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Ultrasonic Studies on Solvation Parameters of Urea in Aqueous Triton -100 at 303K, 308K and 313K

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Abstract

Urea is a synthetic organic fertilizer used for growing all types of crops and soils. It will not abuse the soil. Surfactants or surface active agents, reduce the surface tension of fertilizer and pesticide solutions, allowing to penetrate into the soil quickly for less run-off and waste. Appropriate use of surfactant will furnish optimum performance and increases the effectiveness of fertilizer solutions. This study, discusses the solvation parameters of urea in aqueous tritonX-100. Ultrasonic velocity, density and viscosity of urea in aqueous tritonX-100 as a function of composition have been measured at 303K, 308K and 313K. The ultrasonic experimental values of the systems are applied to derive parameters viz., adiabatic compressibility (β), molal hydration number (n_h), apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_V), limiting apparent molal compressibility (ϕ_K^0), limiting apparent molal volume (ϕ_V^0) and their constants (S_K, S_V) and viscosity B – coefficient of Jones–Dole equation. The results have been explored in terms of intermolecular interaction of urea in aqueous triton X-100. Pot culture experiment was carried out to study the effect of urea in aqueous triton X-100 on the growth of cluster bean crop. The solvation parameters results derived from ultrasonic method are compared with the pot culture experiment. Both the results are consistent with each other.

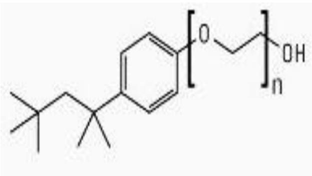
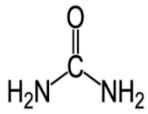
Key words: *Triton X-100, urea, adiabatic compressibility, molal hydration number, apparent molal compressibility, apparent molal volume, pot culture experiment.*

1. Introduction

Fertilizers are commonly used for growing all types of crops, with the application rates depending on the soil fertility. Urea is an organic fertilizer, known as carbamide is the most important nitrogenous fertilizer. It has the highest nitrogen content, equal to 46% and it can be used for all types of crops and soil [1]. All over the world, urea is extensively used as dry granular source of nitrogen. Urea when applied to the soil will enhance the effective yield of crop. The green leafy growth of a crop is afforded by the nitrogen of urea released in the soil. A large number of researchers [2-5] have reported that urea act as a structure breaker in water.

Surfactants consist of organic molecules with hydrophobic and hydrophilic parts and can interact with polar as well as non-polar surface. Surfactant absorption by soil is of great importance due to the wide spread use of these compounds in household and industrial activates[6]. Nonionic surfactant has uncharged head group which are however polar in nature. Head groups are usually based on a polyoxyethylene chain. Non-ionic surfactant is widely used to lyse cells to extract protein or organelles, or to permeabilize the membranes of living cells. It can be used in pesticide and fertilizer formulation. It reduces surface tension of fertilizer solution.

The objective of ultrasonic study of urea in triton X-100 is to identify the type of molecular interactions between urea and triton X-100 and to fetch the changes introduced in the structure of triton X-100. Experimental data have been used to calculate the solvation parameters. The obtained results are discussed in terms of solute-solvent, solute-co solute, ion-ion interactions occurring in the solutions at different temperatures and concentrations of urea and triton X-100.

Structure of triton X-100	Structure of urea
	

The pot culture experiment is used to grow plant in pot. In pot culture experiment, cluster bean seeds are swon in pot atambient temperature. 0.6M of urea concentration in different molarity of triton X-100 solution is applied to the cluster bean plant. In this experiment, biometric observation viz., plant height, dry matter production were recorded at 5, 10, 15, 20, 25, 30, 35 DAS.

