International Journal of Thermodynamics (IJoT)
ISSN 1301-9724 / e-ISSN 2146-1511
www.ijoticat.com

Vol. 14 (No. 2), pp. 87-95, 2011
doi: 10.5541/ijot.345

Viscous and Surface Properties of Upper Critical Solution Temperatures of Immiscible Solvents with Biomolecules, Surfactants and Polymer Resin

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Abstract

Viscosity and surface tension of upper critical solutions (UCS) of water + phenol with $\Delta G > 0$ are reported. The phenol upper critical solutions within before (B) and after (A) UCS temperatures range are depicted as BUCS and AUCS respectively and were used for study. Viscous flow times (t, sec) and pendant drop numbers (n) were measured together with Survismeter for η/N m s^{-2} and γ/mN m^{-1} respectively. The t and n were repeated for UCS with 0.5 millimol/L proteins (casein, pepsin, EA-Egg, albumin), vitamins [thiamine (B_1), riboflavin (B_2), pyridoxine (B_6)], amino acids (glycine, β-alanine, L-leucine), surfactants dodecyltrimethylammoniumbromide (DTAB), trimethylsulphoxoniumiodide (TMSOI), methyltrioctylammoniumchloride (MTOAC), orcinol and melamineformaldehyde-polyvinylpyrrolidone (MFP). Additives formed UCS at lower temperature with about 60% thermal energy saving. The t and n were used to calculate tn sec^{-1} for density calculation with Mansingh equation. The BUCS, UCS and AUCS as pre UCS and post UCS were obtained at 60^{0}C, 70^{0}C and 61^{0}C respectively. The tn with water were obtained for 25 to 70^{0}C and plotted with corresponding densities (± 0.05 kg m^{-3}) for calibration curve used for density calculations. The densities were noted as TMSOI > orcinol > MFP > DTAB > MTOAC, with lower values at 66.5 and higher at 66^{0}C.

Keywords: *Biomolecules; polymer resin; hydrophilic; survismeter; hydrophobic interactions.*

1. Introduction

Physicochemical properties of binary and ternary mixtures at different temperatures are industrially significant. The mixtures undergo molecular reorientations and stabilize by optimizing a particular dipole moment value responsible for interaction dynamics and mixing potential. The temperature and pressure as fundamental coordinates control intrinsic constitutional coordinates such density, viscosity and surface tension and others. In a nutshell, the molecular interaction engineering of aqueous mixtures are monitored with fundamental and constitutional coordinates, and is a most fascinating field of research. However, such studies are challenging and tedious to conduct experiments to design materials of industrial importance. In this context, the water and phenol immiscible solvents were chosen as the most accurate references as these become mutually soluble as an upper critical solution with rise in temperature.

Their mutual miscibility varies with a 3rd chemical component when added as additive. The critical mixtures are highly useful and their physicochemical data are most significant behaving as physicochemical indicators and help to develop critical mixtures in industrial processes. The experimental study of physicochemical data is very difficult because of their maintenance at particular experimental conditions. For example, for maintenance of water + phenol upper critical mixtures, the temperature stabilization at about 65^{0}C with ± 0.01^{0}C is an essential condition. Because of such inherent restrictions in measuring their physicochemical properties such as density, surface tension, viscosity, conductance, it is extremely difficult to design an experimental model for their authentic determination. Due to these reasons, the studies on the viscosities, surface tensions and densities are yet to be reported especially with the additives. Notably, the viscosities as transport and surface tensions as thermodynamic properties are industrially applied (Singh, 2006a; Singh and Kumar, 2007) due to their mixing capacities with different polarity, especially, in printing, anticorrosion, painting, petroleum and oils, polymers and textiles, agrochemicals, cosmetics, sol gels and many others. For measurements of such data fairly constant temperature and pressure are essential conditions. Since the upper critical solutions are obtained at higher temperatures, the instruments such as Antaan Paar or pyknometer, tensiometer and viscometer are not able to measure the density, surface tension, viscosity respectively. Especially, both the viscosities and surface tension measurements of UCS need special attention to maintain a stable temperature as they are temperature dependent parameters. The densities determination with pyknometer or Anton Paar (Singh, Chand, & Gupta, 2005; Singh & Irshad, 2008) is not possible due to loss of a sample in wvaporization during experiments at higher temperatures. Currently the unavailability of any instrumental device for measurement of such data has created a vacuum and serious hurdle in finding an interacting science furnished by physicochemical data of UCS. The UCS with high kinetic energy have additional solubilizing and interaction capabilities and activities with

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many industrial materials such fats, grease, aromatic hydrocarbons, oils and others.

The UCSs are preferred over homogenous mixtures stable at NTP due to their green chemistry capability especially with surfactants. To find an accurate and precise solution of such a difficult tangle, a novel apparatus referred to as Survismeter was used for densities, viscosity, and surface tensions measurements. Interestingly the survismeter measures density, viscosity and surface tension together which is an example of saving materials, manpower, infrastructure and electricity manifolds with 98% saving of resources. The technique has also analyzed additives effect on upper critical solutions including unfolding of biopolymers (Singh & Kumar, 2007) with hydrophobic and hydrophilic interactions. The intermolecular forces (IMF) do play a critical role in designing UCS and their determination could lead to a new breakthrough in the study of UCS sciences.

In general, the structural interactions have a significant impact on the mixtures of industrial interests. The critical solutions are weakly hydrogen bonded and highly useful for several applications where the liquids of low cohesive forces are needed. The analysis of the IMF of the water and phenol UCS constitute an interesting and interacting thermodynamics of non-ideal mixtures. Thereby the green solvents constituted out of the water + phenol + additives have high interacting potential for industrial uses like calending, disinfectants, dyeing, textile, wine purification, fumigation, soaps, detergents, sols-gels, coatings, floor cleaning, dry cleaning, and solubilizing of immiscible solvents of high industrial use such as the water and isobutyl alcohols. Equally, the green solvents which are formulated in our study are assumed to have high capacity to clean electronic and computer components because of their high spraying capacity and volatility. The UCSs have weaker IMF with $\Delta G > 0$ with non-spontaneous thermodynamics.

