Estimated enthalpy of formation of N-[3-(Dimethylamino)propyl] hexadecanamide by experimental approach

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Abstract

The *N-[3-(Dimethylamino)propyl] hexadecanamide* molecule is an important intermediate for synthesizing amphoteric and quaternary ammonium surfactants. Despite its importance for the household and personal care sectors, little to no information about its enthalpy of formation is found in the NIST database or literature, which hinders many industrial operations, especially its chemical production, by consuming much more energy than what is necessary. In this work, we present a first estimative of *N-[3- (Dimethylamino)propyl] hexadecanamide's* standard enthalpy of formation with a simple procedure that can be used to obtain similar parameters in chemical industry laboratories. The enthalpy estimative was obtained by reacting palmitic acid and dimethylaminopropylamine (DMAPA), yielding the desired compound. Hess's law was used to determine the enthalpy of the reaction through the heat associated with the extent of the reaction. The reagents were contacted in a simple calorimeter at room temperature (diluted with acetone) and 100 ºC (without acetone). The extent of the reaction was obtained by quantitative determination of the reaction medium in gas chromatography. The room temperature experiment led to an insignificant reaction extent which generated an unreliable result for the compound's enthalpy of formation. In contrast, at 100 ºC, the estimated standard enthalpy of the reaction was adequately calculated, leading to an enthalpy of formation of -703.93 ± 9.17 kJ/mol for the *N- [3-(Dimethylamino)propyl] hexadecanamide.* With this simple procedure, the industrial reactor's more precise heat consumption can be calculated, yielding economic and environmental benefits.

INTRODUCTION

The quaternary ammonium surfactants are widely used in household and personal care products, such as softeners, conditioners, disinfectants, hair masks, and many others (Bureš, 2019). However, these surfactants can cause uncomfortable feelings, such as rash or sore skin. Therefore, the amphoteric surfactants can provide mildness to the eye and skin, offering a critical micelle concentration reduction. Their structures are different from anionic and cationic surfactants because they have negative and positive charges that are compatible with other surfactants (Mullally and Marangoni, 2004).

Nowadays, these surfactants play a significant role in the customer's consumption struggle against the coronavirus (COVID-19), offering security and life protection sensation while providing desirable dermal properties for the personal care sector. This increase in worldwide demand has led companies to seek ways to improve their productive capacity and reduce energy requirements throughout their production process (Karamov et al., 2022).

The *N-[3-(Dimethylamino)propyl] hexadecanamide* is an important intermediate for synthesizing these surfactants. This molecule is a product of the amidation reaction between palmitic acid and dimethylaminopropylamine (DMAPA) (Fig. 1) (Wang et al., 2018). However, there is little to no information about its enthalpy of formation in the NIST database or literature, which has impaired energy process analysis by the chemical industry and consequently leads to much higher energy consumption.

Capuani do Brasil is a Brazilian enterprise acting on fragrance and surfactants for the chemical industry, which produces ca. 25t/month of *N-[3-(Dimethylamino)propyl] hexadecanamide*. Its process operates at 160ºC to get high reaction conversion. In addition, it uses a distillation process to remove residual DMAPA from the product, as residual levels of this reagent can impact product quality. Although the temperature at which the reactor operates is considered to be adequate for the production of the intermediate, it is an empirical assumption based solely on the experience of the operators.

Therefore, this work aims to present a first estimative using simple calorimetry techniques for the *N-[3-(Dimethylamino)propyl] hexadecanamide*'s standard enthalpy of formation which could improve the knowledge of energy requirements for the chemical process.

EXPERIMENTAL

Palmitic acid (98%) was purchased from Peter Cremer L.P., batch no. 9800829, 3- (dimethylamino)-1-propylamine (99%) was purchased from BASF CORP, batch no. GA2029902 and acetone (HPLC grade) was purchased from Macron Fine Chemical™, batch no. 0000117627. All experimental procedures were performed in Capuani's laboratory.

Given that the experimental setup was designed with materials commonly present in chemical industries laboratories, primarily used for quality analysis, the calorimeter consisted of a beaker thermally insulated by elastomeric foam and styrofoam equipped with a temperature gauge from the MT-512E 2 HP Full Gauge controller.

The calorimeter was calibrated by mixing distilled water at room temperature with warm water at approximately 35°C. Then, after the system reached equilibrium, the final temperature was measured, and this procedure was repeated four times to get the medium calorific capacity of the system.

Acetone dilution was necessary for the room temperature experiment, given that the palmitic acid is solid at this condition. Hence, both reagents were diluted in this solvent to avoid mass transfer limitation and deviation due to heat of dissolution. The palmitic acid was diluted in its solubility limit, one gram in thirty grams of acetone, and one gram of DMAPA was diluted in nineteen grams of acetone to achieve a slight excess in reaction proportion

The reagents were placed to react in the calorimeter at room temperature, and the system was kept undisturbed to reach thermal equilibrium. The final temperature was measured, and an aliquot was taken from the calorimeter after one hour for quantification by gas chromatography.

