




Research Article

An insight into thermodynamic and association behaviours of cocamidopropyl betaine (CAPB) surfactant in water and water–alcohol mixed media

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Abstract

This article presents new experimental data about the conductivity and surface of Cocamidopropyl Betaine (CAPB) surfactant in pure H₂O and organic–H₂O mixed solvent (methanol, MeOH; ethanol, EtOH and glycerol, GlyOH) media containing various mole fractions of alcohols over the temperature range 298.15 to 313.15 K, in steps of 5 K using conductometric and surface tension measurements. The experimental data for conductivity and surface tension have been used in order to determine the critical micelle concentration (CMC). It has been observed that the CMC increases with increasing temperature and proportion of alcohol. Moreover, the association constant (K_a) of CAPB was also determined, depending on the conductivity data, using the Shedlowsky equation. The study showed that, as the temperature and alcohol ratio increased, the association constant of CAPB decreased. In addition, it was found that the CMC increased with MeOH > EtOH > GlyOH and the association behaviour was observed to be spontaneous. The thermodynamics behaviour of (CAPB) surfactant have been thoroughly assessed from the temperature dependence of the micellization and association constants. In all media studied, densities and refractive indices of CAPB were also measured under atmospheric pressure, in the solvents used at T = (298.15 K). The molal volume was estimated based on the density data and some additionally parameters such as molar refraction and the polarizability were also estimated and discussed depending on the refractive index values. These parameters have been utilized to comprehend the association and solvation behaviour of the CAPB surfactant.

Keywords CAPB · Conductivity · CMC · Association constant · Molar volume · Refractive index

1 Introduction

Over the last few year surfactants have been utilized in several application, such as chemical industry, environmental protection and pharmaceuticals, as well as other applications such as in paints, cosmetics, food processing, detergents, etc. This is due to their attractive

properties such their strong dipole or ion–dipole interactions with water, with surfactant molecules considered for applications in systems of ionic surfactants in mixed solvents. Nevertheless, the hydrogen bonding and dispersion interaction between the H₂O molecules has a tendency to push the alkyl chain out of the water and, therefore, these chains are held to be hydrophobic,

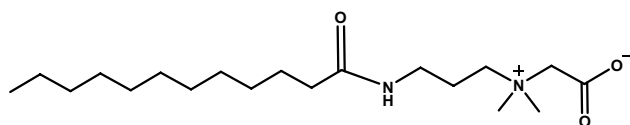
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but at low concentrations most of their features are comparable to those of a classic electrolyte. Notably, surfactant molecules have one important exception their surface tension which rapidly decreases with rising surfactant concentration. This is notwithstanding, all the properties (bulk and interfacial) appear to unexpectedly altered at a particular concentration, which suggest that at and above this specific concentration, molecules or ions in solution associate to form larger units known as micelles. The critical micelle concentration (CMC) is the concentration at which the association phenomenon takes place. The distinguishing CMC for surfactant can be observed at a particular temperature and therefore, below the CMC, most of the surfactant is in the monomeric state whereas above it any additional surfactants enters the micellar state [1]. In the context of the nature of the surfactant, self-association depends on the chemical and physical parameters of the surfactant, as has been reported in the literature. Several techniques have been utilized for CMC determination which includes gel filtration spectrophotometrically, ion activity, counter ion magnetic resonance, light scattering state, solubility, viscosity, surface tension and conductivity state [2–6]. Conductivity measurements have been used by various authors to study the micellization of SDS surfactant [7–14] and ionic liquids [15–19]. The molar volume of other substances in different solutions [20–24] have been determined as depending on density measurements. Based on refractive index measurements, the solvation of various substances in solution has been also reported [25–27]. Even although several studies have been published for the association and solvation behavior of surfactant molecules in solution, quantitative results are quite little. The present work aims to study the solvation of Cocamidopropyl Betaine (CAPB, Scheme 1) utilizing conductivity, density, surface tension and refractive index measurements in pure H₂O and in organic–H₂O solvent mixes over the temperature range 298.15 to 313.15 K, (in steps of 5 K). The conductivity and surface tension measurements utilized should allow the CMC to be identified and the association constants of CAPB in the various media used herein examined. Based on the densities technique, the molar volumes were determined while the refractive index technique



Scheme 1 Cocamidopropyl betaine (CAPB)

has been utilized to estimate the molar refraction and the polarizability of CAPB.

2 Experimental

2.1 Chemicals and solutions

Cocamidopropyl Betaine (CAPB) (30.0%) was obtained from sigma Aldrich. Ethanol (EtOH, 99.8%), Methanol (MeOH, 99.9%) and Glycerol (GlyOH \geq 99.0%) as solvents, were obtained from Sigma Aldrich. All solutions were prepared in clean volumetric flasks using double distilled H₂O so as to have conductivities between 0.05 and 0.5 $\mu\text{S cm}^{-1}$. Stock solution (0.1 mol l⁻¹) of the CAPB surfactant was prepared. The remaining proportion of the CAPB solution (70%) was water, the volume of which was taken into account when preparing the stock solution.

