Studies on the Critical Micelle Concentration and Thermodynamic Properties of Mono(2-ethyl-hexyl)-2-ethyl-hexyl Phosphate Salts in Organic Solvent + *sec*-Octyl Alcohol Systems at 298.15 K Using a Microcalorimetric Method

Xu Zhang*

State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, Shanghai, 200237, P. R. China

The power−time curves of the micelle formation process were determined for quasi-surfactants [mono(2-ethyl-hexyl)-2-ethyl-hexyl phosphate nickel and mono(2-ethyl-hexyl)-2-ethyl-hexyl phosphate cadmium] and two kinds of solvent, n-chain alkanes (decane, dodecane, and tetradecane) and single-ring aromatic hydrocarbons (benzene, toluene, and dimethylbenzene), with *sec*-octyl alcohol by titration microcalorimetry. The critical micelle concentration (cmc), aggregation number (*n*), formation constant of the micelle (*K*), and thermodynamic functions ($\Delta_r H_m^\theta$, $\Delta_r G_m^\theta$, and $\Delta_r S_m^\theta$) are obtained. For different quasi-surfactants and solvents, the relationships between the solvent properties with the cmc and the thermodynamic functions of the surfactants are discussed.

1. Introduction

The properties of surfactants in organic solutions are not similar to those in aqueous solution because of interactions between the organic solvent and the surfactant. The surfactant can form micelles in organic solution. The development of micelles depends on the action of the steric hindrance of dipole−dipole interactions. Therefore, the aggregation number (*n*) of the micelle is small (usually under 10)[1] in organic solution.

The critical micelle concentration (cmc) is one important characteristic for surfactant solutions. There are many methods to determine the cmc, such as density, interfacial tension, electric conductance, and viscosity measurements. Among them, the method of microcalorimetry is sensitive, quick, and easy.

In extraction chemistry, the structure of the extractant is similar to that of the surfactant. Therefore, the extractant can exist in the single molecular state instead of the micelle state[2−5] in an organic solution. A few reports about the research of organic solvents have been published in recent years.[6−10]

In previous papers,[11] we reported a microcalorimetric study on the cmc and thermodynamic functions of di(2-ethyl-hexyl) phosphate salts in organic solvent + *sec*-octyl alcohol systems at 298.15 K.

In this paper, we studied the properties of mono(2-ethyl-hexyl)-2-ethyl-hexyl phosphate EH[EHP] salts {(Cd)EH[EHP], (Ni)EH[EHP]} in different organic solvents. The cmc, aggregation number (*n*), formation constant of micelle (*K*), and thermodynamic functions ($\Delta_r H_m^\theta$, $\Delta_r G_m^\theta$, and $\Delta_r S_m^\theta$) were obtained according to the mass action model and thermodynamic theory. The relationships between the solvent properties with the cmc and the thermodynamic functions of the quasi-surfactants are discussed. Few reports about the microcalorimetric study of these aspects are publicly available in the literature.

2. Theory

An ionic surfactant can form a micelle in an organic solvent. This process of dispersion and dissociation is an endothermic process. In this process the mass action model is used to investigate the corresponding properties, if there exists an association−dissociation equilibrium of the micelle state and nonmicelle state of the surfactant.[1,11]

$$n\mathrm{S} \overset{K}{\rightleftharpoons} \mathrm{M} \tag{1}$$

where *K* is the formation constant of the micelle, *n* is the aggregation number, S is the monomer of surfactant, and M is the micelle.

