A Calorimetric Determination of the Standard Enthalpy and Heat Capacity Changes that Accompany Micelle Formation for Four Long Chain Alkyldimethylphosphine Oxides in H_2O and D_2O Solution from 15 to 79 °C

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Abstract: Relative partial molar enthalpy data were obtained at five degree intervals between 15 and 79 °C for n-C_8-, C_9-, and C_{10}-dimethylphosphine oxides and between 15 and 60 °C for n-C_{11}-dimethylphosphine oxide in H_2O and D_2O. The results were used to calculate the standard molar enthalpy and heat capacity changes for micelle formation for comparison with the data previously reported for the C_{12} homologue. These values were then used to calculate the temperature dependence of the cmc, which was always lower in D_2O than in H_2O solutions. A small temperature dependence of the heat capacity change for micelle formation was observed in both solvents. Changes in thermodynamic parameters that accompany the transfer of the surfactant from H_2O to D_2O solution were also determined. It is interesting that differences in heat capacity noted for micelle formation or transfer of monomeric surfactant between the two solvents exhibited a greater dependence on the molecular weight of the surfactants than the corresponding enthalpy and entropy changes.

Introduction

Thermodynamic data for surfactant solutions are useful because they can provide insights into the mechanism of micelle formation or be used as a reference for understanding related processes. Most of the data currently in the literature have been obtained from first and second derivatives of the Gibbs energy change that is assumed to describe some aspect of micelle formation.[1] However, it has been recognized in the past,[2] and again more recently,[3] that possible problems are associated with these methods and the results need to be verified by calorimetry. This has been difficult for long chain surfactants, especially nonionic ones, due to the lack of convenient commercially available instruments with the necessary sensitivity and precision. Fortunately, that has changed recently and we may expect more data of this type to be forthcoming soon. The purpose of this study was to investigate one aspect of micelle formation with titration calorimetry, namely, the effect of the solvent isotope effect on the thermodynamic changes that accompany micelle formation for a fairly long chain nonionic surfactant homologous series. Such information may be compared with previous solubility data for low molecular weight solutes and other nonionic surfactants to examine the contribution of different portions of the surfactant molecule to the thermodynamic changes that accompany micelle formation and transfer between the two solvents.

Experimental Section

The alkyldimethylphosphine oxide samples used in this study were obtained from BoiAffinity Systems (Rockford, IL), dried over P_2O_5, and used without purification. Each sample was examined by ^{31}P and proton NMR and found to exhibit characteristic spectra,[4] i.e., a single sharp phosphorus peak located near 52 ppm relative to 85% H_3PO_4 and a $P-CH_3$ doublet centered at 1.5 ppm. Elemental analysis of duplicate samples yielded results that were within experimental error of theoretical values. Stock solutions of each surfactant 5−20 times greater than the cmc were prepared by mass in deionized water or D_2O (99.9% ± 0.1%, MSD Isotopes). Final concentrations were converted to units of molality for subsequent data analysis by using specific volumes of 1.09, 1.10, and 1.11 mL/g for C_8DPO, C_{10}DPO, and C_{12}DPO reported by Benjamin[5] and interpolated values of 1.095 and 1.105 mL/g for C_9DPO and C_{11}DPO. The density of D_2O was taken as 1.1045 g/mL.[6]

Heat of dilution experiments were performed by using a titration microcalorimeter (ITC, MicroCal Inc., Northampton,MA) as previously described.[7,8] Only one filling of the syringe was required to obtain a complete relative partial molar enthalpy curve from infinite dilution to about twice the cmc for the longer chain samples. However, successive titrations without removal of the contents of the calorimeter were required due to the large heat of dilution and high cmc for the two shortest chain length samples. The worksheets from as many titrations as were necessary to complete the titrations for C_8DPO and C_9DPO were merged and the final molarity in the cell was calculated by using the standard Origin software. The volume of each injection ranged from 2 to 20 μL depending upon the magnitude of the heat change and the steepness of the titration curves, larger volumes being added when the curve was nearly flat. A buret with a capacity of either 100 or 250 μL was used for the titrations. The cell volume was 1.3373 mL. Concentrations expressed on the molality scale were used for final data analysis. The relative partial molar enthalpy, $\bar{L}_2$, of the surfactant was determined as previously described.[3] Visual inspection of the data