2. Methodology

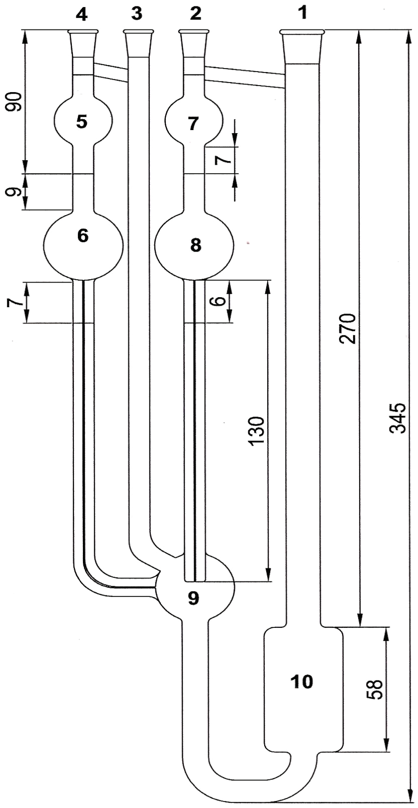
2.1. Chemicals

Above 99.99% pure chemicals (BDH, Fluka) B_1, B_2 and B_6, casein, pepsin and egg albumin, glycine and L-leucine (E. Merck, India), β-alanine (E. Merck, India), DTAB, orcinol (Sigma, USA), TMSOI, MTOAC (Fluka, USA), phenol (E. Merck, India) were used as received. The MFP was prepared. The chemicals were dried for 24 h, before their MP and stored in a P_2O_5 filled desiccator until use. Stock solutions of 0.5 mm L^{-1}, w/v, with Millipore water were prepared with a 0.01 mg electronic balance, Dhona, 100 DS, Instr. Pvt, Ltd, Calcutta, India.

2.2. Experimental:

Initially, the BUCS, UCS and AUCS were prepared in Borosil Mansingh Survismeter reservoir (Figure 1) with several prescribed ratios of water + phenol maintained at constant corresponding temperatures for continuum and non-continuum flows.

Density determination through friccohesity model: The BUCS, UCS and AUCS solutions were separately filled in reservoir bulb no.10 and the Survismeter was mounted in a water bath vertically. A schematic diagram of the Survismeter is shown in Figure 1.



Bulbs nomenclature
10: Reservoir
9: Carburetor
6: for viscous flow
5, 7: buffer
8: for dropwiase flow

Limbs nomenclature
9 to 3: for pressure
10 to 1: overhead pressure
Sockets: 1,2,3,4 for blocking pressure
10 to 8: Surface tension capillary
10 to 9: Hyphenating bend

Figure 1. Schematic illustration of survismeter unit.

A fairly constant temperature was maintained during experimental measurements. The liquid was pulled up from the reservoir to bulb no. 5 via 9 and 6. The pulling was made with a piston pump and viscous flow time (t) was measured within fiducial marks of the bulb no.6. Similarly, the pendant drop numbers (n) were measured in bulb no. 8. The procedural details are reported elsewhere (Singh, 2006b). The numbers 1, 2, 3, 4 marked on the top end of the Survismeter are sockets of the limbs. The limb between bulb nos. 9 to 3 is a pressure limb to control pressure in bulb no. 9 for measurements. Bulb no. 9 is a carburetor to systematically bypass a liquid to loops 10-9-6-5-4 and the 10-9-8-7-2 for the t and n respectively. These loops work alternatively by blocking the respective unit with the stopper based on a lock and unlock device. The MCF (molecular constitutional forces) and CBF (covalent bonding force) control frictional and cohesive forces which were correlated to the UCS sample density. Initially, the water was used to determine t and n data for friccohesity value calculations. The friccohesity and water densities were plotted for a calibration curve and the regression constants obtained from the regression analysis were used to calculate the density of the sample.

The Survismeter was calibrated with calibration no.06070582/1.01/C-0395, at NPL, Govt. of India. The Survismeter is a novel analytical device and works on R4M4 as Reduce Reuse Recycle Redesign Multipurpose Multidimensional Multitracking Multitasking for surface tension and viscosity measurements together. It was patented with patent no. 126089, by Singapore Govt. An entire range of upper critical solution compositions and corresponding mutual solubility temperatures (MST) along with procedural details is reported elsewhere (Singh, 2006a; Singh & Kumar, 2007). Initially, the phenol and water in particular ratios were cautiously filled in bulb no 10 of the Survismeter (Singh, 2006b) as the reference phases for the BUCS, UCS and AUCS preparations. The adequate and controlled heating was made for obtaining the BUCS, UCS and AUCS upper critical solution temperatures (UCST). The 0.5 mg/100 mL aqueous vitamins, proteins, amino acids, surfactants, orcinol and MFP resin were prepared, w/w, as stock solutions. The Survismeter was mounted vertically at a 90^0 angle on stainless steel stand and kept in a paraffin oil filled thermostat with $\pm\ 0.05^0$C control. The thermostat was kept on a shock absorbing and jerkless Bakelite sheet base to avoid disturbance in fluid flow during the study. The contents were heated at a rate of 1^0C min^{-1} and stirred with a glass stirrer at 50 rpm until the phases disappeared. The miscibility approached to form a homogenous single phase solution at a particular temperature, which was noted as MST. Significantly the single phase solution in the Survismeter (Singh, 2006b) was accurately maintained at a constant temperature for measuring viscous flow times and drop numbers. The viscous flow time with an electronic timer of $1\mathrm{x}10^{-2}$ sec and pendant drop numbers with electronic counter were measured respectively. In viscous flow time and drop numbers, the frictional and cohesive forces operate respectively to monitor fluid dynamics. Each measurement was repeated several times for reproducibility and precision in data. A statistical data analysis was made and a 95.5 % confidence interval was noted in measurements.

