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Solubility of NaBr, NaCl, and KBr in Surfactant Aqueous Solutions

Xiangzhu Zhou and Jingcheng Hao*

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, P. R. China

ABSTRACT: The solubility of inorganic salts in surfactant aqueous solutions is very important for both scientific research and inorganic salt industry. In this work, we determine the solubility of three commercially available inorganic salts, NaBr, NaCl, and KBr, in cationic tetradecyltrimethylammonium bromide (TTABr) or anionic sodium dodecyl sulfate (SDS) surfactant solutions from 298.15 to 353.15 K. The data show that the solubility of the three salts in SDS and TTABr solution increases progressively with increasing temperature, which is similar to that in water. The solubility of NaBr, NaCl, and KBr in surfactant aqueous solutions with the concentration under the TTABr or SDS cmc is higher than that in the solutions above the TTABr or SDS cmc. The solubility of NaCl and NaBr in SDS is much lower than that in water and increases slowly along with increasing temperature. For the case of KBr and NaBr in TTABr, it becomes more complicated. Below $T = 312.15$ K, the solubility of KBr and NaBr is much lower than that in water, but the data becomes higher when it is above $T = 340.15$ K. This is similar to that in water between $T = (312.15$ and $340.15)$ K. The data and the results of inorganic salts in surfactant aqueous solutions should provide the basic data and understanding for the inorganic and surfactant industries.

INTRODUCTION

The solubility of inorganic salts is a significant physicochemical parameter in areas such as ionic equilibrium, ion−solvent and ion−ion interactions in aqueous,[1,2] and technical applications, e.g., desalination processes and food processing.[3] Usually, people focus their attention on the solubility of inorganic salts dissolving in water or organic solvents.[1−6] It is easy to gain a large amount of solubility data on inorganic salts that dissolve in water or a pure organic solvent from the literature. In surfactant solutions, the salt effect or ionic strength[7−9] could induce phase and property transitions. However, solubility data of inorganic salts in surfactant aqueous solutions are lacking.

In order to provide the basic solubility data and an understanding of inorganic salts in surfactant aqueous solutions, we employed a simple method to measure the solubility of NaBr, KBr, and NaCl in cationic TTABr and anionic SDS solutions from $T = (298.15$ to $353.15)$ K. The data not only provide the basic solubility data but also help to understand the phase behavior of inorganic salts in surfactant aqueous solutions.

EXPERIMENTAL SECTION

Chemicals and Materials. In all experiments, water (resistivity = 18.25 MΩ·cm) was purified by an UPH Ultrapure Water System. Inorganic salts, NaBr, NaCl, and KBr, were supplied by the Sinopharm Chemical Reagent Co., Ltd. having purities higher than 99.0 %. The salts were dried in an oven before use. Cationic TTABr (Amresco) and anionic SDS (99 %, Sigma) surfactants were used without purification. All chemicals were employed without further purification.

Experimental Procedure. The solubility of NaBr, NaCl, and KBr in surfactant aqueous solutions was determined by the isothermal method. The experiments were carried out in a thermostat which kept a constant temperature (± 0.1 K). A cuvette (20 mL) was weighed by a 0.1 mg precision electronic balance (Adventure, Ohaus). The desired amounts of surfactant solution were displaced into the cuvette, and then the solution and cuvette were weighed together to obtain the precise amount of solution. The inorganic salt was accurately weighed and quickly introduced to the cuvette which was vortexed for several minutes at the working temperature. The cuvette was then closed and wrapped with laboratory film to prevent water evaporation. Additional portions of salts, which also were accurately weighed, were put into the solution until the onset of precipitation began to separate out, indicating the critical point of salt solubility. The highest weight of salt is considered as the salt solubility under these conditions. Every experimental datum was an average of at least three different measurements obeying the following criterion: the relative standard deviation (RSD) should be less than 0.5 %.