The same procedure was repeated without acetone, in the proportion of 7 grams of acid for 3 grams of DMAPA and at 100°C. Both reagents are liquid at this temperature, and a previous dilution was unnecessary. After four hours, the system reached thermal equilibrium, the final temperature was measured, and an aliquot of 20 µL was diluted in 25 mL of acetone for quantification by gas chromatography.

Chromatography analysis was performed with an HP 6850 series GC equipped with FID and 19091 N-133E INNOWAX column (Agilent, 30 m length, 0.25 mm internal diameter, and 0.25 μm thickness). The chromatography conditions used were: 1 minute of heating until 120°C, 10 minutes of heating until 250°C, 14 minutes at 250°C and 5 minutes of post-run until 120°C. Helium at 1.8 mL/min was used as a carrier gas, and the detector used hydrogen gas at 40 mL/min with synthetic air at 450 mL/min, and nitrogen gas at 80 mL/min flows as flame and make-up gases, respectively.

RESULTS AND DISCUSSION

The calorimeter was calibrated by measuring the temperature change due to the heat transferred by the warm water to the room temperature water until the system reached thermal equilibrium. The heat difference between the theoretical calculation and experimental data relates to the heat absorbed by the calorimeter walls. This value, divided by temperature variation, is the calorimeter's calorific capacity. Table 1 provides the measured property, and the results of the calorimeter's calibration, the transferred heat by water was calculated considering 4.184 J/g°C as its specific heat capacity (Taylor and Jackson, 1986). The suffix "C" represented room temperature water, "H" warm water, and "F" the equilibrium values.

Table 1
Calorimeter's calibration parameters

Calibration	mC(g)	TC (°C)	mH(g)	TH (°C)	TF (°C)	QH (J)	QC (J)	Ccal (J/°C)
C1	41.21	27.0	42.44	34.0	29.9	728.03	500.03	78.62
C2	41.81	26.6	46.49	35.0	30.3	914.22	647.25	72.15
C3	41.11	27.2	40.95	34.0	29.9	702.47	464.41	88.17
C4	43.70	27.3	40.13	33.0	29.4	604.45	383.97	104.99

The Shapiro-Wilk test was used to identify whether the calorimeter calorific capacity values are normally distributed. The test resulted in a p-value of 74,25%, indicating that the data is normally distributed. Hence, the average calorific capacity of the calorimeter is 85.99 J/°C with a standard deviation of 14.28 J/°C.

Then, the reagents diluted in acetone were placed to react in the calorimeter at room temperature (ca.25°C). Table 2 shows the results of these tests.

Qr represented the reaction heat and was calculated by Eq. 1, considering 2.16 J/g°C as the acetone specific heat capacity (Low and Moelwyn-Hughes, 1962).

Table 2
Heat of reaction for experiments at 25°C

Experiment	Ti (°C)	TF (°C)	ΔT (°C)	m(acetone) (g)	Qr (J)
EXP1	24.8	25.1	0.3	49.53	-57.89
EXP2	25.0	25.3	0.2	46.55	-37.31
EXP3	25.1	25.3	0.2	50.51	-39.02

$$|Qr| = m(acetone)Cp(acetone)\Delta T + Ccal\Delta T \quad (1)$$

The standard enthalpy of reaction was calculated by the division between the reaction heat and the extent of the reaction (ξ), which was determined by the difference of initial (ni) and final (nf) palmitic acid amount in the calorimeter. Table 3 shows the results of these reactions conducted at 25 ºC.

Table 3 Enthalpy of reaction for experiments at 25°C

Experiment	ni (mmol)	nF (mmol)	ξ (mmol)	ΔHr (kJ/mol)
EXP1	4.08	2.76	1.32	-43.93
EXP2	4.07	3.10	0.97	-38.47
EXP3	3.96	3.08	0.87	-44.68

The intermediate's enthalpy was calculated by Hess's law considering the vapor water's enthalpy (Eq. 2) and liquid water's enthalpy (Eq. 3). The standard enthalpy of formation values, which were consulted in NIST, for DMAPA, palmitic acid, vapor water, and liquid water are, respectively: -76,9 kJ/mol (Papina et al., 1992), -848,4 kJ/mol (Lebedeva, 1964), – 241,82 kJ/mol (Cox, Wagman, and Medvedev, 1984) and – 285,83 kJ/mol (Cox, Wagman, and Medvedev, 1984).

