The effects of temperature on the critical micelle concentrations of alkyl α-picolinium bromides

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The temperature dependence of the critical micelle concentrations of decyl, dodecyl and tetradecyl α-picolinium bromides has been determined by measurement of conductance. Constants for the equation relating log. CMC and alkyl chain length have been calculated for the temperature range 5° to 70°, in increments of 5°. An estimate of the effect of temperature upon the degree of counterion binding is recorded. Thermodynamic parameters have been calculated using the uncharged phase-separation model and a theoretical interpretation of the process of micellization given.

The enthalpy change, ΔHm, accompanying the aggregation of surfactant monomers into micelles may be determined by calorimetry (Goddard, Hoeve & Benson, 1957; White & Benson, 1959; Benjamin, 1964, 1966; Corkill, Goodman & Tate, 1964; Corkill, Goodman & others, 1966) or from the temperature dependence of the critical micelle concentration (CMC) (Flockhart & Ubbelohde, 1953; White & Benson, 1959; Hermann, 1962; Ingram & Jones, 1969).

A limitation to the calorimetric method is that with surfactants having dodecyl or longer alkyl chains the CMC has a low value. Consequently the total heat evolved upon the destruction of micelles in such dilute solutions is small, thereby putting a strain on the sensitivity of measurement. As a result many workers have been obliged to use short-chain compounds, which have higher CMCs and give more readily detectable heat changes on dilution of their solutions from above to below the CMC. Such measurements often do not agree with the enthalpies of micellization derived from the temperature dependence of CMC. This is to be expected as the CMCs are of such magnitude that it is probably unjustified to consider that the activities of such solutions can be replaced by concentrations. Recent measurements of ΔHm for sodium dodecyl sulphate by Pilcher, Jones & others (1969), using a twin differential calorimeter, would appear to have an accuracy greater than that of previous reports.

Because of the difficulties of attaining a high degree of accuracy using the calorimetric method, many workers have preferred to use the indirect method of obtaining ΔHm from CMC values. Results obtained in this laboratory for certain cationic surfactants have been previously published (Adderson & Taylor, 1964, 1967).

The present results extend these data to a homologous series.

EXPERIMENTAL

Materials

Decanol (purissima grade, Fluka A. G.) of greater than 99·5% purity as determined by gas-liquid chromatography, dodecanol and higher homologues absent.

Dodecanol (purissima grade Fluka A. G.) of greater than 99% purity, higher homologues absent, up to 1% of decanol present.

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Tetradecanol (purissima grade, Fluka, A. G.) of greater than 99·5% purity. Up to 0·25% of an unidentified contaminant having a longer retention time, when examined by gas-liquid chromatography, than tetradecanol but shorter than hexadecanol.

α-Picoline, Hopkins and Williams laboratory reagent, was fractionally distilled twice and the fraction distilling at 128° collected. A gas-liquid chromatogram showed the absence of the β- or γ-isomers.

Other reagents of Analar or laboratory reagent quality.

The alcohols were converted to the corresponding alkyl bromides (Organic Syntheses, 1935). Equimolar quantities of alkyl halide and α-picoline were refluxed on a boiling water bath for 12 h. The reaction products were agitated with light petroleum (40–60°) to remove unchanged alcohol or halide. The solid was separated and dissolved in a mixture of 80% methyl isobutyl ketone and 20% acetone and allowed to crystallize at 0°. This was repeated twice. The surfactants were continuously extracted with light petroleum (40–60°) for 12 h and then twice re-crystallized from a mixture of 10% methanol and 90% sodium-dried ether.

An elementary analysis was performed for the decyl homologue for which no melting point was available in the literature. Equivalent weights were determined by a non-aqueous titration of the bromide with perchloric acid in glacial acetic acid in the presence of mercuric acetate.

Bromine content was determined by coulometric analysis.

