Chapter 2 : Experimental

[A] Introduction to Experimental Techniques

(I) Surface Tensiometry Measurements

Molecules inside a liquid and those at the surface of a liquid have different environments . Molecules in the interior are surrounded by the same kind of molecules , whereas molecules at the surface are subject to different environments above and below the surface layer .

Surface / interfacial tension is a physically measurable macroscopic quantity . Its origin lies in the intermolecular attraction forces operating between the molecules of a liquid . In order to increase the surface of the liquid , energy is required to overcome this attraction forces . The work required for increasing the surface by a defined unit area is referred to as specific surface work . The values and the dimension of this quantity are equal to the surface tension , γ .

The SI units for surface tension are $N\,m^{-1}$ or $J\,m^{-2}$; cgs units, which are still widely used in many tabulations , are $dyn\,cm^{-1}$. ($1\ N\,m^{-1} = 1000\ dyn\,cm^{-1}$) .

There are many experimental techniques for measuring the surface tension of liquids . In the ring method (Du Nouy tensiometer) one determines the force necessary to pull a metal ring free from the surface of a liquid . If instead of a ring ,one can also use a thin vertical plate (Wilhelmy plate technique) . In the drop-weight method one determines the weight of a drop which falls from a tube of known radius . In the bubble-pressure method one determines the maximum gas pressure obtained in forming a gas bubble at the end of a tube of known radius immersed in the liquid [79] .

It is found that the surface tensions of solutions are in general different from those of the corresponding pure solvents . It has also been found that solute whose addition results in a decrease in surface tension tend to concentrate slightly in the neighborhood of the surface (positive surface concentration) ; those whose addition results in an increase in surface tension tend to become less concentrated in the neighborhood of the surface (negative surface concentration) .

The surface tension value for water is 72.75 $mN\,m^{-1}$ at 20 °C . Common organic solvents have surface tensions around 20-30 $mN\,m^{-1}$.

Measurement of surface tension temperature derivative $\frac{d\gamma}{dT}$ for aqueous solutions of 1,1 electrolytes had been studied by Johansson and Eriksson [80]. Table 2-01 lists values for $\frac{d\gamma}{dT}$ for some electrolytes .

Table 2-01: $\frac{d\gamma}{dT}$ for some electrolytes [80]

solution	$\frac{d\gamma}{dT}$
water	-0.1608
NaCl	-0.1602
KCl	-0.1589
NaI	-0.1570
KI	-0.1560

* Concentration of electrolyte in 1 mole per kg H_2O

Table 2-02 : Surface tension of water at various temperature [81]

t (°C)	γ (mN m^{-1})
0	75.64
10	74.23
20	72.75
30	71.20
40	69.60
50	67.94

For water, variation of surface tension with temperature is shown in Table 2-02 . The surface tension is lowered with increasing temperature (Table 2-02) and becomes zero near the critical temperature (T_c) . The relationship between γ and T is given by [82]

$$\gamma V^{2/3} = k(T_c - T) \qquad (2\text{-}01)$$

where

V = molar volume ($V = \frac{M}{\rho}$)

T_c = critical temperature .

The value of k for normal liquids is found to be approximately 2.1 erg K^{-1} [83] .

Table 2-03 : Surface tension of NaCl at 20 °C [81]

%	γ (mN m^{-1})
0.58	72.92
2.84	73.75
5.43	74.39
10.46	76.05
14.92	77.65
22.62	80.95
25.92	82.55

% = weight % of solution

Salts are typical surface-inactive solutes in water . In solutions of electrolytes such as NaCl (Table 2-03) , the surface tension increases with concentration indicating a negative surface concentration . In such solutions the surface layers are poorer in solute . This is a result of interionic electrostatic attraction , which tends to make the ions drawn together and away from the surface .

