

Interactions of Proline in Non-aqueous Anionic, Cationic and Nonionic Surfactants at Different Temperatures

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Abstract: Density and viscosity data of proline (Pro) in sodium dodecyl sulfate/cetyltrimethylammonium bromide/poly (oxyethylene) isoctyl phenyl ether in formamide were measured at 298.15, 303.15, 308.15, and 313.15 K and 0.1 MPa. The density data were utilized to evaluate standard partial molar volumes (ϕ_v^0) and partial molar isobaric expansibility (ϕ_E^0). The viscosity data were used to evaluate *A*- and *B*-coefficients, free energy of activation of viscous flow ($\Delta\mu_1^{0*}$) and ($\Delta\mu_2^{0*}$), per mole of solvent and solute respectively, enthalpy (ΔH^*) and entropy (ΔS^*) of activation of viscous flow. The results obtained were utilized in the qualitative elucidation of the Pro–surfactant/formamide and Pro–Pro interactions in the present systems.

Key Words: Partial molar volume; Viscosity coefficient; Interaction

Surfactant–protein interactions have been under investigation^[1–7] due to various applications of surfactants and the role of protein in the very existence of life. Surfactants are widely used in pharmaceutical^[8,9], biological, and technological fields^[10–12].

It has been found that commercial cleaners for lubrication and grease stripping applications normally contain halogenated solvents in their formulations. Generally halogenated substances are toxic and pose a threat to biosphere. So, it is required to develop non-toxic, biodegradable, inexpensive, and environmental-friendly formulations. The blending of water with polar organic solvents along with common surfactants may prove to be an effective formulation for various cleaning operations^[13], or for doing sol-gel processes.

The surfactants utilized in areas such as lubrication require water-free or water poor environment. Therefore, surfactant aggregation process in non-aqueous media has acquired considerable interest in recent years. Polar solvents with properties resembling those of water, such as ethylene glycol, glycerol, and formamide, have been employed^[14–16].

Studies reveal that a liquid capable of replacing water should be of high polarity to make it immiscible with oils and to make it a good solvent for the hydrophilic part of surfactant molecules. Further, hydrogen bonding plays an important role in solvation of both ionic and nonionic surfactants and in the hydrogen bonded network in the liquid itself^[13].

Literature survey reveals that the study of proteins in non-aqueous surfactant media is rare^[17–19]. So, in the present investigation, we have taken amino acid, proline (Pro) in presence of three surfactants, sodium dodecyl sulfate (SDS), cetyltrimethylammo-

nium bromide (CTAB), poly (oxyethylene) isoctyl phenyl ether (TX-100), and polar solvent, formamide (FA). Since proteins have complex structural organization and their direct study is somewhat difficult, simpler units of proteins, i.e., amino acids (AA) are employed. The surfactants used belong to three broad classes, i.e., anionic, cationic, and nonionic. The different classes of surfactants were used to have complete understanding of the effect of the nature of surfactants on proline in non-aqueous media.

To the best of our knowledge, no data has been reported on thermodynamic and transport study of amino acids in non-aqueous surfactant media so far. Therefore, we have measured densities and viscosities of solutions to evaluate various parameters of interest. These parameters are used to study the interactions prevailing in proline+non-aqueous surfactant systems.

1 Experimental

Biochemical reagent grade proline (Thomas Baker, India, mass fraction >0.99), analytical reagent grade SDS (s.d. fine. Chem. Ltd., India, mass fraction 0.99) and CTAB (E. Merck, Germany, mass fraction 0.995) were used after recrystallization from ethanol-water mixtures and drying in vacuum over P₂O₅ at room temperature for at least 72 h. Analytical reagent grade TX-100 (BDH Chem. Ltd., Poole, England, mass fraction 0.995) was kept over molecular sieves (0.4 nm, Sigma Union Carbide type) to reduce the water content, if there was any. Spectroscopic grade FA (s.d. fine. Chem. Ltd., India) was purified as described in the literature^[20].