Decyl α-picolinium bromide: m.p. 117°C, equiv. wt found 314·5, calculated 314·22. Found: C, 61·2; H, 9·0; Br, 25·5; N, 4·5; calculated: C, 61·1; H, 9·0; Br, 25·4; N, 4·5%. No optical effects characteristic of liquid crystals were observed on heating to 140° or on subsequent cooling.

Dodecyl α-picolinium bromide: m.p. 124°C (124°, Kolloff, Wyss & others, 1942), equiv wt, found 346·4, calculated 342·37. Found: Br, 23·3; calculated, 23·6%. No optical effects as of liquid crystals observed up to 160°.

Tetradecyl α-picolinium bromide: m.p. 125 and 192°C (125, 192°C, Kolloff, Wyss & others, 1942), equiv wt, found 370·9, calculated 370·43. Found: Br, 21·6; calculated 21·4%. The lower melting point, corresponding to the transition to a non-mobile translucent gel, was extremely sensitive to moisture and required storage of the compound for several days above phosphorus pentoxide to give a consistent value. In plane-polarized light the gel exhibited characteristic effects as of liquid crystals some 30° above the temperature of transition from solid to a gel. On complete melting at 192° and subsequent cooling Grandjean terraces were observed.

The surface tension–concentration curves did not exhibit minimum values with subsequent increase to constant values.

CMC determinations

CMC values were determined according to Adderson & Taylor (1964) using ion-exchange water equilibrated with laboratory air ($K = 1·91 \times 10^{-6}$ ohm^{-1} cm^{-1}).

<div align="center">RESULTS AND DISCUSSION</div>

CMC values were calculated in terms both of mol fraction (Table 2) and as molalities. The latter system was used to test the application of the equation

$$\text{Log CMC} = A + BM \text{ (Table 2)}$$

where A and B are constants and M the number of carbon atoms in the principal alkyl chain. The constants A and B were obtained by a least squares treatment of the CMC data (Table 1).

Table 1. *Constants for the equation Log CMC (molal)* $= A + BM$

Temperature °C	A	B
10	1·842	−0·3175
15	1·809	−0·3151
20	1·788	−0·3134
25	1·772	−0·3118
30	1·756	−0·3098
35	1·737	−0·3073
40	1·715	−0·3040
45	1·689	−0·3003
50	1·661	−0·2961
55	1·634	−0·2918
60	1·608	−0·2875
65	1·587	−0·2835
70	1·572	−0·2801

The values of the constant B are similar to those found for alkyl trimethylammonium bromides and alkyl benzyl dimethyl ammonium bromides (this laboratory) suggesting that at any one temperature the addition of a further methylene group would have a similar effect upon the CMC values, and upon $\Delta G_m°$, the free energy change upon micellization, for any of these homologous series.

The predicted constants gave CMC values that differed by up to 8·5% from the experimental values obtained. This is in contrast to the results of a similar treatment of the CMC values of alkyl trimethyl ammonium bromides (this laboratory, to be published). This lack of agreement for alkyl α-picolinium bromides may be a reflection of the total hydrocarbon content of the surfactants. A similar result has been noted for compounds having long straight hydrocarbon chains whereas shorter homologous compounds obeyed the above equation (Evans, 1956).

Table 2. *Critical micelle concentrations, mol fractions*

Temperature °C	Decyl	Dodecyl	Tetradecyl salt
5	8·74 × 10⁻⁴	—	—
10	8·59	1·87 × 10⁻⁴	4·60 × 10⁻⁵
15	8·43	1·84	4·61
20	8·30	1·83	4·66
25	8·32	1·84	4·70
30	8·36	1·86	4·88
35	8·56	1·19	5·05
40	8·81	2·01	5·31
45	9·00	2·08	5·71
50	9·33	2·15	6·13
55	9·71	2·28	6·57
60	10·1	2·39	7·19
65	10·6	2·55	7·73
70	11·0	2·71	8·48

