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Vapor Pressure of the Aqueous Solution of Sodium Dodecyl Sulfate

Peixun Li,[†] Buxing Han, Haike Yan,* and Ruilin Liu

Institute of Chemistry, Academia Sinica, Beijing 100080, China

Vapor pressures of aqueous sodium dodecyl sulfate solutions have been measured at (298.15, 303.15, 308.15, and 313.15) K and at concentrations m_1 up to 0.03 mol of solute/kg of solution. The vapor pressure of the aqueous solution decreases with m_1 in the range of m_1 from (0 to about 0.005) mol·kg^{-1} and exhibits negative deviation from Raoult's Law. The vapor pressure increases with m_1 when 0.005 mol·kg^{-1} < m_1 < 0.009 mol·kg^{-1}. The vapor pressure is approximately independent of m_1 for m_1 > 0.009 mol·kg^{-1} (the critical micelle concentration). From the anomalous behavior of the vapor pressure, it is deduced that when m_1 is less than about 0.005 mol·kg^{-1}, the surfactants in the solution exist mainly in the form of monomers. When m_1 is in the range from (0.005 to 0.009) mol·kg^{-3}, the surfactant in the solution begins to aggregate even though the concentration is lower than the critical micelle concentration.

Introduction

Aqueous solutions of sodium dodecyl sulfate (SDS), a typical anionic surfactant, have been studied extensively using different techniques, such as NMR (Zhao and Fung, 1993; Ceglie et al., 1993), ESR (Panatta et al., 1992), small angle neutron scattering (Pilsl et al., 1993), conductivity measurements (Evans, 1956), and some other methods (Matheson and King, 1978; Hoskins and King, 1981; Tartar and Lelong, 1955). There appear to be no vapor pressure measurements for these solutions.

In this paper, the vapor pressure of the aqueous solution of SDS has been determined at different temperatures in concentration regions below and above the critical micelle concentration (cmc). On the basis of the vapor pressure data, the interactions between SDS and water and the existing state of SDS in the solution are discussed.

Experimental Section

The SDS was supplied by Bethesda Research Laboratories and was ultrapure. The water was distilled twice, and its conductivity was less than 10^{-4} S·m^{-1}.

The experimental apparatus used in this work has been described in detail previously (Han et al. 1993). Very briefly, a known mass of solution of a known concentration was charged into a vessel with a stopcock. The solution in the vessel was degassed under vacuum with the solution being stirred. The stopcock of the vessel was closed after the degassing process, and then the vessel was weighed. The mass of water lost during the degassing process was known accurately from the mass difference. The vessel was connected to a U-shaped mercury manometer, and then both were put into a thermostat which was maintained within ±0.02 K of the desired temperature. The air in the tube connecting the vessel and the manometer was evacuated until the pressure was lower than 1 Pa. The stopcock of the vessel was opened after thermal equilibrium was reached. The vapor pressure of the solution was determined on the basis of the height difference of the two mercury levels of the U-shaped mercury manometer. An altimeter (height measuring equipment) with a resolution of 0.01 mm was used to measure the height difference of the two mercury levels. DT-100 and Mettler MP1200 balances were used to determine the mass of the solid SDS and the solutions, respectively, and their sensitivities were, respectively, (0.000 05 and 0.001) g.

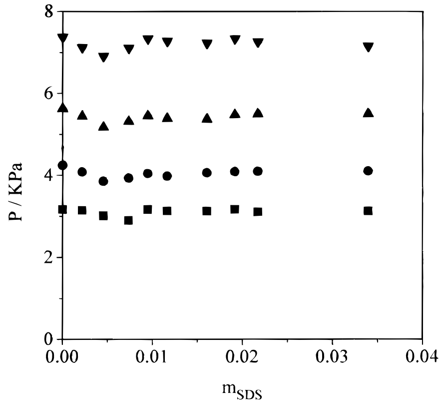

Figure 1. Vapor pressure of the aqueous solution of SDS: (■) 298.15 K, (●) 303.15 K, (▲) 308.15 K, (▼) 313.15 K.

Table 1. Vapor Pressures for the SDS (1) + Water (2) System and the Activity Coefficients of Water

$m_1 \times 10^5$/	298.15 K		303.15 K		308.15 K		313.15 K	
(mol·kg^{-1})	P/kPa	γ_2	P/kPa	γ_2	P/kPa	γ_2	P/kPa	γ_2
0	3.173	1.000	4.256	1.000	5.626	1.000	7.391	1.000
218.0	3.126	0.985	4.084	0.960	5.437	0.966	7.123	0.964
454.0	2.976	0.938	3.853	0.905	5.169	0.919	6.909	0.935
734.0	2.933	0.924	3.932	0.924	5.313	0.944	7.107	0.962
947.0	3.169	0.999	4.049	0.951	5.445	0.968	7.335	0.992
1164	3.125	0.985	3.994	0.938	5.381	0.957	7.274	0.984
1604	3.126	0.985	4.064	0.955	5.365	0.954	7.229	0.978
1914	3.169	0.999	4.090	0.961	5.473	0.973	7.234	0.979
2170	3.108	0.976	4.098	0.963	5.493	0.977	7.261	0.983
3394	3.126	0.986	4.102	0.964	5.492	0.977	7.154	0.969