Surface Tension Measurement. The Processor Tensiometer-K 100, purchased from KRÜSS Company (Germany) was used for measuring the critical micelle concentration (cmc) at different salinity. For controlling the temperature constant at (298.15 ± 0.01) K, the equipment was attached to a circulating water bath. A series measurement was adopted with Wilhelmy platinum. The plate was cleaned well and heated briefly in an alcoholic flame until it glowed before each measurement. A 50 mL salt solution at a fixed concentration was used as the starting solution, and then a small amount of surfactant solution (a few microlitres) was dropped and stirred, of which the concentration can be calculated. The time interval between each measurement was 5 min.[10] The precision in the measurements was ± 0.001 $mN \cdot m^{-1}$.

RESULTS AND DISCUSSION

It is widely known that addition of salts will greatly influence the aggregate structures of surfactants in solutions. Thus the

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Table 1. Solubility (Mass Fraction, % by Weight) of NaBr in TTABr Aqueous Solutions and Water at Different Temperatures

	100 W		
T/K	$1.0 \cdot 10^{-3}$ mol·L^{-1} TTABr	$2.0 \cdot 10^{-2}$ mol·L^{-1} TTABr	H_2O^a
298.15	32.32	29.91	48.620
303.15	41.38	33.98	49.583
313.15	50.77	43.34	51.571
318.15	52.21	48.34	52.673
323.15	52.94	50.94	53.838
328.15	53.35	52.75	54.014
333.15	53.54	52.92	54.087
343.15	55.86	54.58	54.281
348.15	56.06	55.16	54.369
353.15	56.11	55.89	54.495

[a] Data from ref 5.

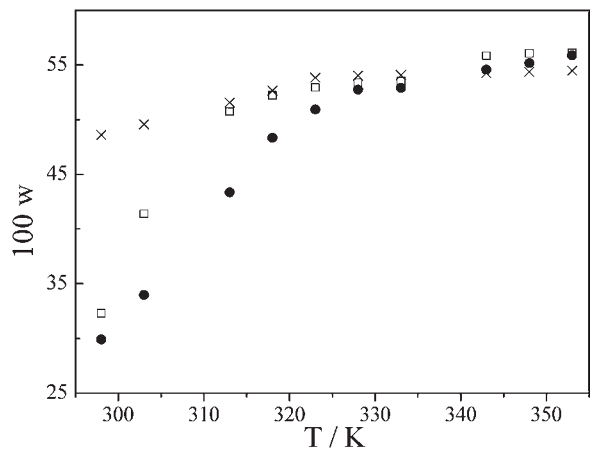

Figure 1. NaBr solubility in TTABr with different concentrations and water at different temperatures. The concentrations of TTABr (mol·L^{-1}): $1.0 \cdot 10^{-3}$ (□), $2.0 \cdot 10^{-2}$ (●), and H_2O (×).

Table 2. Solubility (Mass Fraction, % by Weight) of KBr in TTABr Aqueous Solutions and Water at Different Temperatures

	100 W		
T/K	$1.0 \cdot 10^{-3}$ mol·L^{-1} TTABr	$2.0 \cdot 10^{-2}$ mol·L^{-1} TTABr	H_2O^a
298.15	35.49	33.64	40.713
303.15	40.29	38.32	41.670
313.15	43.79	42.18	43.359
323.15	45.73	43.86	44.932
333.15	47.70	45.36	46.360
343.15	48.78	46.89	47.725
348.15	49.60	48.84	48.349
353.15	50.13	49.72	48.961

[a] Data from ref 1.

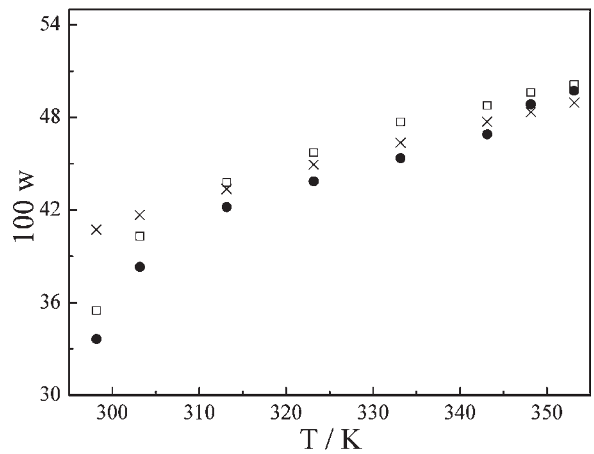

Figure 2. KBr solubility in TTAB with different concentrates and water plotted against temperature. The concentrations of TTABr (mol·L^{-1}): $1.0 \cdot 10^{-3}$ (□), $2.0 \cdot 10^{-2}$ (●), and H_2O (×).

