

## Solvodynamics of Benzene and Water Phases by DTAB, MTOAC, TMSOI and Orcinol Studied with Interfacial Tension, Surface Tension and Viscosity Measured with Survisometer

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### Abstract

Both benzene and water immiscible phases when mixed together develop an energetic interface that remains tense due to individual surface tensions. Physics of a tense interface does equilibrate tensional forces to have an optimized surface force which is denoted as Interfacial Tension (IFT, mN/m). The IFT between water and benzene with addition of surfactants: dodecyltrimethylammonium bromide (DTAB), trimethylsulfoxonium iodide (TMSOI), methyltrioctylammonium chloride (MTOAC) and 3,5-dihydroxytoluene monohydrate (Orcinol) critically decrease to 15.69, 12.86, 10.59, 8.36, 2.97 mN/m for DTAB, TMSOI, water, orcinol, MTOAC respectively. This lowering of IFT infers a higher mutual miscibility (MM) of the phases denoted as wetting. The DTAB and orcinol increased surface tension of water from 71.25 to 79.55 and 72.70 mN/m respectively at 304.65 Kelvin temperature due to stronger cohesive forces.

*Keywords:* DTAB, interfacial tension,  $\pi$ -conjugation, mutual miscibility, buoyancy, inductive effects, steric effects, alkyl chains.

### 1. Introduction

Immiscible solvents phases have been used as a unique model for study of interfacial tension with different chemical potentials of the phases (Singh 2005a; Singh 2007a; Yue et al 2004; Verdes et al 2004; Andelija et al 2006). The mutual miscibility is obtained by adding the surfactants to a set of immiscible solvents that cause hydrophilic and hydrophobic interactions. The surfactants decrease chemical potential of individual solvent due to interactions as per LLI (liquid-liquid interfacial) model solvents. The mutual miscibility of immiscible solvents is industrially significant for developing mixed solvents of a controlled polarity. It also helps in designing solvents of required density and refractive index for biomedical and biophysical uses. And the interfacial tension makes an energetic zone that catalyzes the growth of certain enzymatic process using biomolecules due to availability of energy at interface. Such systems are highly fascinating for study of viscosities for estimation of a type of the liquids which are formed on mutual miscibility. The type of liquid could be Newtonian or non-Newtonian. So such systems develop self deriving forces with gradient in the chemical

potentials. Electronic configurations of surfactants with functional groups and alkyl chains do contribute to generate chemical potentials due to inductive and steric effects (Singh 2006a; Kuznetsov and Kazansky 2008; Wan et al 2007). An electronegativity of O, I, and S<sup>-</sup> of trimethylsulfoxonium iodide (TMSOI); Cl<sup>-</sup>, and N<sup>+</sup> of methyltrioctylammonium chloride (MTOAC); N<sup>+</sup> and Br<sup>-</sup> of dodecyltrimethylammonium bromide (DTAB); OH<sup>-</sup> groups and  $\pi$ -conjugation of 3,5-dihydroxytoluene (Orcinol) are interesting models for mutual wetting of both the benzene and water (Singh 2006a; Singh 2007b; Singh 2005b; Rosen and Zhu 1993; Selcan et al 1988; Vollmer and Vollmer 2000). These models are thermodynamically most significant and active along with electronegativities of the functional units (Singh et al 2007; Hilal et al 1999). The CH<sub>3</sub> group with the surfactants causes hydrophobic interactions and the positively charged N<sup>+</sup> or S<sup>+</sup> atoms develop hydrophilic interactions. So the mutual mixing is directly controlled by a ratio of the hydrophobic and hydrophilic interactions. The surface tension, viscosity and interfacial tension data depict an integrated behavior of molecular interactions

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(Singh et al 2005). A study on the effect of the buoyancy of a medium is useful but very few studies are conducted on this parameter of the phases. For example both the MTOAC and TMSOI surfactants decrease the IFT of benzene + water interfaces by 42.67 and 3.6 mN/m respectively. Their effects on cloud points of the water and phenol phase are reported elsewhere (Singh and Kumar 2007; Al-Sabagh et al 2003; Vora et al 1999). In this context the viscosity and surface tension and IFT data are of industrial significance in cosmetics, extraction, pharmaceuticals etc. areas.

## 2. Materials and method

### 2.1. Solution preparation

Stock solutions of 0.5 mm kg<sup>-1</sup> DTAB, TMSOI, MTOAC and orcinol were prepared separately with ultrapure water, w/v.

