CURRENT TRENDS IN SUSTAINABLE ENERGY, ENGINEERING, MATERIALS AND ENVIRONMENT

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Thermodynamic characterization of a non-commercial emulsifying agent for asphalt emulsion

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Abstract
The objective of the present work was to characterize a non-commercial emulsifying agent: dodecylpyridinium thiocyanate (C12PCNS). This study was carried out by conductimetry technique in the temperature range 25–50 °C. Assuming the system conforms to the pseudo-phase separation model, change of standard Gibbs free energy, ΔG_m^0, enthalpy, ΔH_m^0, and entropy of micellization, ΔS_m^0, were estimated. Values for critical micelle concentration (cmc) and the ionization degree, β, were determined directly from the experimental data. The results show that the influence of the counter ion is very relevant, because the cmc for this compound is appreciably greater than the cmc of other pyridinium homologs of the same chain length. Finally, the compensation rule for this system has been found and the compensation temperature and the intercept ΔH^*—it is an indication of the stability of the micelle—were estimated.

Keywords Dodecylpyridinium thiocyanate · Emulsifying agent · Critical micelle concentration (cmc) · Change of standard Gibbs free energy of micellization · Change of enthalpy of micellization · Change of entropy of micellization · Compensation temperature

Introduction

The benefits of asphalt emulsion are very relevant when they are used as on-site techniques, because the energy and gas emissions are lower than in the conventional ones.

The balance of intermolecular forces drives the stability of bituminous emulsions. Although this kind of emulsions are being used for many paving applications, further improvement will be possible when the whole principles of physical chemistry that ruled the colloidal behavior are included to the applied engineering.

The interfacial area between the asphalt and the water is about 500 m^2 per liter of bituminous emulsion. In order to prevent the coalescence and providing stability to the emulsion, surfactants are required.

Surfactants are materials that concentrate at interfaces—oil and water, for example—and surfaces. This particular

behavior let them to lower interfacial tension; consequently, they are involved in several applications such as detergency, cosmetics (Ontiverosa et al. 2014), water purification (Gonzalez-Perez and Persson 2016), production of silica-based mesoporous materials (Yang et al. 2017), and phase transfer catalysis (Gang et al. 2017).

A typical surfactant molecule is made up of two different parts: polar or hydrophilic head group and non-polar or hydrophobic chain group. The first one makes them soluble in water, and this group is very important for the aqueous surfactant solution properties.

Taking into account the charge carried by the head group, surfactants can be classified as anionic, cationic, non-ionic, and zwitterionic ones.

One of the most important properties of cationic surfactants is the emulsification, which is relevant in many applications, such as secondary oil recovery and emulsifiers in asphalt emulsions. In addition, their properties can be modified easily by the substitution of the counterion. Another important property is its resistance to bacteria, fungus, and other microorganisms.

As it was said, surfactants play an important role as emulsifiers in asphalt emulsions. Some of them, such as dodecylbenzene and p-toluene sulfonic acids, were used as additives in crumb-rubber-modified asphalt binders (Zhou et al. 2015). More recently, Schulz et al. studied the properties

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of sodium oleate and hexadecyltrimethylammonium bromide mixtures in order to establish their applicability in the asphalt emulsification for pavement production (Schulz et al. 2016). Rodriguez-Valverde et al. used a commercial cationic surfactant—a blend of N-alkyl propylendiamines and alkylamidoamines, both derived from tallow—in order to characterize bituminous emulsions using imaging techniques (Rodríguez-Valverde et al. 2008). Urbina-Villalba et al. carried out an interesting theoretical study about the surfactant structure and the stability of their oil/water emulsion (Urbina-Villalba and García-Sucre 2000). On the other hand, Gómez-Meijide et al. studied the mechanical properties of cold mix (Gómez-Meijide and Pérez 2014) and the effect of using demolition waste in cold asphalt mixtures (Gómez-Meijide and Pérez 2013).