3. Density Calculation

The densities of water taken from literature and (Singh et al, 2005; Singh & Irshad, 2008) were used as reference data against t and n data. The densities of the UCST were calculated with newly developed equations which were patented with Indian Govt. with patent no. 232429. Individually in viscosity and surface tension, the frictional and cohesive forces respectively play key roles in generating fluid flow phenomenon. However the fluid flow within rigid boundaries works on dual force theory (DFT) influenced partly by the frictional force work and partly by the cohesive force. Unfortunately, a product of frictional and cohesive forces was never considered as a potential phenomenon while in fact they are complementary to each other to attain the fluid dynamics. Basically the fluid dynamics is also controlled with intramolecular shared electron pair shift (IMSEPS) and molionics. To date no example, application or study of frictional and cohesive forces in combination is reported. However their product develops a new parameter and if it is taken into account, then it could be a most effective physicochemical property which could be very near to core sciences of IMF and IMSEPS in UCST sciences. In this paper a new equation which combines both forces is used for determining densities, viscosity and surface tension. Through this equation the frictional and cohesive forces were applied to illustrate a chemistry of new phenomenon listed as friccohesity. The frictional forces do depict the forces operating in the bulk phase while the cohesive forces do reflect the dimension of molecular forces at the surface or air-liquid interface. Density is a static property as a function of integrated forces due to IMSEPS. Thus, the t and n data reflect the above said forces integrated mutually and are hand in glove or complementary to each other with complementary strength to colloids and emulsion technologies. Hence the product of the t and n data is denoted as tn data and referred to as friccohesity $(\sigma_{,}\, m^{-1})$ (Singh, 2006). Since the friccohesity integratedly differentiates the functional molecular force factors responsible for developing internal pressure establishing a relationship between the volume and density, it was applied for density calculations in this paper. The water was taken as the reference liquid with its corresponding densities in kg m^{-3}. Any other liquid which is stable within a chosen temperature can also be used as reference liquid for such study.

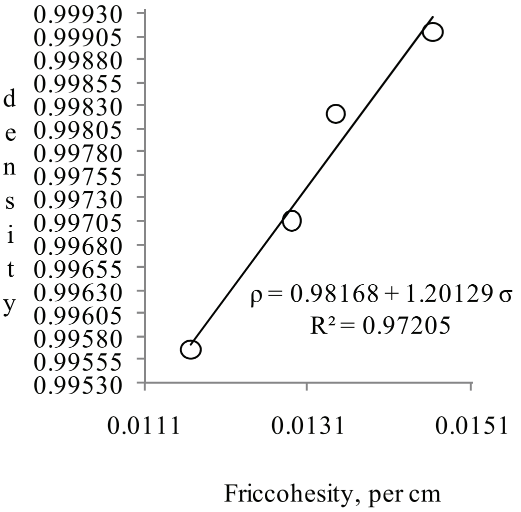


*Figure 2. Calibration curve determined with water densities (*kg m^{-3}*) with its corresponding tn data.*

Since the UCST is function of the temperature, the t and n data for water sample were measured for 25 to 70^0C range and fitted to the Mansingh equation (Singh, 2006b) Eq. (1).

$$\sigma = \sigma_0\left[\left(\frac{t}{t_0} \pm \frac{B}{t}\right)\left(\frac{n}{n_0} \pm 0.0012\left(1-\rho\right)\right)\right] \tag{1}$$

The σ is the Friccohesity (sec/cm) of the water used as the unknown sample and σ_0 is the Friccohesity (sec/cm) of the water used as the reference sample. The B/t is a kinetic energy correction to viscous flow in the Survismeter capillary. The 0.0012 is air density and (1-ρ) is the buoyancy correction. The (t and t_0) and (n and n_0) are flow times and drop numbers of water and the reference water sample respectively. The kinetic energy and buoyancy corrections were $3\mathrm{x}10^{-6}$ and $2.5\mathrm{x}10^{-6}$ respectively, and were omitted and then Eq. (1) is finalized as Eq. (2).

$$\sigma = \frac{\sigma_0}{t_0 n_0}\left[\left(tn\right)\right] \tag{2}$$

The σ_0 friccohesity of water was determined with Eq.(3)

$$\sigma_0 = \frac{\eta_0}{\gamma_0} \tag{3}$$

The η_0 and γ_0 are viscosity and surface tension of the reference water sample. The $\sigma_0/(/t_0n_0)$ is a constant for a reference water sample and denoted as Mc, Mansingh constant. The Mc is temperature dependent and associated with Survismeter capillaries. For example, its value at 25^0 C is 0.0029 m^{-1} and was used in calculations. Thus Eq. (2) is written as Eq. (4).

$$\sigma = M_C(tn) \tag{4}$$

The σ values were derived from Eq. (4) with the t and n data. The t and n data were repeated several times for reproducibility and precision. On statistical analysis the 95.5% confidence interval in data was noted with 99.99% reproducibility. Thus the tn and data were measured at different temperatures and σ values were calculated with Eq. (4) and plotted against respective densities for calibration curve depicted in Figure 2. Residual coefficient R is 97.21%. The calibration curve on regression produced an empirical equation depicted as Eq. (5).

$$\rho_{water} = \rho_0' + A\sigma_0 + B\sigma_0^2 \tag{5}$$

The ρ_0' is the limiting density of water within a studied temperature range, both the A and B are regression constants, and σ_0 is the friccohesity of the water. Thus using values of A and B coefficients, the ρ data of the UCST samples were determined. The A and B coefficients were determined taking different references samples and produced similar densities of the UCS samples. The densities of the UCST samples were also regressed against their σ values with Eq. (6).

