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Calorimetric studies on some nonionic surfactants

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Summary

The heats of hydration of some nonionic surfactants at various temperatures between 25 and 55 ° C have been measured using calorimetry. The heat of hydration of a surfactant, in its liquid state, is directly related to its hydrophile-lipophile balance (HLB) and can be used to investigate batchwise variation. The method is accurate, rapid and relatively easy to use. Experiments on the nonylphenol ethoxylates have shown a change in behaviour in those samples with molar ethylene oxide ratios in excess of 10.

Introduction

Derivatives of polyethylene oxide arguably form the majority of the nonionic surfactants used today. They are generally prepared by the addition of ethylene oxide to compounds containing one or more active hydrogen atoms, e.g. alkylphenols, fatty alcohols, fatty acids and polyols. When dissolved or diluted in water, hydration of the ether linkage of the ethylene oxide chain by hydrogen bond formation results in an exothermic reaction. This so-called heat of hydration can be measured calorimetrically and, for materials in the liquid state, related to the hydrophile-lipophile balance (HLB) of the surfactant (Racz and Orban, 1965). This study extends the original work in two areas; firstly, to the measurement at higher temperatures enabling surfactants solid at room temperature to be evaluated and, secondly, to the development of a method for assessing batchwise variation in nonionic surfactants.

Materials and Methods

Two series of nonionic surfactants were studied; the polyoxyethylene sorbitan fatty acid esters (polysorbates, Tweens 20, 40, 60, 80, 81 and 85; ICI Specialty Chemicals) and the nonylphenol ethoxylates of increasing molar ratios of ethylene oxide (Synperonic NP4, NP5, NP6, NP8, NP9, NP10, NP12, NP13, NP15, NP20, NP30, NP35 ICI Chemical and Polymers). In addition, a polyoxyethylene castor oil derivative (PEG (40) hydrogenated castor oil; Cremophor, BASF) was also tested. All materials were used as received.

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The heat of hydration of liquid samples was measured using a Tronac calorimeter (Model 458, Tronac Inc., UT, U.S.A.). The calorimeter, which has been described elsewhere (Lindenbaum and McGraw, 1985) consisted of a reaction vessel (50 ml capacity, silvered glass, vacuum Dewar flask) immersed in a thermostatted, insulated water-bath. The surfactant in its liquid state was contained in a sealed, thin-walled, glass ampoule mounted on a rotating support (which also doubled as a stirrer for the water in the reaction vessel). After equilibration to the required temperature the ampoule was broken and the temperature rise monitored by means of a thermistor. This was compared to a similar temperature rise initiated using a heating coil in the reaction vessel and from the applied current, voltage and time used an enthalpy of the reaction could be calculated. Data capture and processing were carried out using a microcomputer linked to the calorimeter via an interface. Experiments were carried out in triplicate.

Results and Discussion

Before discussing the results in detail it is important to note the following:

(a) All the experiments were performed using surfactants in the liquid state – for materials in the solid state superimposed phase changes would cause enthalpy changes in addition to energy release by hydration.
(b) The concentration of the aqueous solution of each surfactant after completion of the reaction (2% w/w) was an order of magnitude greater than its critical micelle concentration (Becher 1966).

Effect of temperature

Fig. 1 shows the linear relationship between the measured heat of hydration (Q) at both 25 and 45 °C and the HLB values (manufacturer's data) of the polysorbates. If the relationship is expressed in the same format as used by Racz and Orban (1965), i.e.

$$\text{HLB} = AQ + C \tag{1}$$

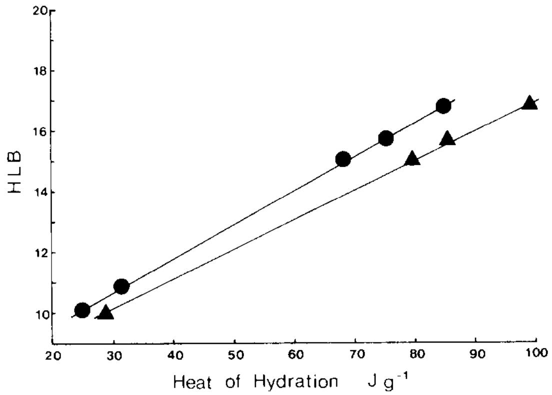

Fig. 1. Relationships between HLB and the heat of hydration for the polysorbates: (●) 45°C, (△) 25 °C.

where A and C are constants, then values for these constants determined using regression analysis are comparable with those calculated from their data (Table 1), despite the fact that the ultimate concentrations in this work were some 3-times greater. The decrease in the heat of hydration with temperature is a manifestation of the inverse temperature solubility of these materials in water. It is interesting to note that the relative decrease in the heat of hydration with temperature varies with the HLB of the surfactant, those with higher HLB values being larger (Fig. 2). Similar results were obtained with the nonylphenol ethoxylates (Figs 3 and 4) but in this case the regression constants were different (Table 2).