2. Experimental details

The chemicals used in the present study are, urea fertilizer of molecular weight 60.06 g/mol and triton X -100 surfactant of molecular weight 646.87 g/mol respectively purchased from Sd Fine Chem. limited, Mumbai and Kemphasol, Mumbai respectively. Triton X-100 surfactant added with deionized water had been used as solvent for preparing urea fertilizer solution of different concentrations. The ultrasonic velocity was measured using the 2MHz fixed frequency of ultrasonic interferometer (Model F-81, Mittal Enterprises, New Delhi). The density was measured using a specific gravity bottle and digital balance (Denver digital electrical balance). The accuracy in the measurement of density was the order of $\pm$ 0.1 kg m^{-3}. The viscosity of the solutions was measured by Ostwald's viscometer. The overall accuracy of the measurement of viscosity in this method was $\pm$0.001Nsm^{-2}. The temperature was kept constant using constant temperature water bath (Raaga Industries, Chennai Model PT 100) with an accuracy of $\pm$ 0.1° C. The measurements are taken at 303K, 308K and 313K temperatures.

3. Pot culture experiment

Cluster bean (Cyamopsis tetragonoloba) is an annual legume crop and one of the famous vegetable, popularly known as "Guar" in India. Cluster bean grown well in warm climatic conditions and this crop can be cultivated in both summer and rainy season. Cluster bean grown on sandy loam soil, soil pH range of 7 to 8 should result in good yield and quality. Pot culture experiment was conducted for 60 days. 21 pots were used for the experiment. The pots are arranged in 7 sets having 3 replications each. 10 Kg of red soil and sand in the ratio of 3:1 are filled in pots separately. Seed of cluster bean was collected from local market in Pudukkottai. The 3 seeds are sown in each pot. Each pot is irrigated at only one time with different concentrations of triton X-100 with 0.6M urea. The biometric observation are recorded at equal intravals of time.

4. Theory

Molal hydration number (n_H), apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_v), are the parameters which are used to explain the solute–solvent, solvent–solvent and solute–solute interactions and structure making/breaking properties of the solution. The experimental velocity, density and viscosity data were used to calculate the physical parameters of urea in aqueous triton X-100 solution using the standard formula.

Adiabatic compressibility

$$\beta = \frac{1}{U^2\rho} \qquad (1)$$

Molal hydration number

$$n_h = \frac{n_1}{n_2}\left(1-\frac{\beta}{\beta_0}\right) \qquad (2)$$

Apparent molal compressibility is given by

$$\phi_K = \frac{1000}{m\rho_0}(\rho_0\beta - \beta_0\rho) + \left(\frac{\beta_0 M}{\rho_0}\right) \qquad (3)$$

where, β, ρ and β_0, ρ_0 are adiabatic compressibilities and density of solution and solvent respectively. n_1 and n_2 are the number of moles of solvent and solute. M is the molecular weight of solute, m is the molar concentration of the solute.The apparent molal compressibility ϕ_K is the function of m as obtained by Gucke (1993), [7] from Debye Huckel theory (1923) [8] and is given by

$$\phi_K = \phi_K^0 + S_K\sqrt{m} \qquad (4)$$

where, ϕ_K^0 is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. ϕ_K^0 and S_K are calculated by graphical method.

Apparent molal volumeis given by

$$\phi_V = \frac{1000}{m\rho_0}(\rho_0 - \rho) + \frac{M}{\rho_0} \qquad (5)$$

The apparent molal volume ϕ_V has been found to differ with concentration.

According to Masson's, (1929) [9] empirical relation,

$$\phi_V = \phi_V^0 + S_V\sqrt{m} \quad (6)$$

where, ϕ_V^0 is the limiting apparent molal volume at infinite dilution and S_V is constant. These values were determined by graphical method.

In the year (2002) M S. Chauhan et.al., were established the importance of viscometric study of electrolytic solution in mixed solvent [10]. The entire viscosity data have been analysed in the light of Jones-Dole semi-emprical equation [11].

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad (7)$$

where η and η_o are the viscosities of the solution and solvent respectively and m is the molar concentration of the solute-solvent system. A and B are constants which are distinct for a solute-solvent system. A is known as the Falkenhagen coefficient [12] which characterises the ionic interaction and B is Jones-Dole coefficient which depends on the size of the solute and nature of solute-solvent interactions.

5. Result and discussion

The experimentally determined values of density, viscosity and ultrasonic velocity for different molar composition of urea in aqueous triton X-100 solution at 303K, 308K and 313K are shown in table (1).