$$\rho = \rho^0 + A'\sigma + B'\sigma^2 \tag{6}$$

The ρ and ρ^0 are density and limiting density of the UCST samples respectively, and A' and B' are their coefficients. Thus the t and n data determined the ρ with the σ values. Since the temperature varies in the case of the UCST samples, the densities of the water used as the reference sample were determined with varying temperatures. The ρ values of the UCS samples were used for their viscosities (η) and surface tensions (γ) calculations using Eqs. (7) (8) respectively.

$$\eta = \left[\left(\frac{t}{t_0}\right)\left(\frac{\rho}{\rho_0}\right)\right]\eta_0 \tag{7}$$

$$\gamma = \left[\left(\frac{n_0}{n}\right)\left(\frac{\rho}{\rho_0}\right)\right]\gamma_0 \tag{8}$$

The η_0 and γ_0 are viscosities and surface tensions of the solvent respectively. Apart from analysis of routine surface tension and viscosity data, the friccohesity was used for calculation of the densities and behavior of the mixtures. The purpose of applying the friccohesity here was to determine the density of subcritical, critical and supercritical mixtures due to lack of any provision for density determination of such mixtures at high temperatures. Thus, the tn data are most significant (Singh 2006b) and their precise and reproducible values under standard experimental conditions could be used as more authentic data for derivation of the densities of the upper critical solution temperatures. The Survismeter capillaries were uniform and cleaning was made as per standard methods. As the Survismeter was of standard make and of high authenticity, both the B/t and 0.0012(1-ρ) correction terms in practical uses were negligible and omitted. The constant $\sigma_0/(/t_0n_0)$ as Mc was carefully determined and is temperature dependent. Effective and direct method for calculation of the Mansingh constant Mc could also be made by using the t_0 and n_0 data for water at each experimental temperature using the η_0 and γ_0 data of the water reference sample with Eq. (9).

$$M_c = \left[\left(\frac{\eta_0}{\gamma_0}\right)\left(\frac{1}{t_0n_0}\right)\right]_0 \tag{9}$$

Thus the Mc values could be easily determined and be kept in Eq. (4). The Mc value at 25^0 is 0.0029 m^{-1}. The M_c also depends on the nature of the solvent along with temperature where it could act as an indicator to detect strongly, moderately and weakly polar solvents. Thus the tn data are the most effective device for density determination of water-phenol upper critical solution temperatures and could be most useful to other similar systems at desired experimental conditions. Especially, the emulsion and sol gel type materials could easily be studied where there is a trouble to measure physicochemical properties at higher temperatures.

4. Result and Discussion

The t and n data in combination resulted in a unique model for the study of physicochemical properties such as density, surface tension and viscosity of upper critical solutions. These properties are comfortably studied at normal temperature and pressure (NTP) as several methods like pyknometer, viscometer and stalagmometer are in use for their measurements with the homogenous mixtures at NTP. But our model used in the present study is efficient and safe to determine physicochemical data of upper critical solutions and hence the mixtures of several mole fractions given in Table 1 were studied. The viscosities and surface tensions of the water were used from the literature (Singh et al., 2005; Singh & Irshad, 2008) and were extended for their determination of the UCST. The viscosities and surface tensions of the UCST were found with close agreement with experimental values. The phenol-water mixtures showed changes in the densities with their mole fractions as well as temperatures with variable strength and weakening of hydrogen bonds respectively (Table 2). The internal force on the molecules is weakened with increases in the temperature due to a partial neutralization of the IMF and IMSEPS. The electrons of the bonds absorbing thermal energy gained kinetic energy and oscillate with weaker intermolecular forces. Thus the thermal energy and activity of the molecules are interrelated. A comparative analysis of BUCS, UCS and AUCS data was made for structural illustration. The vitamins with the BUCS showed densities as $B_2 > B_6 > B_1$, due to stronger interacting activity of the B_2 as compared to the B_6 and the B_1 due to single heteroatomic benzene ring (Table 2). So the single benzene ring is more interacting as compared to the many benzene rings of the B_6 and B_1. It makes the vitamins more responsive to the temperature of critical solutions. However, the UCST and AUCS values, with larger water mole fractions, the densities of the B_6 are higher than those of the B_2 and B_1 with $B_6 > B_1 > B_2$ and $B_6 > B_2 > B_1$ respectively (Table 1).

Table 1: Mole fractions at BUCS, UCS and AUCS, micromole of additives = μ x.

System	Temp, ^{0}C	x_{water}	x_{phenol}	μ x	System	Temp, ^{0}C	x_{water}	x_{phenol}	μ x
Phenol	66.0	0.1316	0.8684	0	β-Alanine	65.0	0.1333	0.8667	5.61
	68.5	0.1893	0.8107	0		68.0	0.0811	0.9189	5.61
	66.5	0.2486	0.7514	0		67.0	0.0822	0.9178	5.61
B1	60.5	0.1168	0.8832	1.53	L-Leucine	66.5	0.1529	0.8471	3.81
	68.0	0.1707	0.8293	1.53		68.0	0.0811	0.9189	3.81
	65.0	0.2353	0.7647	1.53		66.0	0.0833	0.9167	3.81
B2	62.0	0.1143	0.8857	1.33	TMSOI	66.5	0.1739	0.8261	2.27
	66.5	0.1739	0.8261	1.33		67.0	0.0822	0.9178	2.27
	66.0	0.2326	0.7674	1.33		66.0	0.0833	0.9167	2.27
B6	65.0	0.1096	0.8904	2.96	MTOAC	60.5	0.0902	0.9098	1.24
	68.0	0.1707	0.8293	2.96		67.0	0.0822	0.9178	1.24
	66.0	0.2326	0.7674	2.96		65.5	0.0839	0.9161	1.24
Pepsin	65.0	0.1333	0.8667	0.01	Orcinol	66.0	0.1316	0.8684	3.52
	67.0	0.1928	0.8072	0.01		66.8	0.0824	0.9176	3.52
	65.4	0.2517	0.7483	0.01		66.0	0.0833	0.9167	3.52
Casein	59.5	0.0916	0.9084	0.01	DTAB	64.0	0.1111	0.8889	1.62
	67.5	0.1509	0.8491	0.01		66.5	0.0828	0.9172	1.62
	66.5	0.2130	0.7870	0.01		66.0	0.0833	0.9167	1.62
Egg-Albu	64.0	0.1351	0.8649	0.01	MFP-resin	64.0	0.1111	0.8889	0.01
	68.0	0.1905	0.8095	0.01		68.5	0.0805	0.9195	0.01
	66.0	0.2500	0.7500	0.01		66.0	0.0000	1.0000	0.01
Glycine	64.0	0.1111	0.8889	6.66					
	67.0	0.0822	0.9178	6.66					
	66.0	0.0833	0.9167	6.66					

