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Effect of DMSO on micellization behavior of SDS in aqueous mixtures of L-tryptophan at different temperatures

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ABSTRACT

This paper represents the effect of Dimethyl sulfoxide on the micellar behavior of SDS in aqueous mixtures of tryptophan. The critical micellar concentration (CMC) of SDS is represented in terms of mole fraction unit (X_{CMC}) and was determined at different temperatures i.e. (293.15, 298.15, 303.15 and 308.15 K) using electrical conductivity method. The dependence of X_{CMC} on temperature and concentrations of tryptophan and DMSO reveals the presence stronger intermolecular interactions between tryptophan and SDS. The negative value of ΔG^{o}_{m} represents the spontaneity of the system. The positive values of entropy of micellization ΔS_{m}^{o} indicate the dominance of hydrophobic interactions in tryptophan-SDS system.

Keywords: Conductivity, DMSO, SDS, Tryptophan.

INTRODUCTION

Use of soap by humans in order to clean proteinaceous dirt molecules is a very common example of protein-surfactant interactions [1]. Due to complex structure of protein molecules [2] it is difficult for the researchers to generalize the consequences of protein-surfactant interactions. In order to reduce this complexity we used amino acid (Tryptophan) as model compound as amino acids are major constituents of proteins and also represent many important properties of proteins [3-5]. Tryptophan is a biologically important amino acid [6, 7]. It has pharmaceutical importance and also administered as nutraceutical. The major role of this amino acid is to act as a main constituent in protein synthesis. Tryptophan contains indole ring consisting of N-H hydrogen bonding group, which can interact with solvent in folded proteins [8]. The anionic surfactant (SDS) is selected because it shows high binding affinity for many proteins [9, 10]. SDS plays vital role in various biochemical processes and is commonly used in many industries such as food, cosmetic and pharmaceuticals [11]. Renewed interest in the field of amino acid -surfactant interactions is due to the numerous application in industrial and biochemical processes [12]. Amino acids surfactant interactions have been extensively studied using various techniques [13-15]. Use of co-solvent (DMSO) is another interesting feature of this work. The role of co-solvents in such studies shows the importance of structural consequences of intermolecular interactions between these two solvent components. DMSO an oxidized product of Dimethyl sulfoxide and is widely used as commercial solvent. It is polar aprotic solvent and has low toxicity. Due to its high penetrating power it is used as a cryoprotectant and a vehicle for transport of various chemicals through skin [16, 17]. It is also used to extract oxidized amino acids from unoxidized peptide chains. The oxidative property of DMSO is responsible for the changes in amino acid structure and amino acid oxidation is frequently observed in protein hydrolysis [18].

MATERIALS AND METHODS

Ordinary tap water of conductivity in the range 3 -5 x 10^{-6} S cm^{-1} was distilled thrice in the presence of alkaline $KMnO_4$. The distillation was carried out through a 750-mm long vertical fractionating column. The triple distilled water of conductivity range is 0-2x10^{-7} S cm^{-1} and pH 6.8-7.0 were used in all the experiments. Sodium dodecyl sulfate (SDS) of AR grade was obtained from LOBA Chemie Pvt. Ltd. SDS was recrystallized twice using ethanol (99.9% pure) as suggested in literature [19]. Tryptophan 99:9% pure was obtained from TITAN Biotech Ltd. and was used as such after drying over night in vacuum oven in the presence of P_2O_5. Dimethyl Sulfoxide of 99% purity was supplied by Finar Ltd. and was used without further purification.

Aqueous solutions of SDS of different molar concentration in the range 2-16 mM were prepared by the addition of small aliquots of stock solution of SDS to 50ml of 0.0005, 0.001, 0.005 and 0.01M tryptophan solutions. Similar experiments were repeated in presence of 1 %, 2%, 3% and 4% w/v DMSO solution at 293.15, 298.15, 303.15 and 308.15 K. All the conductivity experiments were performed by digital conductivity meter supplied by Labtronics Pvt. Ltd. (India). Digital water thermostat [Bombay scientific Pvt. Ltd. (India)] was used to maintain temperature accuracy of 0.05 K. The conductivity cell was calibrated by 0.01 M KCl solution supplied s. d. fine Pvt. Ltd. (India) and cell constant was determined equal to 1 cm^{-1}.

RESULTS AND DISCUSSION

The specific conductance, were plotted against the molar concentration of the surfactant and CMC values were determined at concentration corresponding to the break point observed in these plots.

