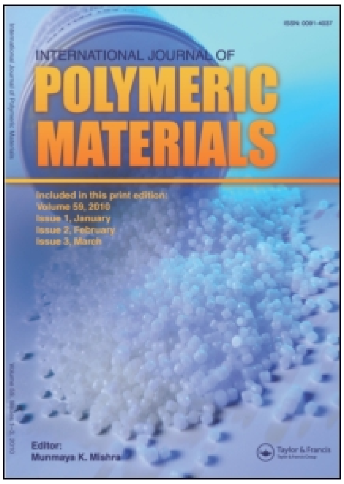


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Surface Activity of Monomeric and Polymeric (3-alkyloxy aniline) Surfactants

S. M. Sayyah[a]; H. M. Abd El-Salam[a]; E. M. S. Azzam[b]
[a] Faculty of Science, Beni-Suef Branch, Cairo University, Beni-Suef, Egypt [b] Egyptian Petroleum Research Institute, Elzhoor, Nasr City, Cairo, Egypt

To cite this Article Sayyah, S. M. , El-Salam, H. M. Abd and Azzam, E. M. S.(2005) 'Surface Activity of Monomeric and Polymeric (3-alkyloxy aniline) Surfactants', International Journal of Polymeric Materials, 54: 6, 541 — 555
To link to this Article: DOI: 10.1080/00914030390278662
URL: http://dx.doi.org/10.1080/00914030390278662

International Journal of Polymeric Materials, 54:541–555, 2005
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390278662

Surface Activity of Monomeric and Polymeric (3-alkyloxy aniline) Surfactants

S. M. Sayyah
H. M. Abd El-Salam
Faculty of Science, Cairo University, Beni-Suef Branch,
Beni-Suef, Egypt

E. M. S. Azzam
Egyptian Petroleum Research Institute, Elzhoor,
Nasr City, Cairo, Egypt

The adsorption and micellization processes of 3-alkyloxy aniline namely [3-decyloxy aniline (C10M), 3-dodecyloxy aniline (C12M) and 3-cetyloxy aniline (C16M)] and their polymers [C10P, C12P and C16P] have been investigated using surface tension (γ) measurements at different temperatures. The synthesized monomers and polymers have been characterized by IR and elemental analysis. The surface and thermodynamic parameters of these monomeric and polymeric surfactants are investigated. The results show that the critical micelle concentration (CMC) of the polymeric surfactants is lower than that of monomers. The CMC values decreases as the hydrophobic chain lengthens for both monomeric and polymeric surfactants. The surface parameters show the ability of monomeric and polymeric surfactants to adsorb at the air/water interface and decrease the surface tension. The thermodynamic parameters reveal that the micellization process is spontaneous for all investigated surfactants. The specific conductance measurements show that the specific conductance increases with increasing chain length of the substituted alkyl groups, the synthesized polymeric surfactants have higher values of specific conductance than the corresponding monomers and the specific conductance increases with rising solution temperature.

Keywords: monomeric and polymeric surfactants, critical micelle concentration (CMC), surface parameters, thermodynamic parameters, specific conductance

Received 12 November 2003; in final form 24 November 2003.

Address correspondence to S. M. Sayyah, Faculty of Science, Cairo University, Beni-Suef Branch, Beni-Suef, Egypt. E-mail: smsayyah@hotmail.com

INTRODUCTION

Water-soluble polymers are ordinarily used as surface active agents due to their amphipatic structure and surface activity [1–3]. They are used commercially in many different applications, among which stabilization of dispersions is probably the most widespread [4]. The polymeric surfactants consisting of hydrophilic and hydrophobic parts have become the subject of many studies on their solutions, solid state, and surface properties [5–9]. Systematic investigations employing some ethoxylated alkyl phenol-formaldehyde (APF) polymeric surfactants have been carried out. Their surface and interfacial tension behavior have been investigated [10–12]. By far, the most extensively studied polymeric surfactants are the block copolymer polyols. To the best of the authors' knowledge no one had investigated, the conducting polymeric surfactants. Surface and thermodynamic parameters of some polymeric surfactants have been determined in previous investigations [13–16]. The present work intends to investigate the surface and thermodynamic parameters of the prepared monomers and their poly (3-alkyloxy anilines) as conducting polymeric surfactants and the effect of the alkyl chain length on these parameters.

MATERIALS AND SYNTHESIS PROCESS

The chemicals used in the synthetic process were obtained from Aldrich Chemical Co., England.

Synthesis of Monomeric (3-alkyloxyanilines)

3-decyloxy aniline (C10M), 3-dodecyloxy aniline (C12M), and 3-cetyloxy aniline (C16M) monomers were prepared by the equimolar reaction between 3-aminophenol with decyl bromide, dedecyl bromide, and cetyl bromide, respectively, in the presence of sodium ethoxide as a medium as mentioned by Azzam et al. [17].