solubility of salts in surfactant aqueous solutions should provide a basic understanding of surfactant aggregates in high salinity solutions. We applied cationic and anionic surfactant aqueous solutions instead of water to investigate the solubility of commercially available inorganic salts. Cationic TTABr and anionic SDS are commonly used in laboratory research and industry applications. The solubility of NaBr, NaCl and KBr was determined at the concentrations of surfactants above and under the critical micelle concentration (cmc). The obtained experimental solubility of NaBr, NaCl, and KBr in TTABr and SDS aqueous solutions was compared with that in water.

Solubility of NaBr in TTABr Solutions. The solubility of NaBr in TTABr solutions was determined from T = (298.15 to 353.15) K. The investigated concentrations of TTABr were $1 \cdot 10^{-3}$ mol·L^{-1} (lower than the cmc = $3.8 \cdot 10^{-3}$ mol·L^{-1})[11] and $2 \cdot 10^{-2}$ mol·L^{-1} (higher than the cmc). The experimentally determined solubility of NaBr in TTABr aqueous solutions is summarized in Table 1 and illustrated in Figure 1. For comparison, the solubility of NaBr in pure water from the report of Pinho[5] is also included in Table 1 and Figure 1. From Table 1 and Figure 1, it can be clearly seen that a sharp increase of NaBr solubility is caused by an increase of temperature. Under 315.15 K, the solubility of NaBr in TTABr solutions is much lower than that in water, whether the concentration is below or above the TTABr cmc. When the temperature was kept between (320.15 and 340.15) K, the solubility of NaBr in TTABr aqueous solutions is similar to that in water. The solubility in TTABr solutions becomes higher than that in water when the temperature is above 340.15 K. The solubility of NaBr in $1.0 \cdot 10^{-3}$ mol·L^{-1} (below cmc) TTABr solution is always higher than that with the concentration of $2.0 \cdot 10^{-2}$ mol·L^{-1} (above cmc) at the same temperature.

Solubility of KBr in TTABr Solutions. The solubility of KBr was determined in TTABr solutions with two different concentrations, $1.0 \cdot 10^{-3}$ mol·L^{-1} (below the cmc) and $2.0 \cdot 10^{-2}$ mol·L^{-1} (above the cmc). The measured data are tabulated in Table 2 and presented graphically in Figure 2. The solubility of KBr in water, which was measured by Pinho,[1] is also listed in Table 2 and graphed in Figure 2 for comparison. For the data of KBr in TTABr solutions, the situation in Figure 2 becomes a little complicated. One can see that the solubility of KBr in TTABr solutions smoothly increases with the increasing of temperature. It is interesting to note that the solubility of KBr in TTABr aqueous solutions is much lower than that in water under T = 305.15 K,