The CMCs have minimum values at specific temperatures; these temperatures are chain length dependent. Similar effects have been observed in alkyl trimethyl-ammonium, alkyl dimethylbenzylammonium and alkyl pyridinium bromides (Adderson & Taylor, 1964 and unpublished data of this laboratory). Decyl cationic surfactants have a minimum CMC at approximately 23–25°, dodecyl at 18–20° and

tetradecyl at 10°.   Emmerson & Holtzer (1967) have suggested that the minimum is the resultant of two opposing effects, namely the decrease in dielectric constant of water with increase in temperature, which increases the electrostatic repulsion of the heads, and a hydrocarbon effect.   The latter is postulated as arising from the occurrence of "water-cages" stabilized by the hydrocarbon chain, the degree of structured water decreasing with temperature increase.

Butler, Stead & Taylor (1969) consider the observed minimum value of the CMC to be an artifact.   In systems in which dimers have been detected in co-existence with monomers, the use of the monomer concentration only in the calculation of CMC values removes the conventional minimum value.   It is, however, noteworthy that minimum values appear in the temperature dependence of the CMC of decyl compounds whereas specific investigations to detect dimers have not produced supporting evidence for their existence in such compounds (Mysels & Kapauan, 1961; Clunie, Goodman & Symons, 1967).

Evans (1956) has suggested that the charge on the micelle may be obtained from the specific conductance–concentration plots using

$$\frac{p^2}{N^{4/3}} (1000\, S_1 - \Lambda_R) + \frac{p\Lambda_R}{N} = 1000\, S_2$$

where p = the effective charge on the micelle, N = the aggregation number, Λ_R = the equivalent conductance of the counterion at infinite dilution, $S_1 = (dK_1/dC_1)$ = the slope of the specific conductance–concentration plot below the CMC, $S_2 = (dK_2/dC_2)$ = the similar slope above the CMC.

The concentrations in the present work have been expressed in terms of weight in weight, whereas Λ_R relates to a weight in volume relation.   To correct the experimental measurements for this discrepancy the slopes dk/dc, with c (the concentration) in molal units, have been adjusted by a factor $1/D$ where D is the density of water at the requisite temperature.   The difference between the density of water at 25°C and the most concentrated solution used is less than 0·1%.

The aggregation numbers N for alkyl α-picolinium bromides are not known. However, Evans has shown that p/N is insensitive to change in N.   It is commonly observed that an increase in alkyl chain length is accompanied by an increase in N, for example for alkyl trimethylammonium bromides $N_{C10} = 36$, $N_{C12} = 50$, $N_{C14} = 75$ (Debye, 1949).

Limited values are available for alkyl pyridinium bromides; $N_{C11} = 42$, $N_{C14} = 79$ (Trap & Hermans, 1955).   It seems reasonable therefore to assume that alkyl α-picolinium bromides would exhibit similar values and, for the purposes of subsequent calculations, values of N of 36 for the decyl, 50 for the dodecyl and 75 for the tetradecyl salts have been assumed.

The use of an invariant aggregation number has only a slight effect upon p/N. If $N = 50$ is assumed for all the homologues at 25°C, p/N becomes $C_{10} = 0·29$, $C_{12} = 0·22$ and $C_{14} = 0·21$ so that the observed relations are scarcely altered.   The use of a gradually decreasing value of N, such as would be expected with rise in temperature (Debye, 1949; Trap & Hermanns, 1955) enhances the increase in p/N with temperature.   For the decyl compound at 55° if $N = 32$, $p/N = 0·34$.   Thus the degree of dissociation increases, as expected with temperature.   The extent of counterion binding increases in the order decyl<dodecyl<tetradecyl compound (Table 3).

A similar result has been observed in the alkyl trimethylammonium bromides (this laboratory), and has been reported for anionic surfactants (Evans, 1956).

