Evaporation from Water−Ethylene Glycol Liquid Mixture

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Evaporation rates were determined for water−ethylene glycol liquid mixtures with different mole fractions, where the evaporation rate expressed as mg min^{-1}/area was used because of the presence of two kinds of molecular species. The rate increased with increasing temperature and decreased with increasing mole fraction of ethylene glycol, almost obeying ideal mixing of the two components, although a small positive deviation was observed over the mole fraction from 0 to 0.5 of ethylene glycol at higher temperatures. The activation energy of evaporation was determined from the temperature dependence of the evaporation rate, where the energy was an apparent one because the composition of evaporated species was not determined. The activation energy increased with decreasing temperature and with increasing mole fraction of ethylene glycol, where the energy obeyed the ideal mixing at lower temperatures while it positively deviated at higher temperatures. The evaporation rates were examined by surface tension of the liquid mixture, but any definite relation between them was not found. Both the evaporation rate and the activation energy were found to be determined mainly by the mole fraction in the surface layer from which the evaporation takes place. Finally, the new concept of surface excess was presented, where the surfactant molecules were concentrated and formed a bimolecular layer at a certain distance beneath the air/solution interface.

Introduction

Evaporation rate measurement of water molecules across the air/aqueous solution interface modified by amphiphilic molecules is quite valuable for a basic study on the interface and the transport of water molecules across the interface. This can be done by using the remodeled apparatus for a thermal gravitational analysis.[1] The activation energy of water evaporation is very useful for observing the process through which evaporation takes place, which can be carried out by the temperature dependence of the evaporation rates. In the preceding study, the soluble surfactants examined to modify the interface were cationic, anionic, and nonionic to find out if there exists any difference in the rate among kinds of the surfactant species employed.[2] The rate was also examined from the viewpoint of molecular surface area of the surfactants derived from the Gibbs adsorption isotherm. The effect of an insoluble monolayer on water evaporation was also examined by using long 1-alkanols as an insoluble amphiphile.[2,3] Indeed, these results were found quite useful in considering where the surface excess material was concentrated or what kind of reasonable model should be drawn for the surface excess of soluble surfactant solution. Retardation of the water evaporation due to concentration of the surfactant molecules would be evaluated by a change in the activation energy of the evaporation. At the same time, the evaporation rate of the liquid must present quite useful information on a gas/

liquid interface, because the evaporation takes place just from the interface. On the other hand, from the viewpoint of a dynamic surface tension study which considers a mechanism of the adsorption process, there still exists uncertainty in the transport of the surfactant molecule from a subinterface to an interface.[4−7] The several experimental results mentioned later will give new insight into conventional amphiphile adsorption at the air/solution interface.

Evaporation rate and the activation energy from liquids certainly become a useful index of the characteristics of the gas/liquid interface as mentioned above. There have appeared several papers on the evaporation of water across insoluble monolayers spread on a water interface;[8−10] in addition, some theoretical discussions have already been made on the evaporation rates.[11,12] However, the studies of liquid evaporation from mixed liquids are quite small in number,[13,14] although physicochemical properties of bulk liquid mixtures have been investigated in great detail.[15,16]

The authors have reported a few papers on the evaporation of liquids published in the last few years[1,2,3,12]

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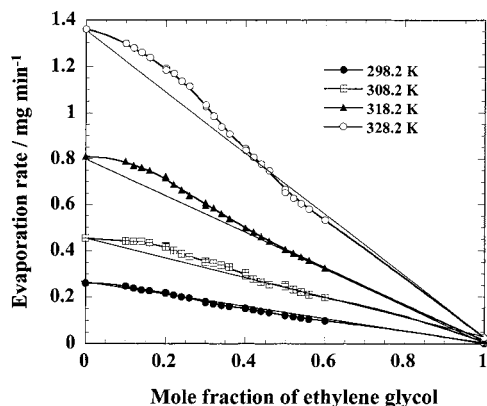
Figure 1. Change of evaporation rate from a water−ethylene glycol liquid mixture with the mole fraction of ethylene glycol at different temperatures, where the lines represent the ideal mixing.

in which soluble surfactant molecules were found to concentrate not just at the air/solution interface but at some distance beneath the interface.[2] Soluble surfactants in water must mix with water molecules in both the surface layer and the inner bulk, and it is easy for the mole fraction of the surfactants in the surface layer to become more than 0.5 from the molecular surface area due to the Gibbs surface excess.[17] If the mole fraction of surfactant in the surface layer becomes truly more than 0.5, the evaporation should be smaller than that of purified water. However, experimental observation indicated no difference in either the evaporation rate of water or the activation energy between water and surfactant solution within experimental error.[1,2]

The above fact strongly suggests no condensation of surfactant molecules just around the air/solution interface. To support this, the fact that the evaporation rate of water molecules truly depends on the mole fraction of the molecules in the surface layer should be experimentally verified. This study is aimed at observing whether the evaporation of molecules from the liquid mixture depends on the mole fraction of the molecules in the mixture. The second component employed in the present mixed system is ethylene glycol, which can mix with water at any mole fraction.

