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Aggregation in the aqueous solutions of alkylpyridinium chlorides

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Aggregation in the aqueous solutions of decylpyridinium chloride, dodecylpyridinium chloride and tetradecylpyridinium chloride has been investigated by conductivity measurements at 20–40 °C, and thermodynamic characteristics of micellization have been analysed.

The physico-chemical properties of micellar solutions are of interest.[1–7] The increase of concentration range and investigation of micelle polymorphism have shown the possibility of the existence of CMC$_1$, CMC$_2$ which are accompanied by the existence of extremes in the region of CMC on the relation of equivalent electroconductivity λ *vs.* $c^{1/2}$ (where c is the surfactant concentration).[8] This phenomenonon was explained by Rusanov,[9] who theoretically showed the possibility of extremes appearance on the λ *vs.* $c^{1/2}$ relation in surfactant aqueous solutions in the process of micellar formation when aggregation numbers and degree of counterion binding change.

The expansion of investigated temperature range made it possible for the Lyklema research group[10] to detect the existence of a minimum of CMC at 30 °C. Kochurova *et al.*[11] found that such peculiarities can be explained by the change of hydration type of surface active ions at temperature change due to the change of aqueous structure.

Decylpyridinium chloride (DePCl), dodecylpyridinium chloride (DPCl) and tetradecylpyridinium chloride (TPCl) were used as test substances. Kraft's point for these substances in aqueous solutions lays in negative area of temperatures.[12,13] Criterion of a cleanliness of the surfactants was the absence of a minimum on an isotherm of an equilibrium surface tension that has been checked up by measurements of a surface tension by the ring detachment method (Table 1).[14,15]

Table 1 Values of CMC ($\times 10^2$ mol dm^{-3}) of aqueous solutions of *n*-alkylpyridinium chlorides at different temperatures.

Surfactant	*T*/°C	CMC$_1$	CMC$_2$	CMC$_3$	CMC$_4$
DePCl	20	6.75	7.9	9.0	—
	25	6.45, 6.55 (ST),[a] 6.33[10]	7.9	9.0	—
	30	5.99	7.9	9.0	—
	35	7.26	7.9	9.0	—
	40	7.48	7.9	9.0	—
DPCl	20	1.9, 1.72 (ST)[a] 1.75[10]	2.56	3.24	3.42
	25	1.77, 1.62[16]	2.14, 3.29[16]	3.24	3.42
	30	1.37, 1.24[10]	1.88	3.24	3.42
	35	1.98	2.30	3.24	3.42
	40	2.17	2.6	3.24	3.42
TPCl	20	0.426	0.744	—	—
	25	0.349, 0.320 (ST),[a] 0.350,[10] 0.418[16]	0.682, 0.759[16]	—	—
	30	0.223	0.396	—	—
	35	0.475	0.782	—	—
	40	0.588	0.850	—	—

[a] ST is the surface tension.

The results of electroconductivity measurements are given in Figure 1.[14,15,†] The equivalent electroconductivity decreases with the increase of concentration as the number of charge carriers rises but their mobility falls due to interaction between ions and enlargement of sizes of the moving micelles. Minima and maxima can be seen on the given curves as in ref. 8. Maximum of equivalent electroconductivity increases with the rise of temperature and the length of the hydrocarbon radical.

First maximum corresponds to the CMC$_1$ which is defined by the sharp bend of the λ *vs.* $c^{1/2}$ curve. Rusanov[9] found that the equivalent electroconductivity in the micellar region has a maximum, which is preceded by a minimum. There is a rather narrow concentration region of micellar transition in which changes of aggregation numbers and degree of counterion binding take place, which causes the existence of minima and maxima (abnormal character of λ). CMC$_2$ corresponds to the next maximum *etc*. The values of CMC given in Table 1 correspond to the published data.[10,16]

In a procedure technique described,[1] the numbers of aggregation (n) (1) and a degree of counterions binding (β) by micelles (2) have been counted:

$$n = 4\pi l_C^3/3v_C, \tag{1}$$

where n is the number of aggregation for a spherical micelle, l_C is the length of the unwrapped radical and v_C is the volume of a hydrocarbon radical. The length and volume of a hydrocarbon radical were calculated subject to the length and volume of the benzene ring. The value of benzene ring length is 3.7 Å,[12] the volume of benzene ring 56.68 Å^3 was calculated using the Le Ba method.[17]