Surface active compounds even at low concentrations can considerably lower the surface tension of water . These molecules contain both polar hydrophilic and non-polar hydrophobic group . The hydrophobic groups of the solutes would be extremely "uncomfortable" in the interior of an aqueous solution (in a state of high free energy) , and little work is required to bring them from the interior to the surface . Such solutes tend to accumulate strongly at the surface where , in many cases , they form a unimolecular film of adsorbed molecules . When the concentration of a surface-active solute increases , the surface tension of the solution decreases until the film is substantially complete and can accept no more solute molecules when the bulk concentration attains some small value , and hence the surface concentration undergoes little change when the bulk concentration is increased further over a wide range . The surface tension becomes constant or continues to decrease but at a much smaller rate so that the curve of surface tension versus logarithm concentration shows a distinct kink . Concentration at that kink is taken as the critical micelle concentration (CMC) .

Surface tension is one of the most popular methods to detect impurities present in the surfactant . A minimum in the surface tension-concentration curve in the region of the CMC is known to be due to the impurities (contamination or products of hydrolysis) which is more surface active but removed from the surface by solubilization in the micelles above the CMC [84] . The difficulty of removing small amounts of these highly surface-active impurities has been one of the major obstacles hampering the accumulation of reliable surface chemical data on surfactants , such as sodium dodecyl sulfate [85] .

(II) Electron Spin Resonance (ESR)

ESR is experimentally concerned with resonant position , line width , line shape and intensity . The resonant position of ESR is referred to as the *g* value and is directly determined by the separation of the energy levels of the system under investigation . The variation of the *g* value is interpreted in terms of the first and the second order perturbation by the spin-orbit interactions . The line width is produced by the relaxation of the spin energy state [86].

The free ion of Cu^{2+} has an electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ and a spectroscopic term , ^2D . When the Cu^{2+} ion is placed in a complex , the ^2D state is split into a number of states , and the energy levels are shifted from the free ion position . In solution , the complexed cupric ion generally exhibits in its ESR spectrum four hyperfine lines with varying line widths . Molecular orbital theory had been applied to interpret the observed parameters , example : $Cu(acac)_2$ under D_{4h} symmetry .

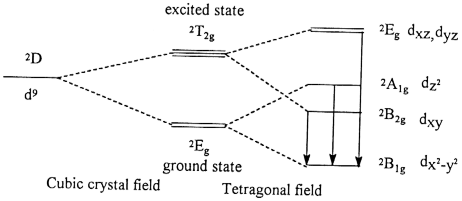


Figure 2-01 : Splitting of ^2D state under tetragonal field (D_{4h}) for copper(II) complex .

If a molecule containing Cu(II) has a tetragonal structure stretched along the symmetry axis (taken as the z axis) , ${}^2B_{1g}$ ($d_{x^2-y^2}$) is the ground state . By group theory , the proper linear combination of ligand orbitals can be combined with the copper *d* orbitals to form the following antibonding wave functions . The wave functions are in order of increasing energy [87].

$$\Psi_{B_{1g}} = \alpha d_{x^2-y^2} - \tfrac{1}{2}\alpha'[-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}] \qquad (2\text{-}02)$$

$$\Psi_{B_{2g}} = \beta d_{xy} - \tfrac{1}{2}(1-\beta^2)^{1/2}[p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)}] \qquad (2\text{-}03)$$

$$\Psi_{A_{1g}} = \gamma d_{3z^2-r^2} - \tfrac{1}{2}(1-\gamma^2)^{1/2}[\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}] \qquad (2\text{-}04)$$

$$\Psi_{E_g} = \begin{cases} \delta d_{xz} - (1-\delta^2)^{1/2}[p_z^{(1)} - p_z^{(3)}]/\sqrt{2} \\ \delta d_{yz} - (1-\delta^2)^{1/2}[p_z^{(2)} - p_z^{(4)}]/\sqrt{2} \end{cases} \qquad (2\text{-}05)$$

The B_{1g} and A_{1g} states account for the σ bonding to the copper . The B_{2g} state represents the in-plane π bonding and the E_g states represent the out-of plane π bonding .