Temperature dependence of X_{CMC}

Effect of temperature on the X_{CMC} of SDS in the aqueous solution of tryptophan at each concentration (fig.1) shows that CMC of SDS is directly proportional to temperature. The dependence of X_{CMC} on Tryptophan concentration (fig. 2) shows a complex behavior with respect to temperature. A plot between X_{CMC} vs. Temperature for different concentrations of tryptophan reveals that the X_{CMC} increases with the addition of tryptophan, The data further indicate that above 0.001M concentration of tryptophan, the X_{CMC} of SDS become relatively insensitive to the tryptophan concentration. Firstly it increases linearly with tryptophan concentration but suddenly stops responding at higher tryptophan concentrations and SDS-Tryptophan system does not hold good above 0.005 M [Tryptophan]. This complex micellar behavior of SDS at higher Tryptophan concentrations can be attributed to hydrophobic interactions due to the extra hydrophobicity provided by the aromatic part of amino acid.

Thermodynamics of SDS- Tryptophan System

In order to derive further information about amino acid surfactant interaction from the experimental data, different thermodynamic parameters of micellization were determined and examined. The Xcmc data has been reported in the tables (1-4) were used to calculate the standard enthalpy of micellization ΔH^o_m of SDS in aqueous solution of amino acid from the equation (1).

$$\Delta H_m^o = -RT^2(2-\alpha)\frac{d\ ln(X_{CMC})}{dT} \quad (1)$$

Where R is gas constant, T is temperature in Kelvin and $\frac{d\ ln(X_{CMC})}{dT}$ is the slope of straight

line obtained by plotting ln X_{CMC} against T and α is the degree of the counter ion dissociation which has calculated from the relation (2).

$$\alpha = \frac{post\ micellization\ region\ (S_2)}{pre\ micellization\ region(S_1)} \quad (2)$$

Where, S_1 and S_2 are the slopes of pre and post micellar region obtained by plotting conductivity data against surfactant concentration. The standard free energy of micellization ΔG^o_m and standard entropy of micellization ΔS^o_m were calculated by using the following relations (3) and (4) respectively.

$$\Delta G_m^o = RTlnX_{CMC} \quad (3)$$

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \quad (4)$$

The derived thermodynamic parameters are reported in tables (1 - 4). The thermodynamic parameters show that the micellization of SDS in Tryptophan is an energy driven process. The negative values of ΔH^o_m and ΔS^o_m shows that addition of tryptophan enhances the micellization of SDS and shows strong electrostatic interactions between the amino acid- surfactant systems. Positive values of ΔS^o_m show the hydrophobic nature of interaction between tryptophan and SDS [20]. Decrease in ΔS^o_m values with increase in temperature and an additive is because of the resistance offered by additive to the freely moving surfactant molecules. ΔHom show similar behavior with respect to temperature. Moreover Negative free energy of micellization suggests spontaneity of tryptophan-SDS system. The increase in Gom values with increase in temperature shows that the micellization process is not favored at high temperatures. The effect of temperature on thermodynamics of SDS-tryptophan suggests the increase in X_{CMC} is due to decrease in hydrophobic hydration and decrease in X_{CMC} is due to increase in hydrophobic hydration of surfactant molecules [21].

Effect of DMSO on micellization of SDS in presence of L- tryptophan

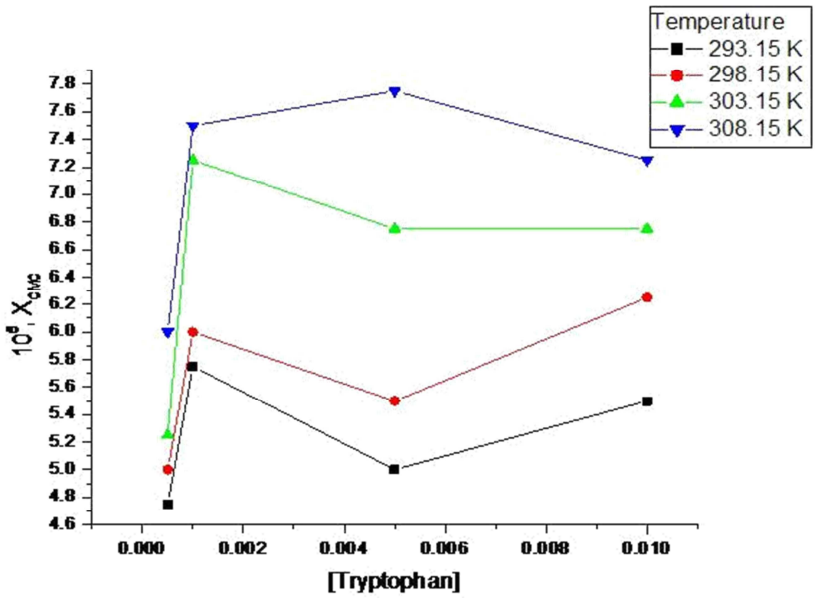
Use of Co-solvent in amino acid - surfactant interactions is more informative than studying these systems in aqueous solutions. Use of surfactants in different solvent environments is common in various industries like pharmaceutical, cosmetic and agrochemicals, so study of co-solvent effect in such systems reveal some useful information in context of physicochemical as well as application point of view. To explore more about SDS-tryptophan system we used DMSO as a co-solvent. The dependence of X_{CMC} on the DMSO concentration is shown in fig. 3.