### 2.2. Chemicals

Dodecyltrimethylammonium bromide (Sigma, 5047), Orcinol (Sigma 1875), Trimethylsulphoxonium iodide (Fluka, 92763), Methyltrioctylammonium chloride (Fluka, 69485) and Benzene (E. Merck) were used as received. The chemicals were dried for 24 h, at 110<sup>0</sup> C and stored in P<sub>2</sub>O<sub>5</sub> filled desiccator till use.

### 2.3. Experimental

Survismeter (Calibration no. 06070582/1.01/C-0395, NPL, Govt. of India) was used for the measuring viscosity, surface

tension and interfacial tension simultaneously (Figure 1).

The survismeter minimized the use of resources and user's time more than 80% as compared to individual instruments. It prevents an escape of poisonous and volatile liquids or mixtures to environment (Singh, et al 2005; Singh, 2006b; Singh, 2006c) during experiments.

#### 2.3.1. Operation

A liquid sample is filled in bulb no. 10 and after use the same is taken out via tube no. 11 whose inner diameter is 2 mm. The sample from bulb no. 10 was siphoned out with a manually operated suction pump no. 14. So for changing a sample from bulb no. 10, the position of instrument remained as such. Thus the working with survismeter is simple and fascinating. The Survismeter was cleaned with freshly prepared chromic acid and at last with acetone. An analysis of economics of resources was compared with individual instruments and found more than 80 % saving of solvents, time and the laboratory occupation, so it is user friendly. The Units 4-5-6-7-9-10, 2-7-8-9-10 and 15-16-18-19-B1-B2-1-10 measure the viscosity, surface tension and IFT respectively (Figure 2). The 2/3 portion of the bulb no.10 is filled with a liquid in question via joint no.1 without fitting a unit 19-B1-B2 in joint no.1. For viscosity joint no. 3 and 2 are stoppered and the piston 14-17-18 is fitted with joint no. 4 to lift a liquid to bulb no. 5 from