[Cu(diamine)(diketonate)]$^+$ belongs to C_{2v} point group , with z axis as the unique symmetry axis and xz plane as corresponding to the chelate plane . The effect of solvation along the y-axis on the energy levels is shown below :

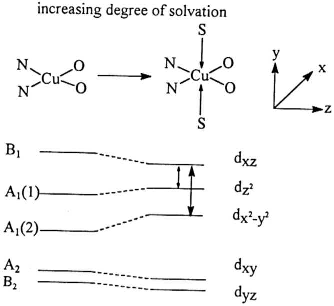


Figure 2-02 : The effect of changing the solvent on the relative energies of d-orbitals in $[Cu(diamine)(diketonate)]^+$ (C_{2v} symmetry) .

For $[Cu(diamine)(diketonate)]^+$, $g_{//}$ is in the range of 2.21 and 2.27 while $g_{\perp}$ is around 2.0 . $g_{//}$ decreases as the β-diketonate ligand becomes more basic (pK_a increase) or more strongly coordinating . Substitution on the diamine ligands has little effect on the $g_{//}$ factor . $g_{//}$ increases as the solvent property changes from noncoordinating to strongly coordinating (i.e. as the solvent increases in donor number) [88].

(III) Ultraviolet and Visible Spectroscopy

One can observe the competition of anions and solvent molecules for the axial coordination sites by means of the visible absorption spectra [89].

$Cu(tmen)(acac)X$ shows the following equilibrium in solution :

$$[Cu(tmen)(acac)X] \rightleftharpoons [Cu(tmen)(acac)]^+ + X^- \qquad (2\text{-}06)$$

(5-coordinated) (4-coordinated, with axial solvation)

, which is shifted to the right hand side with increase of the solvent donor strength and with decrease of the coordination ability of X^- anion . In H_2O and MeOH , the spectra are ascribed to the 4-coordinated ionic complexes $[Cu(tmen)(acac)]^+$ with axial solvation , because solvent with high donor number will be able to pull out the X^- ions from the coordination sphere of $[Cu(tmen)(acac)X]$ more easily than that of a lower donor number . The degree of ionization of $[Cu(tmen)(acac)X]$ increases in the order of $Cl^- < Br^- < I^-$ or in other words , the coordination ability of the halide ions in organic solvents toward $[Cu(tmen)(acac)]^+$ decreases in the order of $Cl^- >$ $Br^- > I^-$.

The band-shift changes linearly with the donor numbers and acceptor numbers of different organic solvents . The colors of the solutions or the υ_{max} of their *d-d* bands were highly sensitive to changes in solvent basicity . For $X^- = ClO_4^-$ and BPh_4^- , υ_{max} (in nm) increases with increasing solvent donor strength , although exceptions can be found in several cases [90] .

[B] Materials , Preparation of Compounds , Instrumentation and Experimental Methods

(I) Materials :

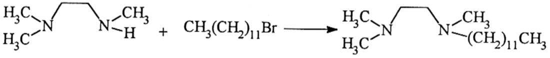
Water was distilled twice in all-glass apparatus . Absolute ethanol , dichloromethane , ether , hexane , toluene , acetone and other solvents were stored over molecular sieves 4A prior to use . $CuBr_2$ (Peking's reagent , China) was used as received . Anhydrous $CuCl_2$ was prepared by heating the hydrate $CuCl_2.xH_2O$ (green) in the oven at 110 °C until it turned brown . N,N,N'-trimethylethylenediamine (tmed) (Fluka Chemica purum > 96 %) , 1-bromododecane (Fluka AG CH-9470 Buchs) , sodium hydroxide (Riedel-de Haen AG Seelze-Hannover) , sodium carbonate anhydrous (A.R. Grade , R & M Chemicals) , sodium sulphate (MERCK-Schuchardt) , acetylacetone (G.P.R. , Hopkin & Williams Ltd.) and 3,5-di-*tert*-butylcatechol (3,5-DTBC) (Fluka , > 98 % (GC)) were used as received . Sodium chloride was analytical reagent grade obtained from R&M Chemical (> 99.8 %) and was recrystallized from water and baked in oven (~120 °C) to remove traces of organic compounds and water (at least 2 hour).