Bitumen emulsions provide an alternative approach in which the bitumen is liquefied by dispersing in water. Bitumen or asphalt emulsions have a great advantage upon asphalt, because the processes with asphalt emulsions need less energy, because their viscosity is lower than the asphalt one. In road construction applications, emulsions are environmentally friendlier system than hot bitumen mix. It does mean less risks of fire; burns are avoided; and, it was already mentioned, the process uses less energy. About 7 L fuel/t (270 MJ/t) is consumed in a typical hot mix asphalt at 150 °C, while a half-warm mix consumes just only around 1 L fuel/t (46.45 MJ/t) (Almeida-Costa and Benta 2016). Furthermore, warm mix releases less ozone-generating hydrocarbons. In other words, asphalt emulsions are a good alternative to the conventional asphalt paving process, because the lower the energy needed is, the lower the emissions of carbon dioxide to the atmosphere are. In addition, the amount of bitumen used is considerably reduced. Amount about of 0.01 to 0.2 M of surfactant is needed for a rapid-setting emulsion, and even larger quantities should be used for cationic quick-setting emulsions (Takamura and James 2015). Critical micelle concentration (cmc), solubility of ionic surfactants, and the capacity to be ionized are very important aspects of the emulsifier. Thermodynamic properties of a micellar system are of major importance to obtain relevant information on the behavior of it. Particularly, enthalpy, entropy, or standard free Gibbs energy change upon the micellization process (Perger and Bešter-Rogac 2007); hence, the changes in hydrophobic interactions leading to micellization can be better evaluated. These main thermodynamics quantities can be derived from the critical micelle concentration with temperature, and all of them undergo changes upon micellization (Gonzalez-Perez and Sanchez-Dominguez 2013).

The main goal of this work was to analyze the influence of temperature on the micelle formation for a non-commercial cationic emulsifier: dodecylpyridinium thiocyanate (C12PCNS) and compare our results with literature data.

Experiment

Material and methods

Dodecylpyridinium thiocyanate is not a commercial emulsifier; it was synthesized in the following way:

A solution of 0.1 mol of dodecylpyridinium chloride (Aldrich) in 200 cm^3 of water was treated with a fivefold excess of aqueous solution of potassium thiocyanate.

The precipitate was filtered off and washed through by rinsing it with the KCNS solution.

The raw material was dissolved in warm water and re-precipitated by adding an excess of KCNS solution. The crude product was then purified by several recrystallizations from cold water. Thus, purified dodecylpyridinium thiocyanate was air-dried.

Conductivity measurements were made with a Wheastone bridge conductometer type CM-177 from Kyoto Electronics and a cell type K-212 from Kyoto Electronics too. The cell constant was determined by calibration with several dilute concentrations of potassium chloride solutions (Barthel et al. 1980). All measurements were carried out in a thermostat bath (Polysciencie 9010), maintaining the temperature constant to within ± 0.05 °C.

A special measuring cell was designed in order to optimize material. As Fig. 1 shows, the cell has a smaller base radius than at the central and upper sections. This way, we used a small amount of C12PCNS. The initial concentration of the water solution of C12PCNS inside of the cell was equal to twice the expected cmc. Then, it was being diluted by means of a calibrated dispenser.
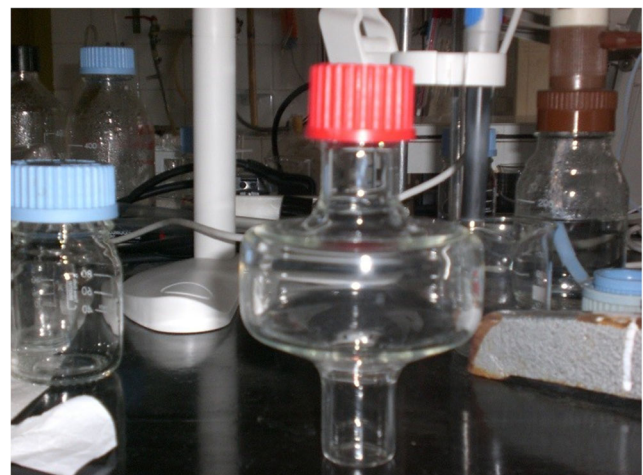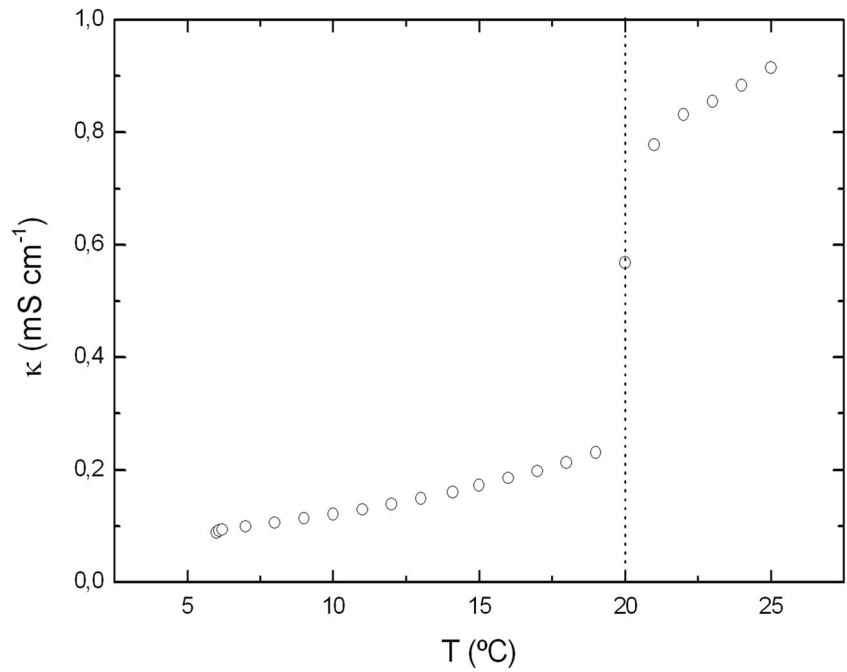