X_{CMC} of SDS in presence of DMSO shows similar trend as observed in aqueous solutions of Tryptophan. General increase in X_{CMC} values on addition of DMSO is observed up to 3% w/v DMSO but at higher concentrations of DMSO it decreases slowly. This type of micellar behavior of SDS can be attributed to the formation of water-DMSO complexes and due to increased solubility of tryptophan in the structured water-DMSO complex. The alteration in water structure on addition of DMSO is responsible for the changes in surfactant-surfactant and amino acid -surfactant interactions and the consequences of these changes are shown in terms of changes in micellar behavior of SDS [22].

Dependence of ΔH^o_m and ΔS^o_m on tryptophan concentration in aqueous rich mixtures of DMSO at 298.15 K is presented in Fig. 4. The interesting feature of this observation is that both H_m^o and S_m^o behave in same way. The decrease in ΔH^o_m is due to electrostatic interactions between SDS and tryptophan whereas increase in ΔH^o_m and ΔS^o_m values show dominance of hydrophobic interactions with respect to DMSO concentration [23]. Both ΔH^o_m and ΔS^o_m decreases sharply to a minimum at around 1% w/v DMSO to 4% w/v DMSO as a function of DMSO. Sudden increase in ΔH^o_m and ΔS^o_m is observed to occur at 3% w/v DMSO. This Non-linear behavior of thermodynamic parameters shows that the structural consequences of intermolecular interactions are qualitatively independent of amino acid concentration. Effect of DMSO on the salvation thermodynamics of SDS-tryptophan system is due to hydrogen bonding between water and DMSO. The change in ΔH^o_m and ΔS^o_m values can be seen to compensate the effect of each other giving rise to relatively small changes in the magnitude of ΔG^o_m value with respect to DMSO concentrations.

CONCLUSION

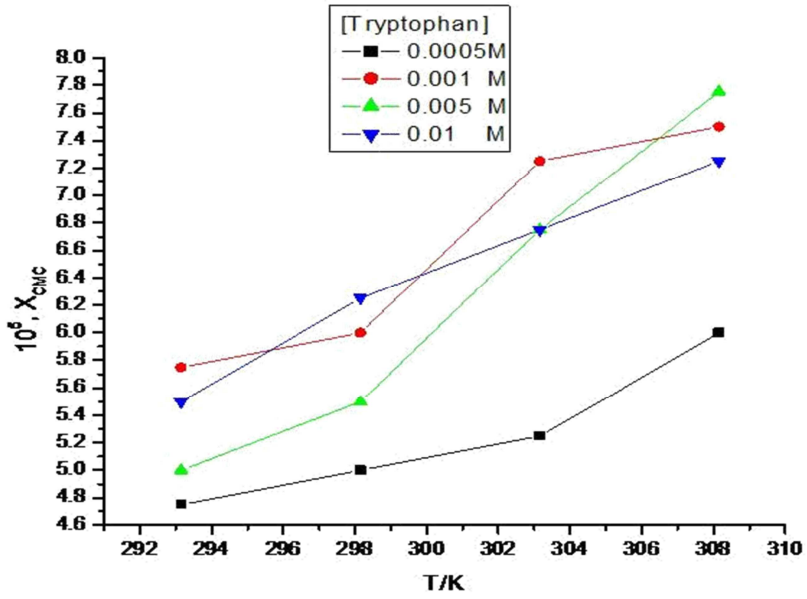
These observations seem to clearly indicate that tryptophan - surfactant interactions are governed by the behavior of the tryptophan in solutions. Cooperative binding of SDS molecules to tryptophan is observed in the tryptophan- SDS system. Micellization of SDS is less favored at lower concentration of tryptophan and at higher concentration it



decreases. As hydrophobicity is the major driving force behind the micellization phenomena so the extra hydrophobicity provided by tryptophan is responsible for lowering the X_{CMC} of SDS at higher tryptophan concentrations. Such interdependence between the packing of polar head groups and hydrocarbon chains may have important implications in the behavior of biological membranes. DMSO shows prominent effects on the thermodynamics of tryptophan -SDS system which are mainly due to salvation of hydrophobic side chains and changes in water structure.