The number of aggregation increases with the length of a hydrocarbon chain in homologous series of test surfactants: $n_{\mathrm{DePCl}} = 51$, $n_{\mathrm{DPCl}} = 87$, $n_{\mathrm{TPCl}} = 109$.

$$\beta \approx -0.5k - 1, \tag{2}$$

where k is the tangent of angle of an inclination of dependence lg $C_{\mathrm{CMC}}(x_C)$, where x_C is the number of carbon atoms in the

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[†] Conductometric measurements were perfomed with the use of a V3-60 ac bridge at 2.5 kHz, which made it possible to smooth the polarization effects. Cell calibration was carried out by the standard solution of KCl (0.01 N). Temperature was maintained with the accuracy ±0.05 °C. Electroconductivity measurement error was ≤ 2%. The measurements were performed at 20, 25, 30, 35 and 40 °C and the folowing concentrations of aqueous solutions: DePCl (4.5–9.5)$\times 10^{-2}$ mol dm^{-3}, DPCl (1.0–4.0)$\times 10^{-2}$ mol dm^{-3} and TPCl (0.9–1)$\times 10^{-2}$ mol dm^{-3}.

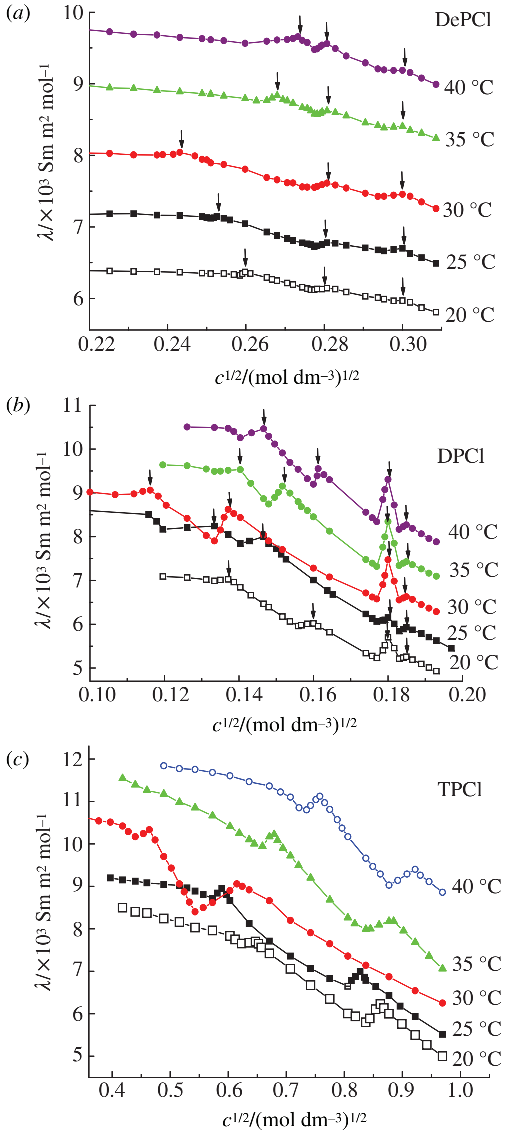

Figure 1 Concentration dependences of equivalent conductivity of aqueous solutions of (*a*) DePCl, (*b*) DPCl and (*c*) TPCl at different temperatures.

chain. The degrees of counterion binding for *n*-alkylpyridinium chlorides are as follows: 20 °C, 0.667; 25 °C, 0.563; 30 °C, 0.389; 35 °C, 0.667; 40 °C, 0.786. Estimations of β are pertinent to the case when the degree of binding of counterions is considered to be the same for all homologous series and allows one to calculate β only for CMC$_1$.