From reaction 1,

$$K = \frac{[\mathrm{M}]}{[\mathrm{S}]^n} \quad \text{or} \quad nK = \frac{n[\mathrm{M}]}{[\mathrm{S}]^n} \tag{2}$$

$$\log(nK) = \log\{n[\mathrm{M}]\} - n\log[\mathrm{S}] \quad \text{or} \quad \log\{n[\mathrm{M}]\} = \log(nK) + n\log[\mathrm{S}] \tag{3}$$

If the total concentration of surfactant is C_s

$$[\mathrm{M}] = \frac{\{C_s - [\mathrm{S}]\}}{n} \tag{4}$$

When eq 4 is substituted into eq 3 then

$$\log\{C_s - [\mathrm{S}]\} = \log(n\mathrm{K}) + n\log[\mathrm{S}] \tag{5}$$

A plot of $\log\{C_s - [\mathrm{S}]\}$ against $\log[\mathrm{S}]$ allows the aggregation number (*n*) and formation constant of micelle (*K*) to be calculated. The values of C_s and [S] were calculated from the following equation

$$[\mathrm{S}] = \frac{V^1}{2 + V^1} C \text{ (original solution concentration)} \tag{6}$$

where V^1 is the corresponding titrated volume of the titrated solution, [S] is the concentration of solution of surfactant, and 2 is 2 mL of solvent.

$$C_s = \frac{V_t}{2 + V_t} C \text{ (original solution concentration)} \tag{7}$$

where V_t is the volume of the titrated solution, C_s is the total concentration of surfactant, and 2 is 2 mL of solvent.

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* Corresponding author: E-mail: zhangxu@ecust.edu.cn.

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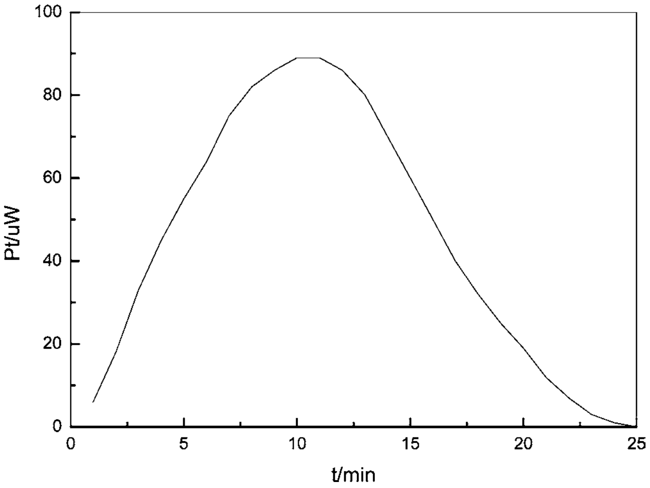

Figure 1. Power−time curves of the (Ni)EH[EHP] toluene solution system at 298.15 K.

From the power−time curve, the area (under the curve) represents the heat effect (Q). The concentration corresponding to the peak point of the curve is the cmc. From the heat effect (Q) and the cmc, the standard enthalpy change ($\Delta H^{\theta}_{\mathrm{m}}$) of the micelle formation process was obtained.

According to the equations $\Delta_{\mathrm{r}}G^{0}_{\mathrm{m}} = -RT \ln K$ and $\Delta_{\mathrm{r}}G^{0}_{\mathrm{m}} = \Delta H^{\theta}_{\mathrm{m}} - T\Delta_{\mathrm{r}}S^{0}_{\mathrm{m}}$, the thermodynamic functions ($\Delta_{\mathrm{r}}G^{0}_{\mathrm{m}}$, $\Delta_{\mathrm{r}}S^{0}_{\mathrm{m}}$) could be calculated.

3. Experimental Section

3.1. Instrument. The 2277 thermal activity monitor (Sweden) was an isothermal thermostat containing 23 L of water, which holds up to four independent calorimetric units. A 4 mL stainless steel titration ampule unit was inserted into the thermostat. The titration ampule unit was equipped with a stirrer and a stirrer motor, which rotated the stirrer shaft at the desired speed [0 to 120) rpm]. A Kelf turbine was used as a 4 mL ampule to be filled with (2 to 3) mL of solution.

The working temperature range of the thermostat instrument was in the range of (283 to 353) K. It was maintained at a given temperature constant to within $\pm 2 \cdot 10^{-4}$ K. The system is very sensitive with a detection limit of 0.15 μW and a baseline stability (over a period of 24 h) of 0.2 μW.