The values of density are found to increase with increase in urea and triton X-100 concentration and decrease with increase in temperature for all the systems. The increasing value of density indicates the increase in solvent-solvent, solute-co solute, and solute-solvent interactions taking place in the solution. The increase in density with the addition of urea is due to the shrinkage in the volume of the solvent which in turn is due to the presence of solute molecules. The decreases in density with elevation of temperature in the system indicate the decrease in intermolecular forces due to increasing in the thermal energy of the system, which causes increase in volume expansion. Urea breakdown the hydrogen bonded structure of water and interact either with hydrophobic or hydrophilic parts of triton X-100. The same behaviour was observed by Rathika et.al (2014), in the measurement of acoustical parameters of organic fertilizer urea at various temperatures [13].

From the values of ultrasonic velocity, it is observed that the velocity increases with increase in concentration of urea and triton X-100 as well as with increasing in temperature. The increase value of ultrasonic velocity of urea in aqueous triton X-100 may be attributed to the cohesion brought about by ionic hydration. The structural rearrangement of solvent occurs with increase in temperature. This lends to comparatively more ordered state as a result of hydration. This is the reason for the increase in ultrasonic velocities of the solution with temperature. Punitha and Uvarani, (2012) also obtained similar variations in ultrasonic velocity of SLS (Sodium Lauryl Sulphate) [14]. The orientation of solvent molecules around the solute is determined by adiabatic compressibility [15]. An intermolecular association (or) dissociation (or) repulsion between the solute and solvent molecules are measured by adiabatic compressibility [16]. The compressibility of solvent is higher than that of solution is noted from table (1). The Adiabatic compressibility values decreases generally with increase in molarities of urea and triton X-100. The β values are greater in 3mM triton X-100 than in other two systems which shows molecular association is greater in 3mM triton X-100. The decrease in compressibility implies that there is a greater molecular association in the systems with increase of urea in aqueous triton X-100. This may be due to the dimmer and trimer formation of urea molecules [17].

The solvation approach is used to interpret ion-solvent interaction [18]. The hydration number reflects the dynamic situation of the ion as its moves around in the solution [19]. From the table (2), it is noted that the values of n_h are found to increase with increase in the concentration of triton X-100, but it is found to decrease with solute concentration and temperature. The decreasing behaviour of n_h values lead to reduction in elecrostriction. The decreasing value of hydration number with the temperature indicates structure breaking tendency of urea due to higher thermal energy over interaction energy. This reveals that urea has a dehydration effect on triton X-100.

Apparent molal compressibility is an important acoustic parameter which explains the solute-solvent, solute–co solute and solute-solute interaction in solutions. From table (2), it is found that ϕ_K values are negative for urea in triton X-100 solution over the entire range of molarities of urea and temperatures. The apparent molal compressibility values decrease with increase in triton X-100 concentration and increase with increase in urea concentration at all temperatures. The negative values of ϕ_K reveal the existence of hydrophilic and ionic interaction occurring in the systems. The increasing behaviour of ϕ_K suggests that the existence of strong solute–solvent interaction in the systems studied. The maximum value of ϕ_K is observed in 3mM triton X-100 solution irrespective of molarity and concentration which shows that greater molecular association occurs at 3mM triton X-100. The limiting apparent molal compressibility has been computed by using graphical method. ϕ_K^0 Provides information regarding solute-solvent interaction and S_K provides that of solute- solute interaction in the solutions. It is noted from table (3) that ϕ_K^0 values are negative in the systems. Such a negative values of ϕ_K^0 in the systems reinforce the earliest view that the persistence of solute-solvent interaction. Further the S_K values are positive in all the systems. It indicates the strong solute-solute interaction in the solution. The ϕ_K^0 and S_K values decrease with increasing concentration of triton X-100. The magnitude of ϕ_K^0 and S_K of urea in triton X-100 is in the order 3mM > 5mM > 7mM.

