

Apparent Molar volume, Viscosity and Ultrasonic Studies on the effect of Urea and Alkylureas on the Micellization of Aqueous Sodium Cholate

D. Gopinath^{1*}, P. Baby Shalini², R. Margretlurdubenasir³

1,2,3Department of Physics, Mailam Engineering College, Mailam – 604304

Villupuram, Tamil Nadu, India

Corresponding Author:

D. Gopinath

Department of Physics, Mailam Engineering College, Mailam – 604304.

Email id : gopinathphysics@mailamengg.com

ABSTRACT

Apparent molar volume, viscosity, ultrasonic velocity and absorption studies have been carried out in aqueous solution of some bile salt namely sodium cholate (SC) in the concentration range of 7-17mM by adding 0.1M, 0.2M and 0.3M of urea, N-methylurea (MU) and N,N-dimethylurea (DMU) using a digital ultrasonic pulse echo velocity meter at a fixed frequency of 2MHz and at a fixed temperature of 303.15 K. The variation of apparent molar volume and ultrasonic velocity with concentration exhibits a break at the critical micelle concentration (CMC) of aqueous surfactants with addition of urea and alkylureas (MU and DMU). The results are discussed on the basis of solvent-solvent interactions brought about by the modification of hydrophobic interaction in the medium due to the addition of urea, MU and DMU. The results obtained from apparent molar volume, ultrasonic velocity and apparent molar compressibility studies are confirmed by the equivalent conductance measurements.

Keywords : Apparent molar volume, Ultrasonic velocity, Apparent molar compressibility, Ultrasonic absorption, Micelles

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INTRODUCTION

Urea and its derivatives are well-known denaturants of proteins [1,2], because of their ability to weaken hydrophobic interactions in aqueous solution [3]. For the same reason, one expects that urea may have a profound effect on the properties of micellar solutions [4,5]. Two different mechanisms have been proposed for the action of urea on surfactants namely (i) indirect mechanism, in which urea changes the structure of interfacial water surrounding the solute, and (ii) direct mechanism, where urea replaces some of the water molecules in the hydration shell of the solute [6]. The indirect mechanism has received most of the attention and has been widely accepted in the past. It has been established that the addition of urea alter the properties of micellar solutions by a delicate modulation of the balance of hydrophilic and hydrophobic interactions and increases the critical micellar concentration of ionic and nonionic surfactants [7,8]. Apparent molar volume is one of the important thermodynamic properties which are more helpful in understanding the solute-solvent, solute-solute and solvent-solvent interactions present in the medium.

Various studies have been reported in the literature [9-12] to investigate the mechanism of the action of urea on the micellization of single chain aliphatic surfactants. But no attention has been paid so far to study the effect of urea and alkylureas on the micellization of bile salts in aqueous solutions. Moreover, urea is considered as a water structure breaker, whereas alkylureas (MU and DMU) are considered to be water structuring agents. Nevertheless, urea and alkylureas weakens hydrophobic effect in aqueous solution. In addition, our earlier ultrasonic studies carried out in aqueous solutions of sodium oleate and sodium taurocholate with urea revealed interesting results [13]. Hence, in continuation of our previous work, the present apparent molar volume and ultrasonic studies have been undertaken in aqueous solutions of sodium cholate (SC) with 0.1- 0.3M of urea, methyl urea (MU) and dimethyl urea (DMU) in order to understand the effect of urea and alkylureas on the aggregation behavior of sodium cholate.

2. MATERIALS AND METHODS

The sodium cholate and additives namely urea, MU and DMU used in the present study are of AR/BDH grade with

*Author for Correspondence: D. Gopinath

a purity of >99% purchased from Merck chemicals, India. The purity of the chemicals was checked using TLC method. All the chemicals used in the present study produced single spot in TLC showing that their purity is greater than 99%. The sodium cholate having different concentrations are prepared by dissolving the required amounts of SC and additives namely urea, MU and DMU in Millipore water. The ultrasonic velocity and absorption studies are measured using a digital ultrasonic velocity meter (Model VCT-70A, Vi-Micro systems Pvt. Ltd., Chennai, India) at a fixed frequency of 2MHz and at a fixed temperature of 303.15 K. The accuracy of velocity measurement is ± 2 parts in 10⁵. The viscosity and density of aqueous solutions of SC containing 0.1- 0.3M of urea, MU and DMU are determined using an Oswald's viscometer and a graduated dilatometer respectively. The accuracy in the measurements of density and viscosity are ± 2 parts in 10⁵ and ± 0.1 % respectively.

From the measured values of ultrasonic velocity, density, viscosity and observed absorption, various other parameters such as apparent molar volume (ϕ_v), adiabatic compressibility (β_s), apparent molar compressibility (ϕ_k), hydration number (h), intermolecular free length (Lf) and classical absorption (α/f^2)_{cl} are calculated using standard formulae [14-16]. The equivalent conductance measurements of aqueous SC with addition of urea, MU and DMU are carried out using a digital LCR bridge (Model 8118, Hameg, West Germany) with an accuracy of

0.005%. The apparent molar volume and molar compressibility values calculated for aqueous solutions of sodium cholate with the addition of urea, MU and DMU at different concentration are fitted to Masson's equation to determine ϕ_v^0 (molar volume at infinite dilution), ϕ_k^0 (molar compressibility at infinite dilution), and the slopes of the plot (S_v and S_k), respectively. The viscosity data is fitted to Jones-Dole equation ($\eta_{sp} = AC^{1/2} + BC$) using least square fitting method to determine the coefficients A and B respectively [17].