Synthesis of Polymeric (3-alkyloxyanilines)

The polymerization of 3-decyloxy aniline (C10P), 3-dodecyloxy aniline (C12P), and 3-cetyloxy aniline (C16P) were carried out as reported by Sayyah et al. [18].

Experimental Technique

Elemental Analysis and Infrared Spectroscopic Analysis

The elemental analysis of the prepared monomeric and polymeric surfactants was carried out in the micro analytical laboratory at Cairo University.

The infrared measurements were carried out using a shimadzu FTIR-430 Jasco spectrophotometer and KBr disc technique.

Surface Tension Measurement

Surface tension was measured using Du Nouy tensiometer (KRUSS Type 8451) for the hydrochloride form of synthesized monomeric and polymeric surfactants using different concentrations at different temperatures (25, 40, and 55°C) as mentioned by Gad et al. [19].

Specific Conductance Measurement

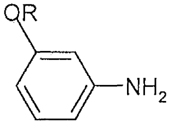
An electrical conductivity meter (Type 522; Crison Instruments S.A., Barcelona, Spain) was used to measure the specific conductance of 1% solution of the synthesized monomeric and polymeric.

RESULTS AND DISCUSSION

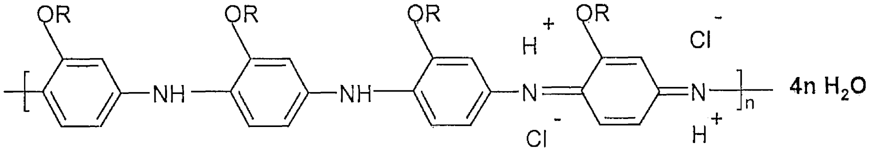
Structure Determination of the Prepared Surfactants

The elemental analysis of the monomeric and polymeric surfactants was carried out in the micro analytical laboratory at Cairo University. The C%, H%, Cl%, and N% are found to be in good agreement with the calculated one for the suggested structure present in Scheme 1. The elemental analysis data are given in Table 1.

The infrared absorption bands and their assignments of the three prepared monomers and their polymeric surfactants are summarized in Table 2. The strong absorption band appearing in the region 500–546 cm^{-1} in case of polymers, which could be attributed to the torsional oscillation of NH_3^+ group, disappears in case of monomers. The medium band appearing in the region 620–883 cm^{-1} in case of monomers appears as a weak or sharp band in case of polymers; it may be attributed to the CH out of plane deformation for 1,3-disubstituted benzene ring. The weak bands appearing in the region of 909 to 1003 cm^{-1} in case of polymers could be attributed to the CH out of plane bending for 1,4-disubstituted benzene ring. The stretching vibration bands of both C–O and C–N and the out of plan binding vibration of CH_3 group of monomers and polymers appear in the region between 1041 and 1488 cm^{-1}. The strong band appearing at 1622 cm^{-1} in case of the polymers could be attributed to C=C in



A: Structure of monomer



B: Structure of polymer

Where R is equal to decyl ($C_{10}H_{21}$), Dodecyl ($C_{12}H_{25}$) and Cetyl ($C_{16}H_{33}$)

SCHEME 1 Structure of monomeric surfactants (A) and polymeric surfactants (B).

benzene ring or C=N in quiniod structure (c.f. Scheme 2A). These bands appear in case of monomers at 1500, 1601, and 1640 cm^{-1}. The two weak bands, which appear at 2334 and 2369 cm^{-1} for the monomers, could be attributed to the hyperconjugation of monomer unit (B) in Scheme 2 or combination and overtone bands for C–N. These bands also appear in case of polymers, but with slight shift. The stretching vibrations of the aliphatic C–H and aromatic C–H of monomers appear at 2855, 2926, and 3091 cm^{-1} respectively.

TABLE 1 Elemental Analysis of the Prepared Monomeric and Polymeric Surfactants

		Elemental analysis							
		C%		H%		N%		Cl%	
Compound type	Molecular formula	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
C10M	$C_{16}H_{27}NO$	77.10	76.50	10.84	10.50	5.62	5.10	—	—
C10P	$C_{64}H_{108}N_4O_8Cl_2$	67.90	65.30	9.55	9.20	5.66	6.00	6.28	6.70
C12M	$C_{18}H_{31}NO$	77.98	77.60	11.19	10.70	5.05	5.60	—	—
C12P	$C_{72}H_{124}N_4O_8Cl_2$	67.51	67.30	9.98	9.60	5.15	4.90	5.71	6.30
C16M	$C_{22}H_{39}NO$	79.28	78.70	11.71	11.50	4.20	3.90	—	—
C16P	$C_{88}H_{156}N_4O_8Cl_2$	71.98	68.90	10.63	10.10	4.36	4.70	4.84	5.20

For the polymers these bands appear at 2850 and 2929 cm^{-1}. The stretching vibration of NH_2 group for monomers appears at 3237 and 3379 cm^{-1}. The sharp or broad bands in the region between 3337 and 3414 cm^{-1} are due to the stretching vibration of N–H group or strongly bonded O–H group.

