BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 275—277 (1971)

Distribution of Aqueous Sodium Perchlorate into Some Polar Organic Solvents

Yuko HASEGAWA, Teruhiko ISHII, and Tatsuya SEKINE
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

(Received June 3, 1970)

As sodium ions or perchlorate ions are usually believed to form only very weak complexes, sodium perchlorate has often been used in order to control the activity coefficients of ionic species in aqueous solutions.

However, in the systems where anionic species are extracted as ion pairs with sodium ions into an organic phase, the sodium concentration in the aqueous phase should be taken into account, and if the extracted ion pairs dissociate in the organic phase, the sodium-ion concentration in the organic phase is also important. In the extraction of mercury(II) complexes with halide or thiocyanate ions into polar solvents, some part of the complexes is assumed to consist of ion pairs of mercury(II) complex anions with sodium ions,[1] and the extraction of indium(III) halides or thiocyanate into polar solvents is very much effected by the aqueous sodium concentrations,[2] an effect which can also be explained in terms of the extraction of ion pairs of anionic indium complexes with sodium ions.

The present study has been carried out in order to obtain further, more detailed information about the liquid-liquid distribution behavior of sodium perchlorate as ion pairs.

Experimental

Reagents. The sodium-24 radioactive tracer was obtained as a sodium chloride solution. This was diluted with a large amount of water in order to prepare the stock tracer solution. The sodium perchlorate was prepared from perchloric acid and sodium carbonate and was recrystalized three times from water. The TBP(tributylphosphate), MIBK-(methylisobutylketone), methylisobutylcarbinol, and nitromethane were obtained from the Tokyo Kasei Co. They were washed with perchloric acid, water, and aqueous sodium hydroxide successively, and then several times with water. The hexane used was of a reagent grade and was used without further purification.

Procedures. All of the procedures were carried out in a thermostatted room at 25°C. Stoppered glass tubes (volume, 20 m*l*) were always used for the equilibration of the two phases. Sodium perchlorate solutions labelled by a radio-

---

[1] T. Sekine and T. Ishii, This Bulletin, **43**, 2422 (1970).

[2] Y. Hasegawa, H. Takeuchi, and T. Sekine, to be published.

active tracer and the organic solvent were placed in the tubes. The initial volume of the two phases was always 5 ml. The two phases were agitated mechanically for thirty minutes and then centrifuged. The γ-radioactivity of both phases was measured with a well-type (NaI) scintillation counter, and the distribution ratio of sodium was calculated as;

$$D = \frac{[Na(I)]_{org,\ total}}{[Na(I)]_{total}} = \frac{\gamma\text{-count rate per m}l\text{ of the org. phase}}{\gamma\text{-count rate per m}l\text{ of the aq. phase}}$$

Results and Discussion

In an aqueous phase, sodium salt could usually be assumed to dissociate. In an organic phase, on the other hand, the extracted ion pairs of the sodium ion and a large univalent anion, A^-, could dissociate completely or partially, or they could remain in the associated form. The distribution of sodium ion pairs from an aqueous phase to an organic phase can be described as:

$$Na^+ + A^- \rightleftharpoons Na^+A^-(org) \tag{1}$$

$$K = \frac{[Na^+A^-]_{org}}{[Na^+][A^-]} \tag{2}$$

When the dissociation occurs in the organic phase:

$$Na^+A^-(org) \rightleftharpoons Na^+(org) + A^-(org) \tag{3}$$

$$K^o_{diss} = \frac{[Na^+]_{org}[A^-]_{org}}{[Na^+A^-]_{org}} \tag{4}$$

The distribution ratio of sodium(I) can be described as:

$$D = \frac{[Na^+A^-]_{org} + [Na^+]_{org}}{[Na^+]} \tag{5}$$

When only one kind of sodium salt is present in the system, it is assumed that the concentration of the sodium ions is equal to that of the total number of anions, and that, consequently, $[Na^+]=[A^-]$ and $[Na^+]_{org}=[A^-]_{org}$. Then, by introducing Eqs. (2) and (4) into Eq. (5), the following equation is obtained:

$$D = K^{1/2}(K^{1/2}[Na^+] + (K^o_{diss})^{1/2}) \tag{6}$$

As no control of the activity of the chemical species in the two phases was made in the present study, only a qualitative discussion can be made of the results.