Fig. 1 Measuring cell

Fig. 2 Krafft temperature for C12PCNS

Results and discussion

The great temperature dependency of solubility in many ionic surfactants is one of the most remarkable effects in this kind of materials. Solubility may be very low at low temperatures and then increase by orders of magnitude in a narrow temperature range (Jönsson et al. 1998). This is a well-known phenomenon; the temperature at which the solubility increases strongly is called Krafft temperature or Krafft point.

Krafft point depends not only the length of alkyl chain but also on the head group and counterion.

Krafft point was first estimated for this non-commercial emulsifier in order to establish the onset temperature of the measurements.

For this purpose, we have used the same method that we reported in a previous paper (Galan and Rodriguez 2010); that is, an oversaturated water solution of C12PCNS was prepared at temperature below 6 °C. Afterwards, the specific conductivity of this solution against temperature was measured without changing the concentration of the emulsifier (Fig. 1).

As Fig. 2 shows, the Krafft temperature, T_K, is around 20 °C. T_K varies as a function of both the nature of the hydrophobic

Fig. 3 Specific conductivity vs molality from 25 to 50 °C
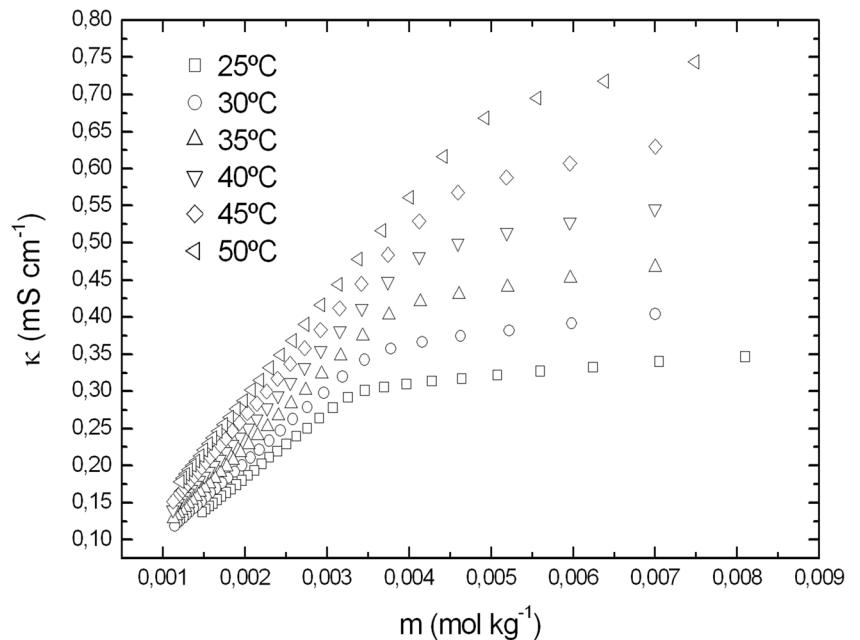
Table 1 *cmc* (mol kg^{-1}) values for C12PCNS and other pyridinium homologs

T (°C)	C12PCl[a]	C12PBr[a]	C12PCNS	C14PCl[b]	C14PBr[b]
15	1.81^{-2}	1.190×10^{-2}	–	4.5×10^{-3}	2.5×10^{-3}
20	1.65×10^{-2}	1.124×10^{-2}	–	4.4×10^{-3}	2.6×10^{-3}
25	1.57×10^{-2}	1.120×10^{-2}	3.4×10^{-3}	4.3×10^{-3}	2.7×10^{-3}
30	1.58×10^{-2}	1.135×10^{-2}	3.6×10^{-3}	4.4×10^{-3}	2.8×10^{-3}
35	1.67×10^{-2}	1.192×10^{-2}	3.8×10^{-3}	4.6×10^{-3}	2.9×10^{-3}
40	1.81×10^{-2}	1.223×10^{-2}	4.1×10^{-3}	$4.7 \times 10{-3}$	3.1×10^{-3}
45	–	–	4.4×10^{-3}	–	
50	–	–	$4.9.10^{-3}$		