Calculation of a degree of counterion binding by the Hoffmann method[16] allows us to determine β for each substance not only for CMC$_1$ but also for CMC$_2$:

$$\beta \approx 1 - k'/k, \qquad (3)$$

where k'/k is the tangent angle ratio of an inclination of straight lines [$k(c)$] from specific conductivity dependences on surfactant concentration at the same temperatures, which were used for definition of CMC. Calculations show that the increase of the surfactant concentration results in strengthening counterions binding at polymorphic transformations of micelles.[8] Note that β, calculated by the method of homologous series (2) and by the Hoffmann method (3), has the minimal value in the region of 30 °C (Table 2).

Table 2 Degree of counterion binding for CMC$_1$ (β_1) and CMC$_2$ (β_2).

T/°C	DePCl		DPCl		TPCl	
	β_1	β_2	β_1	β_2	β_1	β_2
20	0.314	0.343	0.667	0.766	0.586	0.971
25	0.330	0.389	0.479	0.795	0.518	0.875
30	0.264	0.357	0.537	0.839	0.591	0.611
35	0.366	0.436	0.716	0.870	0.596	0.842
40	0.532	0.579	0.744	0.921	0.693	0.708

Calculation of a degree of counterion binding is directly connected with CMC values (1), (2). CMC, in turn, has the minimal value in the region of 30 °C (Table 1), that is associated with the change in the structure of water and a character of hydration of surface active ions.[11,14,15] Therefore, β has minimal value that corresponds to the CMC minimum in the region of 30 °C.

Figure 2 shows the CMC value decrease in the following order: CMCn_{14} < CMCn_{12} < CMCn_{10}. This is a consequence of the increase of a degree of hydrophobicity.[1,18,19]

Using concentration dependences of the equivalent conductivity of aqueous solutions of *n*-alkylpyridinium chlorides (Figure 1), one can observe, that DePCl has three abnormal areas – CMC$_1$, CMC$_2$, CMC$_3$; DPCl has four – CMC$_1$, CMC$_2$, CMC$_3$, CMC$_4$; and TPCl has two – CMC$_1$, CMC$_2$. Note that aggregation with CMC$_2$,[8,16,20,21] CMC$_3$ and CMC$_4$[22,23] was reported. Surfactants were investigated by conductometric and calorimetric methods, and viscosimetry.

Values of CMC$_3$ and CMC$_4$ for DPCl are close enough (Table 1). The maximum in the region of CMC$_4$ is expressed more poorly, than maximum in the region of CMC$_2$ (Figure 1). It is reasonable to consider this region of surfactant concentrations as the region of formation of micelles with the new form.

Figures 1 and 2 show that the height of a maximum of the equivalent conductivity grows with a temperature for all test compounds. It is well-known that an increase in temperature results in a decrease of aggregation number (n) and an increase of a degree of ionization of micelle, which in turn results in the increase of the height of a maximum.[8,9]

The maximum poorly manifests itself for the aqueous solution of DePCl. For DPCl it is well defined, and for TPCl becomes even more expressed. The similar picture was observed for decyltrimethylammonium bromide.[8] It is known that for a straight line micelles the number of aggregation is an accelerated growing function of length of a hydrocarbon radical,[9] therefore we come to a conclusion: the larger is the length of a hydrocarbon radical of a surface active ion, the more probable is the occurrence of a maximum of an equivalent conductivity.

The following data have been calculated for the CMC$_1$ aggregation: the standard change of Gibbs energy (ΔG^0_m), the standard change of enthalpy (ΔH^0_m) and entropy (ΔS^0_m) of micellization of *n*-alkylpyridinium chlorides investigated by a conductivity method, using equations from ref. 1.

$$\Delta G^0_m = (1 + \beta)RT\ln X_{\mathrm{CMC}}, \qquad (4)$$

where β is the degree of counterion binding, X_{CMC} is the surfactant concentration (in mole fraction) at CMC.

$$\Delta H^0_m = \Delta G^0_m - T\partial\Delta G^0_m/\partial T = \partial(\Delta G^0_m/T)/\partial(1/T). \qquad (5)$$

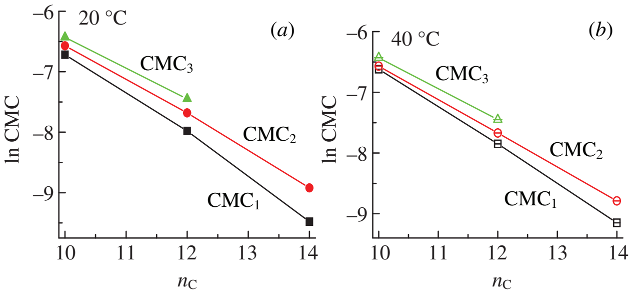

Figure 2 Dependence of CMC logarithm on a hydrocarbon chain length of DePCl(n_{10}), DPCl(n_{12}), TPCl(n_{14}) at (*a*) 20 °C and (*b*) 40 °C.