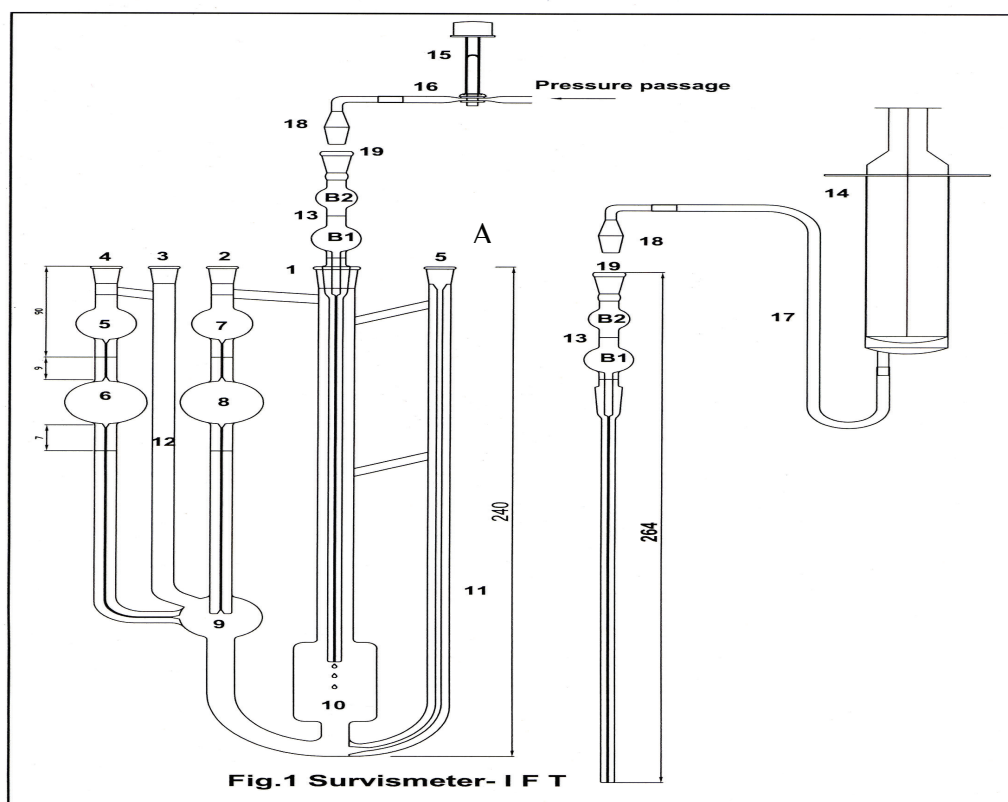


Figure 1. Sketch diagram of Survismeter assembly for simultaneous measurements

bulb no. 10 via bulbs 9 and 6. A stopper from joint no. 3 is withdrawn to evacuate liquid from bulb no. 9 to 10. The piston stopper no. 18 of unit 17-14 is withdrawn and a viscous flow time (t sec) for a liquid within two fiducial marks of bulb no. 6 was noted. Similarly the liquid is lifted up to bulb no. 7 via bulb no. 9 and 8, after the joint no. 4 and 3 were stoppered and the stopper 18 with unit 17-14 was fitted in joint no.2. The liquid from bulb no. 9 is evacuated like previous operation and piston stopper no. 18 is withdrawn and a pendant drop formation and detachment from capillary hanging in bulb no. 9 were counted for a liquid within fiducial marks of bulb no. 8.

#### 2.4. Interfacial tension (IFT)

Denser liquid is filled in bulb no. B1 and B2 of unit 13 fitting hollow stopper no. 18 and using piston. When B2 was filled, the piston stopper no. 18 is lifted and airtight stopper is fitted in joint no. 19 and unit 13 is fitted in joint 1. The bulb no. 10 contains benzene (lighter liquid) and capillary of B1 remains dipped in it. The stopper is removed from joint no. 19 and pressure passage unit 15-16-18 was fitted in it for 4-7 drops  $\text{min}^{-1}$  in a benzene medium out of water within the marks of B1. Similarly the drops are counted in air.

### 3. Results and discussion

The data measured and calculated from primary measurements are given in Table I. Accuracy of Survisometer was analyzed with absolute methanol with 0.3656 % error. Survisometer constant k was  $0.00358 \text{ cm}^2 \text{ s}^{-2}$  at  $31.5^\circ\text{C}$ , the detailed data are given in Table II. The t, n and  $n_{\text{if}}$  (drops in benzene interface) data were fitted in usual equations (Singh, et al 2005; Singh, 2006b) for the viscosity, surface tension and interfacial tension values respectively. The data were with 95.5% confidence level. Literature data (Singh and Kumar 2006; Singh 2005c) closely matched with the experimental data of the IFT (TABLE I).

The benzene applied a buoyant force on the outer surface of the pendant drop which is under flow. The flow times in air medium are lower than those of the benzene due to a buoyancy of the benzene medium. The buoyancy resists drop

falls at interface with a higher decrease in the surface tension values of water at an interface of benzene.

The IFT values are as  $\text{DTAB} > \text{TMSOI} > \text{water} > \text{orcinol} > \text{MTOAC}$  with a 15.69, 12.86, 10.59, 8.36 and 2.97  $\text{mN/m}$  which are very lower as compared to the values in air medium. As the air and liquid interfaces allow hanging of surfactants on interface with a normal decrease in surface tensions of the water-surfactants solutions but the surfactants when added with water-benzene interfaces interact with both the water and benzene interfaces with much lowering in IFT values. The MTOAC, orcinol, DTAB, and TMSOI develop higher hydrophilic and hydrophobic interactions between water and benzene. The MTOAC enhances mutual solubility than those of DTAB, TMSOI and orcinol with 2-OH groups and 1- $\text{CH}_3$  with slightly weaker hydrophilic and hydrophobic interaction (Figure 2). The molecular structure of DTAB (Figure 3) with alkyl chain of 12 carbon atoms infers stronger hydrophilic interaction but the MTOAC and TMSOI with alkyl chain of 12 carbon atoms and the 3  $\text{CH}_3$  groups develop weaker hydrophobic and stronger hydrophilic interactions due to  $\text{N}^+$  and  $\text{Cl}^-$  with MTOAC and the O atom of TMSOI.

