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Solvent Effect on the Dimerization of Tetracyanoquinodimethane Anion Radical

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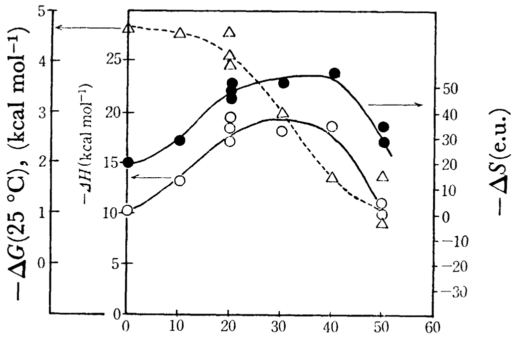
Synopsis. The thermodynamic quantities of the dimerization of tetracyanoquinodimethane (TCNQ) anion radical in water–ethanol mixtures were determined. The free energy of dimerization $-\Delta G$ showed a monotone decrease with an increase in ethanol content, whereas the enthalpy and the entropy of dimerization, $-\Delta H$ and $-\Delta S$, showed a maximum. This unusual behavior is explained by proposing a solvation model in which the water molecules are attracted more strongly around the $TCNQ^-$ dimer than are the ethanol molecules. The entropy was found to play an important role in the dimerization.

Dimerizations of organic ion radicals in solutions have been extensively studied.[1–7] The dimerization is strikingly influenced by the solvents. For example, the anion radical of tetracyanoquinodimethane ($TCNQ^-$) dimerizes strongly in water at room temperature, whereas it does not in ethanol even at 77K. In order to clarify this remarkable solvent effect we determined the thermodynamic quantities of dimerization of $TCNQ^-$ in the water–ethanol system.

Li^+TCNQ^-, Na^+TCNQ^-, and K^+TCNQ^- used in this experiment were prepared by the method described in the literature.[8] Deionized water and distilled ethanol were used. Since $TCNQ^-$ is easily oxidized by oxygen, all solutions were prepared and transferred to an absorption cell by using the vacuum line technique.

The equilibrium constant K for the dimerization was determined spectroscopically using the molar extinction coefficients of the monomer and dimer anions obtained by Boyd and Phillips.[2] The changes of the extinction coefficients in the mixed solvents were neglected, since the anions were found to exhibit the same spectral features up to 50 volume % of ethanol. The concentrations at various temperatures were corrected by use of the expansion coefficients for water and ethanol, assuming that the volume of the mixture is equal to the sum of the components.[9] The plots of log K *vs.* T^{-1} gave good straight lines, from which the change in enthalpy ΔH and that in entropy ΔS of the dimerization ($2A^- \rightleftarrows (A^-)_2$) were obtained.

Figure 1 shows the dependency of the thermodynamic quantities on the volume ratio of ethanol to water. The change in free energy $-\Delta G$ at 25 °C decreases with an increase in ethanol content throughout the range studied, whereas both $-\Delta H$ and $-\Delta S$ increase at first, reach a maximum at 30∼40% ethanol, and then decrease. In the region where the ethanol content exceeds 50%, the dimer formation was found to be so scanty even at low temperatures (−50 °C∼−60 °C) that the thermodynamic constants could not be determined. In the region of small ethanol content (<20%), the change in the enthalpy $-\Delta H$ with the ethanol concentration is opposite to that in the free energy $-\Delta G$. This behavior shows the important role of the entropy factor $T\Delta S$ in the free energy change $-\Delta G$ for the dimerization of $TCNQ^-$.



Ethanol content in water (vol %)

Fig. 1. Observed thermodynamic quantities for the dimerization of $TCNQ^-$ in the water–ethanol mixture.
△: $-\Delta G$(25 °C), ●: $-\Delta S$, ○: $-\Delta H$

The presence of a maximum for $-\Delta H$ and $-\Delta S$ as seen in Fig. 1 is quite unusual,[10] and hard to explain by the usual understanding of the solvent polarization energy. By using Born's equation and dielectric constants for water and ethanol, the contributions of solvation in the $-\Delta H$ and $-\Delta S$ values can be calculated; the result shows a simple increase with an increase in ethanol content, and amounts to only 0.5 kcal mol^{-1} and 2.6 eu, respectively at 50% in ethanol content. Therefore, a model of a continuous and uniform medium cannot explain the experiment.

In order to understand this unusual behavior, we propose a simple model for the microscopic structure of the solvation sphere. The electrostatic field due to the dimer is considered to be must stronger than that of the monomer, because the charge of the dimer is twice as large as that of the monomer, and the effective radius is less than twice that of the monomer. Therefore, it attracts water molecules rather than ethanol ones into the solvation sphere more strongly than the monomer, since water is more polar than ethanol. Consequently, at small ethanol content, the ratio of the number of molecules in ethanol to that in water inside the solvation sphere may be lower than that in the bulk of the solution. The situation is illustrated schematically in Fig. 2. This will bring about more stabilization for the dimer anion than for the monomer anion, leading to larger $|\Delta H|$ values for the dimer formation. As the ethanol concentration becomes higher, this effect on ΔH and ΔS will diminish. Thus, the changes in enthalpies with the

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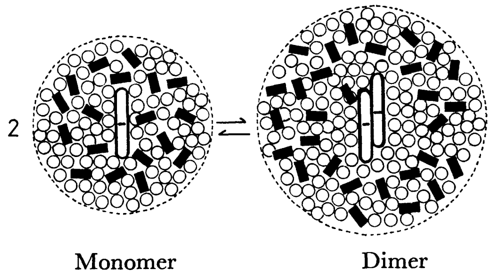

Fig. 2. Schematic illustration representing the enhanced participation of water molecules in the solvation sphere around the dimer compared to the monomer in the water–ethanol mixture.
○: water, ■: ethanol, (⊟): TCNQ$^-$.

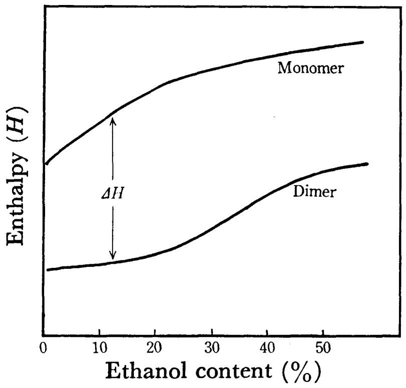

Fig. 3. Qualitative curves explain the behaviors of the enthalpies of the monomer and dimer in the water–ethanol mixture.

ethanol content for the dimer and monomer will be such as given qualitatively in Fig. 3, from which the appearance of a maximum for $-\Delta H$ in the monomer$\rightleftarrows$dimer reaction can be understood. The appearance of a maxima in entropy $-\Delta S$ can be understood similarly.

The influence of counter cations on the thermodynamic quantities in the monomer$\rightleftarrows$dimer reaction in water was also investigated. The result is that there is no essential difference in the thermodynamic quantities by changing the counter ions from Li^+ to Na^+ and K^+. No substantial change was detected for a solution containing LiCl 100 times more than the concentration of TCNQ$^-$. These results suggest that the counter ions exhibit a very small influence on the dimer-monomer equilibrium, and presumably they do not exist in a region very close to the anions in water.

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9) The errors arising from this approximation were estimated from the experimentally obtainable densities of water–ethanol mixtures, and are found to be within the experimental errors.
10) The same behaviors of the thermodynamic quantities were observed in the water–methanol system.