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Thermodynamic Properties of N-Benzyl-N,N-dimethyldodecan-1-aminium bromide Sufractant in Binary Mixture of Propane-1,2-diol and Water

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Micellar systems are colloids with various applications in different branches of industry such as cosmetic, petrochemical, pharmaceutical or food industry. Micelles can be used as nanocarriers of poorly water-soluble substances. This property is often used for drug delivery in medical treatments. Micelle formation is a complex process where multiple interactions take place, but most important are hydrophobic interactions. Propane-1,2-diol (propylene glycol) is a chemical widely used as a food additive while N-Benzyl-N,N-dimethyldodecan-1-aminium (benzododecinium) bromide is quaternary ammonium salt used as preservative and antiseptic in pharmaceutical products. The latter is highly soluble in water and acts like cationic surfactant in aqueous solutions. The research outcome is as the weight percentage of propane-1,2-diol in mixtures increases, the values of critical micellar concentration increase. The negative value of ΔG^0_m show that micellization process is spontaneous. All values of $\Delta H_\mathrm{m}{}^0$ are negative and decrease with increasing precentage of glycol in the mixture. In mixtures zeta potential values decrease as a result of glycol effect to charge of micellar colloid. Result of that effect is collapse of micellar structure. From ^{1}H NMR experiment, upfield shifts of benzododecinium bromide peaks are not consistent with the increase of added propane-1,2-diol in comparison to pure benzododecinium bromide. The shift is caused by the interaction of the polar part of benzododecinium bromide with the alcohol, causing the shielding effect and consequently, the lower ppm values. With increase of weight percentage of propylene glycol caused the rapid increase in the integral value of the peaks corresponding to protons of propylene glycol, whereas the same properties cannot be attributed to benzododecinium bromide corresponding peaks.

Keywords: Thermodynamic, N-Benzyl-N,N-dimethyldodecan-1-aminium bromide, propane-1,2-diol, electrical conductivity, micelles

1. INTRODUCTION

Micelles are a versatile tool that have many applications spanning many different industries. [1-6] Although well researched their versality and different conditions that can interfere with their formation makes them very intersting research topic. Type of solvents [7,8] and/or solvent mixtures[8-10], addition of additives [5-10] such as ionic liquids [11-14] are just a few of those variables that if changed can interfere with formation of micelles by increasing or decreasing the *c.m.c.* value. The other important factor is that by improving already existing micellar solutions the production cost [6-15] and negative effect on environment [6,15,16] can be reduced while their efficiency can be increased. Micelle formation is a complex process where multiple interactions take place, but most important are hydrophobic interactions. [17,18]

Propane-1,2-diol (propylene glycol) is a chemical widely used as a solvent for food colors and flavors in certain food products and farmaceutical industry. [19-21]

A lot of recent research deal with the use of micelles as nanocarriers for drug delivery in medical treatments especially for poorly water-soluble substances. [1,2,22] N-Benzyl-N,N-dimethyldodecan-1-aminium (benzododecinium) bromide is quaternary ammonium salt highly soluble in water and acts like cationic surfactant in aqueous solutions. [23] It is one of the active ingredients in a number of patents mostly used as preservatives [24,25]and sanitizers in pharmaceutical products because of it’s bactericide properties. [26] Research of it’s surfactant properties and micelle formation has been limited. Existing research is of older date and conducted mostly in water as the solvent. [27,28]Research of micelle formation of said surfactant in binary mixtures is limited to addition of alcohols as co-solvents.[29]

In our work, we study how the presence of propylene glycol in mixture affects the micelle structure process. The structure forming of micellar colloid is studied in solvent mixtures with different propylene glycol mass fractions. Also the impact of the temperature gradient on the size and stability of the micellar colloid have been researched.

2. MATERIALS AND METHODS

2.1. Chemicals

The chemicals used in this research were propane-1,2-diol (Sigma-Aldrich St. Louis, USA, purity ≥99.5%) and N-Benzyl-N,N-dimethyldodecan-1-aminium (benzododecinium) bromide (Sigma-Aldrich St. Louis, USA, purity ≥99.0%). The deionised water used in this study was prepared with the Elga Purelab flex.

2.2. Conductivity, Photon Correlation Spectroscopy and ^1H NMR Experiments

Conductivity measurements were conducted at different concentrations of N-Benzyl-N,N-dimethyldodecan-1-aminium (benzododecinium) bromide in aqueous propylene glycol mixtures. The electrical conductivity values were determined using the Mettler Toledo FiveEasy conductivity meter.