Experimental Section

The apparatus used for evaporation rate measurement was the same as the one used for the preceding study,[1] where the sample pan had a large area of 0.739 cm^2 to reduce the edge effects as much as possible. A constant volume (150μL) of liquid sample was pipetted into a shallow platinum pan for the thermogravimetric measurement, where the height from the surface of liquid to the top of the pan was 0.480 cm. Ethylene glycol of analytical reagent grade was used without further purification. Water used was distilled twice from an alkaline permanganate solution. In the former studies, the molecules evaporated could be specified; therefore, the evaporation rate could be given by the unit of mol s^{-1} cm^{-2}. In this study, however, two kinds of molecules evaporate, although the main evaporating molecules are water at the higher mole fractions. Therefore, the evaporation rate expressed as mg min^{-1}/pan area was used in this study.

Results and Discussion

The evaporation rates (k, expressed as mg min^{-1}) as a function of the mole fraction of ethylene glycol are illustrated at different temperatures in Figure 1. As for
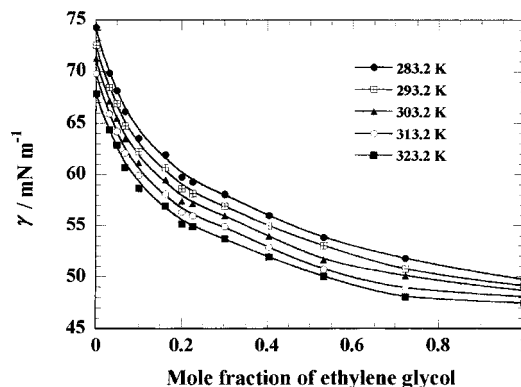
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Figure 2. Change of surface tension (γ) of a water−ethylene glycol liquid mixture with the mole fraction of ethylene glycol at different temperatures.[18]

a water−ethylene glycol mixture, the mole fraction of water in the liquid decreases with the progress of evaporation, which is accompanied by the decrease in evaporation rate with time. The decrease in the mole fraction of water in the liquid with time can be evaluated by the initial weight and the weight loss by evaporation, where the loss at higher mole fractions of water was assumed to be due only to the water molecules evaporated. Therefore, the change in evaporation rate with the mole fraction can be pursued at several mole fractions near the original mole fraction by one run of evaporation rate measurement. This was made possible by the curve fitting of the weight loss by a 2nd-order equation against the running time. Then, the slopes of the initial and reliable part of the curve were used to determine the evaporation rates. The evaporation rates of the liquid mixtures are higher than those expected from the ideal mixture at mole fractions of ethylene glycol below 0.5. In addition, the positive deviation from the ideal line becomes larger at higher temperatures. The increase in evaporation rate suggests (1) a decrease in interaction among water molecules and between water and ethylene glycol molecules or destruction of steric structure of water molecules by intervening ethylene glycol and (2) a higher mole fraction of water molecules in the surface layer than in the bulk. The important experimental fact is that the evaporation of water is roughly proportional to the mole fraction of water in the liquid mixture. The positive deviation from the ideality becomes smaller with decreasing temperature. At any rate, the mole fraction just in the interfacial layer mainly determines the evaporation rate. The decrease in the interaction among the molecules in the system corresponds to higher energy of the system, which results in smaller surface tension of the system. This can be verified by the negative deviation in the surface tension of a water−ethylene glycol mixture from the ideal line (Figure 2).

On the other hand, the activation energy can be evaluated from the temperature dependence of the evaporation rate (see ref 2, Appendix A). The relation between the logarithm of the k values and the inverse of temperature leads to the activation energy of water evaporation at different temperatures from the slope of the relation at the corresponding temperature. Dependence of the activation energy on temperature and the mole fraction are illustrated in Figure 3.