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established the limit of an initial linear region, m', above which concentration the data were clearly sigmoidal. The data were fit to either a linear or sigmoidal equation by using the Origin software provided by MicroCal. The sigmoidal equation used was of the form

$$\bar{L}_2 = \frac{(A_1 - A_2)}{(1 + \exp(m - m_o))/\Delta m} + A_2 \tag{1}$$

The coefficient A_1 is approximately equal to the value of $\bar{L}_2$ at m', A_2 corresponds to $\bar{L}_2$ at the end of the titration, and Δm defines the steepness of the curve at the inflection point, m_o (which is identified as the cmc). The standard enthalpy, $\Delta H°$, and heat capacity, $\Delta Cp°$, for micelle formation over the temperature range investigated were related to their reference values, ΔH_r and ΔCp_r, at the reference temperature, $T_r = 298$ K, by eqs 2 and 3,

$$\Delta H° = \Delta H_r + (\Delta Cp_r - BT_r)(T - T_r) + B/2\,(T^2 - T_r^2) \tag{2}$$

$$\Delta Cp° = \Delta Cp_r + B(T - T_r) \tag{3}$$

The coefficient B, which has units of cal/(mol·K), reflects the temperature dependence of $\Delta Cp°$. The molar enthalpy and heat capacity changes at the reference temperature can be used to calculate the temperature dependence of the cmc with the equation

$$\begin{aligned} R \ln(\text{cmc}) = {} & \\ & R \ln(\text{cmc}_r) + (\Delta H_r - T_r\Delta Cp_r + T_r^2 B/2)(1/T - 1/T_r) - \\ & (\Delta Cp_r - T_r B) \ln(T/T_r) - B/2(T - T_r) \end{aligned} \tag{4}$$

Finally, one can use a pseudo phase equilibrium model[9] to relate the mole fraction of surfactant at the cmc to the standard Gibbs energy, $\Delta G°$, and entropy, $\Delta S°$, for micelle formation from the equations

$$\Delta G° = RT \ln(\text{cmc}) \tag{5}$$

$$\Delta S° = (\Delta H° - \Delta G°)/T \tag{6}$$

The mean standard deviation for data that represents replicates or standard errors for data that result from curve fitting were determined by standard procedures given in the Origin reference manual.

Results

An example of the results obtained from seven successive dilutions of 192 mM C_8DPO in water at 30 °C without removing the contents of the calorimetric cell between dilutions is given in Figure 1a. The concentration of surfactant along the abscissa indicated in this figure represents the amount of sample added during each individual titration. This is based on the assumption that the titration cell only contained solvent prior to the addition of titrant. Thus it represents the actual concentration of surfactant in the cell for the first addition only. The first four dilutions were the most exothermic and consisted of 41 injections of 2 μL from a 100 μL syringe. The fifth dilution consisted of 40 injections of 5 μL and the final two dilutions consisted of 25 injections of 10 μL. The last three dilutions were made with a 250 μL syringe and included a single 2 μL pre-injection. In every case, the data for the first injection from either syringe were discarded. The worksheets that contained data from each of the seven dilutions were merged to give the composite curve shown in Figure 1b.

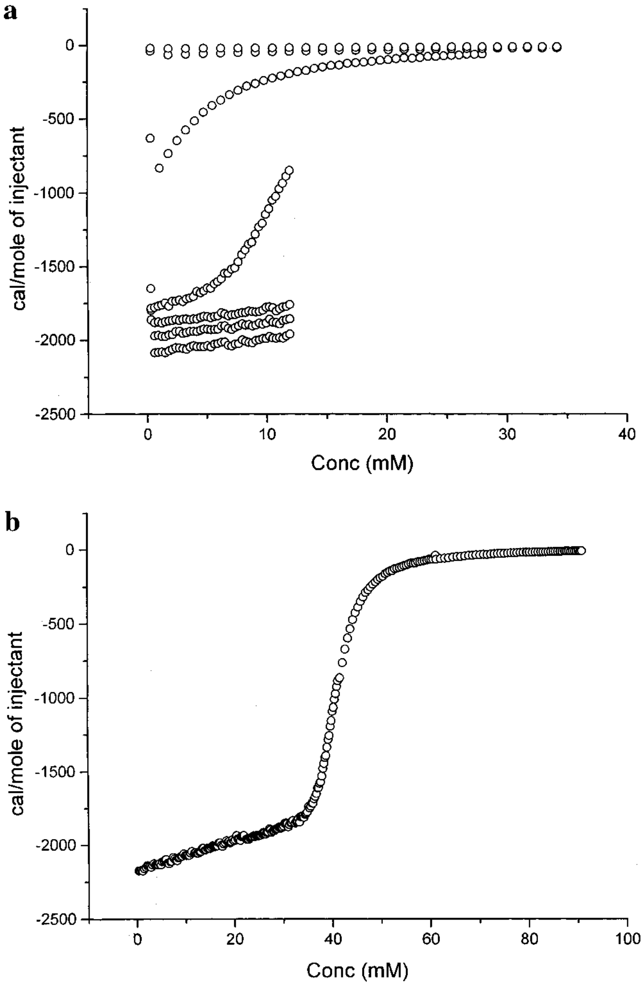

Figure 1. (a) Integrated power data obtained at 30 °C for seven successive dilutions of 192 mM C_8DPO into water as described in the text. The concentration is only apparent for all of the titrations except for the first one since the possible presence of surfactant in the cell prior to the titration was not taken into account until the data from each titration were combined. (b) Results obtained from merging the data depicted in Figure 1a. The final surfactant concentration in the cell was 90.7 mM.