[a] Galan et al. 2002

[b] Galan and Rodriguez 2010

chain and the head group with its counterion. However, there is no a general trend for the counterion dependence; in some cases, the Krafft temperature increases as the atomic number of counterion decreases, and in another, the situation is the opposite (Galan et al. 2003). The most of dodecylpiridinum halides have a very low T_K. In a previous paper, we reported a T_K around 16 °C for pentadecypyridinium bromide C15PBr (Galan and Rodriguez 2010), that is, three more methylene groups in the hydrophobic chain. Therefore, these results show that the interaction between the head group and the CNS$^-$ is very strong. Conventional asphalt hot mixtures ("hot mix") are generally produced at more than 150 °C. The asphalt emulsions are used in half-warm, warm, and in cold mixes. In the first case, the range of the temperature mixes is from 40 to 60 °C; the second from 60 to 120 °C; and in the third one, the materials are unheated and

mixed at ambient temperatures. Due to its high Krafft temperature, this emulsifier is more suitable for half-warm or warm mixes than the cold ones, except when the ambient temperature is much higher than 20 °C, that is, in warm climates.

Specific conductivity against molality concentration plot, in the temperature range from 25 to 50 °C, is shown in Fig. 3. As it is well known, the break in the slopes is due to the micelle formation. The cmc was determined from the intersection of two linear fits above and below on the critical point in the specific conductivity vs molality plot.

In order to establish a comparison, Table 1 shows the results of the cmc for several alkylpyridinium studied previously and determined with the same procedure (Galan et al. 2002, Galan et al. 2003, Galan et al. 2005; Galan and Rodriguez 2010). The cmc values for C12PCNS are more similar to C14PBr and C14PCl than the homologous with the same chain length. This result is consistent with the lyotropic series established by Hofmeinster (Mukerjee 1967); that is, the cmc decreases in the order Cl$^-$ > BrO$_3^-$ > NO$_2^-$ > N$_3^+$ > Br$^-$ > NO$_3^-$ > ClO$_3^-$ > I$^-$ > SCN$^-$.

The degree of micelle ionization, β, was estimated as the ratio of the slopes above and below of cmc of the specific conductivity-molality plot (Bouchal et al. 2016). β displays a linear dependence with temperature. This behavior was expected, because the higher the temperature is, the higher the thermal agitation is; hence, the counterion is easily dissociated from the aggregate.

Figure 4 shows a comparison of the micelle ionization degree of C12PCNS with two homologs with the same chain length, previously reported (Galan et al. 2002). In the present case, β follows the Hofmeinster series too. For that reason, the

Fig. 4 Ionization degree for C12PCNS and other homologs with the same chain length
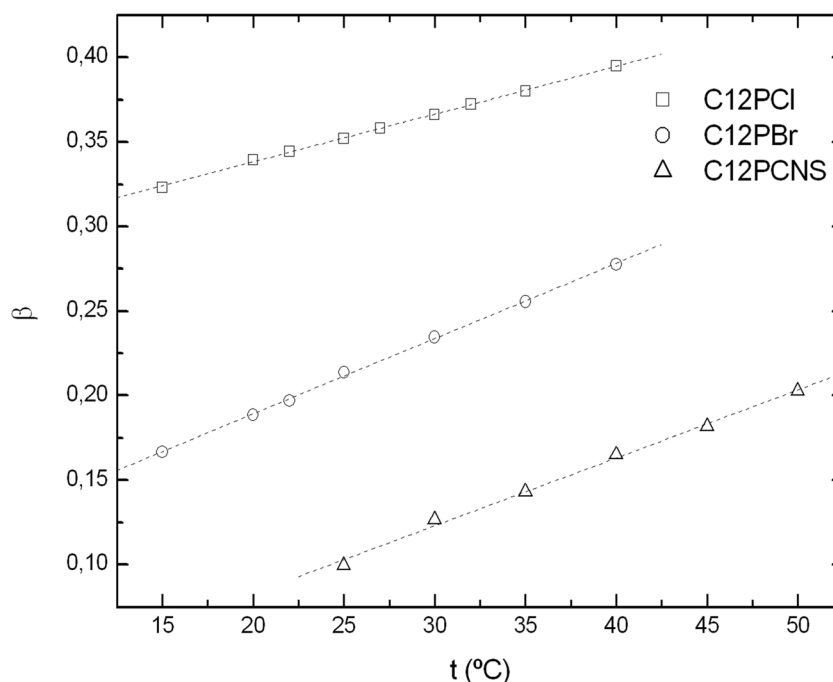
Fig. 5 *cmc* for C12PCNS vs temperature
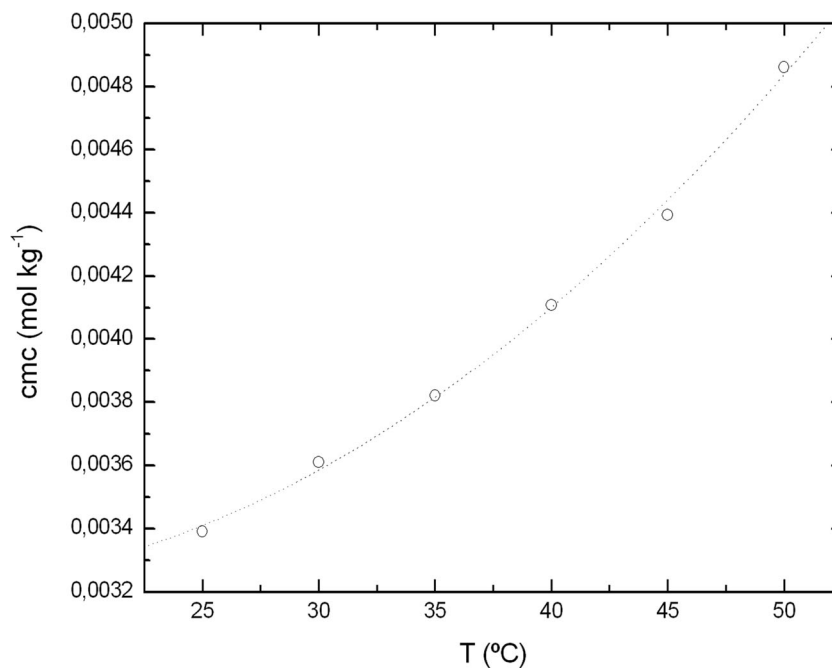
degree of ionization for C12PCNS is lower than of the other homologs of the same chain length. This fact limits its range of application at low temperatures. However, since beta grows linearly with temperature, at temperatures above 30 °C, its behavior can be considered optimal to achieve the flocculation of the emulsion. In fact, the lower temperature was already limited, as stated above, by Krafft temperature. For cold mixtures, Cl^- is more suitable than CNS^- because its degree of ionization is higher and its Krafft temperature is lower.

