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Distribution of Uranyl Nitrate between 1- or 2-Butanol and Aqueous Phases

Norio Yui, Yōichi Kurokawa, and Taketoshi Fujita
Department of Applied Science, Faculty of Engineering, Tohoku University, Aoba, Aramaki, Sendai 980

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The distribution of uranyl nitrate between 1- or 2-butanol and aqueous phases and the effect of nitric acid or sodium nitrate on the distribution at 25 °C have been studied. Conductance measurements have been carried out for the butanol solutions of uranyl nitrate. It was found that high water content in the butanol phase gives rise to the dissociation of the salt. Semi-empirical relations hold for the distribution considering the dissociation of salt in the butanol phase. Observed and calculated slopes agree in the plots of distribution ratio *vs.* nitrate concentration. The results were discussed in comparison with distribution data in literature.

A study of the distribution of electrolyte between aqueous and organic phases provided a method of investigating the thermodynamic properties of organic solutions. However, such a study has been limited to organic solvents almost immiscible with water. Isomeric butanol has a moderate dielectric constant and is miscible with water to a greater extent. Thus, water seems to play an important role in the distribution. The extraction of uranyl nitrate was discussed in some detail.[1] In most cases, the electrolyte was considered to be completely dissociated in aqueous phase and completely associated in the organic phase. Previous conductance measurements on the 1-butanol phase containing alkali halides indicated that these salts were considerably dissociated.[2,3] A marked deviation from thermodynamic distribution ratio could occur depending upon the degree of association in the butanol phase. We investigated the equilibrium composition of alkali halide–1-butanol–water system. A semi-empirical treatment of the distribution of alkali halides was performed, assuming that these salts in the butanol phase are dissociated.[4] This study was undertaken to examine how far the above treatment is applicable to the distribution of uranyl nitrate between the butanol and aqueous phases.

Experimental

Materials. Uranyl nitrate hexahydrate, sodium nitrate, nitric acid, 2-butanol, and 1-butanol were of reagent grade and used without further purification.

Procedure. The electric equipment, conductance cell (flask type) and methods were essentially the same as before, except for the conductance bridge which was of a YOKOGAWA BV-Z-103B type.[2,3] A quartz flask type cell with lightly platinized electrodes was used. The cell constant was determined to be 0.1893 cm^{-1} with 0.1 M KCl. All measurements were carried out in a thermostat at 25±0.01 °C. The conductance of the solute was determined by subtracting the conductance of the solvent from that of the solution. Since the specific conductance of pure 1-butanol was 9.12×10^{-9} (ohm$^{-1}\cdot$cm^{-1}) at 25 °C, solvent correction in pure 1-butanol system was not necessary even for very dilute solution.

100 ml each of aqueous and butanol solutions were taken into a flask with a stopper, and shaken in a thermostat for a few hours. A portion of the solution was then taken from both phases for analysis. In the presence of nitric acid or sodium nitrate, the distribution equilibrium was established within half an hour. The initial concentration of uranyl nitrate in the aqueous phase ranged from 10^{-4} to 10^{-2} M, and that of nitric acid or sodium nitrate from 0.05 to 3 M.

Analysis. *Uranyl Ion*: The method was essentially the same as that reported.[5-7] A sample solution (1—5 ml) from each phase was evaporated to dryness below 80 °C to avoid loss of uranyl salt. A buffer solution of pH 5 and 0.1% solution of neothorin was added to the sample solution.

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[1] Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes" Wiley-Interscience, New York (1969).

[2] Y. Kurokawa and N. Yui, *Tech. Reports, Tohoku Univ.*, **37**, 153 (1972).

[3] N. Yui, Y. Kurokawa, M. Sono, and T. Hiramoto, *Nippon Kagaku Zasshi*, **89**, 483 (1968). N. Yui, Y. Kurokawa, and M. Nakayama, This Bulletin, **46**, 1027 (1973).

[4] N. Yui and Y. Kurokawa, *Nippon Kagaku Zasshi* **89**, 487 (1968).

[5] S. Shibata and T. Matsumae, This Bulletin, **32**, 279 (1959).

[6] E. Hesford and H. A. C. McKay, *Trans. Faraday Soc.*, **54**, 573 (1958).

[7] B. G. W. Hollingshed, "Oxine and its Derivatives" Vol. II Oxine, Part 2, Butterworths, London (1954), p. 497.

The absorbance of the solution was then measured at 600 mμ against a reference solution.