The B_6 caused stronger hydrophilic and hydrophobic interaction than those of the B_2 and B_1, due to 3-OH, groups, hydrophilic 1 N atom and hydrophobic 1-CH_3 groups. It is inferred that the 3-OH groups strongly developed hydrogen bonding by disrupted a bulk dipolar water structure. Similarly due to activities of the hydrophobic part with stronger CBF, it also reoriented the bulk water structure without disrupting the hydrogen bonding but with higher entropic changes. The B_2 caused the stronger hydrophilic and the weaker hydrophobic interactions and the B_1 weakened the hydrogen bonding at BUCS. For larger water mole fractions at UCST and AUCS, the B_6 produced higher densities with stronger hydrophilic interaction. The B_1 and B_2 (Table 2) at the UCST and AUCS developed stronger hydrophobic and weaker hydrophilic interactions. Probably the 1-OH, -NH_2, groups, 2 N, 1 S atom as hydrophilic and 2 -CH_3 groups as hydrophobic with B_1 and the 3-OH, 1 NH, groups, 2 N atoms as hydrophilic and the 2 -CH_3 as hydrophobic functional groups with the B_2 respectively are responsible for such trends of the data. In general, the OH functional group developed hydrophilic while the -CH_3 and the benzene ring developed hydrophobic interactions respectively. These components of the vitamins are not able to disrupt the hydrogen bonded water structures but they are competent to reorient the bulk water. So the latter surrounded such functional sites for solvation. The mechanism of solvation caused different levels of the IMF along IMSEPS that influenced the density data as an indicator of the structural changes. Thus the density of pepsin is higher than those of the casein, egg-albumin at BUCS and AUCS as pepsin > casein > egg-albumin and pepsin > casein > egg-albumin, respectively (Table 2). The densities of egg-albumin are higher than those of pepsin and casein at UCST as egg-albumin > pepsin > casein. The sequential data inferred stronger hydrophilic and hydrophobic interactions of the pepsin than those of the casein and egg-albumin, respectively. The egg-albumin developed stronger hydrophilic interactions but both the pepsin and casein developed weaker hydrophilic interactions. The analysis of IMSEPS of the proteins, biomolecular dendrimers and similar others macromolecules with UCST is a most significant study as the proteins thermally unfolds. Thus the vitamins with different molecular constituents developed different interactions due to their interacting activities or potentials. This could infer stronger water absorbing capacity of the egg-albumin and swelling phenomenon of the protein molecules due to interaction of the water molecules with peptide bonds. Probably peptide bonds have higher affinity towards the water molecules due to the larger number of the amino acids. For example, the pepsin developed stronger hydrogen bonding with water than those of casein and egg albumin (Table 2). Since the proteins are found in folded states, the hydrogen bonded water enters inside the structure and generates internal pressure noted as swelling.

Table.2: Density (ρ, 10^3kg m^{-3}), viscosity (η, 10^{-1}kg m^{-1}s^{-1}), surface tension (γ, mNm^{-1}) at BUCS, UCS and AUCS.

	ρ, 10^3kg m^{-3}			η,10^{-1}kg m^{-1}s^{-1}			γ, mNm^{-1}		
System	BUCS	UCS	AUCS	BUCS	UCS	AUCS	BUCS	UCS	AUCS
Phenol	0.8911	0.9431	0.9753	0.57090	0.52940	0.48020	29.12	31.38	33.04
B1	0.8404	0.9406	0.8913	0.73370	0.51450	0.59150	27.96	30.21	30.19
B2	0.9229	0.8904	0.9781	0.57420	0.58160	0.48200	31.84	29.62	33.74
B6	0.9040	0.9482	0.9985	0.57130	0.53170	0.41370	30.07	32.12	35.1
Pepsin	0.8896	0.8665	0.9891	0.59280	0.59580	0.44810	30.13	28.83	34.13
Casein	0.8541	0.8594	0.9546	0.61250	0.59920	0.52170	28.93	28.59	32.33
Egg-Alb	0.7621	0.9414	0.9111	0.61840	0.52250	0.59720	25.35	30.77	32.03
Glycine	0.8060	0.8845	0.9841	0.62650	0.60720	0.47350	27.03	30.52	34.59
β-Ala	0.7958	0.8627	0.9816	0.61680	0.56730	0.47230	26.47	27.24	33.86
L-Leucine	0.7958	0.8627	0.9816	0.61680	0.56730	0.47230	26.47	27.24	33.86
TMSOI	0.9536	0.9953	0.9954	0.54290	0.43470	0.42200	33.52	35.66	34.34
MTOAC	0.7649	0.9081	0.9601	0.64130	0.60000	0.52140	26.39	31.92	33.13
Orcinol	0.8476	0.9582	0.9896	0.62660	0.52510	0.44630	29.24	33.06	34.14
DTAB	0.7854	0.9706	0.9739	0.64060	0.51930	0.50180	27.10	34.78	34.23
MFP-Resin	0.8216	0.9211	0.9812	0.63490	0.58710	0.48250	28.35	32.38	34.49

The glycine densities are higher than those of β-alanine, L-leucine at BUCS, UCST and AUCS placed as glycine > β-alanine = L-leucine; glycine > β-alanine = L-leucine and glycine > β-alanine = l-leucine, respectively (Table 1). The glycine contains one $-CH_2-$ methylene group which is hydrophobic while its amino and carboxylic groups are hydrophilic in nature and developed stronger hydrophilic interactions than those of the hydrophobic. The glycine developed stronger hydrophilic and hydrophobic interactions than those of the casein and egg-albumin as the IMSEPS seems most effective. The L-leucine with $-CH_2CH(CH_3)_2$ a longer chain and 1–CH group developed the hydrophobic interactions but the 1-N^+H and 1 -COO^- groups caused comparatively weaker hydrophilic interactions.