Critical Micelle Concentration (CMC) and Surface Parameters

The relationships between the surface tension (γ) and $-\log$ concentration of the prepared surfactants at different temperatures (25, 40, and 55°C) are shown in Figures 1–3 (A,B). From the figures it can be noticed that, with raising the solution temperature (in the range 25–55°C), the surface tension deceases in all cases of the investigated monomeric and polymeric surfactants solutions. The critical micelle concentration (CMC) of the prepared monomeric and polymeric surfactants was determined from the abrupt change in the slope of the corresponding plot of the surface tension (γ) versus log concentration. The isotherms plots for monomeric surfactants (C10M, C12M, and C16M) are presented in Figures 1–3 A whereas those for polymeric surfactants (C10P, C12P, and C16P) are presented in Figures 1–3B. Table 3 shows the CMC values for monomeric and polymeric surfactants. The data from Table 3 reveal that the CMC values of all surfactants decrease with increasing alkyl chain length in both cases of monomers and polymers. This is due to the decrease in the solubility of surfactants as the alkyl chain in the hydrophobic part lengthen. It was found that the CMC values of polymeric surfactants are lower than those of monomeric surfactants. This may be attributed to the low solubility of polymeric surfactants, which leads to a continuous shift of the CMC to the lower values as shown in Table 3. From Table 3 it is also clear that, as the temperature increases the CMC values increase, which indicates that raising the solution temperature causes a disruption of the structured water surrounding the hydrophobic group, which disfavors micellization and increases the CMC value.

The surface parameters, effectiveness, Π_{CMC}, maximum surface excess, Γ_{max}, and minimum area, A_{min}, of the surfactants are calculated according to Rosen and Hua [20] and the data are summarized in Table 3. The values of Π_{CMC} at 25, 40, and 55°C show that the most efficient surfactant is C_{16} M and C_{10} P, which give the greater lowering in surface tension at critical micelle concentration. The maximum surface excess (Γ_{max}) values for monomeric surfactants are higher than the corresponding values for the polymeric surfactants (c.f. Table 1). This may be attributed to a higher degree of

TABLE 2 Assignment of Bands in the IR Spectra of the Prepared Monomeric and Polymeric Surfactants

Wave number (cm^{-1})						
Surfactant name						
C10M	C10P	C12M	C12P	C16M	C16P	Assignments
476^{m}	500^{b}	462^{w}	504^{b}	463^{w}	546^{b}	Stretching vibration of Cr–O, NH bending deformation in primary amine, and torsional oscillation of NH_3^+
620^{m}	—	683^{m}	—	687^{m}	—	CH out of plane deformation for 1,3- and 1,4-disubstituted benzene ring
—	—	—	—	722^{m}	749^{w}	
750^{m}	750^{w}	766^{m}	750^{w}	756^{m}	808^{s}	
869^{m}	894^{w}	843^{w}	844^{b}	845^{m}	883^{s}	
—	—	—	848^{w}	—	—	CH out of plane deformation for 1,4-disubstituted benzene ring
—	989^{w}	—	—	—	1003^{w}	
—	1057^{m}	1039^{w}	—	1046^{w}	1041^{m}	CH deformation in benzene ring or C–N stretching vibration or C–O stretching vibration
1121^{w}	1126^{m}	1057^{w}	1088^{b}	1087^{w}	1096^{s}	
1161^{w}	—	1171^{b}	1169^{sh}	1165^{m}	1125^{w}	
—	—	—	—	1194^{s}	1179^{s}	
1251^{w}	1281^{s}	1258^{m}	1285^{sh}	1279^{m}	1281^{sh}	Stretching vibration of C–O group or bending deformation of CH_2