After evaluating ΔH_m^0 and ΔG_m^0 the standard entropy change of micellization[1] has been calculated (Table 3).

$$\Delta S_m^0 = \Delta H_m^0 - \Delta G_m^0/T. \tag{6}$$

The Gibbs energy of micellization (ΔG_m^0) remaining negative, decreases with a growth of temperature and an increase of dissolved surfactant concentration. ΔG_m^0 has a maximum at the points corresponding to minimal value of CMC near 30 °C and decreases with an increase of a hydrocarbon chain length of the test surfactants.

The enthalpy of micellization (ΔH_m^0) increases linearly with a growth of temperature and concentration and becomes positive in the region of 30 °C. Note that the change of the enthalpy of micellization is due to a hydrophobic effect, namely, for ionic surfactant at low temperatures the increase of hydrophobic effect is observed. However, at high temperatures a growth of electrostatic repulsion owing to a reduction of dielectric permeability of water overlaps an increase of hydrophobic effect. The enthalpy of micellization thus changes a sign, and the value of CMC increases.[19,23,24] ΔH_m^0 grows insignificantly with increase of the hydrocarbon chain length.

The entropy of micellization increases with a growth of temperature and concentration of dissolved surfactant. Values of ΔS_m^0 grow with increase in the length of hydrocarbonic chain, *i.e.* $\Delta S_{m\,\mathrm{TPCl}}^0 > \Delta S_{m\,\mathrm{DPCl}}^0 > \Delta S_{m\,\mathrm{DePCl}}^0$, which according to ref. 10 is caused by occurrence of water molecules from so-called 'ice structure' around hydrophobic 'tails' of surfactant monomers, that is the main driving force for micellization process. Formation of micelles is accompanied by liberation of a part of the structured water that is thermodynamicly favourable process as it results in increase of the system entropy.

Thus, the possibility of existence of more than two CMC values has been shown. It is established, that values of CMC decrease with increase of a hydrocarbon chain length, *i.e.*, the hydrophobicity in homologous series of *n*-alkylpyridinium chlorides. The abnormal character of dependence of equivalent conductivity on concentration of investigated surfactant has been revealed. The maximum of equivalent conductivity grows with temperature and the length of a hydrocarbon radical.

The performed analysis of thermodynamic micellization characteristics calculated for aggregations with CMC_1 shows that with increase of temperature the process of micellization changes from exothermic to endothermic one and this transition corresponds to a minimum at CMC in the region of 30 °C, specifying on changes in structurization of a solvent.

Table 3 Thermodynamic parameters of micellization for the aqueous solutions of DePCl, DPCl and TPCl.

Surfactant	T/°C	$C_{\mathrm{CMC}_1}/\times10^{-2}$ mol dm^{-3}	ΔG_m^0/ kJ mol^{-1}	ΔH_m^0/ kJ mol^{-1}	ΔS_m^0/ J K^{-1} mol^{-1}
DePCl	20	6.75	–27.3	–54.0	–91.0
	25	6.45	–26.2	–16.0	34.2
	30	5.99	–23.9	21.0	148
	35	7.26	–28.4	57.0	277
	40	7.48	–30.7	92.0	392
DPCl	20	1.90	–32.4	–61.0	–97.6
	25	1.77	–31.2	–20.0	37.6
	30	1.37	–29.0	20.1	162
	35	1.98	–33.9	58.8	300
	40	2.17	–36.5	96.3	424
TPCl	20	0.426	–38.5	–54.0	–52.9
	25	0.349	–37.5	–14.0	78.8
	30	0.223	–35.3	24.0	195
	35	0.475	–39.8	61.0	327
	40	0.588	–42.5	97.0	445

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