3. RESULTS AND DISCUSSION

The ultrasonic velocity and observed absorption in aqueous solutions of SC containing 0.1 - 0.3M of urea, MU and DMU increase with increasing concentration of SC in the entire concentration range studied exhibiting a break at critical micellar concentration (CMC). The variations of apparent molar volume (ϕ_v), specific viscosity (η_{sp}), ultrasonic velocity, apparent molar compressibility (ϕ_k) and equivalent conductance with concentration of SC studied are shown graphically in Figs. 1–15. The values of density, hydration number and fitted parameters of Masson's equation and Jones-Dole equation are given in Tables 1-6. The various experimental and derived parameters are fitted to straight line equation before and after CMC. The standard deviations along with the fitted straight line equations are given in Table 7.

Table-1. Density and hydration number of sodium cholate with 0.1M urea, 0.2M urea and 0.3M urea in water at 303.15 K.

System	Concentration	Density(ρ) kg/ m ³	Hydration number
SC+ water + 0.1M urea	0.007	984.72	98.0
	0.008	985.58	96.2
	0.009	986.43	95.4
	0.010	987.25	95.0
	0.011	987.77	94.0
	0.012	988.52	93.6
	0.013	989.14	93.3
	0.014	989.75	92.4
	0.015	990.25	91.9
	0.016	990.82	91.1
	0.017	991.43	90.3
SC+ Water + 0.2M urea	0.007	988.42	141.9
	0.008	989.27	133.2
	0.009	989.61	124.4
	0.010	989.87	119.2
	0.011	990.64	115.4
	0.012	991.27	111.5
	0.013	991.47	108.0
	0.014	992.24	105.7
	0.015	992.73	105.4
	0.016	992.88	103.2
	0.017	993.43	101.7
SC+ Water + 0.3M urea	0.007	992.49	198.5
	0.008	993.30	180.8
	0.009	993.74	165.9
	0.010	994.43	156.3
	0.011	994.92	149.7
	0.012	995.19	142.7
	0.013	995.87	137.3
	0.014	996.24	132.3
	0.015	996.73	127.6
	0.016	997.23	126.1
	0.017	997.60	123.9

Table-2: Density and hydration number of sodium cholate with 0.1M MU, 0.2M MU and 0.3M MU in water at 303.15 K.

System	Concentration	Density(ρ) kg/ m ³	Hydration number
SC+ water + 0.1M MU	0.007	989.47	154.6
	0.008	990.25	147.2
	0.009	990.75	138.8
	0.010	991.15	131.6
	0.011	991.64	125.5
	0.012	992.33	121.9
	0.013	992.65	119.9
	0.014	993.21	116.7
	0.015	993.76	115.7
	0.016	994.29	111.4
	0.017	994.54	109.1
SC+ Water + 0.2M MU	0.007	993.29	199.1
	0.008	993.81	180.6
	0.009	994.26	166.8
	0.010	994.64	158.5
	0.011	995.30	150.5
	0.012	995.87	143.5
	0.013	996.23	138.1
	0.014	996.85	133.4
	0.015	997.19	130.5
	0.016	997.61	126.3
	0.017	998.23	124.3
SC+ Water + 0.3M MU	0.007	997.14	251.3
	0.008	997.92	227.4
	0.009	998.22	207.5
	0.010	999.00	193.0
	0.011	999.56	184.4
	0.012	999.93	174.6
	0.013	1000.35	165.6
	0.014	1000.92	159.5
	0.015	1001.39	152.6
	0.016	1001.67	149.2
	0.017	1002.19	145.8

Table-3: Density and hydration number of sodium cholate with 0.1M DMU, 0.2M DMU and 0.3M DMU in water at 303.15 K.

System	Concentration	Density(ρ) kg/ m ³	Hydration number
SC+ water + 0.1M DMU	0.007	993.33	204.2
	0.008	994.57	193.1
	0.009	995.31	180.3
	0.010	995.74	169.3
	0.011	996.38	159.9
	0.012	996.95	153.3
	0.013	997.38	149.1
	0.014	997.92	143.3
	0.015	998.37	139.8
	0.016	998.89	134.8
	0.017	999.41	134.1
SC+ Water + 0.2M DMU	0.007	997.81	250.8
	0.008	998.39	227.4
	0.009	998.89	207.5
	0.010	999.19	194.9
	0.011	999.91	184.8
	0.012	1000.32	174.7
	0.013	1000.75	166.2
	0.014	1001.48	159.9
	0.015	1001.74	153.9
	0.016	1002.22	148.1
	0.017	1002.71	145.1
SC+ Water + 0.3M DMU	0.007	1001.39	300.7
	0.008	1002.23	270.6
	0.009	1002.56	247.1
	0.010	1003.29	227.7
	0.011	1003.83	216.1
	0.012	1004.25	203.7
	0.013	1004.65	192.7
	0.014	1005.18	184.3
	0.015	1005.61	175.2
	0.016	1006.13	171.3
	0.017	1006.51	165.8

Table-4. Fitting parameters(Masson's equation) of sodium cholate with urea, MU and DMU in water at 303.15 K

System	Φ_V^0	Molar volume(Φ_V) ($\text{m}^3 \text{mol}^{-1}$)			
		S_V^0		Standard deviation	
		before	after	before	after
SC+ water +0.1M urea	-1.68	7.78	4.30	0.0119	0.0123
SC+ Water+0.2M urea	-2.88	16.13	8.74	0.0278	0.0103
SC+ Water+0.3M urea	-4.10	23.96	12.76	0.0287	0.0018
SC+ Water+0.1M MU	-3.22	18.42	9.58	0.0207	0.0037
SC+ Water+0.2M MU	-4.52	27.73	13.83	0.0413	0.0086
SC+ Water+0.3M MU	-5.59	34.10	18.54	0.0472	0.0076
SC+ Water+0.1M DMU	-4.37	25.27	14.66	0.0169	0.0068
SC+ Water+0.2M DMU	-5.86	36.22	18.88	0.0570	0.0106
SC+ Water+0.3M DMU	-6.96	43.30	22.35	0.0597	0.0056