Table 3. *The fraction of the theoretical charge, p/N, of alkyl α-picolinium bromides*

Temperature °C	$\Lambda°Br$ · (Robinson & Stokes, 1959)	Decyl, p/N	Dodecyl, p/N	Tetradecyl, p/N
15	63·1 ohm⁻¹ cm²	0·31	0·21	0·19
25	78·1	0·30	0·22	0·20
35	94·0	0·32	0·23	0·21
45	110·7	0·33	0·24	0·21
55	125·4	0·33	0·25	0·21

Thermodynamic parameters

If the micelle is treated as a separate phase the free energy change on micellization may be obtained by $\Delta G°_m = (2 - \alpha)$ RT ln CMC. Variable values for $\Delta G°$ may be derived depending upon the definition of the composition of the phase.

If the phase is considered to consist of the micelles plus bound counterions, "the charged phase model" (Matijevic & Pethica, 1958; Shinoda & Hutchinson, 1962), somewhat lower values are obtained than if the phase is assumed to include all the counterions, whether bound or free "the uncharged phase model". In the latter case α, i.e. p/N as previously defined, is zero.

Values of p/N vary depending upon the method of determination. Estimates using light-scattering techniques (Mysels, 1955), or conductance slopes give values of 0·2 to 0·3, whereas estimates derived from the slopes of the graphs relating CMC values to electrolyte concentration are approximately 0·5 (Shinoda, 1963). With the present uncertainty of choice concerning this parameter, the uncharged model gives as valuable information as the charged model (Table 4).

Using a standard state of a mol fraction of unity for the monomeric species, and the micelle itself as the standard state for its species, and assuming that the heat of dilution from the standard state to the CMC is negligible compared to the heat of micellization, values may be calculated: $- \Delta G°_m = - 2$ RT ln CMC; $- \Delta H_m = 2$ RT² $(\partial$ ln CMC$/\partial$T$)_P$; $- \Delta S_m = - \Delta H_m/T$; $- \Delta S°_m = (\Delta G°_m - \Delta H°_m)/T$.

Two entropy values may be calculated, $\Delta S°_m$ with respect to the change at the standard state, and ΔS_m with respect to the change at CMC. The difference between these values gives the almost constant entropy of dilution (Adderson & Taylor, 1964).

Graphical estimates of the slopes to yield ∂ln CMC$/\partial$T are not accurate. Polynomial expressions relating log CMC and T (the absolute temperature) were therefore obtained using a Stantec Zebra computer. The use of polynomials of higher degrees than those indicated did not give statistically better fits. The experimental and computer-predicted CMC values agree to within 1·2%.

Decyl α-picolinium bromide, log CMC (mol fractions), $= 16·37524 - 1·750665$ T $\times 10^{-1} + 5·161737$ T² $\times 10^{-4} - 4·959002$ T³ $\times 10^{-7}$. Dodecyl α-picolinium bromide, log CMC (mol fractions) $= 19·57319 - 2·104685$ T $\times 10^{-1} + 6·219035$ T² $\times 10^{-4} - 5·97669$ T³ $\times 10^{-7}$. Tetradecyl α-picolinium bromide, log CMC (mol fractions) $= - 1409·548 + 21·97247$ T $- 1·367959$ T² $\times 10^{-1} + 4·238423$ T³ $\times 10^{-4} - 6·535922$ T⁴ $\times 10^{-7} + 4·014295$ T⁵ $\times 10^{-10}$.

Table 4. *Thermodynamic quantities for the micellization of alkyl α-picolinium bromides in water*