Figure 1: Plot of X_{CMC} of SDS with aqueous Tryptophan at different temperatures

Figure 2: Plot of X_{CMC} of SDS vs. temperature in aqueous solutions at different [Tryptophan]



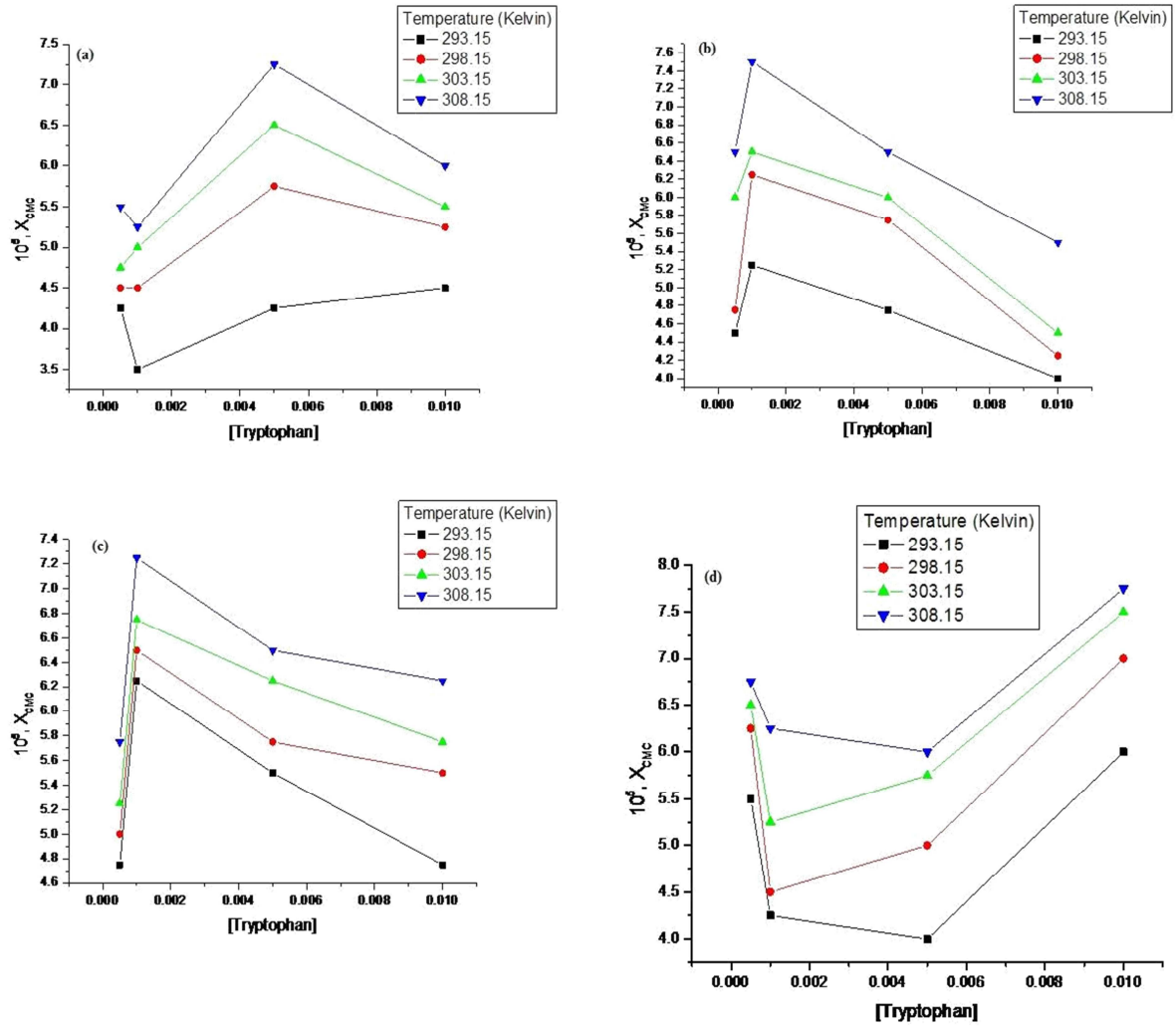


Figure 3: Plot of X_{CMC} of SDS with aqueous Tryptophan containing (a) 1%, (b) 2%, (c) 3% and (d) 4% w/v DMSO at different temperatures.