3.2. Materials. Solvents were as follows: n-chain alkanes (decane, dodecane, and tetradecane) and single-ring aromatic hydrocarbons (benzene, toluene, and dimethylbenzene) (obtained fromTianjin Kermel Chemical Reagents Development Center).

Quasi-surfactants were as follows: mono(2-ethyl-hexyl)2-ethyl-hexyl phosphate nickel, (Ni)EH[EHP], and mono(2-ethyl-hexyl)2-ethyl-hexyl phosphate cadmium, (Cd)EH[EHP] (synthesized in the laboratory, content 99.9 %).

The synthesis method proceeded as follows: The pH of the solution which included HEH[EHP] and methyl alcohol solution was adjusted to 4.50 and 5.30 by the addition of ($Cd(NO_3)_2$ and $Ni(NO_3)_2$) solution, respectively. Then, the solution was flushed, filtered, purified, and dried. Finally, the solid salt of {(Cd)EH[EHP], (Ni)EH[EHP])} was obtained.

The cosurfactant was *sec*-octyl alcohol, analytical grade (Shanghai Chemical Reagents Plant).

Solution (1) was a $3.08 \cdot 10^{-4}$ mol·L^{-1} (Cd)EH[EHP] (containing 10 % *sec*-octyl alcohol) organic solution system.

Solution (2) was a $3.08 \cdot 10^{-4}$ mol·L^{-1} (Ni)EH[EHP] (contained 10 % *sec*-octyl alcohol) organic solution system.

3.3. Method. A 4 mL stainless steel titration ampule unit was used in this experiment. A portion of 2 mL of organic solvent was fed into a 4 mL stainless steel titration ampule. A titrating tube was used to titrate 0.5 mL of solution (1) or solution (2) into the organic solvent in the ampule. The speed of titrant addition was 0.02 mL·min^{-1}, and so the operator rotated the stirrer shaft at a speed of 120 rpm. Every system was determined three times at 298.15 K, and the average values of the power−time curves were obtained with a reported relative error less than 1.5 %.

4. Results and Discussion

4.1. Measurement of cmc for the Quasi-surfactant {(Cd)EH-[EHP], (Ni)EH[EHP]} Organic Solution Systems at 298.15 K. The power−time curves of the micelle formation process were determined at 298.15 K for quasi-surfactant {(Ni)EH-[EHP], (Cd)EH[EHP]} organic solution systems (containing 10 % *sec*-octyl alcohol) and organic solvent (decane, dodecane, tetradecane, benzene, toluene, and dimethylbenzene). A partial curve can be seen in Figure 1.

From the data of the power−time curves, the cmc's were determined. These values for the {(Ni)EH[EHP], (Cd)EH[EHP]} systems are shown in Table 1.

From the values of Table 1, the cmc of the quasi-surfactants decreased with the increment of the carbon number (c) of the single-ring aromatic hydrocarbon and n-chain alkane solvents. For the single-ring aromatic hydrocarbon solvents, the order was demonstrated as (Ni)EH[EHP] > (Cd)EH[EHP] for the same carbon number. For the n-chain alkane solvents, the order was demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

4.2. Determination of the Aggregation Number (n) and Formation Constant of the Micelle (K) of the Quasi-surfactant {(Cd)EH[EHP], (Ni)EH[EHP]} Systems at 298.15 K. According to the data of Figure 1, the curve of $P_{\mathrm{total}}-V_{\mathrm{t}}$ is shown in Figure 2. Then, C_{s} and [S] were calculated, and partial values are shown in Table 2. A curve of $\log\{C_{\mathrm{s}} - [\mathrm{S}]\}$ against log[S] was plotted. The aggregation number (n) and the formation constant of the micelle (K) were calculated, and these values are shown in Tables 3 and 4.