Sodium dodecyl sulfate (SDS) was a gift from Prof. T. Kondo (Japan) . SDS was extracted three times with ether and recrystallized twice from ethanol and dried in vacuum at 60 °C. Cetyltrimethylammonium bromide (CTAB) (Sigma , > 99 % (GC)) was recrystallized from acetone / ethanol mixture and dried in vacuum . Octaethylene glycol monododecyl ether ($C_{12}E_8$) (Fluka , > 98 % (GC)) was used as received .

(II) Preparation of complexes :

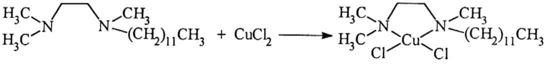
C_{12}tmed and Cu(C_{12}tmed)Cl_2 were prepared according to method by Menger et. al. [7] ; Cu(C_{12}tmed)(acac)Cl was prepared according to ref. [11(b)] , while PNPDPP was prepared according to Gulick's method [91].

(a.) **Preparation of C_{12}tmed**



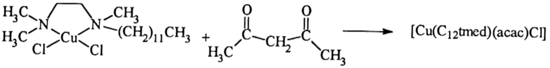
N,N,N'-Trimethylethylenediamine and 1-bromododecane were mixed in 3 : 2 ratio (in absolute ethanol) and refluxed for 10 minutes . A stoichiometric amount of NaOH in minimal water was added dropwise , and the mixture was further refluxed for 9 hours . After cooling , the solution was shaken with a solvent mixture consisting of 1-butanol , benzene and water (1 : 1 : 3 respectively) . The organic layer was collected and washed with water . The mixture was left to stand overnight to allow better separation . The organic layer was again separated and dried in Na_2SO_4 before being filtered . The volatile solvents were reduced by vacuum pump and the remaining liquid was then distilled under reduced pressure . Percentage yield is 60 % .

(b.) **Preparation of Cu(C_{12}tmed)Cl_2**



$CuCl_2$ and C_{12}tmed in absolute ethanol were mixed in stoichiometric ratio . The mixture was cooled in ice and the powder formed was filtered and washed with portions of cold absolute ethanol . The crude product was redissolved in ethanol/CH_2Cl_2 . After filtration , the more volatile CH_2Cl_2 was evaporated off under reduced pressure to result in a suspension of the pure product which was only slightly soluble in ethanol . The product was filtered and dried in desiccator . Melting point 101-102 °C (bright green) . Percentage yield ≈ 50 % .

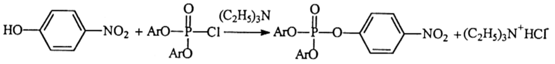
(c.) **Preparation of Cu(C_{12}tmed)(acac)Cl**



Cu(C_{12}tmed)Cl_2 in ethanol/CH_2Cl_2 was first mixed with a 10 % excess of acetylacetone (in ethanol) , followed by the addition of a stoichiometric amount of aqueous sodium carbonate solution . The resulting solution was filtered to remove $Cu(acac)_2$ and NaCl which were formed as by-products . The filtrate was evaporated to dryness using a vacuum pump . The crude product was washed with hexane . A minimum amount of dichloromethane was added to dissolve the product followed by centrifugation to remove $Cu(OH)_2$ and NaCl . The supernatant solution was again evaporated to dryness under reduced pressure . Finally a minimum amount of water was added to redissolve the compound and any remaining $Cu(acac)_2$ was removed by centrifugation . The clear dark blue solution was then evaporated to dryness under vacuum at room temperature to result in greenish powder . The purity was confirmed by the absence of a minimum in the surface tension versus concentration plot and sharp melting points .

Melting point 74-76 °C (greenish) . Percentage yield = 70 %

(d.) <u>Preparation of *p*-nitrophenyl diphenyl phosphate</u>



1.40 g of *p*-nitrophenol and 2.68 g of diphenyl chlorophosphate in ether were mixed with 10 % molar excess of triethylamine (1.11 g) . The yellow precipitate (salt) , triethylamine hydrochloride , was removed by filter paper . Little amount of ether was used to wash the precipitate . When water was added to ether , the water layer turned yellow showing that the unwanted salt was transferred to the water layer .The extraction with water was continued until no more yellow colour appeared in the water layer . The ether layer was collected and evaporated to dryness to result in a viscous liquid , which solidified after leaving in the desiccator overnight . The solid was recrystallized from 95 % ethanol . The solid was filtered and washed with 95 % ethanol . The melting point was determined after drying the solid in the desiccator . Melting Point : 49-51 °C (white)

(III) Instrumentation :

(a) Surface tension measurements were carried out by Du Nouy ring technique using White Elec. Ind. Co. Torsion Balance ,within an accuracy of 0.1 $mN\,m^{-1}$.