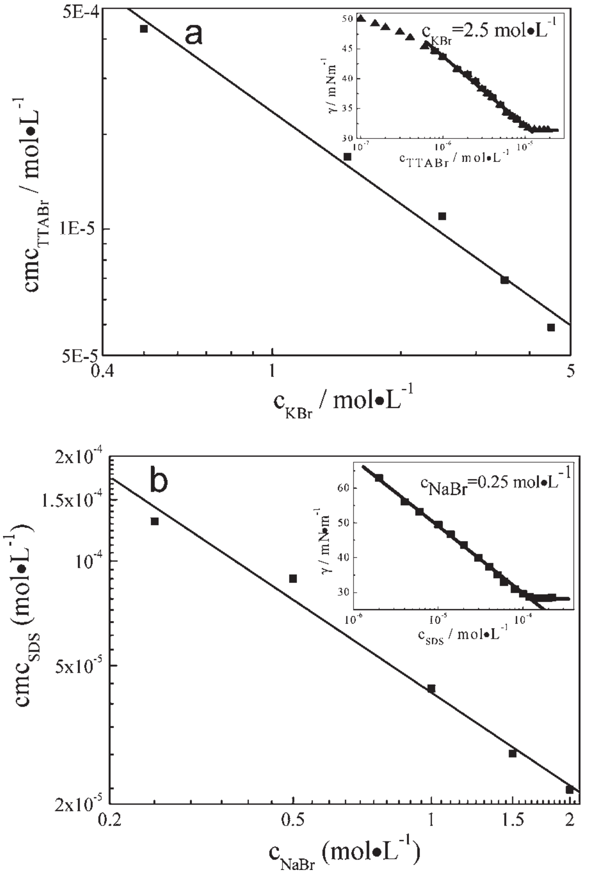

Figure 3. Double logarithmic plot of the critical micelle concentration (cmc) of surfactant versus molar concentration of different salts. Semilog plot of surface tension versus molar concentration of surfactant at a fixed concentration of salt in the inset. (a) TTABr in KBr solution; (b) SDS in NaBr solution.

nevertheless the data become higher than that in water above T = 345.15 K. When the temperature is between T = (310.15 and 345.15) K, the solubility of KBr in TTABr aqueous solutions is close to that in water. As depicted in Figure 2, the solubility of KBr in TTABr aqueous solutions with a concentration of $1.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$ is a little higher than that in water, and the solubility of KBr in TTABr with a concentration of $2.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$ is a little lower than that in water. In other words, the solubility of KBr in TTABr solutions with a concentration above the cmc ($2.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$) is lower than that in TTABr solution with the concentration below the cmc ($1.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$). Similar results were obtained for the solubility of NaBr in TTABr aqueous solutions as indicated in Figure 1. This result could be explained by the common-ion effect in TTABr aqueous solutions. Br^- is dissociated from the cationic surfactant, TTABr, in aqueous solutions, which should decrease the solubility of NaBr or KBr in water.

We observed another strange phenomenon in that the solubility of NaBr and KBr in TTABr aqueous solution is a little higher than that of NaBr and KBr in water at high temperature. In order to explain the result, the effect of high salinity on the critical micelle concentration (cmc) was investigated.

Critical Micelle Concentration (cmc) of TTABr and SDS in High Salinity. The cmc of surfactants in high concentration salts were investigated by surface tension measurements. Different concentrations of KBr solution were taken as the electrolyte solutions for TTABr and NaBr for SDS. Figure 3 gives the curves of the logarithm of the critical micelle concentration (cmc) of the surfactant against the logarithm of the concentration of salt, and the surface tension curves were recorded at fixed concentration of salt in the inset. The straight lines have been calculated and are expressed as follows:

(a) $lg\ cmc_{TTABr} = -4.63 - 0.97\ lg\ c_{KBr}$

(b) $lg\ cmc_{SDS} = -4.38 - 0.88\ lg\ c_{NaBr}$

The result is very consistent with the literature.[12] In Figure 3, the critical micelle concentration of surfactant obviously decreases with the increase of the concentration of salt. In another words, more micelles were formed with the addition of salt. So this may be explained by the large aggregation numbers of TTABr micelles at high temperature, at which the large micelles can bind large numbers of Br^-, as illustrated in Figure 4. This case could reduce the free concentration of Br^- in aqueous solution to increase the solubility of NaBr and KBr.

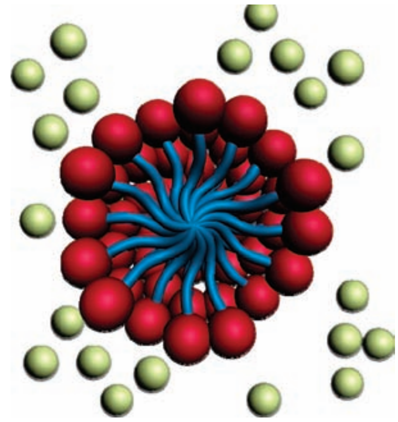

Figure 4. Schematic of a TTABr micelle surrounded by K^+, Na^+, or Br^- ions (yellowish spheres).