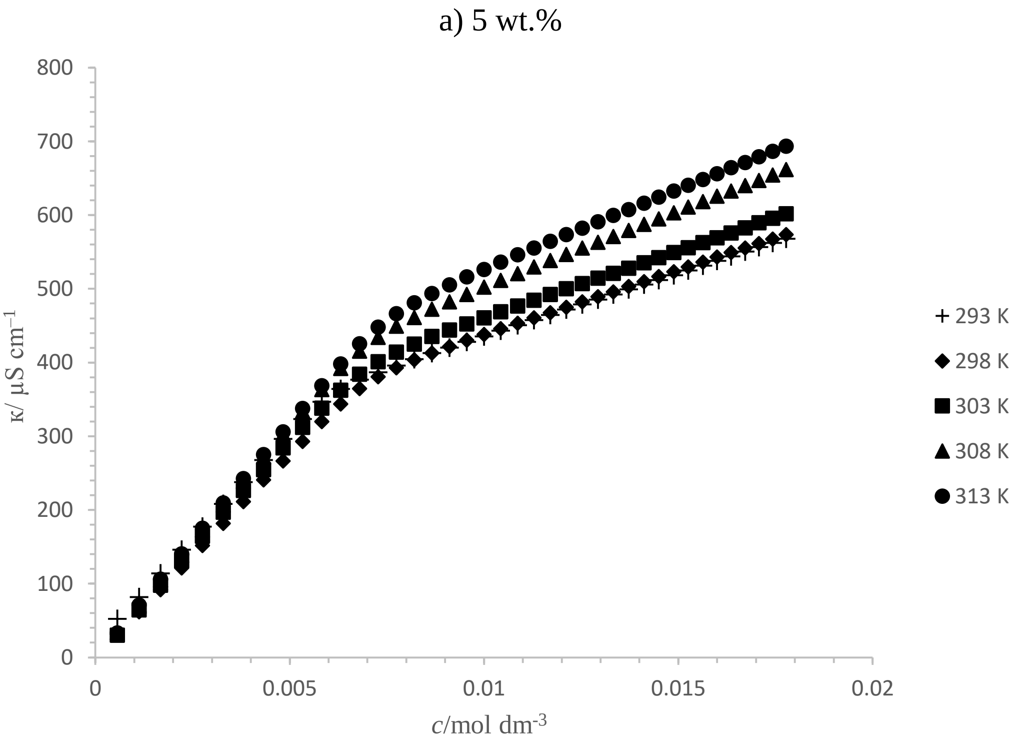
The hydrodynamic radii and zeta potential of solutions were measured by Litesizer 500 (Anton Paar, Graz, Austria) at 25 °C.

^{1}H NMR studies were performed with 300 MHz Bruker NMR machine. All experimental procedures have been performed as described in ref 9.