Figure 5 shows the behavior between the cmc vs temperature. Unlike other homologs with the same chain length (Galan et al. 2002, Galan et al. 2003), in this case, the typical *U*-shaped curve between cmc against temperature does not appear; it is because the Krafft temperature is high enough to prevent the presence of a minimum. As the temperature becomes higher, the hydrophobicity of the emulsifier decreases; therefore, the critical micellar concentration increases (Chen et al. 1998).

The more remarkable thermodynamic parameters of micellization such as the standard enthalpies, ΔH_m^0; entropy, ΔS_m^0; and Gibbs free energy, ΔG_m^0, of micellization for C12PCNS were estimated by means of the pseudo-phase separation model (Shinoda and Hutchinson 1962; Hunter 1993; Blandamer et al. 1995; Kim and Lim 2004). According to this model, the standard Gibbs free energy of micellization can be calculated from the relation

$$\Delta G_m^0 = (2-\beta(T))RT\ln x_{cmc}(T) \tag{1}$$

where X_{cmc} is the mole fraction of the surfactant at the cmc, and it is a temperature function, the same as β.

On the other hand, ΔH_m^0 can be estimated from the Gibbs-Helmholtz relation

$$\Delta H_m^0 = \left[\frac{\partial\left(\Delta G_m^0/T\right)}{\partial\left(1/T\right)} \right] \tag{2}$$

and ΔS_m^0 from the relation

Table 2 Thermodynamics parameters for C12PCNS at several temperatures

| T (°C)	ΔG_m^0 (kJ mol^{-1})	ΔH_m^0 (kJ mol^{-1})	ΔS_m^0 (J mol^{-1} K^{-1})
25	−45.59	−42.13	11.58
30	−45.61	−45.63	−0.062
35	−45.57	−49.20	−11.79
40	−45.47	−52.85	−23.57
45	−45.32	−56.58	−35.41
50	−45.10	−60.37	−47.27

$$\Delta S = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \tag{3}$$

Table 2 shows the results obtained for C12PCNS.