The solutions of 0.01 mol·L⁻¹ SDS+FA/CTAB+FA/TX-100+FA

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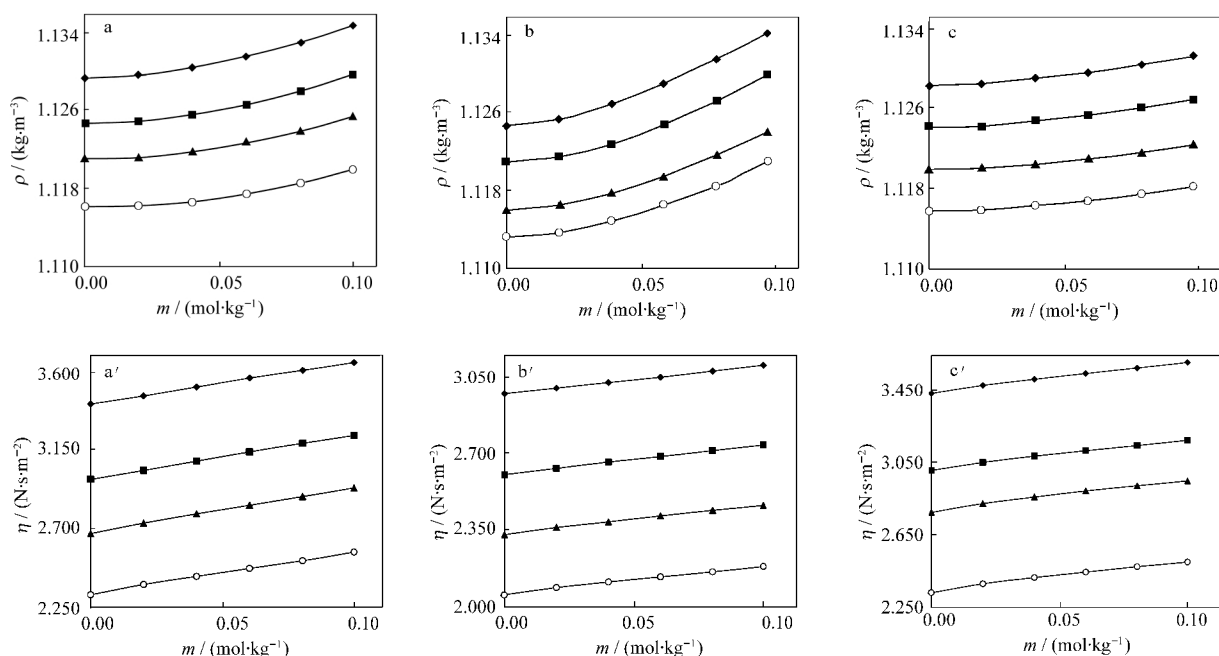


Fig.1 Plots of density (ρ) and viscosity (η) vs concentration of Pro in (a, a') SDS+FA, (b, b') CTAB+FA, and (c, c') TX-100+FA at (\blacklozenge) 298.15, (\blacksquare) 303.15, (\blacktriangle) 308.15, and (\circ) 313.15 K

were used as solvents for preparation of 0.02, 0.04, 0.06, 0.08, and 0.10 mol \cdot L $^{-1}$ Pro solutions. Solutions were prepared by weight on Precisa XB-220 (Swiss-make) electronic balance precise to ± 0.0001 g. The solutions were kept in special air tight bottles to avoid contamination and evaporation.

The densities of ternary solutions were measured using a single stem pycnometer made of Borosil glass with a bulb capacity of 8×10^{-6} m 3 . The stem had graduated marks and a well-fitted glass cap. The viscosity measurements were made using Ubbelohde type suspended level viscometer. The pycnometer and viscometer containing the test solution were kept for about 20 min in an electronically controlled thermostated water bath (JULABO, Model-MD GMBH, Germany) having precision of ± 0.02 K, in order to avoid thermal fluctuations. The details of density and viscosity measurements were given in our earlier papers^[21]. The respective accuracies in density and viscosity are found to be ± 0.01 kg \cdot m $^{-3}$ and $\pm 3 \times 10^{-6}$ N \cdot s \cdot m $^{-2}$.

2 Results and discussion

Density and viscosity data for Pro in SDS+FA/CTAB+FA/TX-100+FA at 298.15, 303.15, 308.15, and 313.15 K as a func-

tion of the molality (m) of Pro are shown in Fig.1.