3. RESULTS AND DISCUSSION

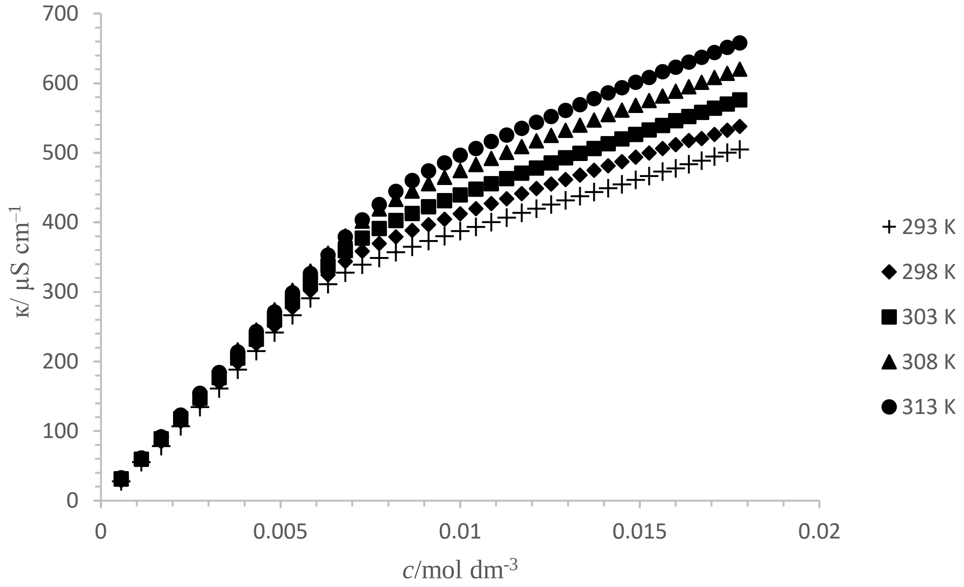
3.1. Critical micellar concentration

Conductometric technique was used to determine the critical micellar concentration (*c.m.c.*) of benzododecinium bromide in in aqueous propylene glycol mixtures which are presented in Table 1. Fig. 1 showed that *c.m.c.* was determined from intersection of the linear slope plots of specific conductance (κ) as a function of surfactant concentration. The results of the study (Table 1) show that as the weight percentage of propylene glycol in mixtures increases, the critical micellar concentration values seem to increase. By nature, propylene glycol has low dielectric constant which effect electrostatic repulsion among the ionic head groups of the surfactant at the micellar surface and on the other side can form hydrogen bonding with water. This effect reduce the movement of surfactant for which obstruction of hydrophobic interaction is expected and a increase of *c.m.c.* [9,30].



a) 5 wt.%

b) 10 wt.%



c) 15 wt.%

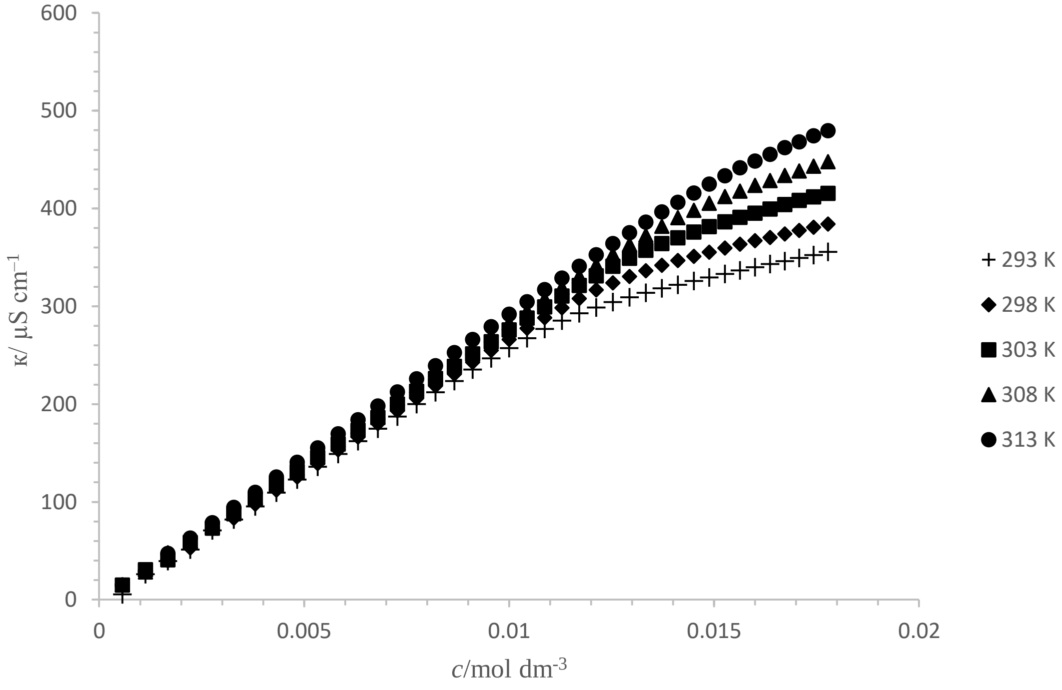


Figure 1. Graph of the relationship of the conductivity vs. molar concentration for benzododecinium bromide in aqueous mixture of propylene glycol at five temperatures, where the weight percentage of propylene glycol: (**a**) 5, (**b**) 10 and (**c**) 0.15.

The solubilization of benzododecinium bromide is more favorable in aqueous propylene glycol media, compared to previous study of SDS in same mixtures, atractive electrostatic interaction among the head group and partial negative charge on oxygen, resulting delayed micellar aggregation [9,31-33].

The degree of counterion dissociation parametar is higher in mixtures than in pure water. With a higher precentage of organic solvent in a mixture, the increase becomes more noticeable. The main reason is that propylene glycol solubilize at the surface of micellar aggregates scaling down the charge density [9,30].