These values are in good agreement with our previous works for pyridinium surfactants (Galan et al. 2002; Galan and Rodriguez 2010) and with other homologs of ammonium quaternary salts (Perger and Bešter-Rogac 2007). At a given chain

Fig. 6 Compensation rule for C12PCNS
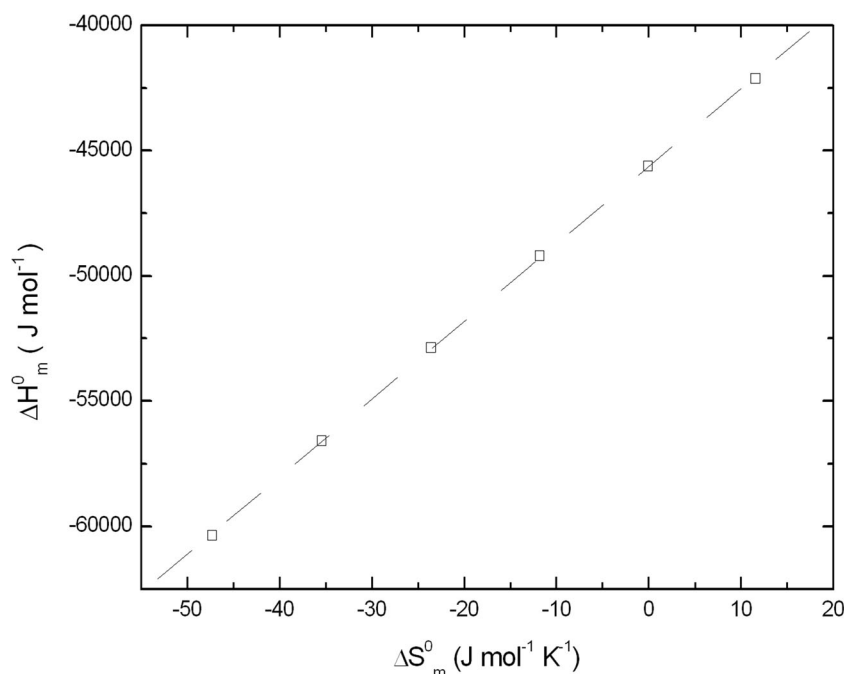
length, as the value of the standard Gibbs free energy is more negative, the larger the counterion.

The micelle formation is an exothermic process in the whole temperature range studied.

Several processes in aqueous solution with small solutes exhibit a linear relationship between enthalpy change and entropy change. This relationship is given by Eq. 4, and it is called compensation rule (Zielinsky et al. [1987]; Moroi [1992]; Mehrian et al. [1993]; Muller [1993]; Chen et al. [1998]; Sugihara and Hisatomi [1999]; Gonzalez-Perez et al. [2003]; Galan et al. [2005]).

$$\Delta H_m^{\circ} = \Delta H_m^{*} + T_c \Delta S_m^{\circ} \qquad (4)$$

Although this phenomenon is unresolved yet (Pan et al. [2016]), we can explain it as follows: the mechanism of micellization is the following: firstly, the hydrophobic tails are dehydrated;

we called it the desolvation part. Finally, the aggregation of the hydrophobic tails happen; this is so-called the chemical part. According to several authors (Chen et al. [1998]), the slope of Eq. (4), T_c, is a measure of the first part, desolvation, and it is known as compensation temperature and the intercept is considered as an index of the second part, the chemical one.

On the other hand, taking into account that in the intercept, ΔH^{*}, there is no any entropy change, ΔH^{*} has the same value as the standard Gibbs free energy change (Eq. (2)); then, the larger the ΔH^{*} is, the less stable the micelle is. So, the value of the intercept can be considered as a measure of the stability of the aggregate.

Figure 6 shows the compensation rule plot for C12PCNS. In this case, the value for T_c is around 310 K and 45.63 kJ for the intercept. Comparing these values with other homologs (Table 3), we observed that the compensation temperature for C12PCNS is higher than the other ones for homologs of the same chain and it is similar to C16PBr.

The value for ΔH^{*} reveals that the aggregates of C12PCNS are very stable, because it reaches a value around −45.63 kJ, which is very close to the C16PBr one, which has two more methylene groups.

Summary

In present work, we have used conductivity measurements to study the micellization process in aqueous solution of a non-commercial emulsifier, dodecylpyridinium thiocyanate (C12PCNS). It has been shown that the inflection point in the specific conductivity against molality plots corresponds

Table 3 ΔH^{*}_m and T_C values for several alkylpyridinium halides

Emulsifier	ΔH^{*}_m (J mol^{-1})	T_C (K)
C12PCl[a]	−33,800 ± 100	300 ± 2
C14PCl[b]	−38,200 ± 100	298 ± 2
C16PCl[b]	−42,420 ± 100	300 ± 2
C12PBr[a]	−37,900 ± 70	301 ± 2
C14PBr[b]	−43,000 ± 100	301 ± 2
C15PBr[b]	−45,400 ± 50	302 ± 1
C16PBr[b]	−47,900 ± 80	310 ± 2
C12PCNS	−45,600 ± 50	310 ± 2

[a] Galan et al. [2002]

[b] Galan and Rodriguez [2010]

to the position of cmc. This process was carried out at several temperatures. The shape of the curve of dependence of cmc on temperature shows only a branch of U-shaped plot. That is due to the high value of Krafft point.