1399^{w}	—	1304^{w}	—	1341^{m}	1300^{w}	Sym. stretching for CH_3 group
—	1403^{s}	1337^{w}	1402^{m}	1391^{m}	1403^{m}	
1461^{w}	1444^{w}	1465^{m}	1475^{m}	1469^{s}	1488^{s}	Scissoring vibration of CH_2 group.
1500^{s}	1622^{s}	1611^{s}	1622^{s}	1505^{m}	1519^{s}	Sym. stretching vibration of C=C in benzene or C=N in quinoid unit
—	—	—	—	1640^{s}	1621^{s}	
2334^{w}	2337^{w}	2334^{w}	2341^{w}	2337^{w}	2341^{w}	Combination and overtone band for C−N or combination for protonated primary amine or symmetric stretching vibration CH aliphatic
2368^{w}	2369^{w}	2369^{m}	2373^{w}	2369^{m}	2370^{m}	
2798^{w}	2781^{sh}	2733^{w}	2728^{sh}	2687^{w}	2650^{sh}	Sym. stretching for CH in CH_3 group
2854^{w}	2841^{w}	2855^{s}	2838^{w}	2851^{s}	2830^{w}	Sym. and asym. stretching for CH aromatic
2926^{m}	2920^{w}	2923^{s}	2910^{w}	2920^{s}	2921^{w}	
3091^{w}	3085^{sh}	3085^{sh}	3075^{sh}	3080^{sh}	3070^{sh}	Symmetric stretching vibration of CH aromatic
3237^{m}	—	3212^{sh}	—	3211^{sh}	—	Sym. stretching for NH in NH_2 group
3415^{s}	—	3406^{b}	—	3379^{b}	—	Asym. stretching for NH in NH_2 group
—	3389^{b}	—	3414^{b}	—	3337^{b}	Sym. stretching for NH group and strong bonded hydroxyl group

w = weak band, m = medium band, sh = shoulder band, b = broad band, and s = strong band.

SCHEME 2

packing for the monomeric molecules than that of the polymeric one. The minimum area (A_{min}) values increase with raising the surfactant solution temperature, which could be due to the increase of thermal kinetic motion [21]. Furthermore, minimum are (A_{min}) values of polymeric surfactants are higher than for the corresponding monomers, which can be ascribed to the increase in the radius of gyration of the molecule as a result of increasing molecular mass.

Thermodynamic Parameters

Some thermodynamic parameters such as the standard free energies (ΔG^0_{mic}), enthalpies (ΔH^0_{mic}), and entropies (ΔS^0_{mic}) of micellization and standard free energies (ΔG^0_{ad}), enthalpies (ΔH^0_{ad}) and entropies (ΔS^0_{ad}) of adsorption for the synthesized surfactants are tabulated in Table 4. These parameters were calculated as mentioned by Rosen and Hua [20]. The standard free energy of micellization for solutions of 10^{-2}M or less containing a completely dissociated 1:1 ionic surfactant (A^+B^-) in the absence of any other solutes is calculated using the following equation [22]: [$\Delta G_{mic} = 2RT \ln CMC$]. The data in Table 4 indicate that the micellization process is spontaneous [$\Delta G_{mic} < 0$]. It is also noticed that ΔG^0_{mic}-values increase as the alkyl chain length increases, which favors the micellization. Analyzing the ΔG^0_{mic} values in Table 4 reveals that the standard free energy of micellization increases with increasing temperature from 25–55°C. It is also noticed that the ΔG^0_{mic} have greater values in case of polymers than in the corresponding monomers in all investigated surfactants, indicating that the polymeric surfactants favor micellization. The positive values of ΔS^0_{mic} are due to the increased freedom of the hydrophobic part in the non-polar interior of the micelles compared to the aqueous bulk of the solution.