Table 1. Values of *c.m.c.* (mol dm^{-3}) of benzododecinium bromide in pure water and aqueous propylene glycol mixtures

Temperature/K	***c.m.c.* (water)**	***c.m.c.* (5 wt.%)**	***c.m.c.* (10 wt.%)**	***c.m.c.* (15 wt.%)**
293.15	0.00563	0.00610	0.00682	0.01167
298.15	0.00591	0.00702	0.00700	0.01268
303.15	0.00594	0.00696	0.00747	0.01337
308.15	0.00579	0.00704	0.00771	0.01425
313.15	0.00608	0.00746	0.00833	0.01471

3.2. Thermodynamic Quantities of benzododecinium bromide in aqueous propylene glycol mixtures

Table 2. Thermodynamic quantities for micellization process of benzododecinium bromide bromide in pure water and aqueous propylene glycol mixtures

Wt.%	**Temperature /K**	**α**	**ΔG^0_m /kJmol^{-1}**	**ΔH^0_m /kJmol^{-1}**	**ΔS^0_m /kJK^{-1}mol^{-1}**	**ΔG^0_{trans} /kJmol^{-1}**
Water	293.15	0.285	-38.44	-3.401	0.119	-
	298.15	0.313	-38.25	-3.403	0.117	-
	303.15	0.300	-39.17	-3.486	0.118	-
	308.15	0.306	-39.79	-3.531	0.118	-
	313.15	0.322	-39.84	-3.555	0.116	-
5	293.15	0.304	-37.5	-10.20	0.0931	0.94
	298.15	0.329	-37.02	-10.22	0.0899	1.23
	303.15	0.323	-37.81	-10.43	0.0903	1.36
	308.15	0.339	-38.01	-10.50	0.0893	1.78
	313.15	0.353	-38.06	-10.58	0.0878	1.78
10	293.15	0.312	-36.72	-12.38	0.0830	1.72
	298.15	0.326	-36.93	-12.48	0.0820	1.32
	303.15	0.341	-36.94	-12.58	0.0804	2.23
	308.15	0.345	-37.32	-12.76	0.0797	2.47
	313.15	0.386	-36.66	-12.64	0.0767	3.18

15	293.15	0.372	-33.12	-13.99	0.0653	5.32
	298.15	0.393	-32.92	-14.04	0.0633	5.33
	303.15	0.446	-32.16	-13.81	0.0605	7.01
	308.15	0.504	-31.22	-13.51	0.0575	8.57
	313.15	0.617	-29.22	-12.69	0.0528	10.62

The thermodynamic quantities of micellization process: Gibbs free energy (ΔG_m^0), enthalpy (ΔH_m^0) and entropy (ΔS_m^0) and the degree of dissociation of the counterion (α) (Table 2) were calculated as described in ref 9.

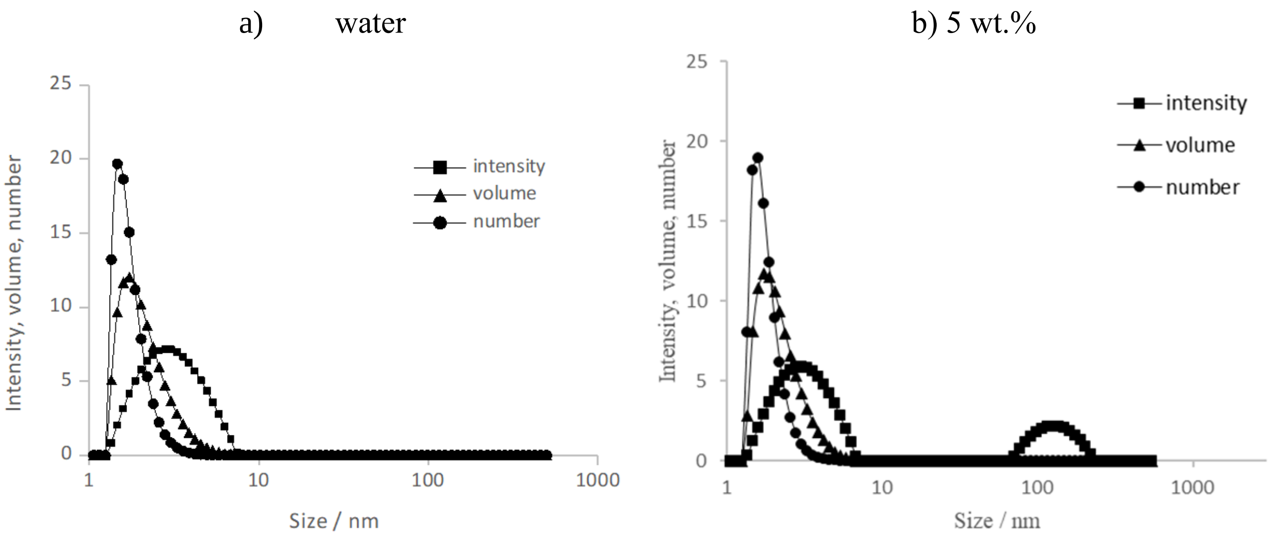
From Table 2, the negative value of ΔG_m^0 show that aggregation process is spontaneous and becomes more positive which can be attributed to micellar unfavorable situation at higher propylene glycol concentration. The main reason for that effect is dominant electrostatic interaction, resulting increase the solubility of non-polar part of surfactant and decomposition of micellar structure [9,17].