The nonylphenol ethoxylates are a useful series of surfactants to study since, by their very nature, they are polydispersed materials with properties close to those of the homogeneous compound having the composition of the mean.

TABLE 1

Regression data for the polysorbates (± standard error)

Temperature (°C)	A	B	r^2
20 [a]	0.100 ± 0.004	7.32 ± 0.26	0.9931
25	0.096 ± 0.020	7.31 ± 1.11	0.9990
35	0.102 ± 0.002	7.43 ± 0.14	0.9983
45	0.108 ± 0.003	7.45 ± 0.17	0.9976

[a] Data from Racz and Orban (1985).

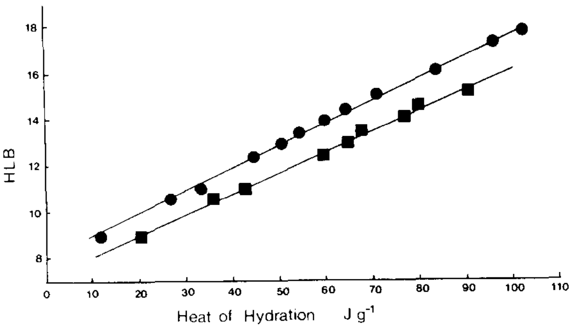

Fig. 2. Relationship between HLB and the heat of hydration for the nonylphenol ethoxylates: (●) 55 °C, (■) 25 °C.

Hence, it is possible to convert the heat of hydration data into molar units assuming each surfactant has a mean molar ratio of ethylene oxide units equivalent to its designated number (i.e. NP4 will have an average of four ethylene oxide units per nonylphenol unit) – a reasonable approximation in the light of recent chromatographic data (Allan et al., 1989). Fig. 5 shows the results for the series at four temperatures. For all temperatures the molar heat of hydration increases to a maximum at a molar ethylene oxide ratio of 10 and then decreases at higher ratios. It is interesting to note that the curves are analogous to those showing the effect of molar ethylene oxide ratio on both detergency (Harris, 1966) and foaming (Gantz, 1966) for a variety of alkylphenol ethoxylates.

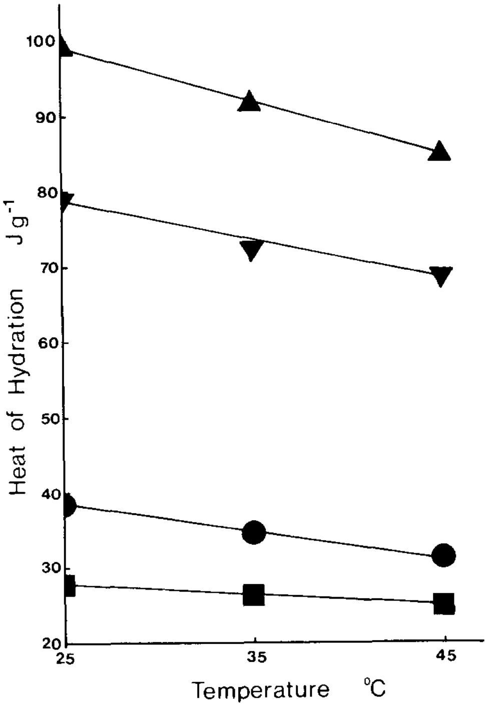

Fig. 3. Relationship between the heat of hydration and temperature for the polysorbates: (▲) polysorbate 20, (▼) polysorbate 80; (●) polysorbate 85, (■) polysorbate 81.

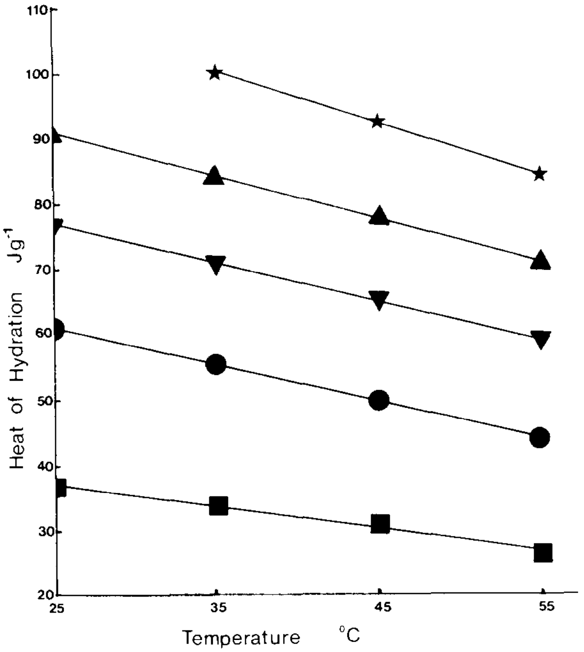

Fig. 4. Relationship between the heat of hydration and temperature for the nonylphenol ethoxylates (★) NP 20; (▲) NP 15; (▼) NP 12, (●) NP 8, (■) NP 5.