The analysis of the thermodynamic parameters of the micellization for this compound shows that ΔH_m^0 becomes more exothermic upon increasing the temperature. The similar ΔG_m^0 values for the whole range of temperature show that the micellization process occurs spontaneously. On the other hand, the ΔS_m^0 values of the emulsifier solution decrease when temperature rises; it reveals that the order of the system increases with the temperature.

The compensation rule phenomenon was studied for this compound, and the values of ΔH_m^* and T_C were compared with other alkylpyridinium halides.

According to the results, this emulsifier is useful for warm asphalt mixes or half-warm mixes, mainly due to high Krafft temperature and low degree of ionization. The latter increases with temperature; therefore, the stability of the mixture will be higher for temperatures above 50 °C. Although taking into account that the range of temperatures of the cold mixes extends from 0 to 40 °C, C12PCNS can be used as emulsifier in cold mixes in countries with warm climates.

References

Almeida-Costa A, Benta A (2016) Economic and environmental impact study of warm mix asphalt compared to hot mix asphalt. J Clean Prod 112:2308–2317. https://doi.org/10.1016/j.jclepro.2015.10.077

Barthel J, Feuerlein F, Neueder R, Wachter R (1980) Calibration of conductance cells at various temperatures. J Solut Chem 9(3):209–219. https://doi.org/10.1007/BF00648327

Blandamer MJ, Cullis PM, Soldi LG, Engberts JBFN, Kacperska A, Van Os NM, Subha MCS (1995) Thermodynamics of micellar systems: comparison of mass action and phase equilibrium models for the calculation of standard Gibbs energies of micelle formation. Adv Colloid Interf Sci 58(2-3):171–209. https://doi.org/10.1016/0001-8686(95)00252-L

Bouchal R, Hamel A, Hesemann P, In M, Prelot B, Zajac J (2016) Micellization behavior of long-chain substituted alkylguanidinium surfactants. Int J Mol Sci 17(2):223–238. https://doi.org/10.3390/ijms17020223

Chen LJ, Lin SY, Huang CC (1998) Effect of hydrophobic chain of surfactants on enthalpy–entropy compensation of micellization. J Phys Chem B 102(22):4350–4356. https://doi.org/10.1021/jp9804345

Galan JJ, Rodriguez JR (2010) Thermodynamic study of the process of micellization of long chain alkyl pyridinium salts in aqueous solution. J Therm Anal Calorim 101(1):359–364. https://doi.org/10.1007/s10973-009-0385-9

Galan JJ, Gonzalez-Perez A, Del Castillo JL, Rodriguez JR (2002) Thermal parameters associated to micellization of dodecylpyridinium bromide and chloride in aqueous solution. J Therm Anal Calorim 70(1):229–234. https://doi.org/10.1023/A:1020678222376

Galan JJ, Gonzalez-Perez A, Rodriguez JR (2003) Micellization of dodecyldimethylethylammonium bromide in aqueous solution.

Thermal parameters. J Therm Anal Calorim 72(2):465–470. https://doi.org/10.1023/A:1024552911066

Galan JJ, Gonzalez-Perez A, Seijas JA, Uriarte E, Rodríguez JR (2005) Effect of counterion on thermodynamic micellar properties of tetradecylpyridinium in aqueous solution. Colloid Polym Sci 283(4):456–460. https://doi.org/10.1007/s00396-004-1206-0

Gang W, Ming Z, Shenying D, Zhou H, Ze Z, Sisi L (2017) Reaction principle of alcohol ether sulfonates by sulfonated alkylation method—a review. Tenside Surfactant Deterg 54(1):5–10. https://doi.org/10.3139/113.110472

Gómez-Meijide B, Pérez I (2013) A proposed methodology for the global study of the mechanical properties of cold asphalt mixtures. Mater Des 57:520–527. https://doi.org/10.1016/j.matdes.2013.12.079

Gómez-Meijide B, Pérez I (2014) Effects of the use of construction and demolition waste aggregates in cold asphalt mixtures. Constr Build Mater 51:267–277. https://doi.org/10.1016/j.conbuildmat.2013.10.096

Gonzalez-Perez A, Persson K (2016) Bioinspired materials for water purification. Materials. https://doi.org/10.3390/ma9060447

Gonzalez-Perez A, Sanchez-Dominguez M (2013) Changes in self-assemblies induced by temperature, concentration and light. Front Biosci 5:611–630

Gonzalez-Perez A, Czapkiewicz J, Del Castillo JL, Rodríguez JR (2003) Micellar behaviour of tetradecyldimethylbenzylammonium chloride in water-alcohol mixtures. J Colloid Interface Sci 262(2):525–530. https://doi.org/10.1016/S0021-9797(03)00064-X