(b) UV-visible and kinetic studies were carried out by using Shimadzu UV-VIS-NIR spectrophotometer (model UV-3101PC) equipped with the NEC Powermate 286 Plus microprocessor , NEC MultiSync 2A monitor and DXY 1100 plotter .

(c) Infra-red spectra were recorded with Perkin Elmer 1600 FTIR , equipped with Epson Extended VGA colour monitor , Epson PC AX2e 286 (IR Data Manager Software) and Hewlett Packard HP-7440 ColorPro Plotter .

(d) ESR spectra were recorded on a Bruker B-R 70 spectrometer (9in.-magnet) equipped with a variable temperature accessory .The ESR spectra were calibrated with DPPH and an NMR oscillator .

(e) Melting point determinations were carried out by using Thomas Hoover capillary melting points apparatus .

(f) pH measurements were done on a Alpha-200 combined pH and conductivity meter at (21±2) °C .

(g) A precision micrometer syringe with an accuracy of ±0.2 μl or 0.002 cm^3 was used in the transferring of standard solutions .

(IV) Experimental methods

(a) Surface Tensiometry

All glasswares (disc , pipette , flask) , platinum ring and magnetic bar were soaked in chromic acid overnight . Mixed surfactant solution was prepared by mixing equal volumes of individual surfactants , then shaken for uniform mixing . To ensure that comparisons between solutions of different ionic surfactants would be made at the same ionic strength , all surfactant solutions were prepared in 0.1 M NaCl .The stock solution was filled into the 2 *ml* micrometer syringe . 10 *ml* of doubly distilled water was pipetted into the sample container . The solution was then injected from the micrometer syringe . The mixed surfactant solution was equilibrated by stirring using magnetic bar . The room temperature was taken while waiting the injected solution to be equilibrated . The measurements were made at room temperature (21 ± 2) °C .The reading was taken at 5-25 min interval when stabilized reading was attained .

(b) pH measurements

pH meter was let to warm up for at least 15 min . The electrode was presoaked in pH 7 buffer . pH meter was then calibrated by 2-point calibration , i.e. pH 7 and pH 4 buffer . In a typical case , 3 *ml* of solution was introduced into the test tube and the pH reading was taken when it was stabilized . The required pH (pH = 5.7) is obtained by injecting HCl or NaOH solution in μl volumes .

(c) Kinetic Studies (UV-visible measurements)

(i) Autooxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC)

The mixed surfactant solution was air saturated by stirring using glass rod . 3 *ml* of solution was introduced to the 1 cm cuvette for both sample and reference compartments . Temperature was thermostated at (25 ± 0.2) °C . pH was adjusted by injecting μl of HCl or NaOH . 5-6 μl of 3,5-DTBC in acetonitrile (final concentration = 5-6 x 10^{-5} M) was injected . The solution was rapidly stirred with glass rod flattened at one end . The formation of 3,5-di-*tert*-butylquinone (3,5-DTBQ) was monitored at 385 *nm* . The cuvette was uncapped to allow the solution constantly exposed to air . The final pH was determined .

(ii) Hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNPDPP)

Approximately 4 μl of PNPDPP in acetonitrile was added into 3 *ml* of solution . The final concentration of the substrate was at least ten times lower than that of the complex in the solution . Liberation of *p*-nitrophenolate was monitored at 400 *nm* for at least five half-lives .

The observed first order rate constants determined under the condition of excess surfactants over substrate were obtained by fitting experimental curves to the first order rate equation using Peakfit program developed by Jandel Scientific .