2.1 Volumetric study

Volumetric property has been regarded as a sensitive structural tool for understanding interactions in solutions^[22]. The apparent molar volumes of solutions were calculated from the density data using the equation:

$$\phi_v = M[\rho - (\rho - \rho_0)/m] / \rho \rho_0 \quad (1)$$

where m is the molality of Pro having molecular weight M ; ρ and ρ_0 are the respective densities of solution (Pro+non-aqueous surfactant) and solvent (non-aqueous surfactant). The ϕ_v values of Pro at the four studied temperatures are plotted against $m^{1/2}$ in Fig.2. Fig.2 depicts that ϕ_v values are large positive for all the three Pro+non-aqueous media, indicating the presence of strong Pro-surfactant/formamide interactions.

2.1.1 Standard partial molar volumes (ϕ_v^0)

The standard partial molar volumes ϕ_v^0 (same as apparent molar volume at infinite dilution ϕ_{v2}^0) are usually obtained by extrapolating the corresponding concentration dependence of the apparent molar volume to infinite dilution, as at infinite dilution $\phi_v = \phi_v^0$. The ϕ_v data were used to evaluate ϕ_v^0 of Pro using Mason's relation^[23]:

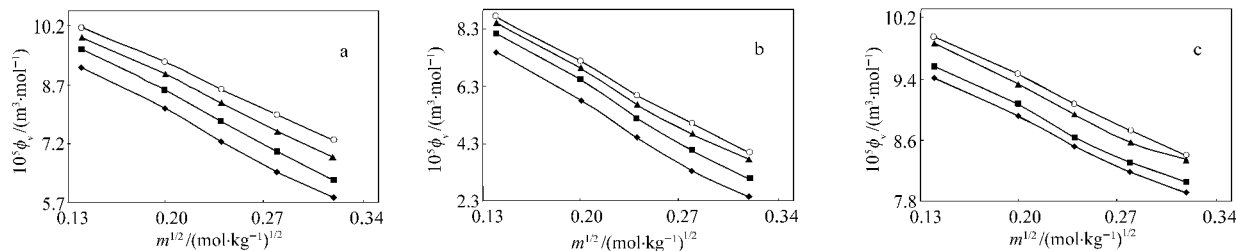


Fig.2 Plots of apparent molar volumes (ϕ_v) vs concentration of Pro in (a) SDS+FA, (b) CTAB+FA, and (c) TX-100+FA at (\blacklozenge) 298.15, (\blacksquare) 303.15, (\blacktriangle) 308.15, and (\circ) 313.15 K

$$\phi_v = \phi_v^0 + S_v^* m^{1/2} \quad (2)$$

where S_v^* is the experimental slope. The values of ϕ_v^0 and S_v^* are given in Table 1. At infinite dilution, Pro-Pro interactions vanish, therefore, ϕ_v^0 provides the information regarding Pro-surfactant/FA interactions, while S_v^* gives an insight into the Pro-Pro interactions. The observed ϕ_v^0 values given in Table 1 are large positive, suggesting the presence of strong Pro-surfactant/FA interactions in all the three Pro+non-aqueous surfactant solutions. It is found that ϕ_v^0 values follow the order: SDS>CTAB>TX-100. The ϕ_v^0 values also increase with the rise in temperature. This may be due to the loosening of solvation layers of Pro in surfactant+FA medium and hence, some of the solvent molecules are released. On the other hand, S_v^* values are negative, implying the presence of weak Pro-Pro interactions. Iqbal *et al.*^[24] reported that negative S_v^* values are associated with hydrophobic solutes. The presence of aliphatic side chain in Pro contributes to its hydrophobicity.

The partial molar volumes ϕ_v^0 of Pro in FA+surfactant solutions can be (qualitatively) interpreted by considering the operations of the following interactions expected in the ternary mixtures.

(i) Ion-ion interactions between SO_4^{2-} of SDS/ Br^- of CTAB and NH_2^+ group of Pro and between Na^+ of SDS/ N^+-CH_3 group of CTAB and COO^- group of Pro.

(ii) Ion-hydrophilic interactions between the charge centres (NH_2^+ , COO^-) of Pro and hydrophilic (polyoxyethylene) part of TX-100.

(iii) Hydrophobic-hydrophilic group interactions between the hydrophobic part $-(\text{CH}_2)_5-$ of Pro and hydrophilic $\text{C}_{12}\text{H}_{25}\text{SO}_4^{2-}$, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$, and polyoxyethylene groups of SDS, CTAB, and TX-100, respectively.