$$\boldsymbol{\Delta H^{\circ}_{r(lower)} = \Delta H^{\circ}_{f(intermediate)} + \Delta H^{\circ}_{f(vapor\ water)} - \Delta H^{\circ}_{f(DMAPA)} - \Delta H^{\circ}_{f(palmitic\ acid)}} \quad \textbf{(2)}$$

$$\boldsymbol{\Delta H^{\circ}_{r(lower)} = 683.48 + \Delta H^{\circ}_{f(intermediate)}}$$

$$\Delta H^{\circ}_{r(higher)} = \Delta H^{\circ}_{f(intermediate)} + \Delta H^{\circ}_{f(liquid\ water)} - \Delta H^{\circ}_{f(DMAPA)} - \Delta H^{\circ}_{f(palmitic\ acid)} \quad (3)$$

$$\Delta H^{\circ}_{r(higher)} = 639.47 + \Delta H^{\circ}_{f(intermediate)}$$

As a result, the average *N-[3-(Dimethylamino)propyl] hexadecanamide*'s enthalpy of formation was estimated as -681.83 ± 3.39 kJ/mol for the reaction at 25ºC considering the higher enthalpy of reaction (Eq. 3). Using this estimated enthalpy of formation leads to a positive lower enthalpy of reaction (Eq. 2), which is impossible given that the global reaction is known to be exothermic. It is possible that the low reaction extent and slight temperature variation contributed to this unreliable result. Moreover, the dilution of the reagents could have also contributed to a low reaction extent.

The reaction temperature was raised to 100ºC, closer to industrial reaction conditions, in which the reagents are both in liquid form to overcome these impairments.

Tables 4 and 5 show the results of the tests conducted at 100ºC.

Table 4
Heat of reaction for experiments at 100°C

Experiment	Ti (°C)	TF (°C)	ΔT (°C)	Qr (J)
EXP1	99.9	108.0	8.1	-696.48
EXP2	100.1	108.1	8.0	-687.88
EXP3	100.1	108.9	8.8	-756.67

Table 5
Enthalpy of reaction for experiments at 100°C

Experiment	ni (mol)	nF (mol)	ξ (mmol)	ΔHr (kJ/mol)
EXP1	0.219	0.209	10.27	-67.80
EXP2	0.219	0.208	10.96	-62.78
EXP3	0.219	0.210	9.39	-80.56

The average enthalpy of formation of *N-[3-(Dimethylamino)propyl] hexadecanamide* was estimated as -703.93 ± 9.17 kJ/mol for the reaction at 100ºC considering the lower enthalpy of reaction (Eq. 2), which is -70.38 ± 9.17 kJ/mol at this temperature, negative as expected. This enthalpy of reaction value is a reasonable estimate because it is close to the standard enthalpy of reaction between acetic acid and ammonia, -76.1 ± 9.17 kJ/mol (Hill and Wadso, 1968), unique likewise reaction of amidation enthalpy value available at NIST.

As an estimated result, the standard deviation is significant, probably due to the increasing volatility of DMAPA with increasing temperature. In addition, the chemical setup of this reaction is challenging for the industry since, at room temperature, the palmitic acid is solid and immiscible with DMAPA. In contrast, at higher temperatures, DMAPA partially vaporizes. However, even as a first estimate with a simple calorimeter setup, the economy in vapor directed to the industrial chemical reactor was significant, as will be shown in a future publication regarding the process operation.

CONCLUSION

In this work, we report a first estimative of the enthalpy of formation of *N-[3- (Dimethylamino)propyl] hexadecanamide*, an important intermediate for synthesizing amphoteric and quaternary ammonium surfactants. The average value was − 703.93 ± 9.17 kJ/mol, obtained at 100ºC. The exothermic characteristic of the reaction is preserved for lower and higher enthalpy of the reaction (Eqs. 2 and 3) at this temperature. The estimated value obtained in this work provides important information for energy balance calculations, allowing the simulation of this reaction and favoring research on improving quaternary ammonium and amphoteric surfactant production processes.

Declarations

Conflict of interest The authors have no conflicts of interest to declare.

Responsibility The responsibility of information about Capuani do Brasil’s manufacturing process, lies entirely with the authors.

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Figures

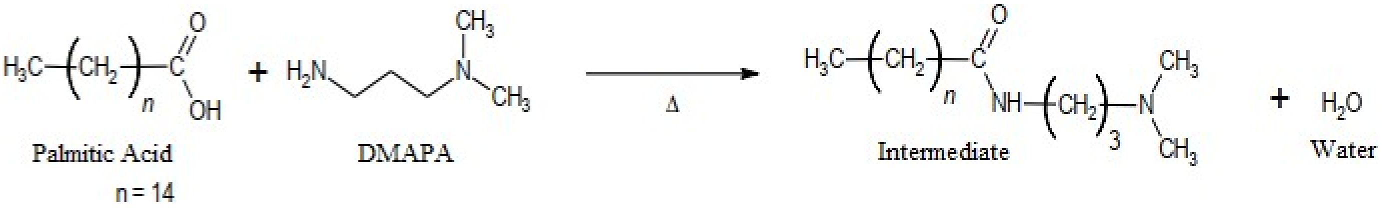

Figure 1

Reaction between palmitic acid and DMAPA (Wang et al., 2018).