Surface Tension and Solubility of Allyl-β-cyclodextrin

Chang-jun Zou,* Hao-min Wu, and Lan Ma

School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, 610500, People's Republic of China

The changes for the surface tension of this derivative of β-cyclodextrin (β-CD) at a pH between 4 and 10 and a temperature of 298.15 K and its solubilities at temperatures between (273.15 and 353.15) K were investigated. The results of these studies show that the minimum value, 40.5 $mN \cdot m^{-1}$, for the surface tension of allyl-β-CD appears in an alkaline environment, that the critical micelle concentration (cmc) is $9 \cdot 10^{-3}$ $mol \cdot L^{-1}$, and that the solubility of allyl-β-CD increases by at least 50 % compared with that of β-CD. Finally, according to the analysis with ideal solution model, the optimal solubility model is obtained.

Introduction

Cyclodextrins (CDs) are widely used as the second important host compounds in supramolecular chemistry research. But, because of their low solubilities, they usually need to be modified before application. On the basis of years of research, CDs and their derivatives have been widely applied in the fields of agriculture, medicine and health, food processing and the spice industry, and so forth.[1−3]

CD has a special cavity structure and is a kind of external cavity hydrophilic and internal cavity oleophilic material. Therefore, it has aroused scientists' attention. Our team also has done some research about the applications of CDs and their derivatives.[4−6]

In previous studies there were a lot of property-related experiments on various CD derivatives such as hydroxypropyl CDs,[7] methylation CDs,,[8,9] and so forth. Allyl-β-CDs are one class of CD derivatives with unsaturated double bonds. They have a wider range of applications than β-CD, such as in chromatographic separation technology, medicine, the environment, and petrochemical technology. They particularly possess an obvious property of surfactant while β-CD does not. In other words, allyl-β-CDs have great research value. Therefore, in this paper the surface property and the solubility of this short-chain derivative were studied systematically.

Materials and Methods

At first, β-CD was recrystallized two times with distilled water before use. Then it was dried for 12 h in a vacuum drying oven at a temperature of 383.15 K to ensure that its purity was higher than 99.0 %. Bromopropylene, chloroacetic acid, acetone, and absolute ethyl alcohol, all described as 99.0+ % pure (analytical grade), were produced by the KeLong chemical reagent factory.

The preparation, isolation, and purification of allyl-β-CDs in this paper were carried out according to literature.[10] This derivative sample was weighed and accurate to one part in 10.[4] Then a series of aqueous solutions were prepared with the sample and ultrapure deionized water, and the concentrations were between ($5 \cdot 10^{-5}$ and $5 \cdot 10^{-2}$) $mol \cdot L^{-1}$. In all cases, the solutions were prepared (60 to 120) min before the experiments were carried out to avoid possible variations in surface tension due to the change of solute. The uncertainty of the concentration of each solution under test was ± 0.02 $mol \cdot L^{-1}$.

NaOH and HCl (analytical grade), produced by the KeLong chemical reagent factory, were used as pH modifiers. The pH measurements were performed with a pHS-4C^{+} pH meter having an uncertainty of ± 0.001 pH.

The surface tension measurements were performed through the circle method, by a ZL-3000 interfacial tensiometer which has an uncertainty of ± 0.1 $mN \cdot m^{-1}$ with the resolution of 0.1 $mN \cdot m^{-1}$ (made in China). The measurements were carried out in a thermostatted container at 298.15 K with an uncertainty of ± 0.2 K. Eight determinations of surface tension were carried out for each solution. The average value taken from eight measurement values (the maximum and the minimum value of which had been removed) was reported. The range of pH was between 4 and 10.[11]

According to the national standard of the People's Republic of China,[12] the solubilities of allyl-β-CD at temperatures between (293.15 and 353.15) K were tested. The main principle is at first to prepare many groups of sample solutions at different mass concentrations (1 % to 5 %) and set them aside for 1 h, thus ensuring that the values obtained for solubility were steady-state values. Second, the temperature range of solubility of different solutions is determined. Third, the limit temperature of every solution is determined. Fourth, steps 2 and 3 are repeated to get a series of limit temperatures. At last, the standard curve of $S-T$ is drawn.

Cite the solution at 1 % mass concentration as an example: take the solution into a test tube with corks and accurate scale marks, and put it into accurate constant temperature water bath. Decrease the temperature slowly to precipitate out solute, and record this instantaneous temperature as t_1; then increase temperature to dissolve the precipitated solute, and when the solute is just completely dissolved, record the temperature as t_2. Next add the prepared 1 % solution into two accurate test tubes. Elevate the temperature of one tube to completely dissolve the solute, and reduce the temperature of another one to get a turbid solution. Then put the two test tubes into a constant temperature water bath together. Slowly adjust the temperature (t_1 to t_2) to make sure that the

* Corresponding author. E-mail: changjunzou@126.com.