2.2 Apparatus and procedure

All conductivity measurements were taken with a precision conductivity meter utilizing a Jenway Conductivity Bridge of certainty $\pm 0.025 \mu\text{S cm}^{-1}$, which had been calibrated using different standard KCl solutions at 298.15 K [28]. The conductivity was measured as a function of the CAPB concentration, and where the concentration of the CAPB solution was incrementally increased by the addition of 0.25 or 0.5 ml of the earlier prepared surfactant stock solution (0.1 and 0.01 mol l⁻¹) to 40.0 ml of pure organic solvent which was placed in a double jacket glass cell after which addition of the surfactant was began. The desired temperature inside the cell was controlled using an ultrathermostate of type MLW 3230 (Germany). With each addition, the liquid was stirred to achieve homogeneous mixing and then submitted for measurement using the conductivity meter. The uncertainty of the conductivity measurement was predestined $\pm 0.025 \mu\text{S cm}^{-1}$. The specific conductance measurements were carried out in triplicate and the average of these measurements utilized to compute the observed results, and thus used in subsequent discussion. The surface tension was measured by means of a digital tensiometer K9 (ring method) with an error of ± 0.10 dyne/cm. The density data for the studied solutions were determined using a Mettler Toledo portable digital density meter (Densito2Go) ($\pm 0.0001 \text{ g/cm}^3$). Both the density meter and tensiometer were calibrated by triply measuring the density of double-distilled water and the surface tension in triplicate by passing dry air, and their results were in good agreement with published reports. Using a Mettler Toledo portable digital refractometer (Refracto 30GS) (± 0.0001), the refractive index has

Scheme 2 CMC formation

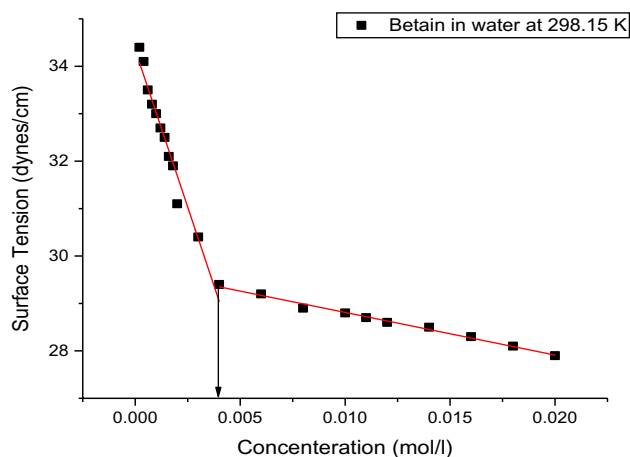
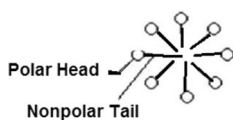


Fig. 1 Surface tension as a function of concentration for CAPB in pure H₂O at 298.15 K

been measured. The refractometer was calibrated against standard samples supplied with the instrument.

3 Results and discussion

3.1 Dependence of conductivity on concentration

In pure H₂O and in organic–aqueous mixed solvents; MeOH, EtOH, and GlyOH–H₂O containing a various mole fractions of organic solvents the conductivity of the CAPB surfactant was determined over the temperature range 298.15 to 313.15 K in each instance, (in steps of 5 K). The relation between the measured conductivity versus CAPB concentration was found to determine the CMC of CAPB (micellization as a result of the surfactant molecules association, Scheme 2) in various media at T=(298.15 to 313.15 K), as presented in Figs. S1–S10 (Supplementary material).

To confirm the CMC obtained from the conductometric measurement, the CMC for (CAPB) was also determined at ambient temperature in H₂O, using the surface tension measurements as presented in Fig. 1.

From Fig. 1 it can be observed that, the surface tension decrease with increase in concentration of CAPB solutions until (*ca.* 0.004 mol l⁻¹), above this concentration, there was almost no further variation in the selected compound Fig. 1. The micellization process of CAPB was rapid this may be those concentrations are greater than

Table 1 The critical micelle concentrations (CMC, mol l⁻¹) for CAPB at different temperatures in various solvent mixes