Table-5. Fitting parameters(Masson's equation) of sodium cholate with urea, MU and DMU in water at 303.15 K

System	Φ_{κ}^0	Molar Compressibility(Φ_{κ}) ($10^{-6} \text{m}^3 \text{mol}^{-1} \text{pa}^{-1}$)			
		S_{κ}^0		Standard deviation	
		before	after	before	after
SC+ water +0.1M urea	-2.30	8.23	3.19	0.0095	0.0169
SC+ Water+0.2M urea	-4.01	20.58	7.64	0.0335	0.0133
SC+ Water+0.3M urea	-5.93	33.23	12.66	0.0624	0.0092
SC+ Water+0.1M MU	-4.45	23.15	11.19	0.0234	0.0115
SC+ Water+0.2M MU	-6.26	36.40	15.30	0.0607	0.0097
SC+ Water+0.3M MU	-7.95	46.79	20.34	0.0843	0.0121
SC+ Water+0.1M DMU	-6.22	34.39	16.42	0.0230	0.0199
SC+ Water+0.2M DMU	-8.04	47.46	22.17	0.0837	0.0133
SC+ Water+0.3M DMU	-9.83	59.41	26.17	0.0102	0.0162

Table-6: Fitting parameters (Jones-Dole equation) of sodium cholate with urea, MU and DMU in water at 303.15K

System	Specific Viscosity (η_{sp})				
	Before CMC			After CMC	
	A (Intercept)	B (Slope)	Standard deviation	B (Slope)	Standard deviation
SC+ water +0.1M urea	-0.2591	11.75	0.0164	16.87	0.0015
SC+ Water+0.2M urea	0.1401	9.06	0.0095	15.92	0.0122
SC+ Water+0.3M urea	0.5452	6.99	0.0335	14.83	0.0006
SC+ Water+0.1M MU	0.1121	9.66	0.0220	15.56	0.0014
SC+ Water+0.2M MU	0.6191	6.59	0.0082	14.53	0.0137
SC+ Water+0.3M MU	0.9832	4.81	0.0327	13.41	0.0007
SC+ Water+0.1M DMU	0.4634	8.32	0.0201	14.24	0.0002
SC+ Water+0.2M DMU	0.9347	5.29	0.0117	13.96	0.0165
SC+ Water+0.3M DMU	1.3853	2.83	0.0323	12.31	0.0004

Table-7: Standard deviation and the fitted equations for ultrasonic velocity, specific viscosity, molar volume, molar compressibility and equivalent conductance against concentration (X) for sodium cholate with urea, MU and DMU in water at 303.15 K.