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Table 1. Surface Tension of Aqueous Solutions of Allyl-β-CD at 298.15 K

C	γ/mN·m^{-1}						
mol·L^{-1}	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
$5\cdot10^{-5}$	70.6	70.5	70.2	69.2	68.2	67.7	67.8
$1\cdot10^{-4}$	70.2	69.8	69.5	68.7	67.4	67.1	67.6
$3\cdot10^{-4}$	67.9	67.8	67.4	66.6	66.1	65.4	65.3
$7\cdot10^{-4}$	65.6	65.3	64.9	64.3	63.6	62.8	62.5
$1\cdot10^{-3}$	64.5	64.2	63.9	62.7	61.2	60.5	60.6
$3\cdot10^{-3}$	61.3	60.8	60.5	59.9	59.3	58.2	57.9
$7\cdot10^{-3}$	54.2	53.9	53.5	52.7	52.5	51.8	51.7
$8\cdot10^{-3}$	48.8	48.9	48.5	48.1	47.6	47.3	47.4
$9\cdot10^{-3}$	43.9	43.8	43.6	43.4	42.9	42.6	42.5
$1\cdot10^{-2}$	41.7	41.6	41.5	41.1	40.8	40.7	40.7
$2\cdot10^{-2}$	41.2	41.1	40.9	40.7	40.5	40.4	40.5
$3\cdot10^{-2}$	40.9	40.7	40.7	40.6	40.5	40.5	40.5
$4\cdot10^{-2}$	40.7	40.7	40.6	40.6	40.6	40.5	40.6
$5\cdot10^{-2}$	40.7	40.7	40.8	40.7	40.5	40.6	40.6

appearances of the two solutions will not change (the observation time is about (2 to 3) h). The temperature at this point is the limit temperature of this 1 % solution. Then, for the next step, repeat the experiment of the solutions at different concentrations to measure a series of the limit temperatures. According to group data, the solubility curve can be drawn. Thus, the solubilities at different temperatures can be finally defined with the curve. The experiment was carried out in a HWC-502 temperature controllable bath (Jingie Industry and Trading Co., Ltd., China), so the temperature variation could be controlled in ± 0.5 K. Each final value was taken from the average of eight measurement values (the maximum and the minimum value of which had been removed) and was accurate to 0.01 g/100 g water. Then all of the final values were brought into regression analysis through the ideal solution model. Ultimately the solubility curve of allyl-β-CD was obtained.[13−15]

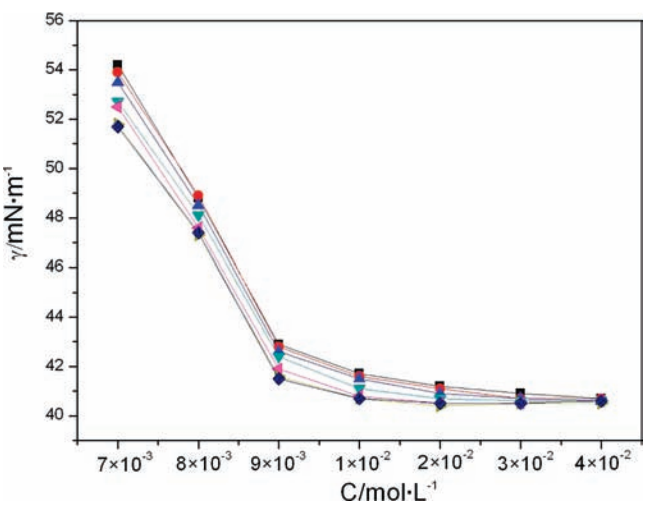

Figure 1. Surface tension vs molar concentration curves of allyl-β-CD: ■, pH 4; ●, pH 5; ▲, pH 6; ▼, pH 7; left-pointing triangle, pH 8; right-pointing triangle, pH 9; ◆, pH 10.

Table 3. Regression Calculation Results of the Ideal Solution Model

system	A	B	σ%
allyl-β-CD/water	4455.226	9.631	9.7

Results and Discussion

The surface tension for aqueous solutions of allyl-β-CD at various pH and different concentrations at a temperature of 298.15 K are shown in Table 1. The values show that the two change trends of the surface tension were consistent in an alkaline environment and in an acidic environment, and the minimum value appeared in the alkaline environment. It can be indicated that the variations of pH have little obvious effect on the surface tension of allyl-β-CD.

According to Figure 1, the variations in the surface tension of allyl-β-CD with the changes of concentration were in accord with the typical $\gamma-C$ curves of surfactants. This point illustrates that allyl-β-CD has a typical property of surfactant. Thus, allyl-β-CD can be classified as an amphiphilic nonionic surfactant theoretically. Simultaneously, on the basis of the analysis of the measurement values and figures, the critical micelle concentration (cmc) of allyl-β-CD is $9\cdot10^{-3}$ mol·L^{-1} at a pH between 4 and 10.

The measurement values of solubility of allyl-β-CD at temperatures between (293.15 and 353.15) K are shown in Table 2. With analysis it can be figured out that the water solubility of β-CD[3] was improved obviously after modification. Then, the values were brought into regression analysis through ideal solution model.

The ideal solution model is a simplified solubility model which is universally applicable for the solid−liquid equilibrium system.[16]

$$\ln x = \frac{A}{T} + B \qquad (1)$$

where x is the molar fraction of solute, A and B are equation parameters, and T is absolute temperature. After regression calculation of the upper measurement values, the result is shown in Table 3.

Conclusion

This paper reports some new experimental data for the surface tension (at different pH values ranging from 4 to 10) and solubility of allyl-β-CD (at different temperatures ranging from (293.15 to 353.15) K) at normal pressure. With a comprehensive analysis of this paper, we can draw the following conclusions: (1) Allyl-β-CD, which was prepared through the allylation reaction of β-CD, has an obvious property of surfactant and the cmc value of $9\cdot10^{-3}$ mol·L^{-1}. (2) The surface tension of allyl-β-CD does not change obviously with the variations of pH. (3) The solubility of allyl-β-CD increases rapidly with the temperature rise. (4) The ideal solution model can represent the solubility data very well.

Table 2. Solubilities of Allyl-β-CD and β-CD in Water at Different Temperatures

	S/g·100 g^{-1} water						
sample	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K
allyl-β-CD	2.49	3.58	5.68	10.81	13.19	23.54	42.04
β-CD[a]	1.64	2.28	3.49	5.27	7.29	12.03	19.66

[a] Ref 3.

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