Solvent mixtures	Alcohol mole fraction	T/K			
		298.15	303.15	308.15	313.15
EtOH–H ₂ O	0.0000	0.0031 (0.0029)* 0.0028	0.0036	0.0049	0.0059
	0.0331	0.0024	0.0035	0.0049	0.0059
	0.0715	0.0036	0.0048	0.0059	0.0069
	0.1166	0.0048	0.0059	0.0070	0.0080
MeOH–H ₂ O	0.0000	0.0031	0.0036	0.0049	0.0059
	0.0470	0.0025	0.0037	0.0049	0.0060
	0.0999	0.0036	0.0049	0.0059	0.0070
	0.1598	0.0049	0.0061	0.0072	0.0081
GlyOH–H ₂ O	0.0000	0.0031	0.0036	0.0049	0.0059
	0.0267	0.0019	0.0025	0.0038	0.0049
	0.0582	0.0026	0.0038	0.0048	0.0059
	0.0958	0.0040	0.0051	0.0061	0.0070

*The values in parentheses are from Dai et al. [29] and the values in bold and italics are from surface tension measurements. Standard uncertainties (u) of CMC is = 0.0002 mol l⁻¹

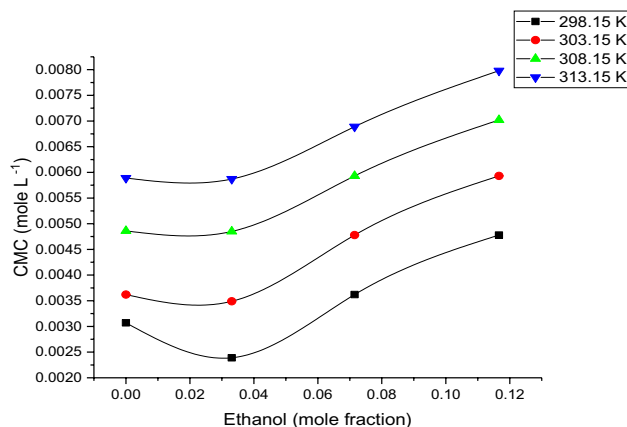


Fig. 2 CMC for CAPB as a function of mole fraction of ethanol at various temperatures

the surfactant CMC. The CMC values of (CAPB) in each solvent are reported in Table 1.

The CMC of CAPB was observed to increase with increasing temperature and ratio of alcohol (see Fig. 2 as an example). In addition, the CMC of CAPB in different solvents increased in the order MeOH–H₂O > EtOH–H₂O > GlyOH–H₂O. This may be a consequence of the higher viscosity in the converse order of these mixture solvents.

The higher the viscosity, the lower the solvation of CAPB leading to reduced micellization and a lower CMC.

The CMC of CAPB in water at 298 K was in good agreement with the literature value [29]. Based on Eq. (1) below, both the degree of ionization in the micelle (α) and the degree of counter ion binding, $\beta = (1 - \alpha)$ of CAPB were suggested: [5]

$$\alpha = S_2/S_1 \tag{1}$$

S_2/S_1 can be defined as the ratio of the slopes of above and below micelle regions, where the slopes were estimated based on the linear relationship between conductivity and concentration. The calculated data of α and β are presented in Table 2. The values of the thermodynamic parameters for get the micellization process were calculated using the following expressions:

$$\Delta G_{mic} = (2 - \alpha)RT \ln [CMC] \tag{2}$$

$$\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic} \tag{3}$$

where α , T and R can be the degree of ionization in the micelle, absolute temperature, and the universal gas constant, respectively. The values of enthalpy and entropy for the micellization process were computed by the slope of the linear plot of ΔG_{mic} vs. T, which gives the value of $-\Delta S_{mic}$, while the intercept gives ΔH_{mic} as per Table 2. Perusal of Table 2 discloses that the observed ΔG_{mic} and ΔS_{mic} have negative values in all the solvents media studied, which suggests that the process of micellization is spontaneous process, this indicates that the spontaneous process increased with the increasing mole fraction of alcohol, where the exothermic nature of the micellization process can be observed from the negative values

of ΔH_{mic} . The $E_{a_{mic}}$ of the micellization process could be treated using Eq. (4), depending on the relation between conductance of ion, ion mobility and temperature degree.

$$[CMC] = A e^{-E_{a_{mic}}/RT} \tag{4}$$

where A is defined as an Arrhenius constant, $E_{a(mic)}$ is the activation energy of the micellization process for CAPB which can be determined by the slope of the linear plot of $\ln[CMC]$ vs. $(1/T)$, where $(-E_{a_{mic}}/R)$ is the slope and $(\ln A)$ is the intercept, the results of which are also included in Table 2.