(iv) Hydrophobic-hydrophobic interactions between the alkyl chains $\text{C}_{12}\text{H}_{25}-$, $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3-$, and $\text{C}_8\text{H}_{17}(\text{C}_6\text{H}_4)-$ of SDS/CTAB/TX-100, respectively, and hydrophobic group $-(\text{CH}_2)_5-$

Table 1 Values of ϕ_v^0 , S_v^* , and ϕ_E^0 of Pro in SDS+FA/CTAB+FA/TX-100+FA at 298.15, 303.15, 308.15, and 313.15 K

T/K	$10^3\phi_v^0/(\text{m}^3 \cdot \text{mol}^{-1})$	$10^3S_v^*/(\text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{L}^{-1/2})$	$10^3\phi_E^0/(\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
{Pro+0.01 mol·kg ⁻¹ (SDS+FA)}			
298.15	11.8267	-19.0494	10.04
303.15	12.3201	-19.0792	6.18
308.15	12.4045	-17.5106	1.98
313.15	12.4786	-16.3330	-2.21
{Pro+0.01 mol·kg ⁻¹ (CTAB+FA)}			
298.15	11.5442	-29.0141	14.5
303.15	12.2421	-29.1074	8.62
308.15	12.3454	-27.3952	2.77
313.15	12.4588	-26.7129	3.63
{Pro+0.01 mol·kg ⁻¹ (TX-100+FA)}			
298.15	10.6545	-8.7143	4.77
303.15	10.8086	-8.7772	4.33
308.15	11.1241	-8.8868	3.88
313.15	11.2338	-8.8890	3.44

of Pro.

Table 1 shows that ϕ_v^0 is positive for all the three Pro+non-aqueous surfactant solutions. The results can be interpreted with the help of Cosphere Overlap Model (COM) proposed by Friedman and Krishnan^[25]. According to the model, the effect of overlap of two cospheres is destructive. Further, Mishra *et al.*^[26] extended this model and observed that overlapping of cospheres of two ionic species caused an increase in volume, whereas overlapping of hydrophilic-hydrophobic and hydrophobic-hydrophobic groups led to decrease in volume. So, in the light of above facts, it is concluded that interactions of the types (i) and (ii) contribute to positive ϕ_v^0 values due to reduction in electrostriction. Because of the interactions of the charged centres (NH_2^+ , COO^-) of Pro with the ions of SDS/CTAB and with the hydrophilic part of TX-100, the electrostatic interaction between (NH_2^+ , COO^-) of Pro and polar FA molecules is partially shielded. As a result, the electrostriction of FA caused by these centres of Pro will be reduced, thereby, resulting an increase in volume, and leads to positive ϕ_v^0 values. While, negative ϕ_v^0 values result from the interactions of the types (iii) and (iv) because of the weakening of hydrogen-bonded structure of FA around non-polar groups of surfactants and Pro as a result of the overlapping of cospheres of these groups. The observed positive ϕ_v^0 values (Table 1), at all the investigated temperatures, suggest that the interactions (i) and (ii) are overall dominant over the (iii) and (iv) interactions in the present ternary solutions.

2.1.2 Partial molar isobaric expansibilities (ϕ_E^0)

Partial molar volume is a useful property which provides information on solute-solvent interactions, however, its temperature dependence may still be more useful in the study of solvation effects as the intrinsic volume of solute is almost independent of temperature^[27,28]. The ϕ_v^0 data are utilized in estimating the precise values of $(\partial\phi_v^0/\partial T)_p$ and $(\partial^2\phi_v^0/\partial T^2)_p$.

The ϕ_v^0 data have been fitted with least-squares method to the following equation similar to that used by Chalikian *et al.*^[29]

$$\phi_v^0 = a + bT + cT^2 \quad (3)$$

where a , b , and c are constants and T is the temperature. The differentiation of equation (3) with respect to temperature leads to the partial molar isobaric expansibility, ϕ_E^0

$$\phi_E^0 = (\partial\phi_v^0/\partial T)_p = b + 2cT \quad (4)$$

The values of ϕ_E^0 are also given in Table 1.

The differentiation of equation (4) yields:

$$(\partial c_p^0/\partial p)_T = -T(\partial^2\phi_v^0/\partial T^2)_p = -2cT \quad (5)$$

and was proposed by Hepler^[30]. The sign of $(\partial c_p^0/\partial p)_T$ elucidates the structure-making/structure-breaking ability of solute. The positive sign represents the structure-making, whereas, negative sign signifies the structure-breaking capability of solute. Thus, in the present investigation, positive $(\partial c_p^0/\partial p)_T$ values indicate that Pro acts as structure-maker in all the three nonaqueous surfactant media.