Apparent molal volume has been proven to be a very beneficial tool in elucidating structural interaction happening in the solution has been studied by Hedaoo,D.S. et al. (2015) [20]. Apparent molal volume is the thermochemical property of solutions, which express the solute-solvent interaction, and it is obtained from density and molarity of solution and molecular mass of the solute. The values of ϕ_V are all positive over the entire range of molarity and temperature is given in table (2). Non-linear variation of ϕ_V values indicates an existence of solute-solvent interactions. Positive values of ϕ_V indicate the strong solute-solvent interaction occurring in the solution. The same behaviour was observed by Sathyvathi, A.V et al. (1973) [21]. The maximum value of ϕ_V is obtained for 3mM triton X-100. This once again proves that molecular association is greater in 3mM triton X-100. ϕ_V^0 Represents the volume behaviour of a solute at infinite dilution is satisfactorily, which is independent of the solute-solute interaction. S_V is a measure of solute-solute interaction. The evaluated values of ϕ_V^0 and S_V are summarized in table (3). The increasing values of ϕ_V^0 and decreasing values of S_V clearly indicate the increase in solute-solvent and decrease in solute-solute interaction with rise in temperature. The values of ϕ_V^0 are positive and the negative value of S_V is found at higher temperature for all the concentration of triton X-100. These values indicates the induced effect of triton X-100 on the solute-solute interaction. Table (1) presents the variation in viscosity with temperature and concentrations of urea and triton X-100. It shows that viscosity increases with concentration of urea up to 0.6M and thereafter decreases at 0.8M. The same behaviour is noted at all temperatures and concentrations of triton X-100. The increasing trend of viscosity with the concentration of urea suggests that the addition of urea increases the effective molecular area. At a given concentration, viscosity decreases with increasing temperature. The addition of urea creates low torsional force. The breaking up of water structure increases by increasing the urea concentration. At higher temperature and concentrations dimmer and trimer formation also decreases and hence viscosity decreases with temperature and concentration. The viscosity coefficients A and B for urea in aqueous triton X-100 solutions are calculated from Jones-Dole equation (7). It is observed that the values of A are positive and B coefficients are negative in all the systems. Since constant A is measure of ionic interaction and it is evident that the positive value of A indicates there is a strong solute-solute interaction and it is greater in 3mM triton X-100. Viscosity B coefficient also known as measure of solute-solvent interaction, it gives an idea of order or disorder introduced by the ion into the solvent structure. Values of B coefficient are negative in the systems. Negative values indicate structure breaking effect of urea in the solution. The magnitude of B value is in the order 7mM > 5mM > 3mM of triton X-100. The structure breaking effect of urea is dominant at 3mM triton X-100. Pot culture studies were carried out to study the effect of triton X-100 urea fertilizer solution on the growth of cluster bean crop during March 2017. In this experiment, biometric observation viz., plant height, dry mater parameters are analysed. Plant height is an important component, as more green area, more will be shared to yield. The plant height was recorded on 5 to 35 DAS and expressed in cm and dry matter production was recorded at 35^{th} DAS and expressed in grams. From the tables (4), it is found that plant height and dry matter of cluster bean increased across the treatments during the growth period compared to the control. The plant height and dry matter in T_1 (3mM triton X-100) and T_{11} treatment (3mM triton X-100+0.6M urea) were greater than the other treatments. Increasing concentration of triton X-100 with 0.6M urea explains the decrease in height and dry mass of cluster bean plant.

6. Conclusion

In the present study, the experimental data viz., ultrasonic velocity, density and viscosity at 303K, 308K and 313K for urea in aqueous triton X-100 solution are found. The observed trends and variation of solvation parameters with molar concentration of triton X-100 + urea provide useful information about the nature of intermolecular forces existing in the solution. The existing ion–ion/solute-solute interaction resulting dipole-

dipole, electrostrictive force enhance the structure breaking properties of urea in aqueous triton X-100 solution. The structure breaking effect of urea is in the order 3mM > 5mM > 7mM. The pot culture experiment results show that the plant height of cluster bean crop is greater in 3mM of triton X-100 and 0.6Murea in 3mM triton X-100. The use of urea with high concentration of triton X-100 reduces the growth of plant.

Table-1. Values of density (ρ), viscosity (η), ultrasonic velocity (U) and adiabatic compressibility (β) of urea in aqueous tritonX -100 solution at 303, 308 and 313K for.