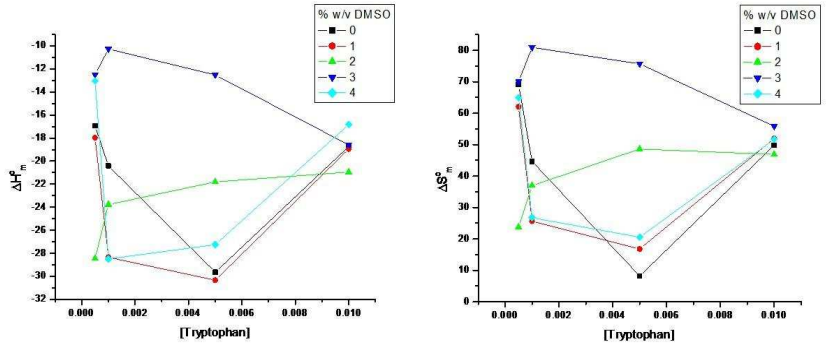


Figure 4: Representative plots of ΔH^{o}_{m} and ΔS^{o}_{m} vs. tryptophan concentration in aqueous rich mixtures of DMSO at 298.15 K.

Table1: Standard Thermodynamic Parameters of micellization of SDS in 0.0005 M Tryptophan containing different concentrations of DMSO at different Temperatures.

Temp		0 % w/v		
(Kelvin)		DM SO		
	^{x}cmc	ΔH	ΔG	ΔS
	10^{5}	kJ mol^{-1}	kJ mol $^{-1}$	JK^{-1} mol^{-1}
293.15	4.75 0.41	-16.92	-38.33	73.04
298.15	5.00 0.49	-16.95	-37.56	69.13
303.15	5.25 0.51	-16.38	-35.52	63.14
308.15	6.00 0.54	-17.16	-36.11	61.51
		1 % w/v		
		DM SO		
293.15	4.25 0.51	-17.62	-36.55	64.59
298.15	4.50 0.53	-17.98	-36.47	62.02
303.15	4.75 0.57	-18.08	-35.88	58.70
308.15	5.50 0.55	-18.95	-36.44	56.76
		2 % w/v		
		DM SO		
293.15	4.50 0.61	-26.56	-33.91	25.08
298.15	4.75 0.56	-28.46	-35.53	23.73
303.15	6.00 0.63	-27.99	-33.57	18.39
308.15	6.50 0.59	-29.77	-34.83	16.43
		3 % w/v		
		DM SO		
293.15	4.75 0.56	-12.80	-34.94	75.52
298.15	5.00 0.64	-12.50	-33.39	70.04
303.15	5.25 0.62	-13.12	-34.28	69.80
308.15	5.75 0.63	-13.45	-34.27	67.55
		4 % w=v		
		DM SO		
293.15	5.50 0.61	-12.98	-33.23	69.07
298.15	6.25 0.65	-13.04	-32.39	64.91
303.15	6.50 0.73	-12.68	-30.86	59.96
308.15	6.75 0.71	-13.31	-31.74	59.80

Table2: Standard Thermodynamic Parameters of micellization of SDS in 0.001 M Tryptophan containing different concentrations of DMSO at different Temperatures

Temp		0 % w/v		
(Kelvin)		DM SO		
	^{x}cmc	ΔH	ΔG	ΔS
	10^{5}	kJ mol^{-1}	kJ mol $^{-1}$	JK^{-1} mol^{-1}
293.15	5.75 0.50	-21.15	-35.69	49.63
298.15	6.00 0.60	-20.41	-33.74	44.68
303.15	7.25 0.70	-19.60	-31.23	38.38
308.15	7.50 0.60	-21.81	-34.07	39.79
		1 % w/v		
		DM SO		
293.15	3.50 0.48	-28.71	-38.01	31.71
298.15	4.50 0.55	-28.33	-35.97	25.63
303.15	5.00 0.55	-29.29	-36.19	22.76
308.15	5.25 0.60	-29.22	-35.35	19.87
		2 % w/v		
		DM SO		
293.15	5.25 0.48	-24.09	-36.51	42.37
298.15	6.25 0.55	-23.77	-34.79	36.98
303.15	6.50 0.63	-23.22	-33.29	33.23
308.15	7.50 0.71	-22.59	-31.39	28.56
		3 % w/v		
		DM SO		
293.15	6.25 0.68	-09.11	-31.14	75.16
298.15	6.50 0.56	-10.28	-34.41	80.94
303.15	6.75 0.70	-09.60	-31.47	72.14
308.15	7.25 0.57	-10.91	-34.92	77.33
		4 % w/v		