The -COO^- and -H_3N^+ groups of glycine developed stronger hydrophilic interactions while the 1 -CH group developed weaker hydrophobic interactions but the β-alanine and L-leucine with -CH_3-CH_2 and -(CH_2-CH-(CH_3)$_2$) longer alkyl chain developed stronger hydrophobic interactions as compared to the glycine. The L-leucine with -(CH_2-CH-(CH_3)$_2$) chain caused induction and steric effects that supported the stronger hydrophobic interactions. Such interactions which are directly related to molecular constitution and development of IMF have proven to be the most authentic data to develop a background of the UCST to determine physicochemical properties. Due to such vital force generation vis-à-vis structural configurations, the concept is extended to a novel phenomenon of intramolecular multiple force theory (IMMFT). Fundamentally the IMMFT involves the collisions and kinetic energy where friccohesity is a critical parameter and matters a lot. Since with UCS the collisions play a critical role, the IMMFT is a most suitable model to explain the molecular interactions based on their molecular constitutional force (MCF) contributing to IMF. The physicochemical properties which act as a physicochemical indicator (PCI) are functions of the MCF based on the covalent bonding force (CBF). In this context, the surfactants in general and cationic surfactants specifically with vital MFC and CBF are interesting model for UCS and their PCI. Thus the densities of TMSOI are higher than those of orcinol, MFP, DTAB, MTOAC at BUCS, UCST and AUCS are placed as TMSOI > orcinol > MFP > DTAB > MTOAC; TMSOI > DTAB > orcinol > MFP > MTOAC and TMSOI > orcinol > MFP > DTAB > MTOAC, respectively. The TMSOI with 3-CH_3 hydrophobic and O=S^+-I^- hydrophilic groups showed stronger hydrophilic and weaker hydrophobic interactions due to different MCF and CBF. With hydrophobic mechanism the CBF is not shifted to any individual constituent atom and Columbic force = 0 but with hydrophilic the CBF is shifted to more electronegative atom with Columbic force > 0. Thus the dislocation of a covalent bond develops a vacancy for molecular interaction with different magnitude of the PCI which is a concept of IMSEPS. Hence the TMSOI developed stronger hydrogen bonding with the water than those of orcinol, MFP resin, DTAB, and MTOAC at BUCS, UCST and AUCS. The orcinol with 1–CH_3, hydrophilic 2 –OH, hydrophobic 1-benzene ring; the DTAB with longer alkyl chain of 12 C atoms, hydrophobic 3–CH_3 groups and -N^+, -Br^- hydrophilic groups are not able to compete with the interactions of the TMSOI due to different magnitude of the CBF and Columbic forces. Also the MTOAC with 3 octyl chains [$CH_3(CH_2)_6(CH_2)$] with hydrophobic 1–CH_3, the –N^+ and Cl^- hydrophilic atoms; and the MFP resin with 3–(CH-CH_2-)$_n$- vinyl chains, 3 pyrrolidone rings, 3 –CH groups, 1 heteromolecular benzene ring, 6–N atoms, hydrophilic groups 3-OH groups caused comparatively weaker molecular interactions. The orcinol, MFP resin, DTAB, and MTOAC developed stronger hydrophobic and weaker hydrophilic interactions against stronger interactions of the TMSOI. Here, the molionic model is most applicable as the surfactants also behave like salts along with alkyl chains with stronger CBF.

The O=S^+-I^--H_2O interactions of TMSOI are stronger dipolar interactions due to the stronger induced potential or polarizability of I^- but Cl^- atom of the MTOAC caused a slightly stronger hydrophobic interaction. Here, the higher CBF exists that developed stronger Columbic forces. Thus, the O=S^+-I^- with alky chain of 10 carbon atoms dominates over the weaker hydrophilic interactions of N^+-Cl where the Cl^- is a small sized anion with no induced potential. The density of MFP resin is lower than those of the biomolecules (Table 2) which undergo structural changes with different electron densities on positively and negatively charged polar centers. The amino acids act as zwitterions and the vitamins developed multiple force centers with negative and positive charges where the IMMFT is a befitting model to reckon with offshoots of the CBF and MCF. The IMMFT also inferred interacting activities with activation energy due to multiple interacting force centers within a single molecule.

4.1. Viscosity

The viscosity follows a laminar flow controlled by MCF and CBF that results into net interacting molecular forces that decide frictional force. The CBF leads to the generation of van der Waals and Lennard Jones forces and are executed through Le Chatelier and Boltzmann distribution energy tendencies to equilibrium. The molecular reorientations and polarity both contribute to the viscosity phenomenon and hence determination of the viscsosity data retrieves the inbuilt forces and molecular constitution in the mixtures. The viscosity is a transport property and the IMF leads to the infererence of useful information for PCI. In this context, the viscosity of vitamin B_1 is higher than those of B_2, B_6 at BUCS and AUCS, with $B_1 > B_2 > B_6$ and $B_1 > B_2 > B_6$ (Table 2) orders respectively. But with the mole fraction of water, the viscosities of the B_2 are higher than those of B_6, and B_1 at UCST with $B_2 > B_6 > B_1$ orders. The B_1 have stronger hydrophilic and hydrophobic interactions than those of B_2 and B_6. The viscosity of egg-albumin are higher than those of casein, and pepsin at BUCS and AUCS with egg-albumin > casein > pepsin and egg-albumin > casein > pepsin order. But with the mole fraction of water at UCST the viscosities of casein are higher than those of the pepsin, and egg-albumin as casein > pepsin > egg-albumin. Thus the egg-albumin caused stronger hydrophilic and hydrophobic interactions than those of the casein and pepsin. It inferred stronger electronegativity of the egg albumin with shared covalent bonding as per CBF and hence stronger CBF exists with casein fitted in an IMSEPS model with activation energy.