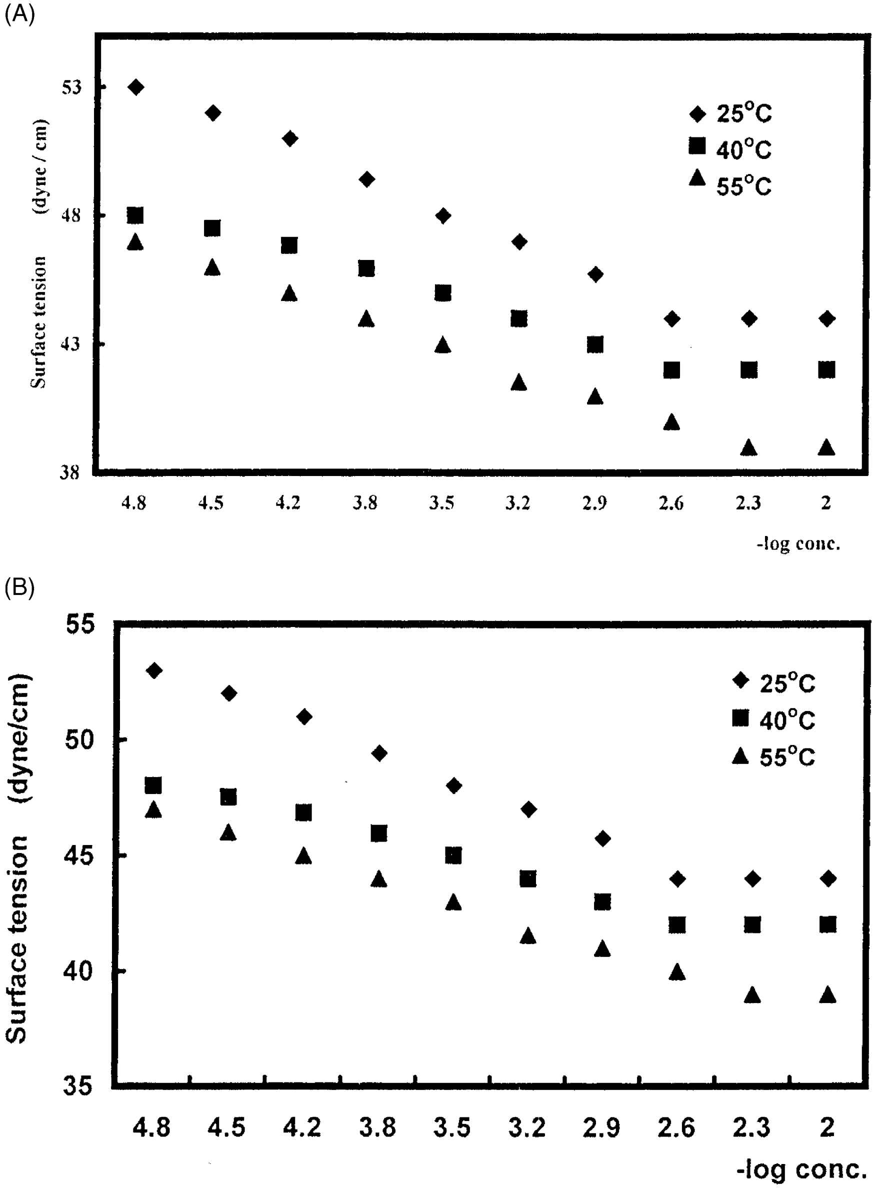


FIGURE 1 Variation of surface tension vs. −log concentration for (A) C10M and (B) C10P at 25, 40, and 55°C.