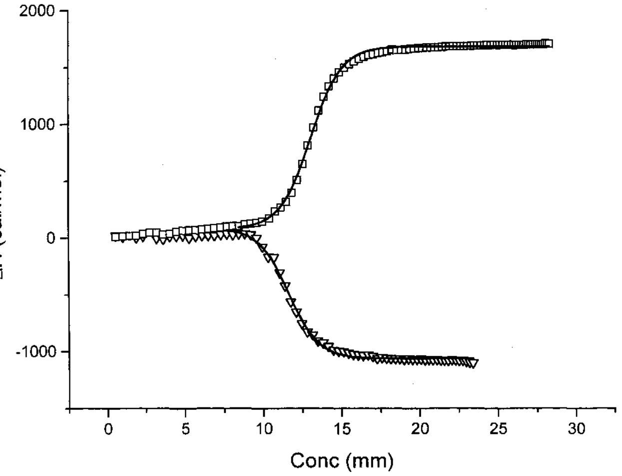

Figure 2. Plot of the experimental data obtained for the dilution of C_9DPO at 30 (open squares) and 65 °C (open triangles). The solid lines correspond to a fit of the experimental data to eq 1 above 8.4 mm in H_2O and 6.2 mm in D_2O.

The dilution curves for all of the alkylphoshine oxide surfactants considered here were exothermic at low temperatures and endothermic at high temperatures. An example of enthalpy data that illustrate this behavior is given for C_9DPO at 30 and 65 °C in Figure 2. The data resemble those for C_{12}DPO previously reported.[3] A summary of the empirical parameters that describe the variation of $\bar{L}_2$ with concentration and temperature between infinite dilution and m' is given in Table 1 for all five alkylphosphine oxide surfactants investigated. The

Table 1. Summary of the Coefficients That Describe the Temperature Variation of the Slope of the Linear Region of the Relative Partial Molar Enthalpy Curve between *m′* and Infinite Dilution for the Surfactants Investigated[a]

surfactant	solvent	*m′* (mm)	T_0 (°C)	*a*	*b*
C_8DPO	H_2O	30	60.0	−0.09 ± 0.02	12 ± 1
	D_2O	21	61.1	−0.08 ± 0.02	13 ± 1
				(2.65 ± 0.35)	(2E−3 ± 5E−3)
C_9DPO	H_2O	8.4	50.7	−0.24 ± 0.04	20 ± 3
	D_2O	6.2	52.5	−0.25 ± 0.04	24 ± 2
				(0.84 ± 0.05)	(1E−3 ± 1E−3)
$C_{10}DPO$	H_2O	3.0	44.8	−0.38 ± 0.1	34 ± 6
	D_2O	2.4	48.1	−1.8 ± 0.1	96 ± 10
				(0.20 ± 0.02)	(7E−4 ± 3E−4)
$C_{11}DPO$	H_2O	0.71	39.5	−2.9 ± 0.9	141 ± 34
	D_2O	0.59	41.5	−5.6 ± 0.7	262 ± 29
				(0.12 ± 6E−3)	(−1.2E−4 ± 1.4E−4)
$C_{12}DPO$[b]	H_2O	0.19	35.0	−6 ± 1	201 ± 27
	D_2O	0.13	37.5	−7 ± 1	251 ± 37
				(3.4E−2 ± 2E−3)	(−3.3E−4 ± 1.9E−4)

[a] Values of the coefficients for Δm are given in parentheses. The temperature at which the observed heat of dilution was zero, T_0, is also included. The equation used to represent the data is as follows: slope (cal mol^{-1} mm^{-1}) = $a + bT$ (°C) or Δm (mm) = $a + bT$ (°C), and the corresponding standard errors are given. [b] Reference 3.

intercepts were usually more positive and the slopes more negative for the D_2O solutions than for the H_2O solutions, likely reflecting differences in solute−solute interactions in the two solvents below the cmc.[10] The positive trends observed for the variation of slopes and intercepts with temperature may be attributed to the same effect. Also, the lower cmc noted for all surfactants in D_2O was accompanied by a lower value of *m′*. The more positive heat of dilution of the surfactants in D_2O than in H_2O at 15 °C persisted well above 25 °C and resulted in a higher temperature at which the heat of dilution (also micelle formation) was zero. The values of Δm were found to be temperature dependent, although not significantly different in H_2O and D_2O. A summary of the coefficients that represent the average values of Δm for the two solvents is also given in Table 1. These values together with the cmc (m_o) and $\Delta H°$ ($-A_2$) may be used with eq 1 to calculate relative partial molar enthalpy curves for each surfactant over the temperature range investigated.