For the aggregation number (n) and the formation constant of the micelle (K), the values of quasi-surfactants decreased with the increment of carbon number (c) of the single-ring aromatic hydrocarbon solvents with the order demonstrated as (Ni)EH-[EHP] > (Cd)EH[EHP] for the same carbon number. The aggregation number (n) and the formation constant of the micelle (K) increased with the increment of carbon number (c) of n-chain alkane solvents with the order demonstrated as (Ni)EH[EHP] > (Cd)EH[EHP] for the same carbon number.

4.3. Measurement of the $\Delta_{\mathrm{r}}H^{\theta}_{m}$ of the Quasi-surfactant {(Cd)EH[EHP], (Ni)EH[EHP]} Systems at 298.15 K. The power−time curve of the micelle formation process was

Table 1. Values of cmc of Quasi-surfactants {(Ni)EH[EHP], (Cd)EH[EHP]} with Different Solvents and 10 % *sec*-Octyl Alcohol Systems at 298.15 K

solvent	benzene	toluene	dimethylbenzene	decane	dodecane	tetradecane
(Ni)EH[EHP] 10^5cmc/mol·L^{-1}	3.23 ± 0.07	2.92 ± 0.06	2.61 ± 0.06	2.38 ± 0.07	2.26 ± 0.06	2.11 ± 0.06
(Cd)EH[EHP] 10^5cmc/mol·L^{-1}	1.91 ± 0.08	1.56 ± 0.07	1.23 ± 0.07	3.25 ± 0.08	3.08 ± 0.07	2.95 ± 0.07

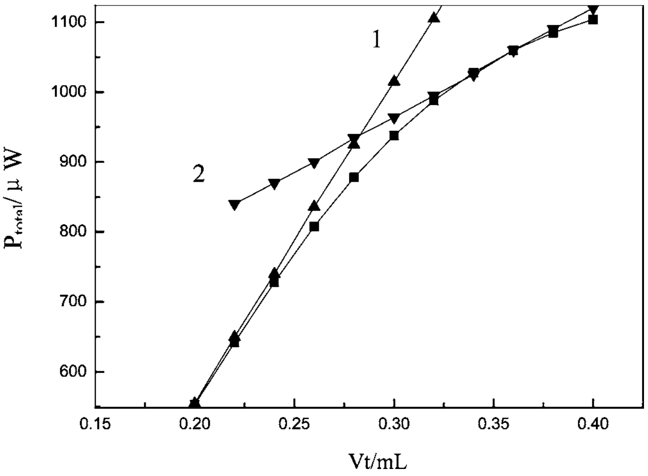

Figure 2. $P_{\mathrm{total}}-V_t$ curve of the (Ni)EH[EHP] toluene solution system.

Table 2. Data of C_s and [S] for the {(Ni)EH[EHP], (Cd)EH[EHP]} Decane Solution System at 298.15 K

	V_t / mL	V^1 / mL	$[S]\cdot 10^5$ / $\mathrm{mol\cdot L^{-1}}$	$C_s\cdot 10^5$ / $\mathrm{mol\cdot L^{-1}}$	−log[S]	$-\log\{C_s - [S]\}$
(Cd)EH[EHP] decane solution	0.22	0.139	2.001	4.023	4.699	4.694
	0.24	0.143	2.053	4.350	4.688	4.639
	0.26	0.147	2.103	4.671	4.678	4.590
	0.28	0.150	2.154	4.986	4.667	4.548
	0.30	0.154	2.205	5.296	4.656	4.510
(Ni)EH[EHP] toluene solution	0.20	0.136	3.412	5.782	4.467	4.625
	0.22	0.140	3.520	6.303	4.453	4.556
	0.24	0.145	3.628	6.814	4.440	4.497
	0.26	0.150	3.735	7.317	4.423	4.446
	0.28	0.154	3.842	7.811	4.416	4.401
	0.30	0.159	3.948	8.296	4.404	4.362

determined. The area under the curve was obtained which represents the thermal effect. Parallel control experiments were conducted to achieve the thermal effect caused by dilution in the organic solvent. According to the cmc and heat effect (Q), the standard enthalpy change ($\Delta_r H_m^\theta$) of the micelle formation process can be calculated. The data of $\Delta_r H_m^\theta$ are given in Table 5.