Molarity M	Density (ρ) Kg.m^{-3}			Viscosity(η) Nsm $^{-2}$			Velocity (U) ms $^{-1}$			β× 10^{-10} (kg^{-1} ms^2)		
	303K	**308K**	**313K**	**303K**	**308K**	**313K**	**303 K**	**308 K**	**313 K**	**303K**	**308K**	**313K**
3mM TritonX-100												
0	996.9893	994.2057	992.5684	1.4392	1.4236	1.4093	1524	1534	1540	4.3186	4.2856	4.2481
0.2	999.7608	996.8101	994.8285	0.9336	0.8747	0.7921	1532	1540	1548	4.2617	4.2301	4.1948
0.4	1002.5769	1001.1991	997.0148	0.9765	0.9060	0.8099	1540	1544	1554	4.2057	4.1897	4.1533
0.6	1006.5662	1004.6965	999.6458	0.9986	0.9527	0.8351	1544	1550	1560	4.1674	4.1429	4.1106
0.8	1009.7944	1007.6071	1003.1019	0.9464	0.8535	0.7638	1548	1554	1564	4.1326	4.1097	4.0755
1	1013.6048	1010.9197	1006.1391	0.9755	0.8685	0.8029	1552	1558	1568	4.0959	4.0752	4.0425
5mM TritonX-100												
0	997.2329	995.7532	993.2015	1.4436	1.4333	1.4160	1540	1548	1556	4.2283	4.1909	4.1586
0.2	1001.1480	999.1086	995.6219	1.1906	1.0902	0.9507	1548	1556	1564	4.1683	4.1339	4.1061
0.4	1004.0832	1003.8255	999.7862	1.2147	1.1176	1.0194	1556	1560	1568	4.1135	4.0935	4.0682
0.6	1006.7092	1005.2642	1001.7566	1.2459	1.1469	1.0546	1562	1568	1574	4.0713	4.0460	4.0293
0.8	1010.2257	1008.1944	1007.1069	1.1496	1.0764	0.9796	1568	1574	1576	4.0262	4.0036	3.9977
1	1014.9211	1011.1810	1008.3302	1.1705	1.0868	0.9905	1572	1578	1582	3.9872	3.9715	3.9626
7mM TritonX-100												
0	998.6893	997.3863	996.1161	1.5200	1.5093	1.4967	1544	1552	1560	4.2003	4.1625	4.1252
0.2	1002.0958	1001.6510	1000.1803	1.2797	1.2496	1.2331	1554	1560	1566	4.1323	4.1024	4.0769
0.4	1005.8773	1005.3350	1003.9943	1.3094	1.2776	1.2611	1562	1566	1570	4.0747	4.0561	4.0408
0.6	1009.5147	1006.5151	1006.1455	1.3372	1.3131	1.2902	1568	1574	1576	4.0289	4.0102	4.0015
0.8	1014.0569	1011.2716	1010.4404	1.2714	1.2379	1.2184	1572	1578	1580	3.9906	3.9712	3.9644
1	1017.9190	1013.4987	1012.6248	1.2874	1.2486	1.2301	1576	1582	1584	3.9553	3.9424	3.9359

Table-2.Values of hydration number (n_H) apparent molal compressibility (ϕ_k) and Apparent molal volume (ϕ_v) of urea in aqueous triton X -100 at 303,308 and 313K for.