The enthalpy data for surfactant concentrations below *m′* were extrapolated to infinite dilution and the relative partial molar enthalpy values were fit according to eq 1. The standard heat of micelle formation, $\Delta H°$, was defined as the difference between the partial molar enthalpy of the surfactant in the micellar and monomeric states.[3] The resulting data were plotted versus temperature, and the results are given in Figure 3 for the five alkylphosphine oxides investigated. The data included in Figure 3 represent the results from more than 5000 individual injections, or differential heats of dilution, which were collected over a two-year period. Although the heat of micelle formation changes sign at different temperatures for each surfactant, it becomes negative at higher temperatures in each case. The rate of change of $\Delta H°$ with temperature is similar in the two solvents. A summary is given in Table 2 of the results obtained from fitting all of the data according to eqs 2 and 3, and the curves drawn through the individual data points presented in Figure 3 resulted from the use of these data. The heat capacity change that accompanies micelle formation is negative for all of the surfactants and the temperature variation of $\Delta Cp°$, represented by the coefficient *B*, generally increases with the molecular weight of the surfactant.

It has been noted that the prediction of the temperature dependence of the cmc is one of the primary justifications for the experimental determination of enthalpy and heat capacity changes for surfactant solutions.[11] The data contained in Table 1 were used to calculate the temperature dependence of the cmc for the four surfactants considered in this study from eq 4, and the results are given in Figure 4. The overall representation of the experimental data is considered to be good. The calculated curves reproduced the cmc for the D_2O solutions a little better than for the H_2O solutions for an unknown reason (probably experimental error).

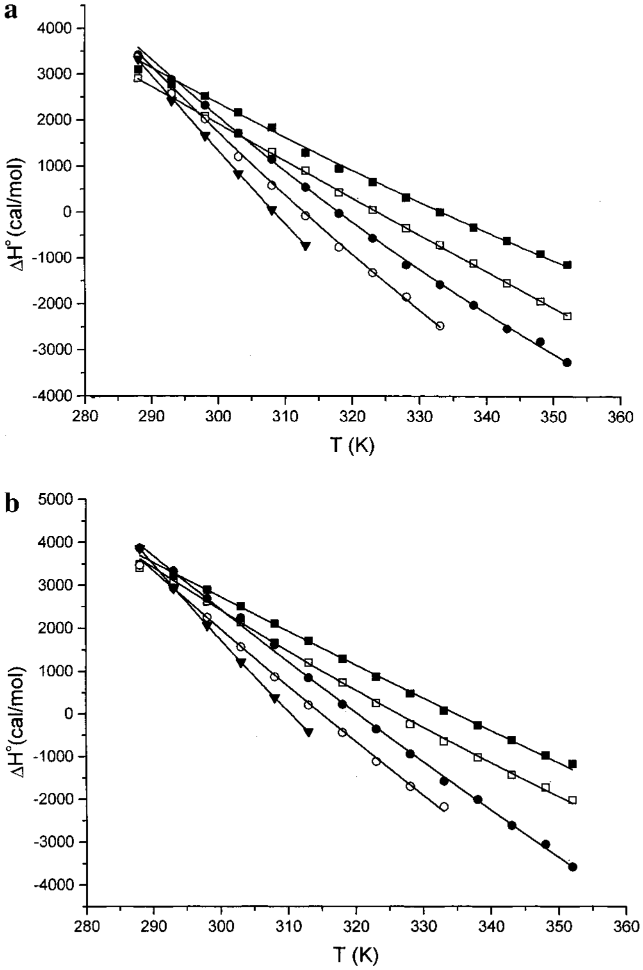

Figure 3. Plot of $\Delta H°$ versus temperature for $C_{12}DPO$ (filled triangles), $C_{11}DPO$ (open circles), $C_{10}DPO$ (filled circles), C_9DPO (open squares), and C_8DPO (filled squares) in H_2O (a) or D_2O (b). The solid lines correspond to the fit of the data to eq 2.