2.2 Viscometric study

The A - and B -coefficients of viscosity for the solutions under study were calculated using empirical equation of Jones-Dole^[31]

$$\eta_r = \eta/\eta_0 = 1 + Am^{1/2} + Bm \quad (6)$$

where η_r is the relative viscosity, η and η_0 are the respective viscosities of solution and solvent (FA+surfactant). The A -coefficient represents solute-solute interactions and can be calculated from interionic theory, while B -coefficient is empirical and provides valuable information in the qualitative elucidation of the effects of ions on solvent structure^[32]. The values of A - and B -coefficients are given in Table 2. The large and positive values of B -coefficients as compared to A -coefficients for solutions of Pro in FA+SDS/CTAB support the respective behaviours of ϕ_v^0 and S_v^* , suggesting the presence of strong Pro-surfactant/FA interactions and weak Pro-Pro interactions. However, in TX-100+FA, the values of A are larger than those of B , indicating strong Pro-Pro interactions.

Eyring and coworkers^[33] proposed that the contribution per mole of solvent to the free energy of activation ($\Delta\mu_1^{0*}$) can be calculated using the relation:

$$\eta_0 = (hN_A/\phi_{v1}^0) \exp(\Delta\mu_1^{0*}/RT) \quad (7)$$

where h , N_A , and ϕ_{v1}^0 are the Planck's constant, Avogadro's number, and standard partial molar volume of solvent, respectively. Rearrangement of equation (7) gives

$$\Delta\mu_1^{0*} = RT \ln(\eta_0 \phi_{v1}^0 / hN_A) \quad (8)$$

Furthermore, Feakins *et al.*^[34] found that B -coefficient is related to contribution per mole of solute to the free energy of activation ($\Delta\mu_2^{0*}$) according to the equation

$$B = (\phi_{v1}^0 - \phi_{v2}^0) + (\phi_{v1}^0 (\Delta\mu_2^{0*} - \Delta\mu_1^{0*}) / RT) \quad (9)$$

which on rearrangement gives:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + (RT/\phi_{v1}^0) [B - (\phi_{v1}^0 - \phi_{v2}^0)] \quad (10)$$

The values of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are listed in Table 2.

Table 2 shows that $\Delta\mu_2^{0*}$ values are positive and larger than $\Delta\mu_1^{0*}$, showing that the formation of transition state in the non-aqueous surfactant solution is less favored in the presence of Pro. According to Feakins *et al.*^[34], greater the value of $\Delta\mu_2^{0*}$, greater is the structure-making ability of solute. So, Pro acts as net structure-maker in all the three non-aqueous surfactant media.

Table 2 Values of A , B , $\Delta\mu_1^{0*}$, and $\Delta\mu_2^{0*}$ of Pro in SDS+FA/CTAB+FA/TX-100+FA at 298.15, 303.15, 308.15, and 313.15 K

T/K	$10^4 A / (\text{dm}^{3/2} \cdot \text{mol}^{-1/2})$	$10B / (\text{dm}^3 \cdot \text{mol}^{-1})$	$\Delta\mu_1^{0*} / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta\mu_2^{0*} / (\text{kJ} \cdot \text{mol}^{-1})$
{Pro+0.01 mol·kg ⁻¹ (SDS+FA)}				
298.15	-0.4228	7.5825	14.4597	66.3210
303.15	-0.8298	8.2548	14.3729	71.4087
308.15	3.9042	8.5190	14.3327	73.8549
313.15	5.2055	8.7232	14.2182	75.7816
{Pro+0.01 mol·kg ⁻¹ (CTAB+FA)}				
298.15	0.7210	4.7851	14.1307	48.3029
303.15	1.0693	4.8199	14.0407	49.3225
308.15	2.9585	4.8432	13.9995	49.9161
313.15	4.3347	4.8800	13.9085	50.6251
{Pro+0.01 mol·kg ⁻¹ (TX-100+FA)}				
298.15	3.9713	4.0100	14.4877	43.3339
303.15	4.7695	4.0348	14.4048	43.8697
308.15	6.6031	4.2714	14.4465	45.9750
313.15	8.7236	4.5932	14.2373	48.2847