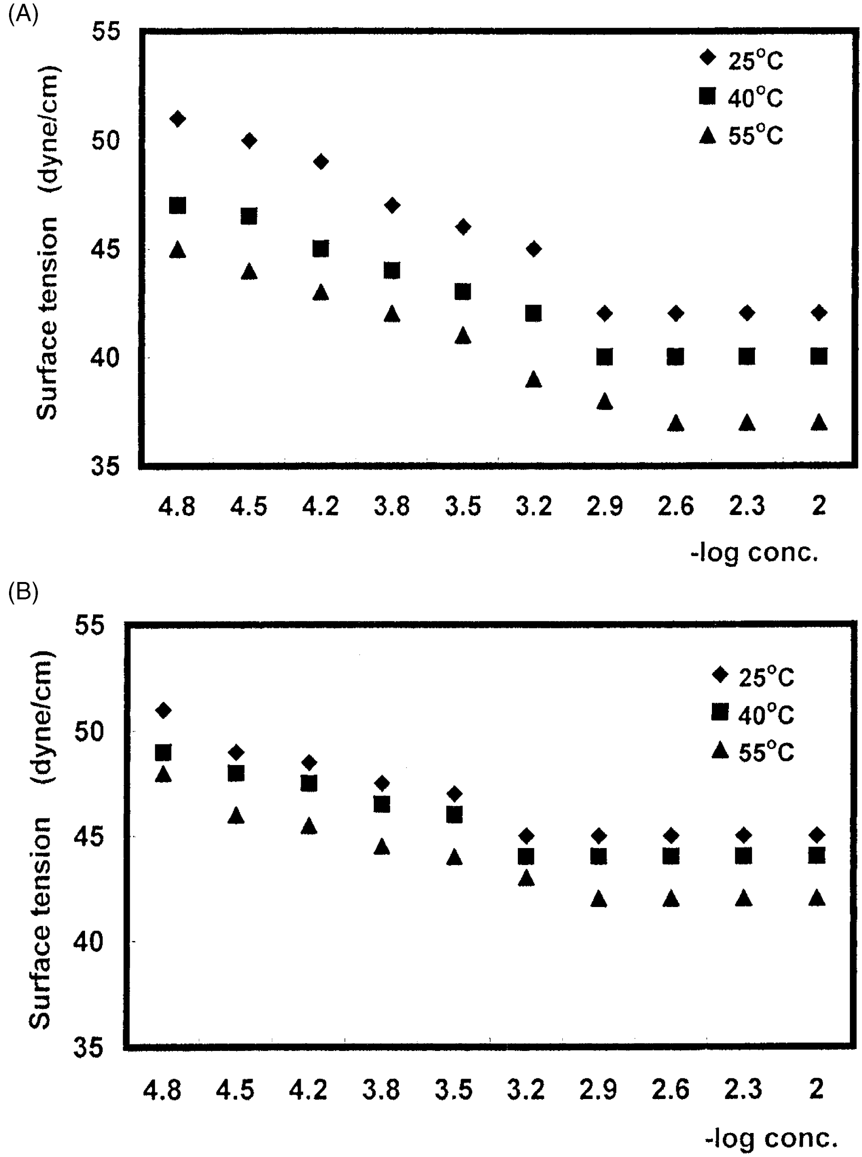


FIGURE 2 Variation of surface tension vs. −log concentration for (A) C12M and (B) C12P at 25, 40, and 55°C.

The values of ΔH_{mic} in Table 4 are a significant factor in the process of micellization. ΔH_{mic} values for the synthesized surfactants are negative due to exothermic solvation associated with micellization.

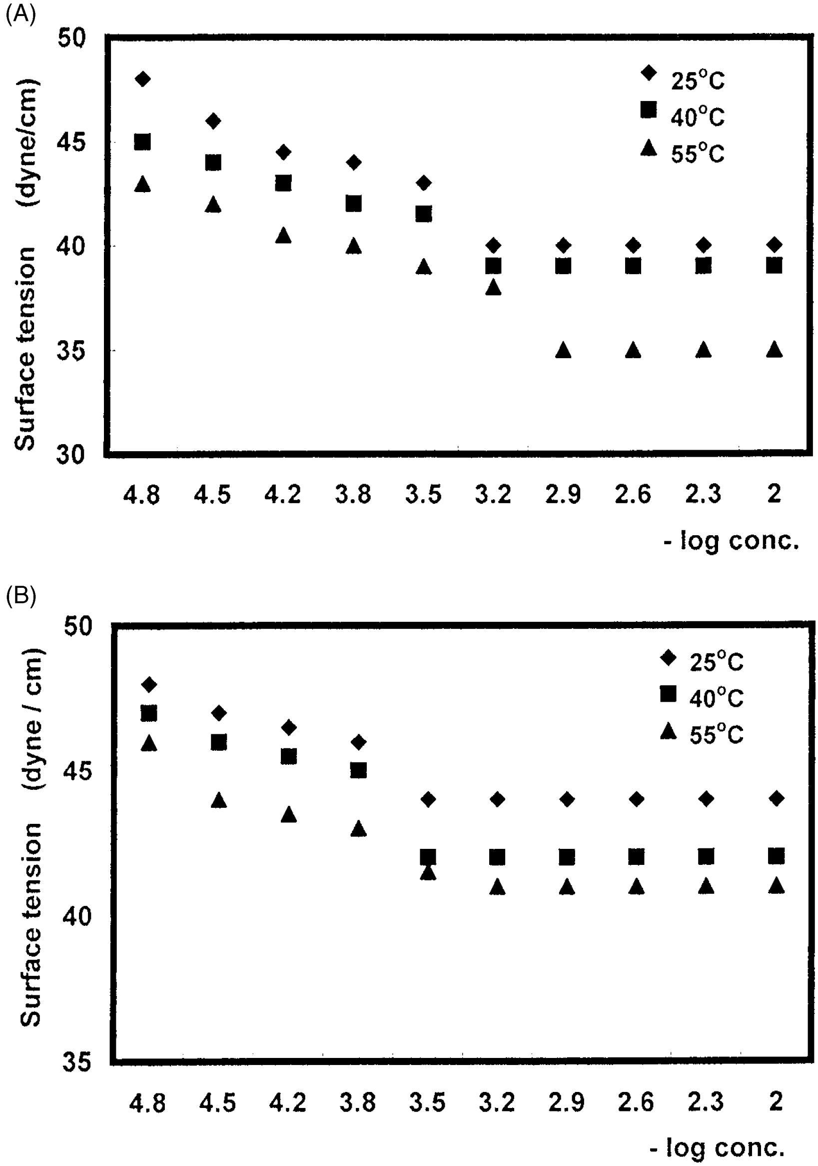


FIGURE 3 Variation of surface tension vs. −log concentration for (A) C16M and (B) C10P at 25, 40, and 55°C.

The obtained behavior is in good agreement with that found by Azzam and Gad [17]. The enthalpies of polymeric surfactants are slightly more negative than those of the monomeric surfactants.