System	Parameters	Standard deviation (σ)		Fitted equation	
		Before CMC	After CMC	Before CMC	After CMC
SC+ water +0.1M urea	C (mol ⁻¹)	0.0337	0.1629	C = 1494.83+1010 *X	C = 1492.78+1207.43 *X
	η_{sp}	0.0016	0.0004	η_{sp} = -0.0122+10.4 *X	η_{sp} = -0.049+13.51 *X
	Φ_V (m ³ mol ⁻¹)	0.0136	0.0120	Φ_V = -1.30+39.79 *X	Φ_V = -1.12 +17.97 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0113	0.0166	Φ_K = -1.90+42.09 *X	Φ_K = -1.64+13.42 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.1504	0.1613	$\wedge$ = 39.55-1604 *X	$\wedge$ = 26.50-450.2 *X
SC+ Water+0.2M urea	C (mol ⁻¹)	0.1291	0.2895	C = 1498.21+922.57 *X	C = 1493.24+1315 *X
	η_{sp}	0.0007	0.0013	η_{sp} = 0.0074+9.71 *X	η_{sp} = -0.0375+13.3 *X
	Φ_V (m ³ mol ⁻¹)	0.0331	0.0097	Φ_V = -2.10+82.94 *X	Φ_V = -1.54+35.8 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0417	0.0127	Φ_K = -3.01+105.73 *X	Φ_K = -2.13+31.34 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.2461	0.1588	$\wedge$ = 39.38-1354 *X	$\wedge$ = 28.30-400.6 *X
SC+ Water+0.3M urea	C (mol ⁻¹)	0.3133	0.1965	C = 1502.65+899.29 *X	C = 1495.07+1452 *X
	η_{sp}	0.0032	0.0003	η_{sp} = -0.0275+9.68 *X	η_{sp} = -0.0207+13.4 *X
	Φ_V (m ³ mol ⁻¹)	0.0409	0.0025	Φ_V = -2.92+120.39 *X	Φ_V = -2.05+51.3 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0797	0.0101	Φ_K = -4.29+166.53 *X	Φ_K = -2.82+50.87 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.4204	0.1296	$\wedge$ = 45.41-1583.5 *X	$\wedge$ = 29.50-323.7 *X
SC+ Water+0.1M MU	C (mol ⁻¹)	0.1038	0.2949	C = 1498.70+1018.29 *X	C = 1497.58+1154 *X
	η_{sp}	0.0020	0.0003	η_{sp} = 0.0049+10.3 *X	η_{sp} = -0.0316+13.46 *X
	Φ_V (m ³ mol ⁻¹)	0.0277	0.0032	Φ_V = -2.33+94.89 *X	Φ_V = -1.66+39.20 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0319	0.0107	Φ_K = -3.34+119.24 *X	Φ_K = -2.49+45.84 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.4272	0.3312	$\wedge$ = 41.93-1683.4 *X	$\wedge$ = 23.91-191.34 *X
SC+ Water+0.2M MU	C (mol ⁻¹)	0.2074	0.2053	C = 1502.08+932.28 *X	C = 1497.80+1274 *X
	η_{sp}	0.0010	0.0016	η_{sp} = 0.0297+9.8 *X	η_{sp} = -0.0156+13.4 *X
	Φ_V (m ³ mol ⁻¹)	0.0529	0.0102	Φ_V = -3.18+142.51 *X	Φ_V = -2.17+56.5 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0758	0.0115	Φ_K = -4.51+186.94 *X	Φ_K = -3.03+62.49 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.2021	0.2338	$\wedge$ = 43.74-1595.4 *X	$\wedge$ = 28.5-344.05 *X
SC+ Water+0.3M MU	C (mol ⁻¹)	0.3082	0.2133	C = 1506.14+935.71 *X	C = 1499.08+1453 *X
	η_{sp}	0.0033	0.0004	η_{sp} = 0.0499+9.61 *X	η_{sp} = -0.0031+13.3 *X
	Φ_V (m ³ mol ⁻¹)	0.0647	0.0090	Φ_V = -3.91+171.18 *X	Φ_V = -2.71+74.5 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.1084	0.0140	Φ_K = -5.64+234.55 *X	Φ_K = -3.72+81.68 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.3203	0.1373	$\wedge$ = 46.16-1475 *X	$\wedge$ = 30.77-284.11 *X
SC+ Water+0.1M DMU	C (mol ⁻¹)	0.1256	0.4038	C = 1502.42+1080.28 *X	C = 1498.02+1395 *X
	η_{sp}	0.0019	0.0003	η_{sp} = -0.0218+10.77 *X	η_{sp} = -0.0103+13.5 *X
	Φ_V (m ³ mol ⁻¹)	0.0233	0.0089	Φ_V = -3.16+130.46 *X	Φ_V = -2.30+59.90 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0342	0.0220	Φ_K = -4.57+177 *X	Φ_K = -3.25+66.97 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.3588	0.1215	$\wedge$ = 40.91-1518.8 *X	$\wedge$ = 26.67-344.92 *X
SC+ Water+0.2M DMU	C (mol ⁻¹)	0.2078	0.2245	C = 1505.28+996.79 *X	C = 1501.58+1267 *X
	η_{sp}	0.0011	0.0020	η_{sp} = -0.046+10.1 *X	η_{sp} = -0.0021+13.7 *X
	Φ_V (m ³ mol ⁻¹)	0.0759	0.0123	Φ_V = -4.07+181.71 *X	Φ_V = -2.76+75.8 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.0108	0.0152	Φ_K = -5.70+237.94 *X	Φ_K = -3.84+89.02 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.3786	0.1204	$\wedge$ = 43.26-1465.3 *X	$\wedge$ = 29.89-398.21 *X
SC+ Water+0.3M DMU	C (mol ⁻¹)	0.2984	0.2450	C = 1509.36+985.12 *X	C = 1500.07+1620 *X
	η_{sp}	0.0034	0.0004	η_{sp} = 0.065+10.13 *X	η_{sp} = -0.0206+13.5 *X
	Φ_V (m ³ mol ⁻¹)	0.0961	0.0817	Φ_V = -4.68+201.31 *X	Φ_V = -3.13+84 *X
	Φ_K (10 ⁻⁶ m ³ mol ⁻¹ pa ⁻¹)	0.1499	0.0072	Φ_K = -6.68+274.27 *X	Φ_K = -4.25+91.75 *X
	$\wedge$ (10 ⁻³ m ² ohm ⁻¹ mol ⁻¹)	0.2765	0.0718	$\wedge$ = 46.57-1476.4 *X	$\wedge$ = 31.58-326.33 *X

3.1 Apparent molar volume studies

Apparent molar volume (ϕ_v) calculated from density data for aqueous solutions of SC containing urea, MU and DMU mixtures is found to be negative for the entire concentration range of SC as shown in Figs 1-3. This may be attributed to the presence of hydrophobic surface at the convex side (β -side) and a hydrophilic surface consisting of hydroxyl and carboxylate groups at the concave side (α -side) of the steroid nucleus of SC, respectively. A similar results of small and negative values for apparent molar volume have been reported by Chauhan et al.[18] in di (dodecyldimethyl ammonium bromide) (DDAB) in aqueous gelatin solutions, where this exceptional behaviour has been explained as due to the presence of a relatively larger hydrophobic group in DDAB. This fact was further confirmed by our recent studies [19] on

aqueous bile salts with 10% v/v of aprotic solvents. Moreover, the negative values of apparent molar volumes of aqueous SC in water with 0.1 - 0.3M of urea, MU and DMU indicate that dipole-dipole interaction between solute and solvent molecules is appreciable. This dipole-dipole interaction would also apply to the solutions in which the SC molecules are associated by hydrophobic interaction. In the aggregates formed by SC molecules, the hydroxyl groups would remain on the outer side, free to interact with surrounding water, urea and alkylureas molecules. More hydroxyl groups are available with bile salts molecules, greater will be the dipole-dipole interaction, and smaller will be the values of ϕ_v . A plot of apparent molar volume of aqueous SC with 0.1 - 0.3M of urea, MU and DMU against concentration also exhibits a break or change of slope at the critical micelle concentration (CMC).

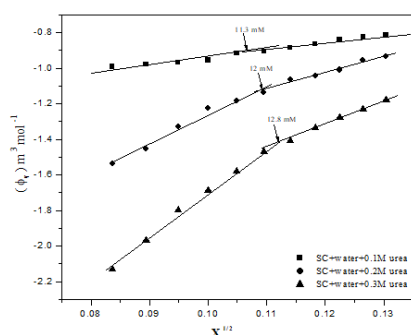


Figure.1. Variation of molar volume (ϕ_v) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC-water=0.1M urea: ■, SC-water=0.2M urea: ●, SC-water=0.3M urea: ▲.