3.2 Association constant and Walden product

Using the conductivity values before the CMC, equivalent conductance (Λ) for CAPB in each studied solvent mixture over the temperature range 298.15 to 313.15 K were estimated according to Eq. (5):

$$\Lambda = 10^3 k/c \tag{5}$$

The limiting equivalent conductance, Λ_o of the (CAPB) was determined from the intercept of the graphical relation of Λ versus $C^{1/2}$ according to the Onsager relation [30].

$$\Lambda = \Lambda_o - BC^{1/2} \tag{6}$$

Using the Shedlowsky extrapolation equation [31], the conductivity data were analysed to obtain the association constant (K_a) (which provides information of the interaction of the charged surfactant ions with their counter ions) of CAPB, as achieved via Eq. (7):

Table 2 The degree of ionization (α), the degree of counter ion binding (β) and the thermodynamic parameters values (ΔG_{mic} , kJ mol⁻¹; ΔH_{mic} , kJ mol⁻¹; ΔS_{mic} , kJ mol⁻¹ and $E_{a_{mic}}$, kJ mol⁻¹) for the micellization process of CAPB in various solvent mixes at various temperatures

s.m.	x	α				$\beta = (1 - \alpha)$				$-\Delta G_{mic}$				$-\Delta H_{mic}$	$-\Delta S_{mic}$	$E_{a_{mic}}$
		T (K ± 15)														
		298	303	308	313	298	303	308	313	298	303	308	313			
EtOH-H ₂ O	0.000	0.880	0.856	0.846	0.826	0.120	0.144	0.154	0.174	16.06	16.20	15.75	15.69	25.50	0.031	34.90
	0.033	0.844	0.871	0.841	0.789	0.156	0.129	0.159	0.211	17.30	16.10	15.82	16.20	61.19	0.015	47.05
	0.071	0.879	0.875	0.850	0.829	0.121	0.125	0.150	0.171	15.63	15.16	15.11	15.17	30.96	0.052	33.38
	0.116	0.695	0.882	0.827	0.764	0.305	0.118	0.173	0.236	17.29	14.45	14.90	15.55	56.83	0.134	26.53
MeOH-H ₂ O	0.000	0.880	0.856	0.846	0.826	0.120	0.144	0.154	0.174	16.06	16.20	15.75	15.69	25.50	0.031	34.90
	0.047	0.887	0.863	0.850	0.838	0.113	0.137	0.150	0.162	16.58	16.06	15.66	15.47	38.66	0.074	46.09
	0.099	0.818	0.867	0.836	0.819	0.182	0.133	0.164	0.181	16.53	15.22	15.29	15.28	43.08	0.089	34.58
	0.159	0.473	0.838	0.806	0.780	0.527	0.162	0.194	0.220	20.12	14.92	15.08	15.32	122.99	0.346	25.52
GlyOH-H ₂ O	0.000	0.880	0.856	0.846	0.826	0.120	0.144	0.154	0.174	16.06	16.20	15.75	15.69	25.50	0.031	34.90
	0.026	0.829	0.855	0.833	0.784	0.171	0.145	0.167	0.216	18.24	17.34	16.68	16.82	47.38	0.099	51.93
	0.058	0.816	0.839	0.829	0.781	0.184	0.161	0.171	0.219	17.46	16.29	16.03	16.27	60.18	0.144	41.92
	0.095	0.701	0.737	0.771	0.721	0.299	0.263	0.229	0.279	17.76	16.79	16.05	16.52	43.98	0.089	28.63

s.m. Solvent mixtures, x Solvent mole fraction. Standard uncertainties (u) of α and β are = 0.002

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{K_a C \Lambda S(z) \gamma_{\pm}^2}{\Lambda_o^2} \tag{7}$$

where, as two Zwitter ions are interacted or associated, the association may be due to the mutual attraction between the negative carboxylic and the positive amino groups from both Zwitter ions. The Shedlowsky function, $S(z)$ can be calculated as follows:

$$Z = A \frac{\sqrt{C\Lambda}}{\Lambda_o^{3/2}} \tag{8}$$

$$S(z) = \left\{ \frac{Z}{2} + \sqrt{1 + (Z/2)^2} \right\}^2 \tag{9}$$

In the above equations, the Onsager coefficient A and can be expressed as $A = 8.2 \cdot 10^5 \Lambda_o / (\epsilon T)^{3/2} + (82/\eta_o) (\epsilon T)^{1/2}$, where η_o , ϵ and T are the viscosity, dielectric constant of the solvent, and temperature, respectively.

Utilizing the Debye–Hückel limiting law as modified by Robinson and Stokes, the mean activity coefficient, (γ_{\pm}) has been assigned by Eq. (11). Using the data of (Λ), $S(z)$ and (Λ_o), the value of the degree of CAPB ionization (α) was calculated using the following equation:

$$\alpha = \Lambda S(z) / \Lambda_o \tag{10}$$

The mean activity coefficients (γ_{\pm}) were evaluated by means of (α) and (ϵ) values according to the equation:

$$\log \gamma_{\pm} = - (Z_+ Z_- A C^{1/2}) / (1 - Br C^{1/2}) \tag{11}$$

where (Z_- , Z_+) and (r) are the charges of ions in solution and the solvated radius, respectively. A and B are the Debye–Hückel constants which can be expressed as $A = 1.824 \times 10^6 / (\epsilon T)^{3/2}$; $B = 50.29 \times 10^8 (\epsilon T)^{-1/2}$.

