides and disinfectants. The alcohols and salts control several physicochemical properties like mixing and solubilizing of the industrials products.

Conclusion

The LA showed stronger accumulation at air-water interfaces and CMC formation and salts with benzene-water interface showed bulk interactions. The Pi-conjugation of benzene caused partial charges on alternative carbons in a ring and attracts dipolar water for interaction.

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