The viscosity of glycine is higher than those of the β-alanine, L-leucine, at BUCS, UCST, and AUCS as glycine > β-alanine = L-leucine; glycine > β-alanine = L-leucine and glycine > β-alanine = L-leucine. Thus the glycine caused the stronger hydrophilic and hydrophobic interactions than those of the β-alanine and L-leucine. This inferred larger shift in covalent bonding of the glycine due to single $-CH_2$- group between amino and carboxylic groups act as point charges (($q^{\delta+}$ and $q^{\delta-}$ at r distance) for Coulomb forces = $(q^{\delta+}q^{\delta-})/r^2$. However the covalent bond shifting strength when larger alkyl chain is introduced between the polar groups of the amino acids is weakened due to $r_{\beta\text{-aniline}}$ or $r_{\text{L-leucine}} > r_{\text{glycine}}$. The viscosity of MTOAC is higher than those of DTAB, MFP, orcinol, TMSOI at BUCS, UCST and AUCS with MTOAC > DTAB > MFP > orcinol > TMSOI; MTOAC >MFP > orcinol > DTAB > TMSOI and MTOAC > DTAB > MFP > orcinol > TMSOI orders. The MTOAC have stronger hydrophilic and hydrophobic interactions than those of the DTAB, MFP, orcinol and TMSOI. The viscosity of B_1, B_2, egg-albumin, casein, glycine and MTOAC exhibited maximum Newtonian or Frictional forces. The molecules collide randomly, with a longer residence time in a flow and collide with solvent molecules on the way, including in Brownian motion. However, the B_1, B_2, egg-albumin, glycine and MTOAC showed higher values than those of the B_1, B_2, egg-albumin, glycine and MTOAC with stronger interaction and hydrogen bonding. It showed no influence of the B_6, pepsin, β-alanine, L-leucine, and TMSOI on the viscous flow. The heteromolecular forces are stronger, maintaining streamline flow with the B_6, B_1, pepsin, β-alanine, L-leucine, and TMSOI, orcinol, DTAB but B_2, egg-albumin, and glycine have a weaker streamline flow with the MTOAC where the Brownian motions is attributed to asymmetry.

4.2. Surface tension

The surface tension is developed due to cohesive forces among similar molecules. The higher the shift in covalent bonding or shared electron from less to stronger electronegative atoms, the higher are the columbic forces with higher tension on the surface which exactly work on the model of the IMSEPS. A larger difference in the CBF of the MCF caused the higher surface forces or tensions. Thus the surface tension of vitamin B_2 is higher than those of the B_6, and B_1 at BUCS as $B_2 > B_6 > B_1$ respectively (Table 2). With the mole fraction of water, the surface tension of B_6 is higher than those of B_1 and B_2 at UCST and AUCS listed as $B_6 > B_1 > B_2$ and $B_6 > B_2 > B_1$ respectively. Thus the B_6 developed stronger hydrophilic and hydrophobic interactions than those of B_1 and B_2. The surface tension of pepsin is higher than those of the casein, egg-albumin at BUCS and AUCS with pepsin > casein > egg-albumin, pepsin > casein > egg-albumin orders, respectively. But with the mole fraction of the water, the surface tension of egg-albumin is higher than those of the pepsin, and casein at UCST with egg-albumin > pepsin > casein sequence (Table 2). Thus, the pepsin caused the stronger hydrophilic and hydrophobic interactions than those of casein, egg-albumin which inferred stronger Columbic force with the pepsin. The surface tension of glycine are higher than those of β-alanine, L-leucine at BUCS, UCST and AUCS with glycine > β-alanine = L-leucine; glycine > β-alanine = L-leucine and glycine > β-alanine = L-leucine order respectively. The glycine showed a stronger surface active interaction than those of β-alanine and L-leucine. The viscosities of the glycine depicted a similar trend of its interacting forces. Thus the CBF and MCF are applicable with frictional as well as cohesive forces which could also be configured by molecular and ionic type activities noted as molionic.

The surface tension of TMSOI is higher than those of the orcinol, MFP, DTAB, MTOAC at BUCS and UCST as TMSOI > orcinol > MFP > DTAB > MTOAC; TMSOI > DTAB > orcinol > MFP > MTOAC, respectively. The surface tension of the MFP is higher than those of TMSOI, DTAB, orcinol, MTOAC at AUCS with MFP > TMSOI > DTAB > orcinol > MTOAC in sequence. Thus, the TMSOI developed stronger hydrophilic and hydrophobic interactions than those of the orcinol, MFP, DTAB and MTOAC. The surface tension of the B_1, B_6, pepsin, glycine, TMSOI, MFP are higher than those of the

B_1, B_2, casein, egg-albumin, MTOAC, orcinol and DTAB. The surface tension (Table 2) at BUCS, UCST and AUCS inferred stronger cohesive forces with the TMSOI with stronger surface interactions. It increased with increases in mole fractions (Table 1, 2). The TMSOI with 3-CH_3 groups with an optimum distance between the S^+ and I^- atoms caused maximum surface forces. The MFP resin with 3 $(CH\text{-}CH_2)_n$ vinyl chains, 3-CH groups due to stronger hydrophobic interactions and 3-OH groups, and 9 N atoms developed lower hydrophilic interactions due to stronger CBF. The covalent bond and van der waal forces of the B_6, pepsin, glycine, TMSOI and MFP resin are stronger than those of B_2, B_1, casein, egg-albumin, β-alanine, L-leucine, orcinol, DTAB and MTOAC.