Table 3 Values of ΔH^* (kJ·mol⁻¹) and ΔS^* (kJ·mol⁻¹·K⁻¹) of Pro in SDS+FA/CTAB+FA/TX-100+FA at 298.15, 303.15, 308.15, and 313.15 K

m (mol·kg ⁻¹)	{Pro+0.01 mol·kg ⁻¹ (SDS+FA)}		{Pro+0.01 mol·kg ⁻¹ (CTAB+FA)}		{Pro+0.01 mol·kg ⁻¹ (TX-100+FA)}	
	ΔH^*	ΔS^*	ΔH^*	ΔS^*	ΔH^*	ΔS^*
0.00	0.1899	0.0002	0.1835	0.0001	0.1873	0.0001
0.02	-5.6460	-0.0307	0.3498	-0.0074	-2.7275	-0.0168
0.04	-11.4819	-0.0615	0.5161	-0.0150	-5.6423	-0.0338
0.06	-17.3178	-0.0924	0.6824	-0.0225	-8.5571	-0.0507
0.08	-23.1537	-0.1232	0.8487	-0.0301	-11.4719	-0.0677
0.10	-28.9896	-0.1541	1.0149	-0.0377	-14.3867	-0.0846

This supports our results obtained by $(\partial^2\phi_v^0/\partial T^2)_p$.

Table 3 presents the enthalpies (ΔH^*) and entropies (ΔS^*) of activation of viscous flow of Pro in non-aqueous surfactant media, which were determined using the relationships:

$$\Delta\mu^{0*} = \Delta H^* - T\Delta S^* \quad (11)$$

and

$$\Delta\mu^{0*} = n_1\Delta\mu_1^{0*} + n_2\Delta\mu_2^{0*} \quad (12)$$

The intercepts ΔH^* and slopes ΔS^* are obtained by the plots of total free energy of activation of viscous flow of the solution, $\Delta\mu^{0*}$ vs T . ΔH^* and ΔS^* are useful in providing the structural information about solute species and solute-solvent interactions. It can be seen from Table 3 that ΔH^* values are positive and increase with the increase in concentration of Pro in non-aqueous CTAB, whereas reverse is observed in non-aqueous SDS/TX-100 media. This indicates that the formation of activated species required for the viscous flow appears difficult, as the concentration of Pro increases in non-aqueous CTAB solution while reverse is the case with non-aqueous SDS/TX-100 media.

The ΔS^* values (Table 3) are negative and show a pronounced decrease as the concentration of Pro increases in all the three non-aqueous surfactant media. This suggests that the system is more structured during the viscous flow rather than in the initial state, therefore, indicating the presence of significant Pro-surfactant/FA interactions in the system under investigation.

3 Conclusions

In the present study, we have investigated the volumetric and viscometric properties of amino acid Pro in SDS+FA/CTAB+FA/TX-100+FA solutions at different temperatures. The positive values of ϕ_v^0 suggest the presence of strong Pro-surfactant/FA interactions and dominance of ion-ion and ion-hydrophilic interactions over hydrophobic-hydrophilic and hydrophobic-hydrophobic interactions in all the three Pro+non-aqueous surfactant solutions. The positive values of $(\partial c_p^0/\partial p)_T$ indicate that Pro acts as structure-maker in all the three non-aqueous surfactant media. The viscosity coefficients, B and A , also support the respective behaviors of ϕ_v^0 and S_v^* , except for TX-100+FA, where Pro-Pro interactions are stronger than Pro-surfactant/FA interactions. $\Delta\mu_2^{0*}$ values show that the formation of transition state is less favored in the presence of Pro and also confirm the structure-making ability of Pro in all the three non-aqueous surfactant media thus, supporting the results drawn from $(\partial^2\phi_v^0/\partial T^2)_p$. ΔH^*

values are found to be positive and increase as the concentration of Pro increases in non-aqueous CTAB, while reverse is found in non-aqueous SDS/TX-100 media, indicating that the formation of activated species required for the viscous flow appears difficult as the concentration of Pro increases in non-aqueous CTAB solution. The ΔS^* values are negative and decrease with the increase in Pro concentration, implying that the system is more structured during the viscous flow than in the initial state, therefore, indicating the presence of significant Pro–surfactant/FA interactions in the system under investigation. The volumetric and viscometric studies are in good agreement with each other.

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