Molarity M	n_h			$-\phi_K\times 10^{-8}$ ($m^2 N^{-1}$)			ϕ_v $m^2 mol^{-1}$		
	303K	**308K**	**313K**	**303K**	**308K**	**313K**	**303K**	**308K**	**313K**
3mM TritonX – 100									
0	-	-	-	-	-	-	-	-	-
0.2	1.0575	0.9401	0.7363	0.8419	0.7446	0.5788	46.3420	47.3217	49.1246
0.4	1.0371	0.7062	0.3492	0.8254	0.5593	0.2745	46.2302	42.8246	49.3105
0.6	0.7667	0.6844	0.2876	0.6102	0.5419	0.2261	44.2317	42.8235	48.6257
0.8	0.5234	0.4181	0.1914	0.4165	0.3311	0.1505	44.1867	43.5607	47.2442
1	0.4338	0.2963	0.0844	0.3452	0.2346	0.0663	43.5757	43.5986	46.8374
5mM TritonX – 100									
0	-	-	-	-	-	-	-	-	-
0.2	1.6284	1.3099	0.7924	1.2830	1.0244	0.6157	40.5968	43.4676	48.2863
0.4	1.3324	0.9682	0.5595	1.0496	0.7571	0.4349	43.0534	40.0493	43.8967
0.6	0.9389	0.7086	0.3055	0.7396	0.5541	0.2375	44.3890	44.3969	46.1150
0.8	0.8492	0.5992	0.2883	0.6689	0.4685	0.2241	43.9406	44.6983	42.9704
1	0.7806	0.4032	0.1008	0.6149	0.3153	0.0783	42.4894	44.8226	45.2389
7mM TritonX – 100									
0	-	-	-	-	-	-	-	-	-
0.2	2.0048	1.7695	0.9809	1.5869	1.3900	0.7654	43.0840	38.838	39.8939
0.4	1.3980	1.2519	0.5613	1.3679	0.9835	0.4379	42.1452	40.2936	40.5219
0.6	1.3726	0.8479	0.3409	1.0865	0.6661	0.2660	42.0728	44.9629	43.5133
0.8	1.1403	0.7759	0.3391	0.9026	0.6095	0.2645	40.9041	42.8153	42.3190
1	0.9251	0.4666	0.1148	0.7323	0.3666	0.0896	42.8839	44.0628	43.7211

Table- 3 Values of limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their constants S_k, S_v, A and B coefficients of Jones-Dole equation of solution at different temperatures.

Temperature	ϕ_K constants		ϕ_V constants		viscosity constants	
	$\phi_K^0 *10^{-8}$ (m^2N^{-1})	S_K*10^{-8} ($m^{-1} N^1 mol^{-1}$)	ϕ_V*10^2 (m^3mol^1)	$S_V *10^{-2}$ ($mol^{-3/2}$)	A	B
3mM TritonX – 100						
303	-1.3036	1.6581	41.983	3.0427	0.7992	-1.0780
308	-1.2008	1.0299	45.899	0.6901	0.8273	-1.1741
313	-1.1866	0.8277	49.549	-0.5983	0.9249	-1.3161
5mM TritonX – 100						
303	-1.5212	0.9014	41.5	2.697	0.3357	-0.4990
308	-1.3558	1.0125	44.487	0.3023	0.5045	-0.7106
313	-1.3018	1.5782	46.864	-0.7856	0.7441	-0.9883
7mM TritonX – 100						
303	-1.6813	0.8909	40.705	2.2024	0.3323	-0.4633
308	-1.3567	0.9943	43.895	0.1663	0.4085	-0.5714
313	-1.3347	1.3559	44.688	-0.8276	0.4134	-0.5826

Phytomorphology of Cluster Bean by Pot Culture Method

Table 4: Pot culture report for height and dry mass of cluster bean plant

Treatment	Height of cluster bean plant in cm							Dry mass in Kg/m^3		
	5 DAS	10 DAS	15 DAS	20 DAS	25 DAS	30 DAS	35 DAS	Stemp	Leaf	Seed
T_0	09.00	11.47	14.77	19.73	22.33	28.40	32.80	5.38	3.28	5.34
T_1	13.33	20.70	24.63	25.27	36.00	41.20	47.60	10.92	4.31	6.46
T_2	11.73	15.87	20.87	24.93	33.97	40.60	44.80	7.95	3.74	6.41
T_3	11.00	12.80	19.40	24.10	29.70	39.10	44.40	6.89	2.7	5.79
T_{11}	10.70	13.30	16.33	21.80	28.13	30.10	38.30	7.28	3.41	5.87
T_{22}	10.00	12.87	16.08	20.57	25.60	29.90	34.40	6.50	3.31	2.97
T_{33}	09.80	11.60	15.53	20.07	24.67	29.70	34.10	4.56	2.41	2.88

T_0- Control soil, **T_1**- Soil + 3mM TritonX-100, **T_2**-Soil + 5mM TritonX-100, **T_3**-Soil + 7mM TritonX-100, **T_{11}**-3mM TX-100 + 0.6M Urea, **T_{22}**-5mM TX-100 + 0.6M Urea, **T_{33}**-7mM TX-100 + 0.6M Urea.

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