TABLE 3 Critical Micelle Concentration (CMC), Effectiveness, (Π_{CMC}), Maximum Surface Excess (Γ_{max}) and Minimum Area (A_{min}) of Both Monomeric and Polymeric Surfactants (C10, C12, and C16)

Surfactant		T (°C)	CMC × 10^4 (mol/l)	Π_{CMC} (dyne cm^{-1})	$\Gamma_{max} \times 10^{11}$ (mol.cm^{-2})	^{A}min nm^2
C10	C10M	25	25.0	28.6	3.54	0.466
	C10P		13.0	34.6	2.51	0.657
	C10M	40	27.0	26.0	3.48	0.474
	C10P		15.0	34.0	2.39	0.690
	C10M	55	50.0	23.0	3.26	0.506
	C10P		25.0	29.0	2.28	0.724
C12	C12M	25	13.0	30.6	2.51	0.657
	C12P		6.30	27.6	1.88	0.877
	C12M	40	15.0	28.0	2.39	0.690
	C12P		6.50	24.0	1.79	0.922
	C12M	55	25.0	25.0	2.28	0.724
	C12P		1.30	20.0	1.71	0.965
C16	C16M	25	6.00	32.6	1.88	0.803
	C16P		3.10	28.8	1.25	1.320
	C16M	40	8.00	29.0	1.79	0.922
	C16P		3.30	26.0	1.19	1.386
	C16M	55	13.0	27.0	1.71	0.965
	C16P		6.30	21.0	1.14	1.417

The ΔG^0_{ad}-values are negative for all the investigated surfactants but have more negative values than ΔG^0_{mic}, indicating that the adsorption at air/solution interface is associated with a decrease in the free energy of the system (c.f. Table 4). The calculated values of entropies show that ΔS^0_{ad} values are all positive and greater than the values of ΔS^0_{mic} for all surfactants under investigation. This is due to the greater freedom of motion for the hydrophobic group at the planar air/solution interface than that in the relatively cramped interior beneath the convex surface of the micelle. The results in Table 4 show that ΔH_{mic} values $> \Delta H^0_{ad}$ values for C16M and C10P, and ΔH_{mic} values $< \Delta H^0_{ad}$ values for the other surfactants C10M, C12M, C12P, and C16P. The ΔH_{mic} values are greater than the ΔH^0_{ad} values, indicating a greater dehydration of the hydrophilic groups is required for micellization that for adsorption at air/solusolution interface. But, the lower values of ΔH_{mic} than those for ΔH^0_{ad} indicate a smaller dehydration for the hydrophilic groups in the molecule, implying that the space available for the hydrophilic groups at the surface of the micelles is less restricted than at the planar air/solution interface.

TABLE 4 Thermodynamic Parameters of Micellization and Adsorption for the Prepared Surfactants (C10, C12, and C16)

Surfactants		T^0_C	ΔG^0_{mic} $(KJ \cdot mol^{-1})$	ΔS^0_{mic} $(KJ \cdot mol^{-1} \cdot K^{-1})$	ΔH^0_{mic} $(KJ \cdot mol^{-1})$	ΔG^0_{ad} $(KJ \cdot mol^{-1})$	ΔS^0_{ad} $(KJ \cdot mol^{-1} \cdot K^{-1})$	ΔH^0_{ad} $(KJ \cdot mol^{-1})$
C10	C10M	25	−29.66	—	—	−37.69	—	—
	C10P		−32.89	—	—	−46.58	—	—
	C10M	40	−30.75	—	—	−38.17	—	—
	C10P		−33.80	—	—	−47.93	—	—
	C10M	55	−28.86	0.027	−20.00	−35.87	0.060	−16.19
	C10P		−32.64	0.008	−30.02	−45.29	0.043	−31.19
C12	C12M	25	−32.89	—	—	−44.99	—	—
	C12P		−36.48	—	—	−51.06	—	—
	C12M	40	−33.80	—	—	−45.44	—	—
	C12P		−38.51	—	—	−51.48	—	—
	C12M	55	−32.64	0.008	−30.07	−43.54	0.048	−27.80
	C12P		−36.20	0.009	−33.25	−47.82	0.108	−12.40
C16	C16M	25	−36.72	—	—	−52.49	—	—
	C16P		−39.99	—	—	−62.89	—	—
	C16M	40	−37.07	—	—	−53.17	—	—
	C16P		−41.68	—	—	−63.38	—	—
	C16M	55	−36.20	0.017	−30.62	−51.89	0.02	−45.33
	C16P		−40.15	0.005	−38.51	−58.45	0.148	−9.91

TABLE 5 Specific Conductance of the Synthesized Monomeric and Polymeric Surfactants at 25 to 55°C and 1% Concentration