Table 2. Summary of the Thermodynamic Parameters Obtained for Five Alkyldimethylphosphine H_2O and D_2O Oxides in Solutions over the Temperature Range Described in the Text. (Reference Temperature 298 K)[a]

	H_2O				D_2O			
surfactant	cmc_r (mm)	B (cal/(mol·K))	ΔH_r (cal/mol)	ΔCp_r (cal/(mol·K))	cmc_r (mm)	B (cal/(mol·K))	ΔH_r (cal/mol)	ΔCp_r (cal/(mol·K))
C_8	46.31 ± 0.07	0.30 ± 0.14	2526 ± 4	−77 ± 3	39.18 ± 0.05	0.11 ± 0.10	2890 ± 4	−80 ± 3
C_9	13.90 ± 0.03	0.03 ± 0.05	2086 ± 4	−81 ± 1	11.61 ± 0.03	0.42 ± 0.12	2618 ± 2	−98 ± 3
C_{10}	4.185 ± 0.01	0.75 ± 0.1	2321 ± 5	−123 ± 2	3.639 ± 0.01	0.30 ± 0.13	2687 ± 9	−124 ± 3
C_{11}	1.250 ± 0.007	0.71 ± 0.3	2020 ± 2	−141 ± 4	1.073 ± 0.006	0.34 ± 0.27	2250 ± 45	−136 ± 4
C_{12}[b]	0.334 ± 0.004	0.50 ± 0.3	1664 ± 30	−162 ± 2	0.276 ± 0.009	1.1 ± 0.1	2068 ± 20	−174 ± 1

[a] The errors given for the cmc and ΔH represent the mean standard deviation and standard errors are included for B and ΔCp. [b] The data for $C_{12}DPO$ were from ref 3.

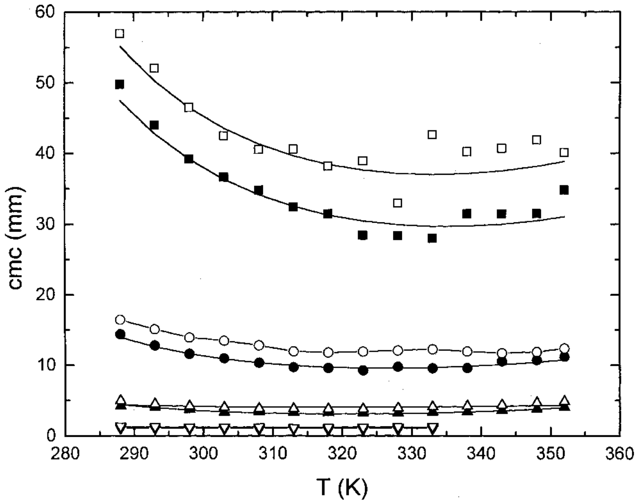

Figure 4. Plot of the cmc versus temperature for $C_{11}DPO$ (down triangles), $C_{10}DPO$ (up triangles), C_9DPO (circles), and C_8DPO (squares) in H_2O (open symbols) or D_2O (filled symbols). The solid lines correspond to the fit of the data to eq 4 using the partial molar enthalpy and heat capacity changes obtained from the use of eq 2.

The standard Gibbs energy and entropy change for micelle formation was calculated for each surfactant over the temperature range considered in this study from eqs 5 and 6, respectively, using the data in Figure 3 for the enthalpy change. The results were used to prepare a compensation plot[1] for each surfactant in water and D_2O and a summary of the values obtained for the resulting linear relationships are given in Table 3. All of the correlation coefficients are close to 1.0, indicating an excellent linear fit of the data. The so-called compensation temperature, or slope, is quite similar in the two solvents. These values may be used as a convenient empirical basis for estimation of the cmc at various temperatures. The data in Table 3 may also be used to estimate the incremental changes in enthalpy and entropy that accompany micelle formation of the alkylphosphine oxides. The enthalpy values so obtained using the difference between the data for each pair of surfactants that differ in size by one methylene group were 850, 660, 540, and 475 cal/mol and the entropy values were 2.43, 2.29, 2.24, and 2.47 cal/(mol·K), respectively. Thus the assumption of a constant value for the contribution of methylene groups to the enthalpy, and perhaps entropy, of micelle formation is not justified. Or in other words, group additivity is not observed.