The ionization degree before CMC (calculated according to Eq. 10) is presented in Table 3. The ionization degree in micelle (calculated according to Eq. 1) is different from that before CMC (calculated according to Eq. 10). This can be noted from the values of the ionization degree before and after micellization process (Tables 2, 3). The values of the ionization degree before the CMC (in the range 0.9600–0.9970) are higher than that after CMC (in the range 0.4700–0.8070). This indicates that ionization after CMC is lower than that before CMC as a result of the steric effect in the micelle which hindered the ionization process.

The calculated values of the triple ion association constant (K_3) were obtained using the expression [32].

$$\frac{\Lambda \sqrt{C}}{\sqrt{\left(1 - \frac{\Lambda}{\Lambda_o}\right)}} = \frac{\Lambda_o}{\sqrt{K_a}} + \frac{C \lambda_3^\circ}{K_3 \sqrt{K_a}} \left(1 - \frac{\Lambda}{\Lambda_o}\right) \tag{12}$$

Table 3 The degree of ionization (α) before the micellization process of CAPB in various solvent mixes at various temperatures (calculated according to Eq. 10)

s.m.	x	T (K ± 15)			
		298	303	308	313
EtOH–H ₂ O	0.000	0.981	0.987	0.992	0.998
	0.033	0.962	0.971	0.977	0.981
	0.071	0.968	0.974	0.983	0.985
	0.116	0.977	0.982	0.986	0.987
MeOH–H ₂ O	0.000	0.981	0.987	0.992	0.998
	0.047	0.985	0.990	0.993	0.994
	0.099	0.988	0.991	0.995	0.997
	0.159	0.989	0.992	0.996	0.998
GlyOH–H ₂ O	0.000	0.981	0.987	0.992	0.998
	0.026	0.958	0.969	0.971	0.981
	0.058	0.961	0.971	0.977	0.985
	0.095	0.964	0.977	0.979	0.987

s.m. Solvent mixtures, x Solvent mole fraction. Standard uncertainties (u) of α is = 0.002

Estimation of the (K_3) values was based mostly on Fuoss Eq. (12) and by utilizing Walden approximation ($\Lambda_o = 3\lambda_o$), from which it was observed that the triple ion association constant takes a negative and extremely small value (-6.0×10^{-5} to -2.5×10^{-5}), suggesting that the triple ion association will not take place. The values of ΔG_a° for the association process have been calculated utilizing the following expressions:

$$\Delta G_a^\circ = -2.303 RT \log K_a \tag{13}$$

where T and R are the absolute temperature and universal gas constant, respectively. The ΔH_a° and ΔS_a° values for the association process of CAPB were identified, as previously estimated using Eq. (3). The conductance of an ion depends on its mobility, so it is quite sensible to treat the rate process by taking into account the alteration in T according to the following classical expression,

$$\Lambda_o = A e^{-\frac{E_a}{RT}} \tag{14}$$

According to Eq. (14) the activation energy of the transfer processes (E_a) has been calculated by plotting $\ln \Lambda_o$ vs. $1/T$, where the (E_a) value is the slope of this graph [33]. The obtained association constant and various thermodynamic parameters for the association process of the CAPB surfactant are reported in Table 4, which show that K_a decreases with increasing temperature of the media, as shown in Table 4 and Fig. 3. It should be noted that, the association constant of the CAPB surfactant first increases then decreases which increasing mole fraction of alcohol. The increase in the K_a values may be due to an increase in

Table 4 The association constant, (K_a , mol⁻¹) and the thermodynamic association (ΔG_a° , kJ mol⁻¹; ΔH_a° , kJ mol⁻¹; ΔS_a° , kJ mol⁻¹; E_a , kJ mol⁻¹) and Walden product ($\Lambda_o\eta_o$, S cm² mol⁻¹cP) of (CAPB) at various temperatures in the solvents used