From these values, the $\Delta_r H_m^0$ of quasi-surfactants decreased with the increment of carbon number (c) of the single-ring aromatic hydrocarbon solvents. For the $\Delta_r H_m^0$ of different quasi-surfactants with the order demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number. The $\Delta_r H_m^0$ of quasi-surfactants increased with the increment of carbon number (c) of n-chain alkane solvents with the order demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

4.4. Determination of the $\Delta_r G_m^0$ and $\Delta_r S_m^0$ of Quasi-surfactants {(Cd)EH[EHP], (Ni)EH[EHP]} System at 298.15 K. The formation constants of the micelle (K) of the association−dissociation between the micelle state and the nonmicelle state were obtained. According to the equations ($\Delta_r G_m^0 = -RT \ln K$ and $\Delta_r G_m^0 = \Delta_r H_m^0 - T\Delta_r S_m^0$), the thermodynamic functions ($\Delta_r G_m^0$, $\Delta_r S_m^0$) were calculated with the data shown in Table 5.

From these values, the $\Delta_r G_m^0$ of quasi-surfactants increased with the increment of the carbon number (c) of the single-ring aromatic hydrocarbon solvents. For the $\Delta_r G_m^0$ of different quasi-surfactants, the order was demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number. The $\Delta_r G_m^0$ of quasi-surfactants decreased with the increment of the carbon number (c) of n-chain alkane solvents. For the $\Delta_r G_m^0$ of different quasi-surfactants, the order was demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

From these values, the $\Delta_r S_m^0$ of quasi-surfactants decreased with the increment of the carbon number (c) of single-ring aromatic hydrocarbon solvents. For the $\Delta_r S_m^0$ of different quasi-surfactants, the order was demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number. The $\Delta_r S_m^0$ of quasi-surfactants increased with the increment of the carbon number (c) of n-chain alkane solvents. For the $\Delta_r S_m^0$ of different quasi-surfactants, the order was demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

5. Conclusions

From the experimental results, the following can be concluded:

(1) Microcalorimetry is a sensitive, quick, and easy method to measure the cmc and study the thermodynamic properties of the micelle formation process.

(2) The cmc decreased with the increment of the carbon number (c) of the solvent. For single-ring aromatic hydrocarbon solvents, the order is demonstrated as (Ni)EH[EHP] > (Cd)EH[EHP] for the same carbon number. For n-chain alkane solvents, the order is demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

(3) The aggregation numbers (n) and formation constant of the micelle (K) decrease with the increment of the carbon number (c) of the single-ring aromatic hydrocarbon solvents with the order demonstrated as (Ni)EH[EHP] > (Cd)EH[EHP]

Table 3. Values of the Aggregation Number (*n*) of Quasi-surfactants {(Ni)EH[EHP], (Cd)EH[EHP]} with Different Solvents and 10 % *sec*-Octyl Alcohol Systems at 298.15 K

solvent	benzene	toluene	dimethylbenzene	decane	dodecane	tetradecane
(Ni)EH[EHP]	5.29 ± 0.07	4.15 ± 0.06	3.14 ± 0.06	4.76 ± 0.07	5.31 ± 0.06	5.86 ± 0.06
(Cd)EH[EHP]	4.66 ± 0.08	3.80 ± 0.07	2.95 ± 0.07	4.29 ± 0.08	4.84 ± 0.07	5.34 ± 0.07