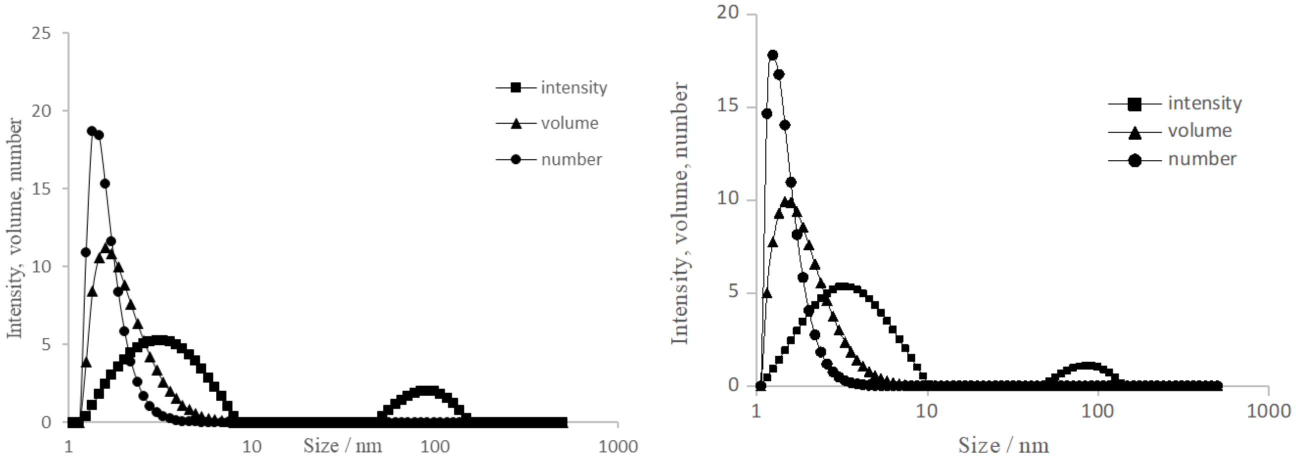
The increase of $\Delta G^0_{\text{trans}}$ is result of reduction of solvophobic interaction and mainly responsible for the increase of *c.m.c.* depending on bulk phase composition. [9,17,30,32]

All the values of ΔH_{m}^0 (Table 2) are negative and decrease with increasing precentage of glycol in solution. The positive values of ΔS_{m}^0 become less positive as the glycol precentage increases. The micellar formation process is induced mostly by the entropy increase, because of the affinity of the hydrocarbon tail of the surfactant to shift from the continuous phase to the structure of the aggregate [9,17,30].

3.3. Micellar Size and Stability

To research the aggregation behaviour, the hydrodynamic radii and zeta potential of the micellar aggregates formed by benzododecinium bromide in water and aqueous propylene glycol mixtures were studied using photon correlation spectroscopy (PCS) (Figure 2 and Table 3).




c) 10 wt.%

d) 15 wt.%

Figure 2. Photon correlation spectroscopy (PCS) measurement of the hydrodynamic radii of benzododecinium bromide (0.01 mol dm^{-3} benzododecinium bromide solution) in water and aqueous propylene glycol mixtures

Table 3. The hydrodynamic radii and zeta potential of benzododecinium bromide in water and aqueous propylene glycol mixtures (0.01 mol dm^{-3} benzododecinium bromide solution).