s.m.	x	T (K±15)								$-\Delta H_a^\circ$	$-\Delta S_a^\circ$	E_a	T (K±15)			
		K_a				$-\Delta G_a^\circ$							$\Lambda_o\eta_o$			
		298	303	308	313	298	303	308	313				298	303	308	313
EtOH–H ₂ O	0.000	12.08	8.06	4.64	1.13	6.18	5.26	3.93	6.18	119.36	0.38	4.80	1.681	1.558	1.447	1.346
	0.033	25.05	18.48	14.75	11.73	7.99	7.35	6.90	7.99	38.83	0.10	9.19	2.070	1.920	1.816	2.445
	0.071	20.87	16.55	11.22	9.64	7.53	7.08	6.20	7.53	41.99	0.12	16.48	2.053	2.026	1.884	2.814
	0.116	15.31	11.71	9.25	8.31	6.77	6.20	5.70	6.77	32.05	0.09	32.40	1.587	1.761	1.790	2.986
MeOH–H ₂ O	0.000	12.08	8.06	4.64	1.13	6.18	5.26	3.93	6.18	119.36	0.38	4.80	1.681	1.558	1.447	1.346
	0.047	9.54	6.12	4.56	3.61	5.59	4.57	3.89	5.59	49.78	0.15	9.39	1.150	1.236	1.309	1.380
	0.099	7.83	5.48	3.33	2.03	5.10	4.29	3.08	5.10	70.75	0.22	14.25	1.031	1.127	1.244	1.354
	0.159	7.22	4.86	2.61	1.14	4.90	3.98	2.46	4.90	95.70	0.30	21.09	0.880	1.034	1.183	1.323
GlyOH–H ₂ O	0.000	12.08	8.06	4.64	1.13	6.18	5.26	3.93	6.18	119.36	0.38	4.80	1.681	1.558	1.447	1.346
	0.026	27.26	19.91	18.30	11.68	8.19	7.54	7.45	8.19	40.85	0.11	14.18	1.629	1.783	1.951	2.144
	0.058	25.86	18.65	14.38	9.56	8.06	7.38	6.83	8.06	50.44	0.14	13.02	1.725	1.864	2.043	2.213
	0.095	23.59	14.68	13.12	8.40	7.84	6.77	6.60	7.84	49.82	0.14	8.41	1.958	2.041	2.180	2.294

s.m. Solvent mixtures, x Solvent mole fraction. Standard uncertainties (u) of $K_a = 0.015$

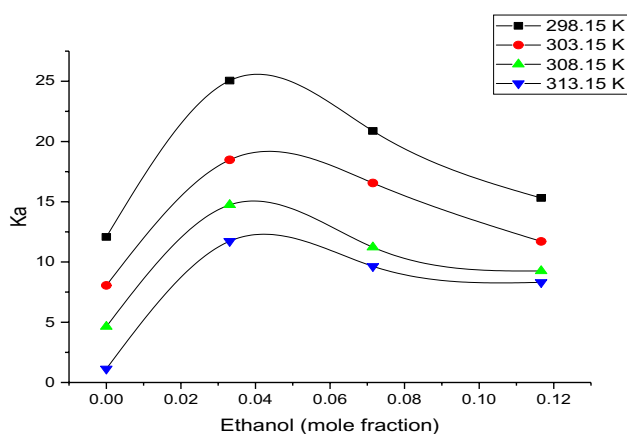


Fig. 3 Association constant (K_a) of CAPB as a function of mole fraction of ethanol in aqueous solutions at different temperatures

the relative permittivity of H₂O compared to that of the alcohols, which is consistent with the literature [15–19, 30, 31]. The association constant decreasing as the mole fraction of alcohol increases is the reverse of the expected behaviour on the basis of previous studies [15–19, 30, 31] which may be attributed to variation in the electrolytic nature of the compounds that previously reported [15–19, 30, 31] and the salt under investigation (CAPB). It was observed that the solvation of the hydrocarbon tail of the CAPB increases with alcohol percentage rise, which is due, therefore, to the association of positive and ions in the CAPB molecule decreasing. In addition, the predominant ordering of the K_a for the studied salt was to increase according to the order GlyOH > EtOH > MeOH, which can

essentially be attributed to the higher dielectric constant as well as lower dipole moment of GlyOH compared to that of EtOH and MeOH. The association process was found to be spontaneous, as subsequently confirmed by the negative value of the free energy change. It is evident from Table 4 that the enthalpy change is negative in all cases, indicating that the association process is exothermic. It is noteworthy that as K_a decreases (which is related to S_1 decreasing) the degree of ionization in the micelle (α) (which is equal (S_2/S_1)) will accordingly rise. The counterion value (β) will then decrease as a consequence of the reduction in the association constant. Positive relationships are found between the association constant and the decrease in CMC (Figs. 2, 3), which mean while the solvation and so the CMC decreases, the association for CAPB increases.