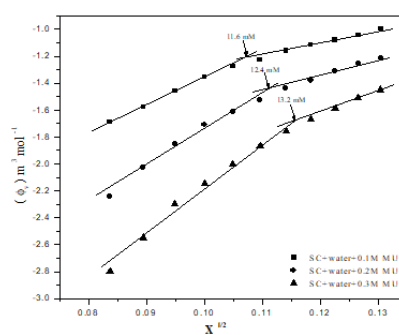


Figure.2. Variation of molar volume (ϕ_v) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC-water=0.1M MU: ■, SC-water=0.2M MU: ●, SC-water=0.3M MU: ▲.

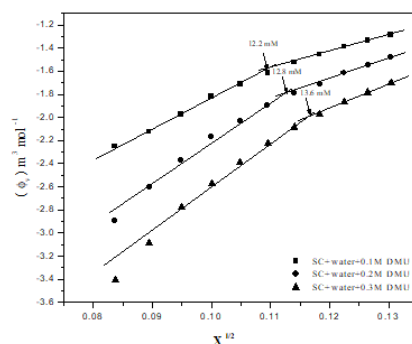


Figure.3. Variation of molar volume (ϕ_v) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC-water=0.1M DMU: ■, SC-water=0.2M DMU: ●, SC-water=0.3M DMU: ▲.

The addition of urea, MU and DMU to aqueous solutions of SC shifts the CMC towards the higher SC concentration. In general, large amount of water-miscible organics will increase CMC value by increasing the solubility of the hydrophobic tail in ordinary surfactants, although opposite effect may occur for highly ionized species, where the lower dielectric constant reduces head group repulsion; as a result micelle formation is favoured [20]. In the present studies, 0.1 - 0.3M of urea, MU and DMU added to aqueous solutions of SC are capable of forming hydrogen bonds with water as well as with the bile salt molecules and thus affect CMC by modifying the bulk water structure. As a result, hydrophobic part of the SC may be weakly induced by lower amount of water structure. This would lead to increase of CMC of SC as observed in the present case due to reduction in the entropy of micellization in water with urea and alkylureas. The extent of shifting towards higher concentration side depends on how the average dielectric constant of the medium is modified by the addition of urea and its derivatives. The effectiveness of urea derivatives in raising the CMC was in the order that the more alkyl radicals are substituted in urea, the stronger their activities. Hence, the effectiveness of urea and its derivatives on the micellization of aqueous SC is in the order $U < MU < DMU$. The change in the CMC value provides a clear evidence that urea and alkylureas appreciably influence the hydrophobic effect which is the deriving force of micellization process. Also, though urea is weak water structure breaker and the alkylureas which are known to be structure makers, show qualitatively the same effects in increasing the CMC [9] (Fig. 16).

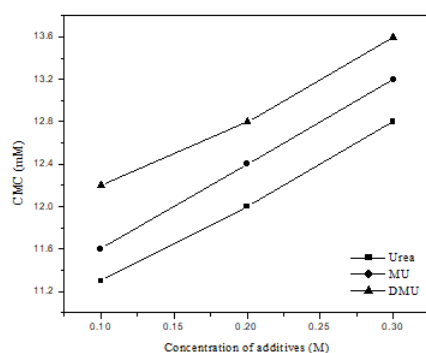


Figure 16. Variation of critical micellar concentration (CMC) with molar concentration of additives at 303.15 K, urea: ■, MU: ●, DMU: ▲.

The values of ϕv_0 obtained for aqueous SC with 0.1 - 0.3M of urea, MU and DMU mixtures is found to be negative. Values of ϕv_0 become more negative with increase in concentration of urea and alkylureas (Table 4). This once again confirms the presence of more structured water in the medium due to the presence of SC, urea and alkylureas, thus suggesting that solvent-solvent interaction to be the dominant factor in the medium than ion-solvent interactions. In aqueous solutions of SC, as we replace urea by methyl urea and then by dimethyl urea, the values of ϕv_0 become more and more negative indicating that the amount of structured water present in the medium also

increases. This is due to the modification of hydrophobic interaction present in the medium with the addition of one or two alkyl groups to urea. This in turn might lead to increased hydration in the medium thereby strengthening solvent-solvent interaction.

The slope (S_v) of Masson's equation is found to be positive above CMC for aqueous SC with 0.1 - 0.3M of urea and alkylureas suggesting the presence of soap-soap interaction in the medium. It is also to be noted from Table 4 that, the values of S_v for aqueous solutions of SC with 0.1-0.3 M urea and alkylureas after CMC are found to be less than their corresponding values before CMC. This indicates that after CMC, the soap-soap interaction is not significant as it is before CMC and it is the solvent-solvent interaction which dominates over any other interactions present in the medium.

3.1.1. Mechanism of action of urea and alkylureas on solvent-solvent interaction

The role of urea and alkylureas in the present studies can be explained using direct mechanism. The addition of urea and alkylureas to aqueous solutions of SC modifies the hydrophobic interaction in such a way that, it leads to a significant increase of solubility of sodium cholate. This in turn increases the CMC of aqueous sodium cholate as observed in the present study. According to the direct mechanism, the fact that urea and alkylureas increases the solubility of hydrophobic solutes is ascribed to an improved solvation caused by the displacement of a number of water molecules by the larger urea and alkylurea molecules in the solvation. In addition, the influence of urea on the hydrogen bonding structure in the apolar region must help the solvation of hydrophobic part of solutes by water molecules. Probably, the observed increase of CMC is also favoured by the increase of solvation of head groups induced by the action of urea and its derivatives. Since, urea and alkylureas have similar effects on the micellization, most probably the interaction mechanism of urea can be extended to alkylureas i.e., urea molecules entering the solvation shell substituting some water molecules. Thus, the addition of urea and alkylureas to aqueous solutions of SC further strengthens solvent-solvent interaction present in the medium.