Sodium Ion: This was analyzed by the potentiometric or EDTA method.[8] The former is as follows. The sample solution was passed through a resin column converted into hydrogen ion form. It was eluted by 2 M HCl. The effluent was evaporated to dryness to remove hydrochloric acid and the residue was dissolved in a small amount of water. The solution was analyzed for chloride by the potentiometric method.

Nitrate Ion: This was analyzed by spectrophotometry.[9]

Hydrogen Ion: This was titrated with sodium hydroxide solution using phenolphthalein as an indicator.

Solvent Composition: Equilibrium compositions in the absence of solute were determined by gas chromatography.[4]

Results and Discussion

Mutual solubilities of 1-butanol–water and 2-butanol–water systems are given in Table 1. Dielectric constant ε was estimated from the values for water and butanol assuming that ε of the mixtures is a linear function of the weight fraction as in the cases of ethanol–water mixture.[10] Both butanols are miscible with water and consequently both butanol phases have high dielectric constants.

TABLE 1. MUTUAL SOLUBILITIES OF 1-BUTANOL–WATER AND 2-BUTANOL–WATER SYSTEMS AT 25 °C (wt %)

	1-Butanol–Water			2-Butanol–Water		
	Water	1-Butanol	ε	Water	2-Butanol	ε
Aqueous phase	92.7	7.3	73	80.5	19.5	67
Butanol phase	20.3	79.7	23	37.5	62.5	38

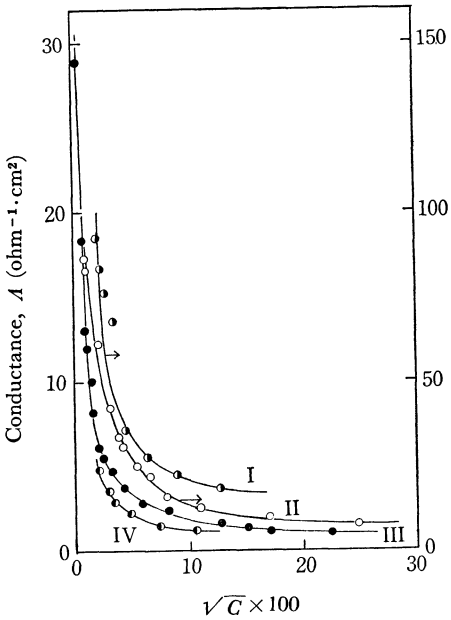

Fig. 1. Conductance Λ vs. square root of molarity.
I: in 1-BuOH-Water (11wt%), II: in EtOH[11], III: in PrOH[11], IV: in 1-BuOH

The conductance of uranyl nitrate Λ(ohm$^{-1}\cdot$cm^2) in a few kinds of pure alcohol and 1-butanol–water(11.0 wt%) isgiven in Fig. 1, by means of the plots Λ *vs.* the square root of concentration. Conductance decreases in the order ethanol(24.3)>propanol(20.1)>1-butanol (17.1) over all concentrations, the order being in line with that of dielectric constant (given in parentheses). The plots show a marked deviation from linearity as in the case of LiI and NH_4I.[12] This indicates that uranyl nitrate behaves as a weak electrolyte. Addition of water to pure 1-butanol causes a large change in conductance. A sharp rise on approaching infinite dilution suggests a possibility of the following dissociation:

$$UO_2(NO_3)_2 = UO_2(NO_3)^+ + NO_3^- \qquad (1)$$

However, concentrated uranyl nitrate solution might not be dissociated in pure 1-butanol. Association constants were not calculated because of a sharp increase in conductance at infinite dilutions. A plot by Shedlowsky's method is not linear for the 1-butanol–water (11 wt%) system. It seems that dissociation in two stages occurs to some extent. Trzebiatowska obtained an association constant of 1.44×10^4 in ethanol and concluded that covalency participates in uranyl nitrate from the very small Bjerrum parameter *a*.[11] However, interpretation of such an adjustable parameter is too uncertain to draw a clear conclusion.