The change in behaviour for these surfactants at a molar ethylene oxide ratio of approx. 10 implies some specific change in chain conforma-

TABLE 2

Regression data for the nonylphenol ethoxylates (± standard error)

Temperature (°C)	*A*	*B*	r^2
25	0.088 ± 0.002	7.18 ± 0.15	0.9953
35	0.093 ± 0.004	7.07 ± 0.27	0.9848
45	0.092 ± 0.002	7.53 ± 0.16	0.9934
55	0.097 ± 0.002	7.88 ± 0.16	0.9932

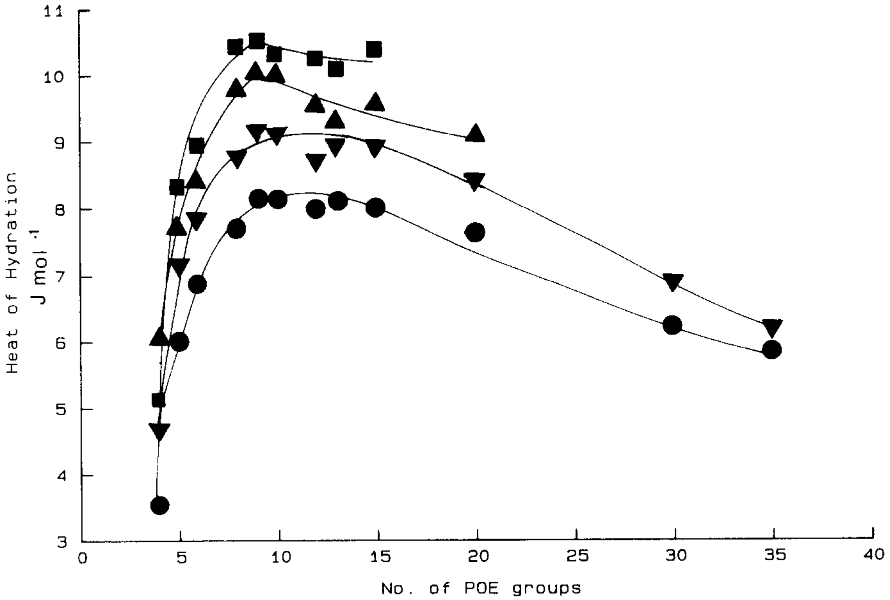

Fig. 5. Relationship between the molar heat of hydration and the molar ratio of the ethylene oxide for the nonylphenol ethoxylates: (■) 25 °C, (▲) 35 °C, (▼) 45 °C, (●) 55 °C.

tion at this ratio followed by a further change in surfactants with molar ratios in excess of 15. The conformation of the oxythylene chain in bulk surfactants has been discussed using the so-called 'zig-zag' and 'meander' models (Rosch, 1966). It is thought that chains with more than 10 ethylene oxide units are predominantly in the form of expanded helical coils (the meander model) rather than in the fully extended conformation (the zig-zag model). Whether the same situation occurs in solution (as opposed to the bulk) is open to debate but the data recorded in this study would confirm this. The gradual decrease in the molar heat of hydration in surfactants with more than 15 ethylene oxide units may well be due to further coiling of the longer chains.

Batchwise variation

Surfactants are, but their very nature, heterogeneous and will exhibit both source and batch variation due to variations in the catalyst, and reaction conditions used to produce them. Measurement of the heat of hydration offers a relatively easy and rapid way of investigating this variation.

Although no batchwise variation was seen with the nonylphenol ethoxylates, variation was found with the polysorbates (Table 3) with the extent being most pronounced in the polysorbate 80. It is interesting to note that a change in the heat of hydration of 10 J g^{-1} can result in the change of HLB of 1 unit. Such a variation could affect the processing and/or stability of a formulation. Such was the case in a formulation prepared using the PEG(40) hydrogenated castor oil where the surfactant was used as a solubiliser for an oil-based flavour. Calorimetric studies performed at 30 °C (i.e. when the surfactant was in its liquid state)

TABLE 3

Batchwise variation in the polysorbates

Batch No.	Heat of hydration (J g^{-1})	
	Polysorbate 20	Polysorbate 80
1	98.83	70.47
2	99.49	81.19
3	96.91	72.92
4	97.77	81.45
5	98.63	76.97
6	–	78.57

TABLE 4

Batchwise variation in PEG (40) hydrogenated castor oil

Batch No.	Heat of hydration (J g^{-1})
1	93.95
2	95.40
3	96.17
4	96.67
5	96.69
6	97.03
7	99.17

showed batchwise variation (Table 4), with those batches having a heat of hydration below 96.7 J g^{-1} performing well but with those with a heat of hydration greater than this value (i.e. those batches with a higher HLB) producing emulsions.

Conclusion

The heat of hydration of a nonionic surfactant above its melting point is directly dependent on its HLB and can be used to investigate batchwise variation and/or control the surfactant. The method is accurate, rapid, relatively easy to use and can be carried out at any temperature enabling surfactants solid at room temperature to be easily evaluated.

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