Table 4. Values of the Formation Constant of the Micelle (*K*) of Quasi-surfactants {(Ni)EH[EHP], (Cd)EH[EHP]} with Different Solvents and 10 % *sec*-Octyl Alcohol Systems at 298.15 K

solvent	benzene	toluene	dimethylbenzene	decane	dodecane	tetradecane
(Ni)EH[EHP]	$3.62\cdot 10^{13}$	$1.93\cdot 10^{13}$	$0.21\cdot 10^{13}$	$3.54\cdot 10^{15}$	$2.59\cdot 10^{18}$	$9.64\cdot 10^{21}$
(Cd)EH[EHP]	$2.90\cdot 10^{10}$	$1.48\cdot 10^{10}$	$0.75\cdot 10^{9}$	$6.61\cdot 10^{14}$	$3.84\cdot 10^{17}$	$1.54\cdot 10^{20}$

Table 5. Values of $\Delta_r H_m^\theta$ ($\mathrm{kJ\cdot mol^{-1}}$), $\Delta_r G_m^0$ ($\mathrm{kJ\cdot mol^{-1}}$), and $\Delta_r S_m{}^\theta$ ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) of Quasi-surfactants {(Ni)EH[EHP], (Cd)EH[EHP]} with Different Solvents and 10 % *sec*-Octyl Alcohol Systems at 298.15 K

	solvent	benzene	toluene	dimethylbenzene	decane	dodecane	tetradecane
$\Delta_r H_m^\theta$ ($\mathrm{kJ\cdot mol^{-1}}$)	(Ni)EH[EHP]	322 ± 5	278 ± 4	251 ± 3	158 ± 2	205 ± 3	251 ± 3
	(Cd)EH[EHP]	365 ± 5	323 ± 5	292 ± 4	180 ± 2	228 ± 3	275 ± 4
$\Delta_r G_m^0$ ($\mathrm{kJ\cdot mol^{-1}}$)	(Ni)EH[EHP]	−77.35	−75.79	−70.30	−88.70	−105.04	−125.42
	(Cd)EH[EHP]	−59.69	−58.02	−56.35	−84.55	−100.32	−115.17
$\Delta_r S_m{}^\theta$ ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)	(Ni)EH[EHP]	1340	1187	1078	828	1040	1263
	(Cd)EH[EHP]	1425	1278	1169	888	1102	1309

for the same carbon number. The aggregation number (*n*) and the formation constant of micelle (*K*) increase with the increment of the carbon number (c) of the n-chain alkane solvents with the order demonstrated as (Ni)EH[EHP] > (Cd)EH[EHP] for the same carbon number.

(4) The $\Delta_r H_m^0$ of quasi-surfactants decrease with the increment of the carbon number (c) of single-ring aromatic hydrocarbon solvents. For the $\Delta_r H_m^0$ of the different quasi-surfactants, the order is demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number. The $\Delta_r H_m^0$ of quasi-surfactants increase with the increment of the carbon number (c) of n-chain alkane solvents; the order is demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

(5) The $\Delta_r G_m^0$ of quasi-surfactants increase with the increment of the carbon number (c) of single-ring aromatic hydrocarbon solvents. For the $\Delta_r G_m^0$ of the different quasi-surfactants, the order is demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number. The $\Delta_r G_m^0$ of the quasi-surfactants decreased with the increment of the carbon number (c) of the n-chain alkane solvents. For the $\Delta_r G_m^0$ of the different quasi-surfactants, the order is demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

(6) The $\Delta_r S_m^0$ of the quasi-surfactants decrease with the increment of the carbon number (c) of single-ring aromatic hydrocarbon solvents. For the $\Delta_r S_m^0$ of the different quasi-surfactants, the order was demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number. The $\Delta_r S_m^0$ of quasi-surfactants increased with the increment of the carbon number (c) of n-chain alkane solvents. For the $\Delta_r S_m^0$ of different quasi-surfactants, the order is demonstrated as (Cd)EH[EHP] > (Ni)EH[EHP] for the same carbon number.

The power−time curves contained much information from which the cmc and thermodynamic properties could be obtained. This information is significant for the studied theory and industrial application of extraction chemistry.

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