Table 3. Solubility (Mass Fraction, % by Weight) of NaBr in SDS Aqueous Solutions and Water at Different Temperatures

	100 W		
T/K	$5.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$ SDS	$4.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$ SDS	H_2O[a]
298.15	9.99	8.27	48.620
303.15	11.36	9.66	49.583
313.15	14.11	11.96	51.571
323.15	15.38	12.88	52.673
333.15	16.57	13.59	53.838
343.15	17.43	14.64	54.014
348.15	18.48	15.15	54.087
353.15	20.04	17.41	54.281

[a] Data from ref 5.

Solubility of NaBr in SDS Solutions. The solubility of NaBr in SDS aqueous solutions is shown in Table 3 and also presented graphically in Figure 5, and the solubility of NaBr in water[5] was also summarized in Table 3 for comparison. The investigated concentrations of SDS solutions were $5.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$ (lower than the cmc = $7.59 \cdot 10^{-3}$)[11] and $4.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$ (higher than the cmc). In Figure 5, the solubility of NaBr monotonically increases with increasing temperature. One can see from Figure 5

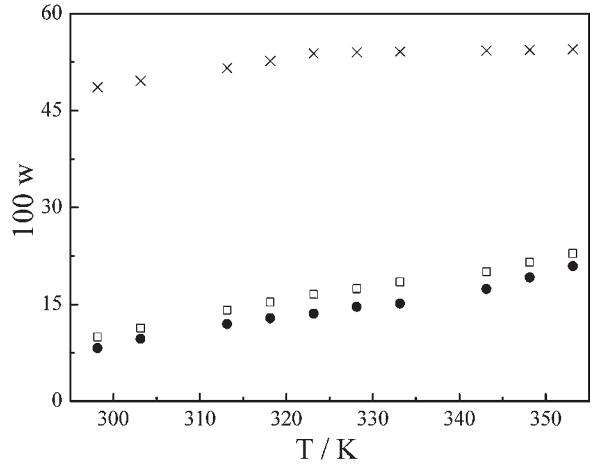

Figure 5. NaBr solubility in SDS aqueous solutions and water plotted against temperature. The concentrations of SDS ($mol \cdot L^{-1}$): 5.0×10^{-3} (□), 4.0×10^{-2} (●), and H_2O (×).

Table 4. Solubility (Mass Fraction, % by Weight) of NaCl in SDS Aqueous Solutions and Water at Different Temperatures

	100 W		
T/K	$5.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$ SDS	$4.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$ SDS	H_2O[a]
298.15	5.24	4.31	26.483
303.15	7.47	6.38	26.550
313.15	10.34	8.99	26.701
323.15	11.64	10.01	26.889
333.15	12.69	10.93	27.106
343.15	13.65	11.57	27.338
348.15	14.00	12.36	27.478
353.15	14.52	13.45	27.602

[a] Data from ref 5.

that the solubility of NaBr in SDS aqueous solutions is much lower than that in water at the same temperature. Due to the common-ion effect, the solubility of NaBr in SDS aqueous solutions with the concentration of SDS below the cmc ($5.0 \cdot 10^{-3}$ $mol \cdot L^{-1}$) is higher than that in SDS solutions above the cmc ($4.0 \cdot 10^{-2}$ $mol \cdot L^{-1}$) at the same temperature (Figure 5). The results show that the presence of anionic SDS in aqueous solutions markedly influences the solubility of NaBr compared to the case of cationic TTABr aqueous solutions.

Solubility of NaCl in SDS Solutions. The experimental solubility of NaCl in SDS aqueous solutions is collected in Table 4 and graphically illustrated in Figure 6. The solubility of NaCl in water is also collected in Table 4 and illustrated in Figure 6 for comparison. The solubility of NaCl in SDS aqueous solutions with the concentration below the cmc ($5 \cdot 10^{-3}$ $mol \cdot L^{-1}$) is higher than that in SDS aqueous solutions above the cmc ($4 \cdot 10^{-2}$ $mol \cdot L^{-1}$). The solubility of NaCl in SDS aqueous solution is much lower than that in water at the same temperature. Figure 6 also shows that an increase in temperature from T = (298.15 to 353.15) K leads to an increase in the solubility of NaCl in SDS aqueous solutions, but the solubility in water hardly increases with increasing temperature.