Distribution of Uranyl Nitrate between 1- or 2-Butanol and Aqueous Phases. The results are shown in Fig. 2 with the plots K_d(U) *vs.* log $(NO_3^-)_a$. The distribution ratio of uranyl nitrate K_d(U) is defined by $\sum(UO_2)_a/\sum(UO_2)_b$, where subscripts a and b refer to the aqueous and butanol phases, respectively. Curve III gives the distribution of uranyl nitrate between

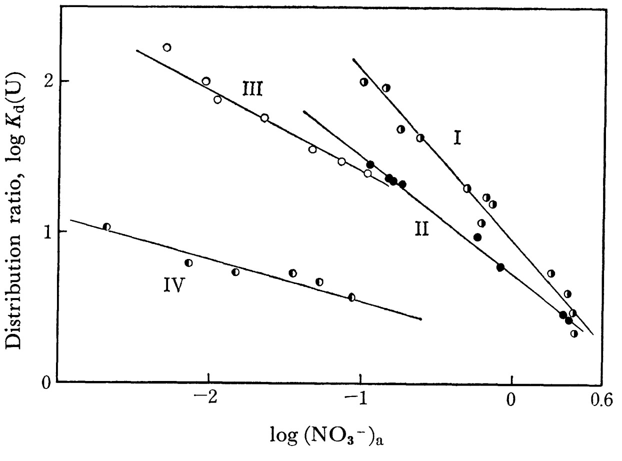

Fig. 2. Distribution ratio K_d(U) *vs.* nitrate ion concentration in aqueous phase.
I: 1-BuOH-nitric acid solution, II: 1-BuOH-sondium nitrate solution, III: 1-BuOH-water, IV: 2-BuOH-water

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[8] B. Sen, *Z. Anal. Chem.*, **157**, 2 (1957).

[9] T. Akisada, *Bunseki Kagaku*, **12**, 614 (1963).

[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., (1964), p. 161.

[11] J. Trzebiatowska and M. Chmielowska, *J. Inorg. Nucl. Chem.*, **20**, 106 (1961); **26**, 837 (1964); **28**, 1435 (1966).

[12] H. Y. Venkatasetty and G. H. Brown, *J. Amer. Chem. Soc.*, **66**, 2075 (1962).

[13] Y. Kurokawa and N. Yui, *Tech. Reports, Tôhoku Univ.*, **29**, 211 (1964).

[14] H. A. C. McKay and A. R. Mathieson, *Trans. Faraday Soc.*, **47**, 428 (1951).

[15] Ref. 1, p. 933.

1-butanol and aqueous phases, and curve IV that between 2-butanol and aqueous phases. The distribution showed the same trend as in the acids, namely it approaches a constant value at higher concentration.[13] This indicates that uranyl nitrate tends to be transferred into the butanol phase with increasing concentration. The ionization constants of uranyl nitrate were determined in various solvents by means of the Walden rule, a slight dissociation being found to take place. However, notable dissociation was found in 1-butanol.[14] Uranyl nitrate showed an appreciable conductivity in diethyl ether on being dissolved in the form of hexahydrate.[15] The relatively high water content in the butanol phase causes the dissociation of salt. Water content is 38 wt% in 2-butanol phase and 20 wt% in 1-butanol phase, causing an increase of conductance (Fig. 1). The first stage of dissociation might therefore occur in the butanol phase. $K_d(U)$ of the 1-butanol system is larger than that of the 2-butanol system over all concentrations. The difference is principally due to the difference in water contents. It seems that water plays the principal role in the distribution of uranyl nitrate. We assume that uranyl nitrate in both phases is dissociated into free ions as follows, the species extracted being the same over all concentrations:

$$(UO_2^{2+})_a + 2(NO_3^-)_a \overset{K}{\longleftrightarrow} (UO_2NO_3^+)_b + (NO_3^-)_b \tag{2}$$

$$K = \frac{[UO_2NO_3^+]_b[NO_3^-]_b}{[UO_2^{2+}]_a[NO_3^-]_a^2} \propto \frac{1}{K_d(U)^2(NO_3^-)_a} \tag{3}$$

If this is the case, the slope of the plot $K_d(U)$ *vs.* log-$(NO_3^-)_a$ should be -0.5 (Eq. 3). The observed values for 1-butanol and 2-butanol systems are about -0.5 and -0.3, respectively. The lower value for 2-butanol system might be due to the second stage dissociation because of high water content of the butanol phase, indicating that mixed species $UO_2NO_3^+$ and UO_2^{2+} are involved. In the case of the solvent extraction with a reagent such as TBP, the slope is -2.[16] Since no data are available concerning activity coefficients in this system, the activity is replaced by concentration.