3.2 Viscosity studies

The Viscosity data for aqueous solution of SC with 0.1 - 0.3M of urea and alkylureas are analyzed using Jones-Dole equation. From the linear plot of $\eta_{sp} / X^{1/2}$ against $X^{1/2}$, Viscosity B-coefficient and Falkenhagen coefficient-A are obtained from the slope and intercept using least square fitting method (figs 4-6). The fitted values of A and B are given in the table 6. Viscosity A-coefficient reflects the solute-solute interactions and B-coefficient reflects solute-solvent interactions. Viscosity B-coefficients also gives the information regarding order and disorder introduced by solute into solution.

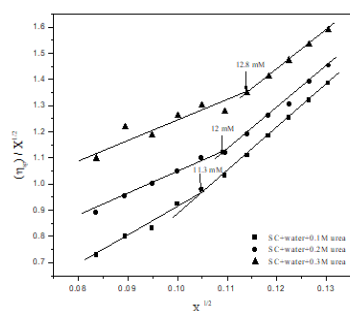


Figure 4. Variation of specific viscosity (η_{sp}) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC+water+0.1M urea: ■, SC+water+0.2M urea: ●, SC+water+0.3M urea: ▲.

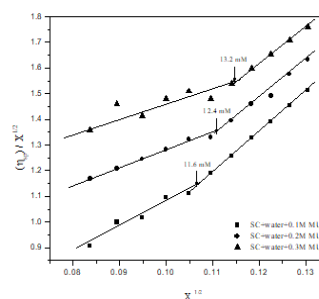


Figure 5. Variation of specific viscosity (η_{sp}) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC+water+0.1M MU: ■, SC+water+0.2M MU: ●, SC+water+0.3M MU: ▲.

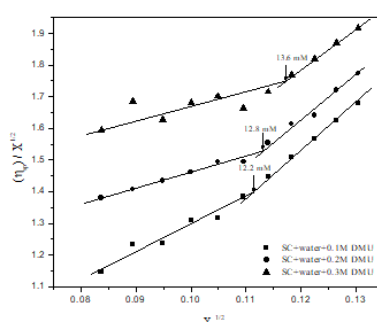


Figure 6. Variation of specific viscosity (η_{sp}) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC+water+0.1M DMU: ■, SC+water+0.2M DMU: ●, SC+water+0.3M DMU: ▲.

In our present studies, the value of viscosity B-coefficient is positive before and after CMC. This indicates the presence of more ordered and favorable state of the solution structure in aqueous SC on adding urea and alkylureas. When 0.1 - 0.3M of urea and alkylureas are added to aqueous SC, they disrupt the already existing solvent structure and forms a new and thermodynamically more feasible arrangement. As a result, urea and alkylurea molecules are tightly bound to water molecules due to the presence of hydrophobic cholate ions in the medium. This supports the conclusion drawn from the partial molar volume studies.

3.3 Ultrasonic velocity studies

Ultrasonic velocity measured in aqueous solution of SC with 0.1 - 0.3M of urea, MU and DMU increases with increasing concentration of SC exhibiting a break or change of slope at CMC (Figs. 7-9). The adiabatic compressibility shows an inverse behaviour with that of

ultrasonic velocity. The increase of ultrasonic velocity in the premicellar region may be due to (i) the formation of hydrogen bonds between water molecules and the hydroxyl group of SC (ii) the Na^+ ion obtained from the dissociation of SC in aqueous medium may also contribute towards the increase of ultrasonic velocity by its water structure making property [21]. The increase of ultrasonic velocity when the concentrations of SC are increased beyond CMC i.e. in the post micellar region may be due to the aggregation of SC molecules leading to micelle formation [22]. Above CMC, aggregation of molecules can occur by hydrogen bonding. The formation of higher aggregates by hydrogen bonding leads to increase of ultrasonic velocity. The increased solvation caused by the displacement of water molecules by the larger urea and alkylurea molecules leads to increased ultrasonic velocity in aqueous solutions of SC with urea and alkylureas.

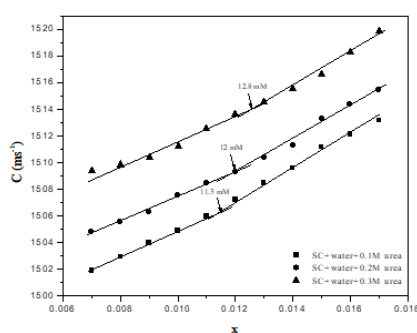


Figure 7. Variation of ultrasonic velocity (C) with molar concentration (x) of Sodium cholate at 303.15 K. SC+water+0.1M urea: ■, SC+water+0.2M urea: ●, SC+water+0.3M urea: ▲.

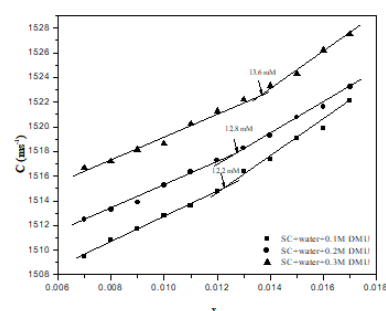


Figure 9. Variation of Ultrasonic Velocity (C) with molar concentration (x) of Sodium cholate at 303.15 K. SC+water+0.1M DMU: ■, SC+water+0.2M DMU: ●, SC+water+0.3M DMU: ▲.