Figure 1 gives the distribution ratio of sodium between TBP, nitromethane, MIBK, or methylisobutylcarbinol and aqueous sodium perchlorate solutions as a function of the initial aqueous salt concentration. It was observed during the experiments with nitromethane that the organic volume decreases, and the aqueous volume increases remarkably, in the highest-salt-concentration region. In such systems, the aqueous salt concentration should decrease upon the volume change and also upon extraction. However, as the correction for these factors will not be easy, the sodium perchlorate concentration in the figures is given by their initial values. The extraction with these solvents is much higher than that with nitrobenzene ($D \simeq 10^{-4}$ at 0.1~5 M $NaClO_4$[3)]).

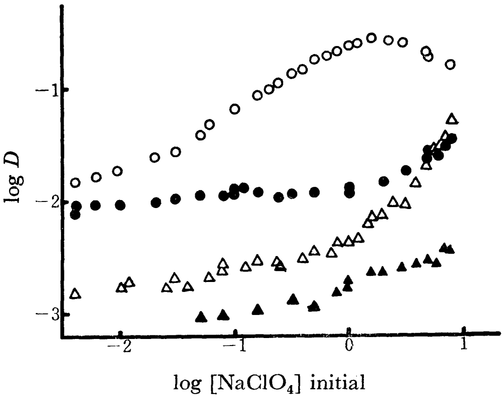

Fig. 1. Distribution of sodium(I) between TBP (○), nitromethane (●) MIBK (△) or methylisobutylcarbinol (▲) and aqueous sodium perchlorate solutions. The aqueous salt concentrations are the intial values.

It may be seen from Fig. 1 that the distribution ratio of sodium in the nitromethane system is almost constant in the lower-salt-concentration region (below 1 M). Equation (6) shows that if the extracted salt dissociates completely, the distribution ratio is independent of the concentration. As the activity coefficients in both the phases may be changed by the changes in the salt concentration, no definite conclusion should be introduced without information about the activities. However, it is probable that the extracted salt is almost dissociated in this organic solvent with a very high dielectric constant ($\varepsilon=34.82$ at 25°C[4)]), at least when the salt concentration is low. However, as the extraction depends somewhat on the salt concentration in the other three solvents, the ions in them should associate to some extent. The increase in the distribution ratio in the higher-salt-concentration region (above 1 M) could be due to the association of the sodium and perchlorate ions in the organic phase (*cf.* Eq. (6)) and/or to the change in the activity coefficients of the ionic species.

Figure 2 shows the extraction of sodium into undiluted, 50% (v/v), and 1 M TBP in hexane as a function of the aqueous sodium perchlorate concentration. The decrease in the extraction upon the dilution of TBP is to be expected from the law of mass action, but it could also be due to the change in the nature of the organic phase (the polarity, the dielectric constants, the activity coefficients of TBP and ionic species, *etc.*).

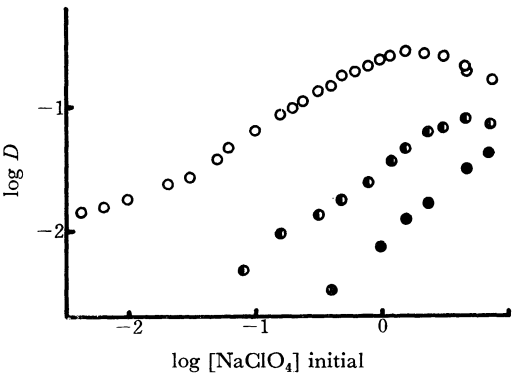

Fig. 2. Distribution of sodium(I) between undiluted TBP (○) 50% (v/v) TBP (◐) or 1 M TBP (●) in hexane and aqueous sodium perchlorate solutions. The aqeuous concentrations are the initial values.

---

3) T. Sekine and D. Dyrssen, *Anal. Chem. Acta*, **45**, 433 (1969).

4) A. A. Maryott and E. A. Smith, "Table of Dielectric Constant of Pure Liquids" NBS Circular 514, Aug. 10, 1951.

It is remarkable that the shape of the extraction curve is changed by the dilution, as may be seen from Fig. 2.

The extractions of sodium perchlorate with these solvents are not very low; for example, when the aqueous phace is 1M Sodium perchlorate solution, 1—10 mM sodium perchlorate is present in all the organic solvents except TBP, and more than 0.1M is contained in TBP; as a dissociation of the extracted salt in the organic phase is assumed in these polar solvents, these organic phases can be regarded as constant ionic media for a small amount of other solutes in these organic phases, such as, for example, an aqueous sodium perchlorate solution at a constant concentration.

These facts should be taken into account when the extraction of ion pairs of sodium with anionic complexes occurs; they are especially important when the extracted ion pairs undergo dissociation in the organic phase.