	Specific conductance (ms)		
Surfactants	25°C	40°C	55°C
C10M	37.8	47.5	49.9
C10P	121.6	147.6	164.5
C12M	39.6	49.6	52.8
C12P	198	218	230
C16M	41.6	51.6	53.6
C16P	211.4	222.6	235.7

Specific Conductance Measurements

The specific conductance of the synthesized monomeric and polymeric surfactants of 1% concentration was measured at different temperatures (25, 40, and 55°C). The data are summarized in Table 5. From it, it is clear that on one hand the specific conductance increases with increasing chain length of the substituted alkyl groups in both cases of monomeric and polymeric surfactants. This may be due to the injection of the alkyl group electrons into the aromatic ring, aiding the conjugation present in the structure. Also, it is noticed that the specific conductance has higher values in case of polymeric surfactants, which could be attributed to the conjugation present in the polymeric structure and doping of HCl molecules in the polymeric unit (c.f. Scheme 1). On the other hand, the specific conductance increases with raising the solution temperature.

CONCLUSIONS

The micellization and adsorption processes are affected by the change in the alkyl chain length in the hydrophobic part.

On the basis of the calculated surface parameters, it is clear that the polymeric surfactants possess lower micellization and higher adsorption affinities than the monomeric surfactants.

The thermodynamic parameters indicate that the affinity of polymeric surfactants for micellization and adsorption is more than in the case of monomeric surfactants.

In all the investigated surfactants, the specific conductance values increase as the alkyl chain length increases whereas the specific conductance values are greater for polymeric surfactants that for the corresponding monomeric ones.

REFERENCES

[1] Lin, S. Y., *Text. Chem. Colorist* **13**, 261 (1981).

[2] Schmolka, I. R., *J. Am. Oil Chem. Soc.* **54**, 110 (1977).

[3] Calderara, F., Hruska, Z., Hurtrez, G., Nugay, T., Riess, G., and Winnik, M. A., *Makromol Chem.* **194**, 1411 (1993).

[4] Jönsson, B., Lindman, B., Holmberg, K., and Kronberg, B. (1998). "Surfactants and polymers." In *Aqueous Solution*, John Wiley and Sons, New York, pp. 201.

[5] Sauer, B. B. and Dee, G. T., *J. Colloid Interface Sci.* **162**, 25 (1994).

[6] Kumar, S. K., Vacatello, H., and Yoon, D. Y., *Macromolecules* **23**, 2189 (1990).

[7] Theodorou, D. N., *Macromolecules* **21**, 1400 (1988).

[8] Chen, K. M. and Liu, H. J., *J. Appl. Polym. Sci.* **34**, 1879 (1987).

[9] Tuzar, Z. and Kratochvil, P., *Adv. Colloid Interface Sci.* **6**, 201 (1976).

[10] Barakat, Y., Gendy, T. S., Mohamed, A. I., and Youssef, A. M., *British Polymer Journal* **21**, 383 (1989).

[11] Barakat, Y., Gendy, T. S., Basily, I. K., and Mohamed, A. I., *British Polymer Journal* **21**, 451 (1989).

[12] Barakat, Y., Basily, I. K., Mohamed, A. I., and Youssef, A. M., *British Polymer Journal* **21**, 459 (1989).

[13] Youssef, A. M., Gendy, T. S., Mohamed, A. I., and Barakat, Y., *Egypt. J. Chem.* **33**(2), 115 (1990).

[14] Youssef, A. M., Gendy, T. S., Mohamed, A. I., and Barakat, Y., *British Polymer Journal* **22**, 339 (1990).

[15] Gendy, T. S. and Barakat, Y., *Polym. Int.* **33**, 247 (1994).

[16] Atta, A. M., *Polym. Int.* **48**, 571 (1999).

[17] Azzam, E. M. S. and Gad, E. A. M., *Mans. Sci. Bull. (A Chem.)* **28**(1), 307 (2002).

[18] Sayyah, S. M., Bahgat, A. A., and Abd El Salam, H. M., *Int. J. Polym. Mater.* **51**, 291 (2002).

[19] Gad, E. A. M., El-Sukkary, M. M. A., and Azzam, E. M. S., *Monatschrifte für chemie (Chemical Monthly)*, **128**, 1085 (1997).

[20] Rosen, M. J. and Hua, X. Y., *J. Colloid and Interfacial Sci.* **86**(1), (1982).

[21] Rosen, M., Dananayake, M., and Cohen, A., *Colloids Surf.* **5**, 159 (1983).

[22] Rosen, M. J. (1978). *"Surfactants and Interfacial Phenomena"*. John Wiley and Sons, New York, p. 61.