Wt.%	**Zeta Potential/mV**	**Size/nm**			
		Intensity Peaks		**Volume Peak**	**Number Peak**
		1.	**2.**		
water	60.3 ± 1.18	3.226 ± 1.108	-	2.158 ± 0.519	1.752 ± 0.295
5	50.7 ± 0.88	3.225 ± 1.132	132.3 ± 35.28	2.227 ± 0.517	1.805 ± 0.326
10	43.5 ± 1.69	3.425 ± 1.330	90.58 ± 23.55	2.101 ± 0.522	1.649 ± 0.285
15	41.3 ± 0.83	3.705 ± 1.630	86.02 ± 20.33	2.021 ± 0.526	1.524 ± 0.279

According to the calculation of experimental data regarding to the volume and number in system are present micelles with hydrodynamic radii of around 3 nm (Table 3). Also there are according to intensity present particles in size around 100 nm and can be attributed to impurities [9].

In mixtures zeta potential values decrease as a result of glycol effect to charge of micellar colloid. The result of that effect is collapse of micellar structure. [9,30,34].

3.4. ^{1}H NMR

According to the Figure 3 there are 6 distinguishing peaks which correspond to protons of benzododecinium bromide: (i) 7.43 ppm (a), which is in correspondence to protons of aromatic ring of benzododecinium bromide; (ii) 4.42 ppm (b), 3.07 ppm (c) and 2.96 ppm (d) peaks are in accordance to protons surrounding the charged nitrogen atom; and (iii) 1.73 ppm (e), 1.21 ppm (f) corresponding to the rest of the methylene groups of benzododecinium bromide where the 0.82 ppm (g) peak is attributed to the protons of the terminal methyl group. With the addition of propylene glycol, there is a slight upfield shift in comparison to D_2O peak.