Decyl α-picolinium bromide

Temperature °K	−ΔG°m kcal	kJ mol⁻¹	−ΔHm kcal	kJ mol⁻¹	−ΔSm cal deg⁻¹ mol⁻¹	J	−ΔS°m cal deg⁻¹ mol⁻¹	J
278·2	7·78	32·6	—2·1	—8·8	—7·7	—32	—35	—150
283·2	7·95	33·3	—1·5	—6·3	—5·2	—22	—33	—140
288·2	8·11	33·9	—0·84	—3·5	—2·9	—12	—31	—130
293·2	8·26	34·6	—0·22	—0·92	—0·73	—3·1	—29	—120
298·2	8·40	35·2	+0·40	+1·7	+1·3	+5·4	—27	—110
303·2	8·53	35·7	0·99	4·1	3·3	14	—25	—100
308·2	8·65	36·2	1·6	6·7	5·1	21	—23	—96
313·2	8·76	36·7	2·1	8·8	6·7	28	—21	—88
318·2	8·87	37·1	2·6	11	8·1	34	—20	—84
323·2	8·96	37·5	3·0	13	9·4	39	—18	—75
328·2	9·05	37·9	3·5	15	11	46	—17	—71
333·2	9·13	38·2	3·8	16	11	46	—16	—67
338·2	9·21	38·5	4·1	17	12	50	—15	—63
343·2	9·28	38·8	4·3	18	13	54	—14	—59

Dodecyl α-picolinium bromide

Temperature °K	−ΔG°m kcal	kJ mol⁻¹	−ΔHm kcal	kJ mol⁻¹	−ΔSm cal deg⁻¹ mol⁻¹	J	−ΔS°m cal deg⁻¹ mol⁻¹	J
283·2	9·66	40·4	—1·5	—6·3	—5·3	—22	—39	—160
288·2	9·85	40·5	—0·71	—3·0	—2·5	—10	—37	—150
293·2	10·0	41·9	+0·06	+0·25	+0·21	+0·88	—34	—140
298·2	10·2	42·7	0·81	3·4	2·7	11	—31	—130
303·2	10·3	43·1	1·5	6·3	5·1	21	—29	—120
308·2	10·5	43·9	2·2	9·2	7·2	30	—27	—110
313·2	10·6	44·4	2·9	12	9·2	39	—25	—100
318·2	10·7	44·8	3·5	15	11	46	—23	—96
323·2	10·8	45·2	4·0	17	13	54	—21	—88
328·2	10·9	45·6	4·5	19	14	59	—19	—80
333·2	11·0	46·0	5·0	21	15	63	—18	—75
338·2	11·1	46·5	5·3	22	16	67	—17	—71
343·2	11·2	46·9	5·6	23	16	67	—16	—67

Tetradecyl α-picolinium bromide

Temperature °K	−ΔG°m kcal	kJ mol⁻¹	−ΔHm kcal	kJ mol⁻¹	−ΔSm cal deg⁻¹ mol⁻¹	J	−ΔS°m cal deg⁻¹ mol⁻¹	J
283·2	11·2	46·9	0·33	1·4	1·2	5·0	—39	—160
288·2	11·4	47·7	0·32	1·3	1·1	4·6	—39	—160
293·2	11·6	48·5	0·76	3·2	2·6	11	—37	—150
298·2	11·8	49·4	1·5	6·3	5·1	21	—34	—140
303·2	12·0	50·2	2·5	10	8·2	34	—31	—130
308·2	12·1	50·6	3·6	15	12	50	—28	—120
313·2	12·2	51·1	4·6	19	15	63	—24	—100
318·2	12·4	51·9	5·6	23	17	71	—21	—88
323·2	12·5	52·3	6·3	26	20	84	—19	—80
328·2	12·6	52·7	6·9	29	21	88	—17	—71
333·2	12·6	52·7	7·2	30	22	92	—16	—67
338·2	12·7	53·1	7·2	30	21	88	—16	—67
343·2	12·8	53·6	7·1	30	21	88	—17	—71

The change in free energy upon micellization, ΔG_m°, per methylene group is between −0·8 and −0·9 k cal mol⁻¹. These numerical values are similar to those for the free energy change in processes which may be considered analagous, though not identical, namely the transfer of medium chain alcohols (Kinoshita & others, 1958), hydrocarbons (McAuliffe, 1963) or long-chain aliphatic acids (Mukerjee, 1965) from an aqueous to a hydrocarbon environment. This agreement may be fortuitous due to the choice of 2 instead of 2-p/N in the calculation of ΔG_m°.