Finally, the standard Gibbs energy of transfer of the monomeric form of each surfactant from water to D_2O was determined from the difference between the Gibbs energy of micelle formation according to eq 5. The corresponding entropy of transfer, $\Delta\Delta S°$, was obtained in a similar manner by using eq 6 and the differences between the standard enthalpy change that accompanies micelle formation in D_2O and H_2O. A summary of the results obtained for each surfactant over the temperature range investigated is given in Figures 5a and 5b, respectively. The results obtained are shown along with a curve that represents an empirical fit of the average of all of the data to a second degree binomial equation with coefficients equal to −25.14 ± 8.56, 0.1957 ± 0.536, and $(-3.542 \times 10^{-4}) \pm 8 \times 10^{-5}$. The enthalpy of transfer data exhibited a similar variation with temperature as shown in Figure 5b, and the average values obtained for all five surfactants were described by a second degree binomial equation with coefficients equal to −6375 ± 4397, 49.30 ± 27.53, and −0.08941 ± 0.04297. The surprising result is the absence of a systematic change in either property with molecular weight of the surfactants.

Table 3. Summary of the Compensation Data Obtained from a Plot of the Standard Enthalpy Change vs the Standard Entropy Change for Micellization for the Surfactants Considered in This Investigation[a]

surfactant	intercept (cal/mol)	slope (K)	R
C_8DPO			
H_2O	−4554 ± 49	314 ± 3	0.99955
D_2O	−4776 ± 30	319 ± 2	0.99986
C_9DPO			
H_2O	−5503 ± 61	324 ± 3	0.99939
D_2O	−5523 ± 36	318 ± 2	0.99981
$C_{10}DPO$			
H_2O	−6106 ± 50	317 ± 3	0.99962
D_2O	−6247 ± 62	318 ± 3	0.99949
$C_{11}DPO$			
H_2O	−6603 ± 70	307 ± 3	0.99962
D_2O	−6828 ± 55	312 ± 2	0.99979
$C_{12}DPO$			
H_2O	−7138 ± 64	298 ± 2	0.99989
D_2O	−7241 ± 71	297 ± 2	0.99988

[a] The uncertainty given for the slopes and intercepts represents the standard error.

Discussion

The values for the cmc that were determined in this study at 25 °C for C_8DPO, C_9DPO, $C_{10}DPO$, and $C_{11}DPO$ of 42 ± 0.1, 14 ± 0.1, 4.2 ± 0.01, and 1.2 ± 0.01 mm are in excellent agreement with the values reported by Clint and Walker[12] from surface tension measurements at 23.6 °C (46 ± 4, 12 ± 4, 3.9 ± 0.01, and 1.1 ± 0.1 mm). Both sets of values also agree with the results from light scattering and surface tension measurements at 30 °C for $C_{10}DPO$ and $C_{12}DPO$ of 41 ± 1 and 4 ± 1 mM by Herrmann et al.[13] and 4.0 ± 0.2 for $C_{10}DPO$

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Table 4. Comparison of Calorimetric and Noncalorimetric Data for Micelle Formation[a]

	$\Delta H°$ (kcal/mol)						$-\Delta Cp°$ (cal/(mol·K))					
	calcd		van't Hoff		empirical		calcd		van't Hoff		empirical	
	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
C_8	2.53 ± 0.01	2.89 ± 0.01	2.21 ± 0.39	3.14 ± 0.25	1.87 ± 0.94	2.82 ± 0.69	77 ± 3	80 ± 3	63 ± 11	87 ± 7	46 ± 2	79 ± 2
C_9	2.10 ± 0.01	2.62 ± 0.01	2.26 ± 0.36	2.94 ± 0.11	1.89 ± 0.69	2.47 ± 0.87	81 ± 1	98 ± 3	88 ± 14	107 ± 4	74 ± 2	85 ± 2
C_{10}	2.32 ± 0.01	2.69 ± 0.01	2.02 ± 0.06	2.17 ± 0.13	1.89 ± 0.25	2.34 ± 0.69	123 ± 2	124 ± 3	102 ± 3	94 ± 6	98 ± 1	109 ± 2
C_{11}	2.02 ± 0.01	2.25 ± 0.05	1.39 ± 0.03	2.59 ± 0.28	1.38 ± 0.25	2.53 ± 3.96	141 ± 4	136 ± 4	96 ± 2	157 ± 17	97 ± 1	135 ± 20
C_{12}[b]	1.66 ± 0.03	2.07 ± 0.02	1.11 ± 0.14	1.78 ± 0.14	1.13 ± 3.8	1.74 ± 4.7	162 ± 2	174 ± 1	111 ± 14	142 ± 11	157 ± 26	157 ± 32

[a] Data from calorimetry evaluated at 25 °C. The errors given for the calorimetric enthalpy data represent the mean standard deviation and standard errors are included for the remaining data. [b] Reference 3.