Hunter RJ (1993) Introduction to modern colloid science. Oxford Univ. Press, Oxford

Jönsson B, Lindman K, Holmberg B, Kronberg B (1998) Surfactants and polymers in aqueous solution. Wiley, Chichester

Kim HU, Lim KHA (2004) Model on the temperature dependence of critical micelle concentration. Colloids Surf A Physicochem Eng Asp 235(1-3):121–128. https://doi.org/10.1016/j.colsurfa.2003.12.019

Mehrian T, Keizer A, Korteweg AJ, Lyklema J (1993) Thermodynamics of micellization of n-alkylpyridinium chlorides. Colloids Surf A Physicochem Eng Asp 71(3):255–267. https://doi.org/10.1016/0927-7757(93)80040-L

Moroi Y (1992) Micelles: theoretical and applied aspects. Plenum Press, New York. https://doi.org/10.1007/978-1-4899-0700-4

Mukerjee P (1967) The nature of the association equilibria and hydrophobic bonding in aqueous solution of association colloids. Colloid Interface Sci 1:241–245

Muller N (1993) Temperature dependence of critical micelle concentrations and heat capacities of micellization for ionic surfactants. Lagmuir 9(1):96–100. https://doi.org/10.1021/la00025a022

Ontiverosa JF, Pierlota C, Cattéa M, Moliniera V, Salagerb JL, Aubrya JM (2014) A simple method to assess the hydrophilic lipophilic balance of food and cosmetic surfactants using the phase inversion temperature of C10E4/n-octane/water emulsions. Colloids Surf A Physicochem Eng Asp 458:32–39. https://doi.org/10.1016/j.colsurfa.2014.02.058

Pan A, Kar T, Rakshit AK, Moulik SP (2016) Enthalpy−entropy compensation (EEC) effect: decisive role of free energy. J Phys Chem B 120(40):10531–10539. https://doi.org/10.1021/acs.jpcb.6b05890

Perger TM, Bešter-Rogac M (2007) Thermodynamics of micelle formation of alkyltrimethylammonium chlorides from high performance electric conductivity measurements. J Colloid Interface Sci 313(1):288–295. https://doi.org/10.1016/j.jcis.2007.04.043

Rodríguez-Valverde M, Ramón-Torregrosa P, Páez-Dueñas A, Cabrerizo-Vílchez M, Hidalgo-Álvarez R (2008) Imaging techniques applied to characterize bitumen and bituminous emulsions. Adv Colloid Interf Sci 136(1-2):93–108. https://doi.org/10.1016/j.cis.2007.07.008

Schulz E, Ambrusi R, Miraglia D, Schulz E, García S, Rodriguez J, Schulz P (2016) Evaluation of oil-in-water emulsions with cationic–anionic surfactants mixtures for potential use in the oil industry. Colloids Surf A Physicochem Eng Asp 490:145–154. https://doi.org/10.1016/j.colsurfa.2015.11.023

Shinoda K, Hutchinson E (1962) Pseudo-phase separation model form thermodynamic calculations on micellar solutions. J Phys Chem 66(4):577–582. https://doi.org/10.1021/j100810a001

Sugihara G, Hisatomi M (1999) Enthalpy–entropy compensation phenomenon observed for different surfactants in aqueous solution. J Colloid Interface Sci 219(1):31–36. https://doi.org/10.1006/jcis.1999.6378

Takamura K, James A (2015) Paving with asphalt emulsions. In: Huang S, Di Benedetto H (eds) Advances in asphalt materials. Woodhead Publishing Elsevier, Cambridge, pp 393–426. https://doi.org/10.1016/B978-0-08-100269-8.00013-1

Urbina-Villalba G, García-Sucre M (2000) Effect of non-homogeneous spatial distributions of surfactants on the stability of high-content bitumen-in-water emulsions. Interciencia 25:415–422

Yang Y, Wang A, Wei Q, Schlesener C, Haag R, Li Q, Li J (2017) Hyperbranched polyglycerol-induced porous silica nanoparticles as drug carriers for cancer therapy in vitro and in vivo. Chem Open 6(1):158–164. https://doi.org/10.1002/open.201600072

Zhou X, Wang F, Yuan X, Kuang V, Song Y, Li C (2015) Usage of slurry oil for the preparation of crumb-rubber-modified asphalt emulsions. Constr Build Mater 76:279–285. https://doi.org/10.1016/j.conbuildmat.2014.11.064

Zielinsky R, Ikeda S, Nomura H, Kato S (1987) Adiabatic compressibility of alkyltrimethylammonium bromides in aqueous solution. J Colloid Interface Sci 119(2):398–408. https://doi.org/10.1016/0021-9797(87)90286-4