The Walden product ($\Lambda_o\eta_o$), has a constant value and is beneficial because it can provide information about ion–solvent interaction [34]. The constant value was attributed to that the Λ_o of the ion relying only upon its speed, and thereby the product of the ion conductance and the viscosity of the medium ought to be independent of the type of solvent being used. Therefore, in a set of solvent mixtures in which the ion–solvent interactions are regular, thus for a given electrolyte the $\Lambda_o\eta_o$ is expected to be constant. The $\Lambda_o\eta_o$ values were calculated for CAPB in the different mixtures and studied at different temperatures, with the results of the associated calculations reported in Table 4. The proportion of the $\Lambda_o\eta_o$ values for the surfactant in solvent mixtures to that in pure water is known as the fluidity ratio (R_f) which was identified in this instance. It can be seen that the $\Lambda_o\eta_o$ values of CAPB solution increase with increasing

proportion of organic mole fraction for EtOH and GlyOH in the solvent mixtures, but decreases in MeOH–H₂O as the mole fraction increases. This may be due to the higher viscosity of the alcohols under investigation than that of pure H₂O. The Λ_o value was observed to decrease as the mole fraction of the solvent under study increased. Consequently therefore, the factor responsible for the change in $\Lambda_o \eta_o$ is the solvent viscosity whereas the effect of Λ_o was almost negligible for the studied salt.

3.3 Molal volumes

The densities of various molal concentrations of CAPB surfactant have been determined in pure H₂O and in organic–aqueous mixed solvents such as MeOH–H₂O, EtOH–H₂O, and GlyOH–H₂O (in various alcohol mole fractions for each) at room temperature 298.15 K). Based on the densities and the molal concentrations, the apparent molal volumes, V_ϕ of CAPB can be obtained through the following expression [35], and the results for which are given in Table 5.

$$V_\phi = \frac{M}{\rho} - \frac{1000}{m} \left[\frac{1}{\rho^\circ} - \frac{1}{\rho} \right] \quad (15)$$

where M , m , ρ° and ρ are the molecular weight of the surfactant, molal concentration of the surfactant solution, and the densities of solvent and solution, respectively.

Table 5 Density (ρ , g cm⁻³), apparent molal volume (V_ϕ , cm³ mol⁻¹), van der Waals volume (V_W , cm³ mol⁻¹) and electrostriction volume (V_E , cm³ mol⁻¹) of CAPB at 298.15 K

<i>s. m.</i>	<i>x</i>	ρ	V_ϕ	V_W	$-V_E$
EtOH–H ₂ O	0.0000	1.0157	354.4335	234.2805	120.1529
	0.0331	1.0113	355.9742	235.2989	120.6753
	0.0715	0.9971	361.0438	238.6499	122.3938
	0.1166	0.9818	366.6701	242.3689	124.3012
	0.2355	0.9525	377.9558	249.8288	128.1270
	0.4182	0.9230	390.0336	257.8122	132.2214
MeOH–H ₂ O	0.0000	1.0157	354.4335	234.2805	120.1529
	0.0470	1.0124	355.5873	235.0432	120.5441
	0.0999	1.0046	358.3473	236.8675	121.4797
	0.1598	0.9814	366.8194	242.4676	124.3518
	0.3074	0.9530	377.7616	249.7004	128.0612
	0.5088	0.9220	390.4615	258.0951	132.3665
GlyOH–H ₂ O	0.0000	1.0157	354.4335	234.2805	120.1529
	0.0267	1.0249	351.2534	232.1785	119.0749
	0.0582	1.0493	343.0855	226.7795	116.3060
	0.0958	1.0743	335.1016	221.5021	113.5994
	0.1981	1.1246	320.1137	211.5952	108.5186
	0.3657	1.1821	304.5425	201.3026	103.2399

s. m. Solvent mixtures, *x* Solvent mole fraction. Standard uncertainties (u) of $\rho=0.002$ g cm⁻³, of $V_W=0.021$ cm³ mol⁻¹)

The relationship between the partial molal volume to the van der Waals volume is recognised as representing the packing density of comparatively large molecules, which is expected to be constant [36, 37]. According to this, the van der Waals volumes (V_W) of the surfactant under investigation were therefore calculated utilizing the following expression [37].

$$\text{Packing density } (P) = (V_W/V_\phi) = 0.0661 \pm 0.017 \quad (16)$$

The electrostriction volume [9] which is the volume compressed by the solvent [36–39], can be calculated using the following equation.

$$V_E = V_W - V_\phi \quad (17)$$

The van Der Waals volumes and the electrostriction volume are presented in Table 5. It can be observed from this table that the ρ values of the CAPB solutions decreased as the mole fraction of the MeOH/EtOH increased, whereas it increased with increasing mole fraction of GlyOH. Moreover, it has been observed that the (V_ϕ) values of the surfactant become significant as the MeOH/EtOH mole fraction increased but decreased for GlyOH solvents with increasing GlyOH mole fraction. The reason for this observation may be attributed to the glycerol having a high density in comparison to H₂O, MeOH and EtOH.