The surfactants with a longer alkyl chain develop stronger hydrophobic interaction due to higher solubility in benzene rather than that of the water. The surfactants with a longer alkyl chain develop weaker hydrophilic interactions, halide ions of their functional groups visa-vise IFTs show their placement as  $\text{Cl}^- > \text{I}^- > \text{Br}^-$ . Thus the IFTs vis-à-vis structures of TMSOI and MTOAC infer that hydrophobic interactions of 3- $\text{CH}_3$  groups of TMSOI outweigh the hydrophilic interactions due to  $\text{O}=\text{S}^+-\text{I}^-$ . Thus the IFT value is higher for  $\text{O}=\text{S}^+-\text{I}^-$  water interfaces as  $\text{O}=\text{S}^+-\text{I}^-$  suits geometry of  $\text{O}=\text{S}^+-\text{I}^- - \text{H}_2\text{O}$ , tending towards water phase with stronger dipolar interactions with  $\text{H}_2\text{O}$ .

The  $\text{I}^-$  also develops stronger induced polarizability but MTOAC's  $\text{Cl}^-$  ion shows slightly stronger hydrophobic interaction than that of  $\text{O}=\text{S}^+-\text{I}^-$  with 10 carbon atoms chain that dominates over the weaker hydrophilic

TABLE I. VISCOUS FLOW TIME (t, sec) DROP NUMBERS (d n), DENSITY ( $\rho$ ,  $1 \times 10^3 \text{ kg m}^{-3}$ ), VISCOSITY ( $\eta$ ,  $\text{N s m}^{-2}$ ) SURFACE TENSION ( $\gamma$ ,  $\text{mN m}^{-1}$ ) FLOW TIME IN BENZENE (t b, sec), DROP NUMBER IN AIR ( $N_a$ ), BENZENE MEDIUM ( $N_b$ ) AND IFT ( $\text{mN m}^{-1}$ ) OF SYSTEMS.

System	t, sec	d n	$\rho$	$\eta$	$\gamma$	t b	$N_a$	$N_b$	IFT
Benzene	0	0	0	0.561	27.87	0	0	0	0
Water	1.2144	29	0.99530	0.7840	71.25	2.2602	48	25	10.59
DTAB	1.1859	26	0.99628	0.7664	79.55	3.2506	44	17	15.69
TMSOI	1.3337	30	0.98547	0.8525	68.19	2.1634	43	19	12.86
MTOAC	1.1669	73	1.00513	0.7608	28.58	6.3787	120	96	2.97
Orcinol	1.1416	28	0.98056	0.7261	72.70	9.3500	44	28	8.36

TABLE II. ACCURACY IN MEASUREMENTS ANALYSED WITH ABSOLUTE METHANOL USING SURVISMETER CONSTANT ( $k, \text{cm}^2 \text{s}^{-2}$ ) AT DIFFERENT TEMPERATURES.

Temp, °C	k	Viscosity ( $\eta/\text{cp}^*$ )	Lit. $\eta/\text{cp}$	Expe. $\eta/\text{cp}$	% error in $\eta$
10	0.00437	0.6498	0.69	-0.0402	$\pm 5.8234$
15	0.00507	0.6004	0.623	-0.0226	$\pm 3.6247$
20	0.00556	0.5641	0.593	-0.0289	$\pm 4.8763$
25	0.00578	0.5513	0.547	0.0043	$\pm 0.7895$
30	0.00646	0.5288	0.51	0.0188	$\pm 3.6949$

\*The cp = centipoises.