			DM SO		
293.15	4.25	0.48	-28.48	-37.29	30.07
298.15	4.50	0.53	-28.49	-36.47	26.78
303.15	5.25	0.57	-28.65	-35.52	22.66
308.15	6.25	0.57	-29.60	-35.46	19.03

Table3: Standard Thermodynamic Parameters of micellization of SDS in 0.005 M Tryptophan containing different concentrations of DMSO at different Temperatures

Temp			0 % w/v		
(Kelvin)			DM SO		
	^{x}cmc		ΔH	ΔG	ΔS
	10^{5}		kJ mol^{-1}	kJ mol^{-1}	JK^{-1} mol^{-1}
293.15	5.00	0.58	-30.83	-34.27	11.74
298.15	5.50	0.68	-29.65	-32.09	8.20
303.15	6.75	0.62	-32.04	-33.40	4.48
308.15	7.75	0.65	-32.39	-32.74	1.13
			1 % w/v		
			DM SO		
293.15	4.25	0.52	-30.15	-35.91	19.65
298.15	5.50	0.56	-30.34	-35.35	16.80
303.15	6.75	0.54	-31.80	-35.48	12.12
308.15	7.25	0.55	-32.64	-35.54	9.42
			2 % w/v		
			DM SO		
293.15	4.75	0.53	-20.66	-35.67	51.19
298.15	5.75	0.50	-21.81	-36.30	48.63
303.15	6.00	0.64	-20.44	-33.32	42.49
308.15	6.50	0.73	-19.72	-31.37	37.80
			3 % w/v		
			DM SO		
293.15	5.50	0.62	-11.53	-32.99	73.21
298.15	5.75	0.55	-12.53	-35.09	75.69
303.15	6.25	0.61	-12.42	-33.91	70.92
308.15	6.50	0.66	-12.37	-33.10	67.28
			4 % w/v		
			DM SO		
293.15	4.00	0.51	-28.87	-36.77	26.96
298.15	5.00	0.64	-27.26	-33.39	20.55
303.15	5.75	0.60	-29.01	-34.45	17.95
308.15	6.00	0.64	-29.12	-33.87	15.42

Table4: Standard Thermodynamic Parameters of micellization of SDS in 0.01 M Tryptophan containing different concentrations of DMSO at different Temperatures

Temp			0 % w/v		
(Kelvin)			DM SO		
	^{x}cmc		ΔH	ΔG	ΔS
	10^{5}		kJ mol^{-1}	kJ mol^{-1}	JK^{-1} mol^{-1}
293.15	5.50	0.50	-19.41	-35.86	56.11
298.15	6.25	0.60	-18.74	-33.59	49.83
303.15	6.75	0.60	-19.37	-33.89	47.88
308.15	7.25	0.70	-18.59	-31.75	42.71
			1 % w/v		
			DM SO		
293.15	4.50	0.48	-19.75	-37.08	59.10
298.15	5.25	0.59	-18.96	-34.44	51.95
303.15	5.50	0.66	-18.62	-33.13	47.84
308.15	6.00	0.69	-18.81	-32.63	44.83
			2 % w/v		
			DM SO		
293.15	4.00	0.56	-20.83	-35.54	50.17
298.15	4.25	0.60	-20.95	-34.93	46.89
303.15	4.50	0.54	-22.59	-36.83	46.98
308.15	5.50	0.61	-22.22	-34.93	41.24
			3 % w/v		

DM SO					
293.15	4.75	0.49	-18.73	-36.64	61.08
298.15	5.50	0.55	-18.60	-35.25	55.84
303.15	5.75	0.60	-18.57	-34.45	52.39
308.15	6.25	0.67	-18.23	-32.98	47.89
4 % w/v					
DM SO					
293.15	6.00	0.57	-17.10	-33.88	57.23
298.15	7.00	0.64	-16.83	-32.25	51.74
303.15	7.50	0.71	-16.50	-30.88	47.44
308.15	7.75	0.69	-17.31	-31.77	46.91

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