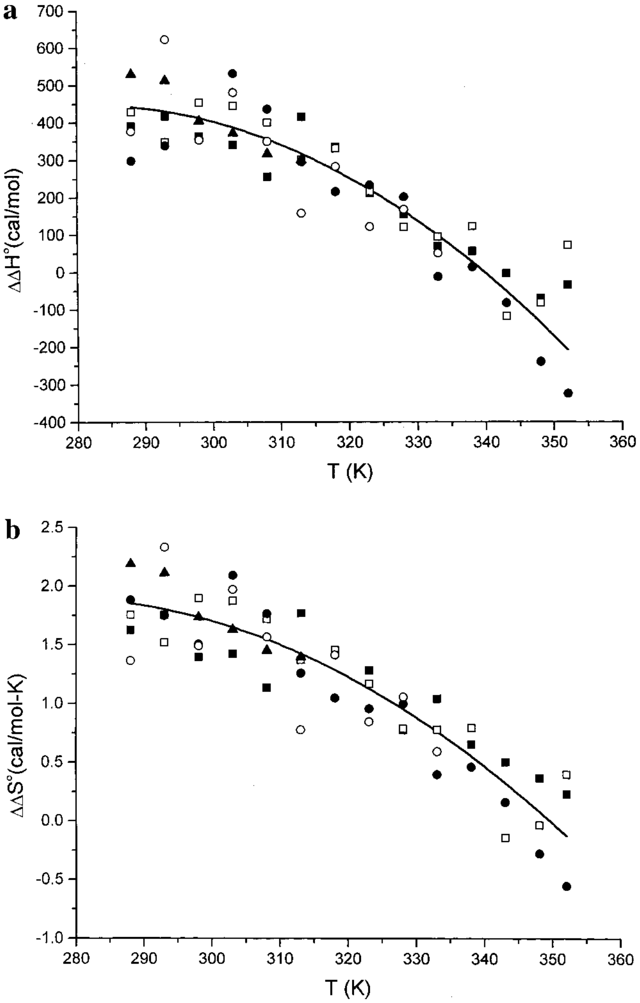

Figure 5. Summary of the variation of $\Delta\Delta H°$ (a) and $\Delta\Delta S°$ (b) with temperature for five alkyldimethylphosphine oxides and an empirical line that describes the variation of their average value with temperature.

from continuous titration calorimetry.[14] All of the samples used were obtained from different sources. The agreement is not as good for the enthalpy values previously reported[12] for C_8DPO and C_9DPO of 3.18 and 2.96 kcal/mol, respectively, and the results from this study (2.53 and 2.10 kcal/mol). The enthalpy changes determined by Clint and Walker from a plot of ln(cmc) against 1/*T* for C_9DPO, C_{10}DPO, and C_{11}DPO were 2.75, 2.65, and 2.61 kcal/mol. Our cmc data were treated with an integrated form of the van't Hoff eq 15 or by an empirical method,[3] and the results are given in Table 4. The values determined by either method are consistently lower than the ones obtained from the slope of a tangent at the temperature of interest.[12] Finally, the current values of $\Delta Cp°$ in water for C_8DPO and C_{10}DPO obtained by titration calorimetry (−77 ± 3 and −123 ± 2 cal/(mol·K)) may be compared with corresponding values from direct measurements of the apparent molar heat capacity[16] of −110 to −117 and −115 to −129 cal/(mol·K) depending upon the model used for extrapolation of the data to the cmc and the value of −133 ± 16 for C_{10}DPO from continuous titration calorimetry.[14] The importance of the procedure used to obtain thermodynamic values for the micellization process from calorimetric data can be appreciated by comparing the enthalpy change of 8 ± 1 kJ/mol reported by Perron et al.[16] for C_6DPO and an extrapolated value of 15 kJ/mol from the work of Clint and Walker. This apparent discrepancy results from the manner by which the data were treated rather than to differences in the measured values themselves. The existence of conflicting methods that have been used for the determination of enthalpy and heat capacity changes for micellization has been previously noted.[11]

We recently summarized the findings of previous investigations of the effect of D_2O on micelle formation for ionic and nonionic surfactants.[3] In all cases, the cmc was lower in D_2O than H_2O. Our calorimetric studies enabled us to describe the enthalpy and heat capacity changes that accompany micelle formation for a single long chain alkylphosphine oxide. The current research represents an extension of this work, and the findings are compatible. Previous calorimetric studies with other nonionic surfactants have identified instances where $\Delta Cp°$ is temperature dependent. The resulting values of *B*, defined by eq 3, were 2.2 cal/(mol·K^2)[10] for octyldimethylamine oxide (C_8-DAO) and −0.2 cal/(mol·K^2)[17] for *n*-octyl tetraoxyethylene glycol monoether (C_8E_4). However, a *B* value equal to zero was reported for Triton X-100 (p-(1,1,3,3-tetramethylnutyl)-phenoxypoly(oxyethylene)glycol).[17] In the case of all of the linear nonionic surfactants investigated, $\Delta Cp°$ is clearly temperature dependent.