Indeed, the evaporation rate of ethylene glycol is very slow compared with that of water, but the rates could be determined at different temperatures with a certain accuracy. Accordingly, the activation energy (E_a) for ethylene glycol could be determined to be larger than that
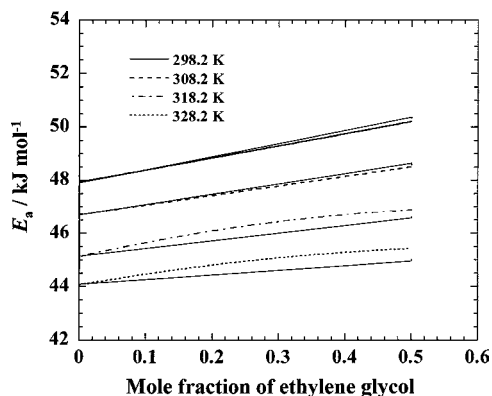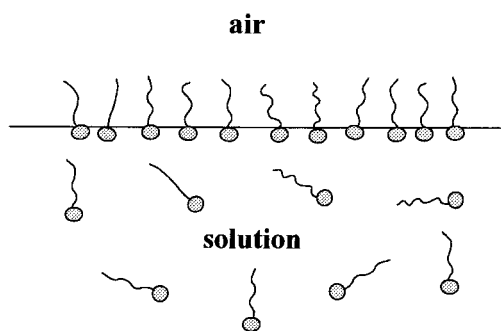
Figure 3. Change of apparent activation energy of vaporization (E_a) with the mole fraction of ethylene glycol at different temperatures, where the lines are those which connect the activation energies of water and ethylene glycol.

of water. The activation energies thus determined are illustrated against the mole fraction of ethylene glycol at different temperatures (Figure 3), where the energy is just an apparent one for the mixture because the molar ratio of evaporated molecules is not known. The activation energy decreases with increasing temperature, which is easily expected from weaker interactions among the molecules at higher temperatures. The important point is that the E_a value increases almost linearly with the mole fraction of ethylene glycol in the liquid mixture. Clear deviation from the ideality was observed for higher temperatures, 318.2 and 328.2 K, as was the case for the evaporation rate.

It is quite difficult to explain the positive deviation of the activation energy from the ideal line at higher temperatures (Figure 3), because the surface tensions negatively deviate from the ideal lines over the whole temperature- and whole mole-fraction range (Figure 2).[18] In addition, the extents of deviation for the surface tensions from the ideal lines are almost the same for the four temperatures. The negative deviation clearly indicates weaker interaction among the molecules in the surface layer with a certain width and suggests, at the same time, the possibility of greater concentration of ethylene glycol molecules than water molecules in the surface layer according to the Gibbs isotherm. In reality, however, the evaporation rate is higher than that of an ideal mixture of the two molecules present, which indicates the possibility of a higher molar ratio of water molecules at the interface than the experimental one. The steric structure of the mixed molecules just at the air/solution interface from which the molecules evaporate breaking the interaction among the surrounding molecules might have special molecular arrangements, resulting in the positive deviation for the activation energy. The mole fraction just at the interface and the steric structure of the mixed molecules at the interface are indispensable for further discussion. At any rate, it became clear from the present study that the evaporation rate and the activation energy depend very much on the mole fraction at the interface.
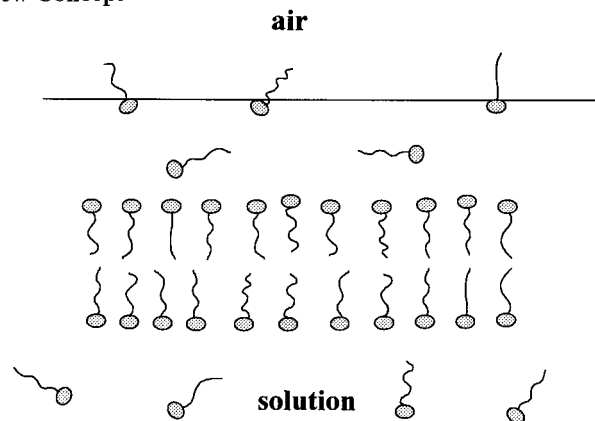
Conventional Concept

New Concept

Figure 4. Schematic illustration of the surface excess for soluble surfactants in aqueous solution: the upper portion represents a conventional concept, while the lower portion is the new concept.

Now that the evaporation rate was found to be subject mainly to the mole fraction of evaporating molecules in the interfacial layer, it becomes quite meaningful to think more about the results of the evaporation rate of water and its activation energy from surfactant solution.[2] As was mentioned in ref 2, there was no difference in either the evaporation rate or the activation energy between just purified water and the surfactant solutions both below and above the critical micelle concentration. Soluble surfactants have been said to concentrate just at the air/solution interface. If this is the real case, the evaporation rate of water molecules should be retarded by the presence of concentrated surfactants near the interface, as was verified by the present study. However, this is not the real case. On the other hand, the molecular surface area from the Gibbs surface excess is just half of the cross-sectional area of the alkyl chain for octaethyleneglycol-*n*-octadecyl ether (C18E8).[19] To compromise the above two, the new concept of surface excess as depicted in Figure 4 should be highly possible. This concept has been verified from BAM images, too.[2]

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