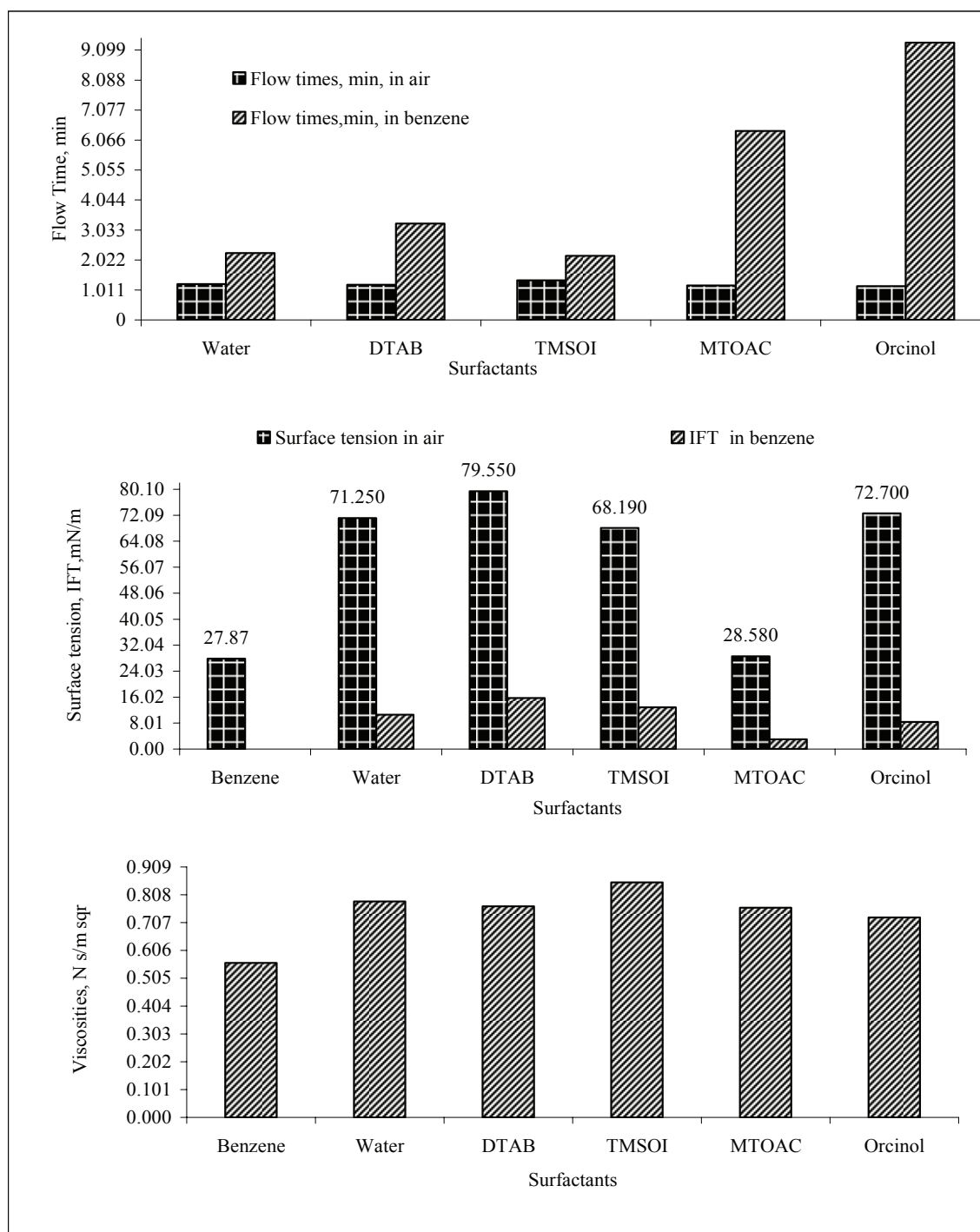


Figure 2. Flow time sec and surface tension  $\text{mN m}^{-1}$  in air and benzene medium, viscosities  $\text{N s m}^{-2}$  in air.

interactions of the  $N^+-Cl^-$ . The  $Cl^-$  is a small sized anion and does not induce any potential. Thus the  $O=S^+-I^-$  compensates more share to the higher IFTs and  $N^+-Cl^-$  does not but the 12 carbon chain does compensate for the same mechanism of interactions.

The DTAB molecules with increase in the surface tension tend to accumulate near a surface of water with a higher surface stretching. So the  $N^+$  and  $Br^-$  interact with water but its dodecyl chain hangs centering towards bottom making surface more stretched. Because the  $N^+-Br^-$  acts as a mild dipole and is unable to disrupt water structure (Singh and Kumar, 2007). Thus a mild interaction of the  $N^+$  further weakened by 3- $CH_3$  groups attached to quaternary nitrogen ion  $N^+$  while on the other side the dodecyl chain also weakens it. Due to this reason both the  $N^+$  and  $Br^-$  are not able to disrupt the hydrogen bonded water surface instead making it more stretched. Hence the DTAB increases the surface tension of water from 71.18 to 79.25 mN/m. The TMSOI does also accumulate near surface of water but because of stronger electronegativity of the  $O^-$  and  $S^+-I^-$ , do disrupt the hydrogen bonding of surface water with decrease in surface tension by 3.6 mN/m. But MTOAC due to  $N^+-Cl^-$  dipole strongly break water structure at surface reducing surface tension to 28.58 mN/m.