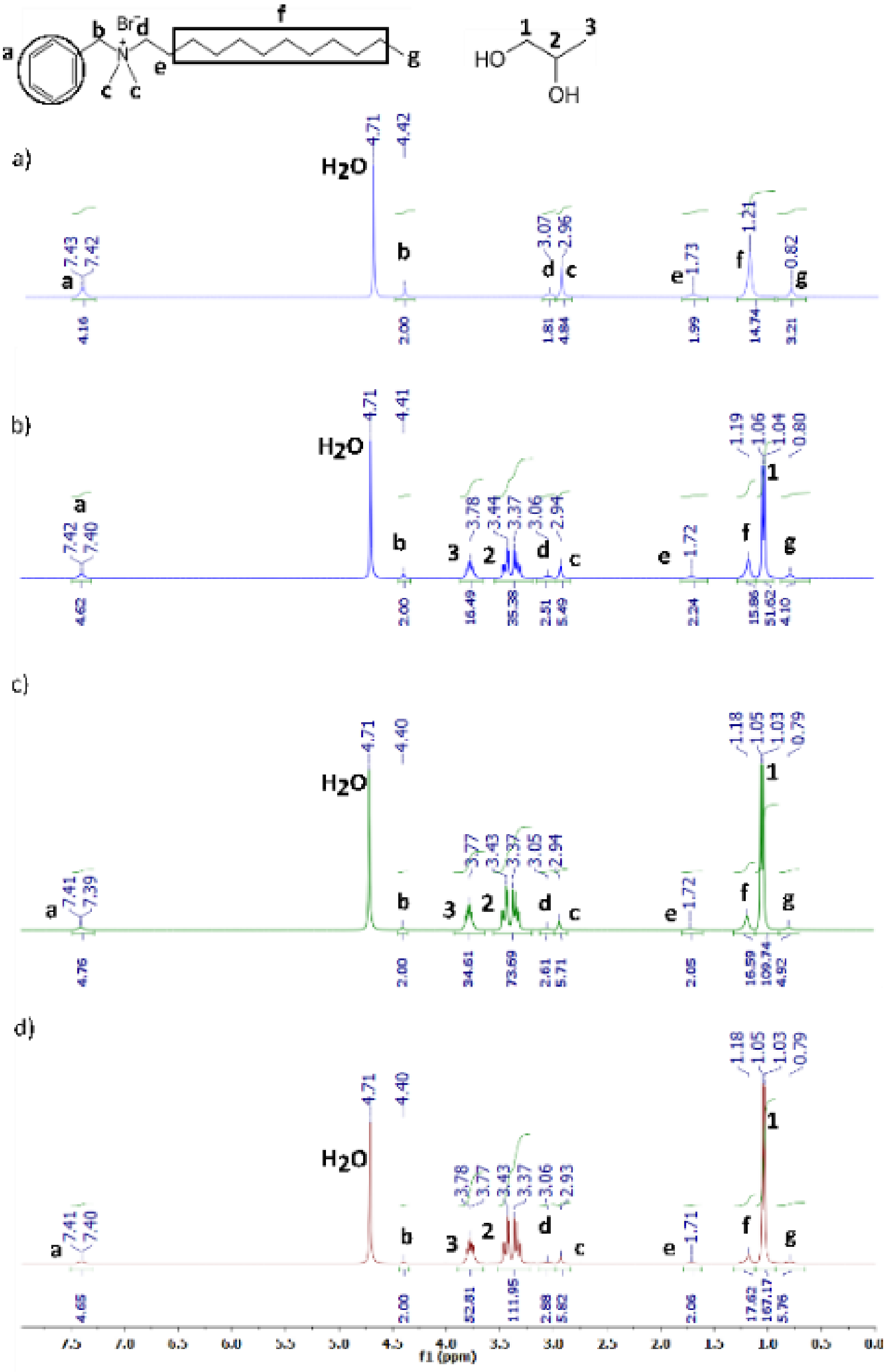


Figure 3. ^{1}H NMR results of benzododecinium bromide (0.01 mol dm^{-3} benzododecinium bromide solution) in a) water b) 5 wt.% of propylene glycol, c) 10 wt.% of propylene glycol, and d) 15 wt.% of propylene glycol

Upfield shifts of benzododecinium bromide peaks are not consistent with the increase of added propane-1,2- diol in comparison to pure benzododecinium bromide. Protons of the aromatic ring shows shift from 7.43 – 7.41 ppm, and is consistent with the 0.15 mass fraction of added propane-1,2-diol. Similar behaviour can be seen with the peaks corresponding to protons in the proximity of cationic charge on the nitrogen atom; from 4.42 ppm – 4.40 ppm (peak marked b), 3.07 ppm- 3.05 ppm (peak marked d) and from 2.96 – 2.93 ppm (peak marked c). However, the upfield shift is caused by the interaction of the polar part of benzododecinium bromide with the alcohol, causing the shielding effect and consequently, the lower ppm values [35,36]. Insertion of the alkyl chain of propane-1,2-diol within benzododecinium bromide micelle is the cause of the shift of propane-1,2-diol peaks (3.78 ppm – 3.77 ppm; 3.44 – 3.43 ppm and 1.06 ppm – 1.05 ppm).

More evident is the decrease of the intensity of the peaks corresponding to the protons of benzododecinium bromide with the increase of the mass ratio of propylene glycol. Especially, the decrease is most evident with the addition of 5 weight percentage of the alcohol. This behaviour can be explained with the decrease of the micelle diameter upon addition of cosolvent, and smaller mobility of the benzododecinium bromide protons [22].

With increase of weight percentage of propylene glycol caused the rapid increase in the integral value of the peaks corresponding to protons of propylene glycol, whereas the same properties cannot be attributed to benzododecinium bromide corresponding peaks [9,22].

4. CONCLUSIONS

Conductometric technique was used to determine the critical micellar concentration of benzododecinium bromide in aqueous propylene glycol mixtures. The results of the study show that as the weight percentage of propylene glycol in mixtures increases, the critical micellar concentration values seem to increase. The negative value of ΔG_m^0 show that aggregation process is spontaneous and becomes more positive which can be attributed to micellar unfavorable situation at higher propylene glycol concentration. According to the calculation of experimental data regarding to the volume and number in examined solution are present micelles with hydrodynamic radii of around 3 nm.

In mixtures zeta potential values decrease as a result of glycol effect to charge of micellar colloid. The result of that effect is collapse of micellar structure.

From ^{1}H NMR experiment, upfield shifts of benzododecinium bromide peaks are not consistent with the increase of added propylene glycol compared to pure benzododecinium bromide.

The shift is caused by the interaction of the polar part of benzododecinium bromide with the alcohol, causing the shielding effect and consequently, the lower ppm values.

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