If the calculated p/N values are used, the free energy change at 25° becomes −0·97 k cal mol⁻¹ per CH_2 group on increasing the length from a decyl to dodecyl chain, and −0·77 k cal mol⁻¹ per CH_2 for the change dodecyl to tetradecyl chain.

In contrast, Mukerjee (1967) derives ΔG_m° as -680 cal mol^{-1} per methylene group from the variation in CMC values with alkyl chain length in a homologous series of non-ionic surfactants. The difference between this and the values for complete transfer from aqueous to hydrocarbon environment is attributed to the inadequacy of the liquid core model. He suggests that chains within a micelle are more constrained than in a liquid hydrocarbon and hence make a lower entropic contribution to ΔG_m°.

The enthalpy and entropy changes are similar to those previously reported (Adderson & Taylor, 1964, 1967) that is that for the shorter chain compounds the enthalpy of micellization is positive at room temperature and becomes negative with temperature increase. For the tetradecyl compound this transition occurs at a lower temperature.

This change in enthalpy from a positive to a negative value with increase in temperature has been recently supported by calorimetric studies of sodium lauryl sulphate (Pilcher & others, 1969).

Benjamin (1964) has reviewed the solution data for aliphatic alcohols in water and derives a value of -590 cal mol^{-1} per methylene group for the enthalpic contribution to the free energy change of solution.

The values of -0.35 k cal mol^{-1} and -0.20 k cal mol^{-1} per methylene group at 25° C, which may be derived from the present data for the increments in ΔH_m between decyl and dodecyl and those between dodecyl and tetradecyl salts are thus smaller than those for the above, somewhat analogous, process. The observed lack of uniformity in values of ΔH_m per methylene group is supported by calorimetric data (Benjamin, 1964).

Increase in surfactant hydrocarbon content either by increase in length of alkyl chain or the incorporation of cyclic structures is always observed to be accompanied by increasing exothermicity. Calorimetric determinations of ΔH_m show that increase in total hydrocarbon content converts an endothermic into an exothermic reaction (Corkill & others, 1966), suggesting that the aggregation of head groups is endothermic and that of alkyl chains exothermic.

Micellization is therefore considered to be accompanied by at least three significant enthalpic changes; those associated with aggregation of charged heads, those with breakdown of hydrocarbon-stabilized water structure and changes due to transfer of hydrocarbon from water to micelle. The two former being endothermic, the latter exothermic. The temperature at which ΔH_m changes from a positive to a negative value (at which the CMC shows a minimum value), will vary with the summation of the above. The gradual decrease of hydrocarbon-stabilized water structure with temperature, with consequent decrease in this endothermic component will explain the change of sign of ΔHm. If the electrical work to assemble the monomers is reduced, for instance due to a greater degree of counterion binding in higher homologues, the minimum will occur at a lower temperature. Change of counterion to one more readily bound has the same effect (Adderson & Taylor, 1964; Mukerjee & Ray, 1966). Increase in alkyl chain length with consequent increase in the area of water-hydrocarbon interface lost and the exothermic formation of a larger amount of "liquid hydrocarbon" micelle interior, will depress the temperature of the minimum CMC.

Thus while it must be appreciated that such thermodynamic evidence cannot give

incontrovertible proof, it may be inferred that micellization is entropy-directed at low temperatures but predominantly enthalpy-directed at room temperature and above.

In contrast, Butler & others (1969) consider that ΔHm, derived from the CMC temperature plot, where the CMC is based solely on the concentration of monomers instead of the total surfactant, is always negative and more nearly constant than the values suggested in the present work. Derivation of ΔHm from their CMC values yields values which appear to be further removed from the somewhat scanty calorimetric values for ionic surfactants; this may be a reflection of the imprecise nature of the calorimetric determinations. Similarly ΔGm per CH_2 group is further removed from similar values for transfer of alkyl chains from aqueous to hydrocarbon environment.

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