Results and Discussions

The vapor pressures of the aqueous solutions of SDS were determined at (298.15, 303.15, 308.15, and 313.15) K and a concentration of SDS up to 0.03 mol of SDS/kg of solution (mol·kg^{-1}). The results are listed in Table 1 and depicted in Figure 1. The accuracy of m_1 in the table is better than ±0.1%. The repeatability for the vapor pressure measurements of pure water was better than ±0.15%. The maximum uncertainty of the vapor pressure data in Table 1 is estimated to be ±0.3%. For the vapor pressures of pure water at the four temperatures studied, the maximum deviation between the results of this work and those in the handbook (Weast et al., 1989−1990) is 0.3%.

[†] Visiting scholar from Lanzhou University, Lanzhou, China.

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Table 2. Activity Coefficients of Water in the SDS (1) + Water (2) System at 373.15 K

c_1/(mol·L^{-1})	0.5	1.0	2.0	3.0
γ_2	0.992	0.985	0.969	0.951

The activity coefficient of water, γ_2, can be calculated from the vapor pressures from

$$\gamma_2 = P_2/(P_2^\circ x_2) \tag{1}$$

where P_2° and P_2 are the vapor pressure of pure water and the partial pressure of water, respectively. x_2 is the mole fraction of water. The activity coefficients of water are also listed in Table 1. The vapor pressure of SDS was neglected in the calculation.

From the data in Table 1 and Figure 1 one sees that the vapor pressure of the aqueous solution decreases with m_1 when m_1 is in the range from (0 to about 0.005) mol·kg^{-1}. The system exhibits negative deviation from Raoult's law. The vapor pressure increases with m_1 when 0.005 mol·kg^{-1} $< m_1 <$ 0.009 mol·kg^{-1}, and it is obvious that the solutions are also nonideal. The vapor pressure, however, is nearly independent of m_1 when m_1 is higher than about 0.009 mol·kg^{-1}.

The vapor pressure of the solution depends mainly on the volatilities of the solvent and the solute, the concentration of the solute, and the interaction between the molecules in the solutions. Under the experimental conditions, the vapor pressure of SDS is extremely low. Thus, it can be assumed that the total vapor pressure of the solution is equal to the partial pressure of water, and so the vapor pressure of the system is dominated by the concentration of the solution and the molecular interactions. SDS consists of a lipophilic hydrocarbon chain and a hydrophilic group, both of them interacting with water molecules and affecting the vapor pressure.

The activity coefficients of water in aqueous solutions of Na_2SO_4 at 373.15 K are listed in Table 2, which are calculated from eq 1 and the reduction of the vapor pressure due to the presence of Na_2SO_4 (Weast et al., 1989−1990). Extrapolating the data in Table 2 to the concentration range of this work, the activity coefficients should be very close to unity. It seems that the effect of the polar head of SDS on the vapor pressure is negligible in the concentration range studied in this work, and thus the effect of the hydrocarbon chains of SDS on the vapor pressure is the main factor. Thus, the anomalous behavior of the vapor pressure may be explained qualitatively as follows.

When m_1 is less than about 0.005 mol·kg^{-1}, the surfactants in the solution exist mainly in the form of monomers. The reason for the decrease of vapor pressure with m_1 may be that the interaction between the hydrocarbon chains of SDS and water molecules enhances the hydrogen-bonded structure of water. Cargill (1978) reported that alcohols also stabilize the hydrogen-bonded clusters of water.

When m_1 is in the range from (about 0.005 to about 0.009) mol·kg^{-1}, the vapor pressure increases with m_1. This is because monomers begin to aggregate although the concentration is lower than the critical micelle concentration (cmc). The hydrocarbon chains of the aggregated SDS overlap. More and more SDS monomers become aggregated as m_1 increases and the number of effective hydrocarbon chains interacting with water molecules decreases. Thus, the effect of enhancing the cluster structure of water becomes weaker and weaker with increasing m_1. Premicellar association of some other surfactants was also discussed by other authors (Zimmels and Metzer, 1976).

When the concentration is higher than about 0.009 mol·kg^{-1}, which is about the cmc (Evans, 1956), micelles are formed in the solution. The unassociated SDS and the micelles should be in equilibrium under fixed conditions. The aggregation number of the micelles is 71 (Tartar and Lelong, 1955) and is almost constant in the concentration range studied in this work (Zhao and Fung, 1993). According to phase separation theory, the concentration of the monomer in the solution is nearly constant when the concentration is higher than the cmc. The concentration of the micelle increases very slowly because the aggregation number is relatively large, so the effects of m_1 on the vapor pressure is not notable above the cmc. On the basis of the vapor pressure data, the cmc should be 0.009 mol·kg^{-1}, which agrees well with that determined using the conductivity method (Evans, 1956).

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