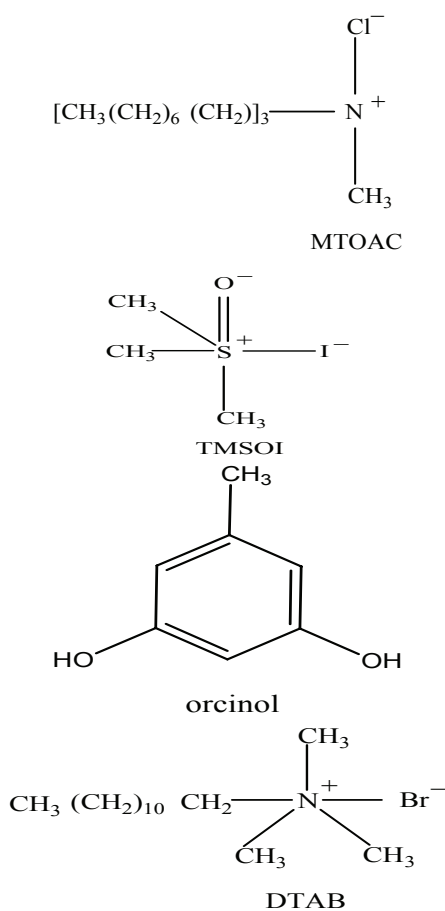


Figure 3. Structures

#### 4. Conclusion

The IFTs of surfactants with halide ions are as  $Cl^- > I^- > Br^-$ , and rationalized with nonbonding electron transitions with stronger electronegativity of  $Cl^-$ . The nonbonding electrons on  $Cl^-$  weakly undergo energy change but of  $I^-$  on TMSOI is loosely bound and reshuffle with energy change. The DTAB and orcinol enhance the surface tensions by 8.3 and 1.45 mN/m with stronger structuredness in solutions. Our data are highly significant for choosing type of surfactants for study of mutual miscibility of immiscible solvents. Further the viscosity data predict type of liquid like Newtonian or non-Newtonian. IFT is a biophysically important to quickly exchange drugs and similar other molecules to inter facial solvents. It assess an inter phases partitioning of drugs. Survisometer does not require any specific light arrangement or any other infrastructure except electricity to run a thermostat for experimental temperature. It saves user's time and electricity manifold, so is environmental friendly.

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#### Nomenclature

IFT	Interfacial Tension
MM	Mutual Miscibility
w/v	Weight by volume
DTAB	Dodecyltrimethylammonium bromide
TMSOI	Trimethylsulfoxonium iodide
MTOAC	Methyltriocetylammmonium chloride
Orcinol	3,5-dihydroxytoluene monohydrate

#### Greek letters

$\rho$	Density
$\eta$	Viscosity
$\gamma$	Surface tension

#### Subscripts

a	air
b	benzene

#### References

- Al-Sabagh, A.M., Ahmed, N.S., Nassar, A.M., Gabr, M.M., 2003, "Synthesis and evaluation of some polymeric surfactants for treating crude oil emulsions part i: treatment of sandy soil polluted with crude oil by monomeric and polymeric surfactants", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 216, No. 1-3, pp. 9-19.
- Andelija, M., Darko, I., Mirjana, M., Biljana, J., Slavko, M., 2006, "Influence of structural and interfacial properties of microemulsion eluent on chromatographic separation of simvastatin and its