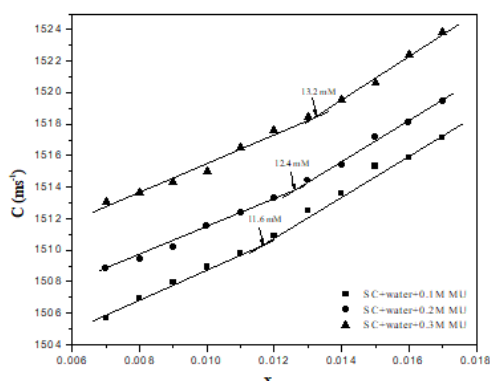


Figure 8. Variation of Ultrasonic Velocity (C) with molar concentration (x) of sodium cholate at 303.15 K. SC-water+0.1M MU: ■, SC-water+0.2M MU: ●, SC-water+0.3M MU: ▲.

3.4 Apparent molar compressibility studies

The apparent molar compressibility (ϕ_k) obtained for aqueous sodium cholate with 0.1 - 0.3M of urea, MU and DMU in the concentration range of 7-17mM studied are found to be negative as shown in Figs. 10-12. This observation indicates that there is an increased amount of

structured water around SC cations due to hydration and the anions due to hydrophobic interaction. The variation of apparent molar compressibility (ϕ_k) with SC concentration also exhibits a break at CMC.

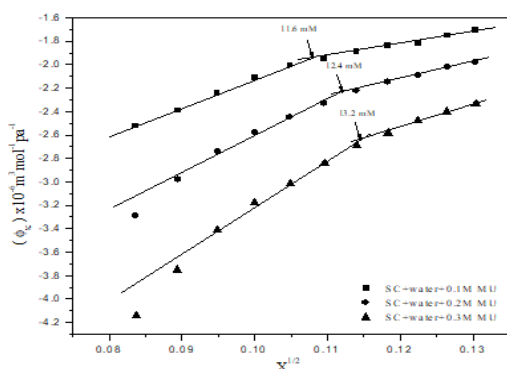


Figure 11. Variation of molar compressibility (ϕ_k) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC-water+0.1M MU: ■, SC-water+0.2M MU: ●, SC-water+0.3M MU: ▲.

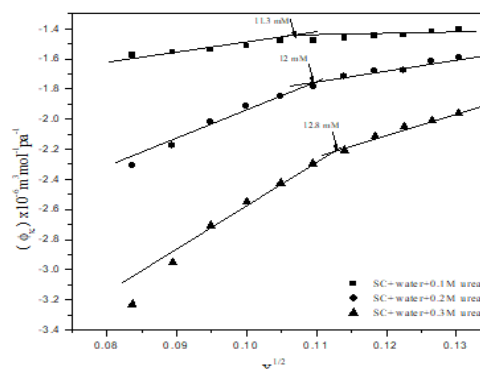


Figure 10. Variation of molar compressibility (ϕ_k) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC-water+0.1M urea: ■, SC-water+0.2M urea: ●, SC-water+0.3M urea: ▲.

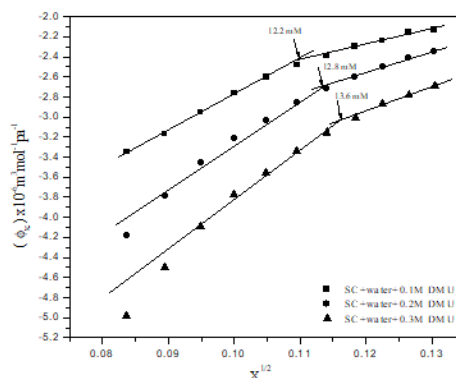


Figure 12. Variation of molar compressibility (ϕ_k) with square root of molar concentration (x) of sodium cholate at 303.15 K. SC-water+0.1M DMU: ■, SC-water+0.2M DMU: ●, SC-water+0.3M DMU: ▲.

The adiabatic compressibility (β_s) and apparent molar compressibility (ϕ_k) decreases with increase of concentration of SC and also with increase of urea, MU and DMU concentrations. This can be explained on the basis of the fact that the hydrophobic cholate ions in the solutions are surrounded by a layer of solvent molecules firmly bond and oriented towards the ion. The orientation of the solvent molecules around the surfactant ions may be due to the influence of electrostatic field of ions. This results in an increase of internal pressure which in turn leads to lowering of compressibility of the solutions, i.e. the solution became harder to compress. The increasing concentration of urea and alkylureas make molar compressibility of aqueous SC more negative. This is due to the fact that, the addition of urea and alkylureas induce the formation of hydrogen bonding (or) electrostriction of water molecules to the detriment of more compressible bulk water. Negative compressibility for both hydrophilic and hydrophobic solutes were already reported by Cabaniet al.,[23] as in the present case. The positive values of S_k indicate the presence of weak soap-solvent interactions in the medium. Also, the values of S_k in aqueous SC with urea and alkylureas after CMC are found to be much lower than their corresponding values before CMC indicating that soap-solvent interaction is not as dominant as solvent-solvent interactions.

3.5 Ultrasonic absorption studies

The observed ultrasonic absorption in aqueous solutions of SC containing 0.1- 0.3M of urea, MU and DMU increases with increasing concentration of SC (Supplementary Tables 8-16). Moreover, the observed absorption is found to be several times higher than the classical absorption. This indicates that the observed absorption is not due to

shear viscosity alone, some another mechanisms are also contributing for the observed absorption [24]. When ultrasonic waves pass through the medium, part of its energy is used in weakening or breaking of hydrogen bonds already formed. So, it is very likely that during the compression cycle of ultrasonic wave, hydrogen bonds are pushed closer resulting in partial irreversible weakening or breaking of hydrogen bonds due to absorption of ultrasonic energy. As the pressure wave passes through the medium completely, hydrogen bonds are formed again between urea and water molecules and also between SC and water. Such type of making and breaking of inter molecular hydrogen bonds as the pressure wave passes on through the medium contributes to the observed increase in ultrasonic absorption. The hydrogen bonding leading to the formation of higher aggregates of SC micelles may also have its contribution superimposed on the increased ultrasonic absorption.