4. Conclusion

The present study depicted unique combination of viscous flow times and pendant drop numbers for continuum and non-continuum flow models respectively. These are most significantly applicable for critical mixtures of biomolecules of different polarity. How do the transport, statistic and surface properties behave in temperature induced homogenous mixtures, are nicely explained. The density, viscosity and surface tension data are unique in nature as no such models of experimental measurements of the PCI and their calculations are reported on the UCST. Our study inferred the activation energies of the biomolecules which are responsible for interaction and potential dynamics. The thermodynamic and transport properties of biomolecules are helpful for analysis of residual forces to estimate Brownian and Newtonian motions along with electrostatic forces. The data are useful for drug disintegration, and distribution of biomolecules in bioprocesses and estimated activities of vitamins: B_1-Thiamine, B_2-Riboflavin, B_6-Pyridoxine, proteins: Casein, Pepsin, Egg-Albumin, amino acids: Glycine, β-Alanine, L-leucine in biological systems. The density, viscosity and surface tension define intermolecular interactions of biopolymers are of bioengineering significance to deal with separations and isolation of biophysically and thermodynamically useful molecules. An excellent combination of IMSEPS and molionic models with interacting activities due to thermal energy has been explicitly and implicitly operational due to multiple force centers within single molecules. The upper critical solution mixtures interestingly act as green solvents due to stronger interactions, solubilizing and hydrogen bonds disruption capacities. They are also useful to develop mixtures of the required polarity for either disruption of CBF or unfolding of biopolymers.

The densities, viscosity, surface tension data calculated with mansingh equation with temperature signify structure breaking effect on the water. The surfactants showed higher densities than those of the amino acids and proteins with stronger hydrophilic and hydrophobic interactions. The CBF of their hydrophobic and hydrophilic parts developed larger difference with higher interacting gradients. The vitamins B_6, pepsin and the glycine showed the density equal to the surfactants. The B_6 pepsin and glycine developed hydrophilic and hydrophobic interactions of equal strength similar to the surfactants and could be used as surfactants in biophysical systems. The (B_1, B_6), (pepsin, egg-albumin), (β-alanine, L-leucine) and MFP made homogenous solutions with stronger mixing and interactions at lower UCST. Conclusively the survismeter approach to physicochemical characterization of molecular interactions of the surfactants, biosurfactants and polymer resin using upper critical mixtures as a suitable medium has been found a most authentic, environmental friendly model in temperature induced molecular interaction engineering. Also the studies are highly significant for interaction efficiency of polymer resins as their solubility and activities significantly vary either to form Newtonian or non-Newtonian liquids. The macromolecules are highly sensitive to temperatures changes as their electrostatic sites get further activated where the friccohesity would be quantitative data to correlate with IMMFT coordinates. Therefore the present studies have industrial implications and impacts for saving and simplifying difficult problem of measurements of density, surface tension and viscosity of upper critical solution temperatures. The studies could also be extended to molar volume data and activation energies of higher temperatures apart from NTP.

Acknowledgement:

The authors are highly thankful to University Grant Commission, Govt. of India and Dr. A. P. Raste, Principal, DBC, for infrastructural support.

Nomenclature

AUCS	After Upper Critical Solution
BUCS	Before Upper Critical Solution
DTAB	Dodecyltrimethylammoniumbromide
MFP	melamineformaldehyde-polyvinylpyrrolidone
MTOAC	Methyltrioctylammoniumchloride
TMSOI	Trimethylsulphoxoniumiodide
UCS	Upper Critical Solution, ^0C

η	Viscosity 10^{-1}kg $m^{-1}s^{-1}$
γ	Surface tension mN/m
ρ,	Density 10^3kg m^{-3}

References:

Singh, M. (2006a). Upper critical solution temperatures for immiscible solvent systems with halides salts, carboxylic acids, surfactants and polynuclear aromatic compounds and benzene derivatives. *J. Chem. Thermodynamics*, *39* (2), 240-246.

Singh, M., Kumar, V. (2007). Effects of biomolecules: vitamins, proteins, amino acids, and surfactants: DTAB, MTOAC, TMSOI, Orcinol on upper critical solution temperatures. *Int. J. of Thermodynamics*, *10* (3), 121-123.

Singh, M., Chand, H., Gupta, K.C. (2005). Studies of density, apparent molar volume and viscosity of bovine serum albumin, egg albumin and lysozyme in aqueous and RbI, CsI and DTAB aqueous solution at 303.15 K", *Chem.& Biodiver. 2*, 809-824.

Singh, M., Irshad, Md. (2008). Study of aqueous biomolecules with magnetic flux using density, viscosity, and surface tension probe at 304.15K. *J. Disp. Sci. Techn.* 29 (6), 895-898.

Singh, M., Kumar, V. (2007). Preparation of melamine-formaldehyde-polyvinylpyrrolidone (MFP) novel resins, their structural with IR-NMR and Friccohesive characterizations with Survismeter, and their Hydrodynamics, *81st Colloid & Surface Science Symposium (Chem. Coll. Mat. III) ACS*, University of Delaware, June 24-27.

Singh, M. (2006b). Survismeter Type 1 and 2 for Surface Tension and Viscosity Measurements of Liquids for Academic, and Research and Development Studies. *J. Biochem. Biophys. Methds.* 67, 151-161.

Yue, P., Feng, J.J., Liu, C., Shen, J. (2004). A diffuse-interface method for simulating two phase flows of complex fluids. *J. Fluid Mechanics*, 515, 293-317