- impurities”, *Journal of Chromatography A*, Vol. 1131, No. 1-2, pp. 67-73.
- Hilal, S.H., Karickhoff, S.W., Carreira, L.A., 1999, Estimation of microscopic, zwitterionic ionization constants, isoelectric point and molecular speciation of organic compounds”, *Talanta*, Vol. 50, No. 4, pp. 827-840.
- Kuznetsov, Y.I., Kazansky, L.P., 2008, Physicochemical aspects of metal protection by azoles as corrosion inhibitors, *Russian Chemical Reviews*, Vol. 77, pp. 219-232.
- Rosen, M.J., Zhu, Z.H., 1993, “Enhancement of wetting properties of water-insoluble surfactants via solubilization”, *Journal of the American Oil Chemists Society*, Vol. 70, pp. 65-68.
- Selcan, K., Kohler, K., Findenegg, G. H., 1988, “Interfacial tensions in simple oil-water-surfactant systems near their three-phase region”, *Colloid & Polymer Science*, Vol. 266, pp. 283-290.
- Singh, M., 2005a, “Studies of intermolecular force coefficient ( $\sigma_{\text{imr}}^0$ ) for methyl derivatives of urea in aqueous solutions with friccohesity, a new physicochemical function, from 293.15 to 303.15K” *Journal of Indian Chemical Society*, Vol. 82, pp. 129-135.
- Singh, M., 2005b, “Studies of molecular interactions of  $\alpha$ -amino acids in aqueous and cationic surfactants systems investigated from density and apparent molal volume at 283.15, 288.15 and 293.15K”, *Pakistan Journal of Scientetific Research*, Vol. 48, No. 5, pp. 303-311.
- Singh, M., 2005c, “A simple instrument for measuring the surface tension and viscosity of liquids”, *Journal of Instrumentl and Expperimental Techniques*, Vol. 48, pp. 270-271.
- Singh, M., 2006a, “Upper critical solution temperatures for immiscible solvent systems with halides salts, carboxylic acids, surfactants and polynuclear aromatic compounds and benzene derivatives”, *Journal of Chemical Thermodynamics*, Vol. 39, No. 2, pp. 240-246.
- Singh, M., 2006b, “Survismeter type 1 and 2 for surface tension and viscosity measurements of liquids for academic, and research and development studies”, *Journal of Biochemical and Biophysical Methods*, Vol. 67, pp. 151-161.
- Singh, M., 2006c, “Measurements of surface tension and viscosity of liquids with survismeter-a green chemistry instrumental approach” *Bulgarian Journal of Chemical Education*, Vol. 15, No. 6, pp. 426-430.
- Singh, M., 2007a, “Contribution of  $\pi$  conjugation electron and  $-\text{CH}_3$  group of aromatic compounds for upper consolute temperature (UCT) of immiscible solvent phases”, *Proceedings of National Academy Science India*, Vol. 77 (A), pp. 17-20.
- Singh, M., 2007b, “Structural interactions of globular proteins-bovine serum albumin, egg albumin, and lysozyme, in aqueous medium, elucidated with molar volumes, viscosities, energy functions, and IR spectra from 293.15 to 303.15 K”, *Journal of Applied Polymer Science*, Vol. 103, No. 3, pp. 1420-1429.
- Singh, M., Chand, H., Gupta, K.C., 2005, “Density and viscosity of bovine serum albumin egg albumin and lysozyme in aqueous and RbI, CsI and DTAB aqueous solutions at 303.15K and molecular interactions”, *Journal of Chemistry and Biodiversity Helvetica Chimica Acta*, Vol. 2, No. 6, pp. 809-824.
- Singh, M., Kumar, A., 2006, “Hydrophobic interactions of methyl ureas in aqueous solutions estimated with density, molal volume, viscosity and surface tension from 293.15 to 303.15 K”, *Journal of Solution Chemistry*, Vol. 35, No. 4, pp. 567-582.
- Singh, M., Kumar, V., 2007, “Effect of bomolecules: vitamins, proteins, amino acids, and Surfactants: DTAB, MTOAC, TMSOI, orcinol on upper critical solution temperatures”, *International Journal of Thermodynamics*, Vol. 10, No. 3, pp. 121-133.
- Singh, M., Pandey, M., Yadav, R.K., 2007, “Thermodynamic studies of molar volume, pair and triplet interactions with increase in length of side-chain of  $\alpha$ -amino acids in aqueous potassium chloride solutions at different concentration and 310.15 K”, *Journal of Molecular Liquids*, Vol. 135, pp. 188-191.
- Verdes, C.G., Urbakh, M., Kornyshev, A.A., 2004, “Surface tension and ion transfer across the interface of two immiscible electrolytes”, *Electrochemistry Communications*, Vol. 6, No. 7, pp. 693-699.
- Vollmer, D., Vollmer, J., 2000, “Bending free energy and spontaneous curvature for micelles and microemulsions with weak and strong surfactants”, *European Physics Journal E*, Vol. 4, pp. 153-159.
- Vora, S., George, A., Desai H., Bahadur, P., 1999 “Mixed micelles of some anionic-anionic, cationic-cationic, and ionic-nonionic surfactants in aqueous media”, *Journal of Surfactants and Detergents*, Vol. 2, No. 2, pp. 213-221.
- Wan, Y., Shi, Y., Zhao, D., 2007, “Designed synthesis of mesoporous solids via nonionic-surfactant-templating approach”, *Chemical Communications*, Vol. 9, pp. 897- 926.
- Yue, P., Feng, J.J., Liu, C., Shen, J., 2004, “A diffuse-interface method for simulating two-phase flows of complex fluids”, *Journal of Fluid Mechanics*, Vol. 515, pp. 293-317.