3.6. Conductivity studies

The equivalent conductance of aqueous solutions of SC with addition of 0.1-0.3 M of urea, MU and DMU are measured. The equivalent conductance decreases with increasing concentration of SC as shown in figs 13-15. This may be due to the dissociation of SC into cations (Na^+ ions) and anions (cholate ions) and also due to the formation of micelles at higher SC concentration. The plot of equivalent conductance against SC concentration also exhibits a break at CMC. The CMC values obtained from equivalent conductance measurements is in agreement with the CMC values obtained from ultrasonic studies.

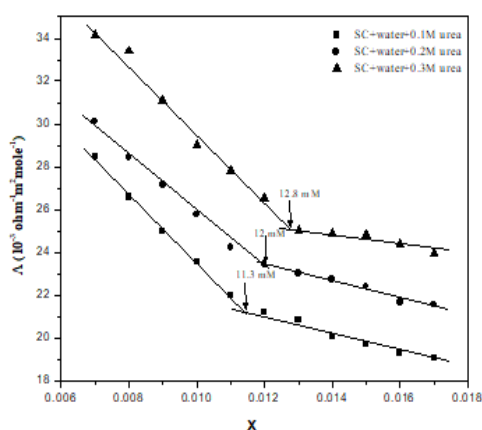


Figure.13. Variation of equivalent conductance (Λ) with molar concentration of sodium cholate at 303.15 K. SC+water+0.1M urea: $\blacksquare$, SC+water+0.2M urea: $\bullet$, SC+water+0.3M urea: $\blacktriangle$.

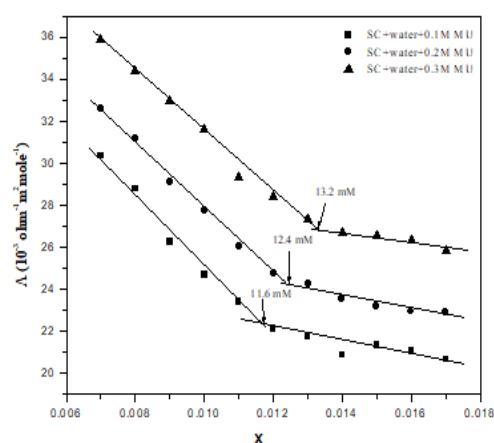


Figure.14. Variation of equivalent conductance (Λ) with molar concentration of sodium cholate at 303.15 K. SC+water+0.1M MU: $\blacksquare$, SC+water+0.2M MU: $\bullet$, SC+water+0.3M MU: $\blacktriangle$.

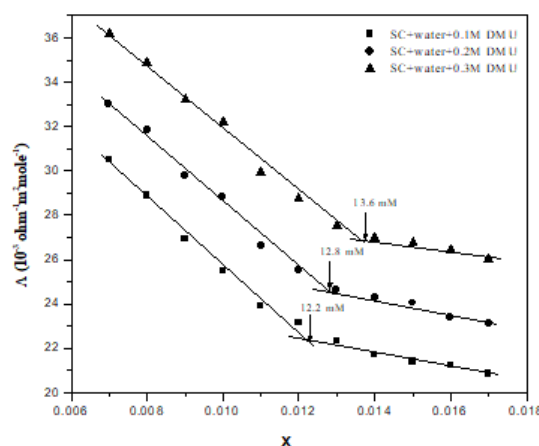


Figure.15. Variation of equivalent conductance (Λ) with molar concentration of sodium cholate at 303.15 K. SC+water+0.1M DMU: $\blacksquare$, SC+water+0.2M DMU: $\blacklozenge$, SC+water+0.3M DMU: $\blacktriangle$.

4. CONCLUSION

Apparent molar volume and apparent molar compressibility values are found to be negative and decreases (less negative), whereas ultrasonic velocity increases with increasing concentration of urea and alkylureas to aqueous SC. This may be due to the increase of more structured water in the medium in the presence of SC molecules and improved solvation caused by the replacement of a number of water molecules by the larger urea and alkylurea molecules. With the addition of each of 0.1 - 0.3M of urea and its derivatives to aqueous solutions of SC, the CMC shifts towards higher concentration side. The extent of shifting towards higher concentration side depends on how the average dielectric constant of the medium is modified by the addition of urea and its derivatives. The observed ultrasonic absorption in aqueous SC with urea, MU and DMU increases with increase of SC concentration due to making and breaking of intermolecular hydrogen bonds in the solutions when the ultrasonic waves pass through the medium.

Author Contributions

D. Gopinath: Conceptualization, methodology, investigation, experimental work, data analysis, interpretation of results, and writing original draft. P. Baby Shalini: Experimental investigation, data collection, data analysis, and validation. R. Margretlurdubenasir: Supervision, methodology, interpretation of results, review and editing of the manuscript. All authors contributed to the discussion of the results, reviewed the manuscript, and approved the final version for publication.

Conflict of Interest

The authors declare that they have no conflict of interest. There are no financial, personal, or professional relationships that could have influenced the work reported in this manuscript.

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Data Availability

The data generated and/or analyzed during the present study are available from the corresponding author upon reasonable request. The authors are willing to provide the relevant experimental data and supporting information to interested researchers, subject to reasonable restrictions..

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