It is recognized that the cmc corresponds to an extrapolated or interpolated concentration that requires some type of molecular modeling to have a detailed physical meaning. Phase separation and mass action models have been successfully employed for this purpose in the past, although they are recognized as being approximate. Nevertheless, useful thermodynamic or quasithermodynamic information has been obtained from their use.[9] Limited validation of the values so obtained has been made. An example recently appeared where experimental enthalpies obtained by using a phase separation model agree with those determined by calorimetry.[18] We have made use of the work of Holtzer and Holtzer,[2] who developed a van't Hoff equation that defined the equilibrium constant for the addition of a surfactant monomer to an existing micelle,

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and the enthalpy change for that reaction. Their final equation contained a term that included the temperature dependence of the aggregation number. Since the molar enthalpy change for several long chain nonionic surfactants does not change with concentration just above the cmc,[3,10,19] there is reason to believe that the problematic term in the Holtzer equation may not be important for some nonionic surfactants over a limited temperature range. This assumption gives rise to the truncated equation used by Clint and Walker,[12] their eq 5, which has certain validity. One may use our data contained in Table 4 for the five alkylphosphine oxides we investigated to address this question. The errors given for each entry represent the precision possible. With few exceptions, the enthalpy and heat capacity changes which were obtained from the van't Hoff analysis were within experimental error of the calorimetric ones, as were most of the values obtained from the empirical analysis. The major difference between the entries in the table is the smaller error associated with the values that were obtained by calorimetry. The sign and magnitude of the differences between the calorimetric and noncalorimetric values appears to be random and are smaller than reported for several equilibria of biochemical interest.[15] Despite the presence of a common polar portion for each of the alkylphosphine oxides investigated, the enthalpy and heat capacity changes for micelle formation are not just a simple linear function of the size of the large alkyl portion of the surfactant molecule as seen from the data contained in Table 2 and discussed with respect to the data contained in Table 3. This behavior is more likely to be due to properties of the surfactant in micellar form, such as different degrees of solvent penetration, than the surfactant monomers.

The recent hydration shell hydrogen bond model introduced by Muller[20,21] was adapted for calculation of the enthalpy, entropy, and heat capacity changes that accompany the transfer of nonpolar solutes in general, or methane in particular, from H_2O to D_2O. The thermodynamic parameters that accompany the transfer C_{12}DPO from H_2O to D_2O were consistent with some aspects of this theory.[3] However, an exact comparison between theory and experiment was not possible due to structural differences between the two compounds for which data were being compared. The current data may be used to test another aspect of the theory, namely, that changes in entropy and heat capacity of transfer between the two solvents should be proportional to the molecular surface area of the solute. For this purpose differences between the entropy change for micelle formation in H_2O and D_2O were obtained from eqs 5 and 6, making use of the cmc and standard enthalpy change for micelle formation over the temperature range investigated. It is clear from the data contained in Figure 5b that the expected proportionality of $\Delta\Delta S°$ with molecular surface area does not exist. Examination of the heat capacity data contained in Table 2 also supports this finding.

Finally, a comparison may be made between the results from this study and a previous one with a different series of nonionic surfactants. The average value of $\Delta Cp°$ for micelle formation at 25 °C in water for three different poly(oxyethylene) surfactants[17] containing a C_{12} alkyl group was -152 ± 20 cal/(mol·K) and our value for C_{12}DPO was -162 ± 2 cal/(mol·K). The corresponding entropy change for the same three poly(oxyethylene) surfactants was 31 ± 2 cal/(mol·K), and our value for C_{12}DPO was 29 ± 0.3 cal/(mol·K). The interpolated values of $\Delta S°$ and $\Delta Cp°$ for micelle formation of a different poly(oxyethylene) containing a C_8 alkyl group in water at 25 °C were 23 ± 1 and -80 ± 23 cal/(mol·K), whereas corresponding values for C_8DPO were 22 ± 1 and -77 ± 3 cal/(mol·K). This remarkable similarity between $\Delta S°$ and $\Delta Cp°$ values for micelle formation of surfactants with totally different headgroups but the same alkyl group emphasizes the dominance of the nonpolar portion of the nonionic surfactant to the energetics of micelle formation. This view is in keeping with previous views of the process.[1,14,17]

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