3.4 Refractive index measurements

In different media (H₂O and in EtOH–H₂O, MeOH–H₂O and Gly–H₂O) mixture solvents with various mole fractions, the refractive indices of (CAPB) were determined at T = 298.15 K and their associated data are summarised in Table 6. The refractive indices were found to increase with increasing alcohol mole fraction. Furthermore, from the data of the measured refractive indices, the molar refraction (R_m) can be calculated [40], using the following equation.

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_\phi = P_A + P_E = P_D + P_T \quad (18)$$

where n is defined as the refractive index of the studied compound in solution. Considering Eq. (18), the right hand side of this equation is essentially equal to the total molar polarization (the distortion polarization), the sum of each the atomic polarization, P_A and electron polarization, P_E , thus, through expression (19) the (P_A) values could then be calculated [41].

$$P_A = 1.05n^2 \quad (19)$$

The mean value of the molecular dipole polarizability (α) could be determined by using the optical refractive

Table 6 The refractive index (n_D), the atomic polarization (P_A), the molar refraction (R_m , $\text{cm}^3 \text{mol}^{-1}$) and the polarizability (α , cm^3) of CAPB at 298.15 K

<i>s. m.</i>	<i>x</i>	n_D	P_A	R_m	α
EtOH–H ₂ O	0.0000	1.3450	1.8995	75.2806	2.9850
	0.0331	1.3490	1.9108	76.3987	3.0293
	0.0715	1.3540	1.9250	78.4865	3.1121
	0.1166	1.3605	1.9435	81.0244	3.2127
	0.2355	1.3675	1.9636	84.9711	3.3692
MeOH–H ₂ O	0.0000	1.3450	1.8995	75.2806	2.9850
	0.0470	1.3460	1.9023	75.7233	3.0025
	0.0999	1.3485	1.9094	76.8086	3.0455
	0.1598	1.3490	1.9108	78.7263	3.1216
	0.3074	1.3520	1.9193	81.7028	3.2396
GlyOH–H ₂ O	0.0000	1.3450	1.8995	75.2806	2.9850
	0.0267	1.3580	1.9364	77.1339	3.0584
	0.0582	1.3710	1.9736	77.7887	3.0844
	0.0958	1.3820	2.0054	77.9854	3.0922
	0.1981	1.4078	2.0810	78.9372	3.1299
	0.3657	1.4371	2.1685	79.8021	3.1642

s. m. Solvent mixtures, *x* Solvent mole fraction. Standard uncertainties (*u*) of $n_D=0.0001$, of $R_m=0.01 \text{ cm}^3 \text{mol}^{-1}$, $\alpha=0.0011 \text{ cm}^3$, $P_A=0.001$

index (n_D) of a substance containing *N* molecules per unit volume. According to the Lorenz–Lorenz formula [23], the refractive index of a substance is associated with the polarizability (α) of its molecules as given by the following expression.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi\hat{n}\alpha}{3} \quad (20)$$

where $\hat{n} = N/V_\varphi$, (*N*) is Avogadro's number and (V_φ) is the apparent molal volume. The values of (CAPB) have been calculated using Eq. (20). The resulting values for (R_m), (α) and (P_A) are listed in Table 6, perusal of which reveals that the variables (R_m) and (α) are directly proportional to the apparent molal volume. It can be seen that both (R_m) and (α) values of the surfactant increased with increasing mole fraction of organic solvent. The reason for this increase in both (R_m), (α) can be attributed to the increase in the apparent molal volume of CAPB.

4 Conclusions

The experimental results for the conductivity of the CMC of cocamidopropyl betaine (CAPB) surfactant in pure water and in alcohol (MeOH, EtOH, and GlyOH)–water

mixed solvents have been presented as a function of mole fractions of alcohols over the temperature range 298.15 to 313.15 K, (in steps of 5 K). Also, from surface tension measurements in water, the CMC of CAPB has been estimated at 298.15 K. It is also important to note from the study that the CMC increases as temperature and alcohol mole fraction increase. Interestingly, the estimated CMC data are in agreement for both conductivity and surface tension measurements. Depending on the conductivity data, the association constant (K_a) of CAPB was also determined using the Shedlowsky conductance equation. The results obtained show that the characteristic behaviours of the association constant for the studied compound was generally decrease with increasing temperature and alcohol mole fraction, and that the association behaviours was observed to be spontaneous. Furthermore it was observed that CMC and K_a of CAPB increased in the order MeOH > EtOH > GlyOH. Based on the density values determined, the molal volumes of the surfactant have been derived and discussed, whose values were found to increase with increasing mole fraction of organic solvent. Moreover, the molar refraction and the polarizability of CAPB were calculated depending on the measured refractive indices. It was demonstrated that both (R_m) and (α) increased with increasing mole fraction of organic solvent, which attributed to the associated increase in apparent molal volume of CAPB.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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