Comparison of Solubility Data. The solubility of NaBr in cationic and anionic surfactant aqueous solutions against temperature

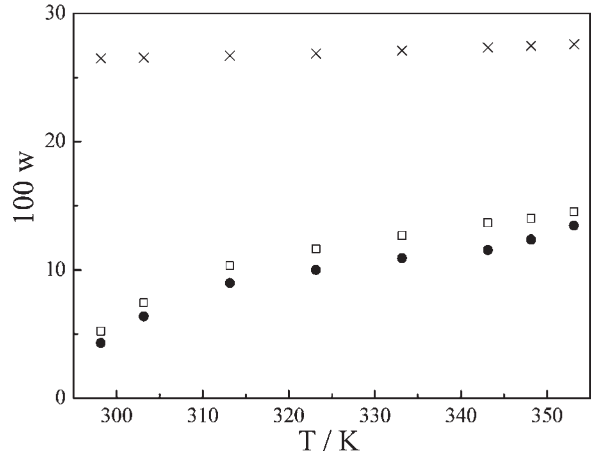

Figure 6. NaCl solubility in SDS aqueous solutions and water plotted against temperature. The concentrations of SDS ($mol \cdot L^{-1}$): 5.0×10^{-3} (□), 4.0×10^{-2} (●), and H_2O (×).

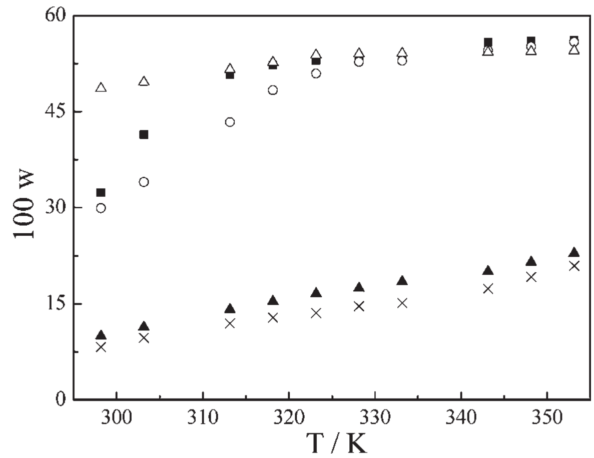

Figure 7. Comparison of the solubility of NaBr in SDS and TTAB aqueous solutions. The concentrations of SDS ($mol \cdot L^{-1}$): 5.0×10^{-3} (▲), 4.0×10^{-2} (×), and H_2O (Δ). The concentrations of TTABr ($mol \cdot L^{-1}$): 1.0×10^{-3} (■) and 2.0×10^{-3} (○).

is compared in Figure 7. We can easily see that the solubility of NaBr in SDS aqueous solutions (below and above the cmc) is much lower than that in TTABr aqueous solutions and in water. The solubility in TTABr aqueous solutions is similar to that in water and mostly lower than that in water. This could be explained because of the common-ion effect from Br^- in solution. In SDS aqueous solutions, the surfactant could be easily separated out after addition of salts (salt-effect), but the solubility of salts may be hardly influenced in the presence of TTABr which has the Br^- counterion. These results could provide an understanding of the cationic surfactant aggregates existence in inorganic salt solutions

■ CONCLUSIONS

We report new experimental solubility data of inorganic salts, NaBr, NaCl, and KBr, in the cationic and anionic surfactant solutions at different temperatures. The solubility of salts in surfactant aqueous solutions increases with increasing temperature, which is similar to the solubility of inorganic salts in water. The solubility of inorganic salts, NaBr and KBr, in cationic

TTABr increases fast with the increase of temperature, but the solubility of NaBr and NaCl in SDS aqueous solution increases slowly. The solubility of inorganic salts in TTABr aqueous solutions is a little lower than that in water at lower temperature, and is almost same as that in water at higher temperature. However, the solubility of inorganic salts in SDS aqueous solutions is much lower than that in water.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jhao@sdu.edu.cn. Phone: +86-531-88366074.

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