Distribution of Uranyl Nitrate Coexisting with Nitric Acid or Sodium Nitrate. Use of a salting-out agent is common in solvent extraction. Nitrate is generally chosen for the extraction of uranyl nitrate.[17] Salting effects of nitric acid and sodium nitrate on the distribution of uranyl nitrate were investigated in the concentration range 0.06—3 M. The results are given in Fig. 2, in which curve I denotes the distribution of uranyl nitrate coexisting with nitric acid and curve II that with sodium nitrate. We see that the effect is enhanced. Distributions of nitric acid and sodium nitrate are given in Fig. 3 by means of logarithms of distribution ratio *vs.* solute concentration in aqueous phase. $K_d(H)$ is the distribution ratio of nitric acid defined by $(H^+)_a/(H^+)_b$ and $K_d(NO_3)$ is that of sodium nitrate by $(NO_3^-)_a/(NO_3^-)_b$, where (H^+) denotes the acid concentration and (NO_3^-) the sodium nitrate concentration in each phase. Nitric acid is extracted into butanol phase more than other mineral acids, indicating its strong interaction with butanol. This may be ascribed to the weak electrolytic behavior and conspicuous covalent character of the acid.[18] Alcock *et al.* studied the extraction of mineral acids from an aqueous solution by TBP and showed that perchloric acid is a strong electrolyte in TBP, but not other acids.[19] In the case of nitric acid, a volume change occurred at the expense of the aqueous phase, apparently due to a much higher uptake of water by the butanol phase which certainly facilitates ionization. We assume that the first stage dissociation occurs in the butanol phase, the species extracted are the same and the concentration is represented in the observed one not in the activity. The following relation is obtained for the system coexisting with nitric acid.

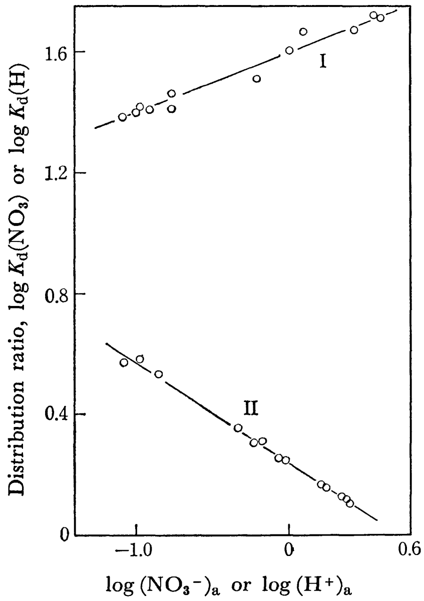

Fig. 3. Distribution ratio of sodium nitrate *vs.* nitrate ion in aqueous phase and that of nitric acid *vs.* acid in aqueous phase.
I: sodium nitrate, II: nitric acid

$$K_d(U) \propto K_d(H) \cdot (NO_3)_a^{-1} \tag{4}$$

$K_d(H)$ is determined to be $K_d(H) \propto (NO_3)_a^{-0.3}$ from Fig. 3. By combining this relation and Eq. (4), a slope of -1.3 equal to the observed value is obtained. In the same way, the following relation can be obtained

$$K_d(U) \propto K_d(NO_3) \cdot (NO_3)_a^{-1} \tag{5}$$

Since $K_d(NO_3)$ is proportional to $(NO_3)_a^{0.2}$ (Fig. 3), the plot $K_d(U)$ *vs.* $(NO_3)_a$ yields a slope of -0.8 by combining this relation with Eq. (5). This is in good agreement with the observed slope -0.8. The degree of ionization of sodium nitrate in TBP is higher than that of uranyl nitrate at an equal solute concentration by an order of magnitude.[20] The ionization in the butanol phase would be still higher because of its high water content. We assumed that the solvent composition remains approximately constant inde-

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[16] K. Naito, This Bulletin, **33**, 363 (1960).

[17] Ref. 1, p. 630.

[18] R. M. Diamond and D. G. Tuck, "Progress in Inorganic Chemistry," ed. by E. A. Cotton, Interscience Publishers, New York (1960), p. 155.

[19] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy, and H. A. C. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).

[20] Ref. 1, p. 704.

pendent of solute concentration. However, the observed phenomenon was more complicated and involved a change of solvent composition accompanied by the solute. Dielectric constant change in the butanol phase caused by solute and water and that in aqueous phase caused by the butanol salted out might affect the equilibrium to a great extent. The distribution of uranyl nitrate in the butanol–water system was given by Morrison and Freiser.[21] They treated the distribution in terms of complex formation in the butanol phase, but their results are not in line with ours. Good agreement was obtained between the observed and calculated slopes by a semi-empirical treatment. This might indicate that distribution is associated with the predominance of ion species in the butanol phase. At a higher concentration the treatment is probably no longer valid. Changes in solvation, association and solvent composition should be taken into consideration.

Thanks are due to Mr. K. Takada for his assitance in the experiments.

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[21] G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley & Sons, Inc. New York (1957), p. 65.