BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2074—2076 (1969)

The Separation Factor for Alkali Metals in Solvent Extraction with Hexyl

Shoji MOTOMIZU,* Tadashi IWACHIDO** and Kyoji TÔEI*

* *Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama*
** *College of Liberal Arts and Sciences, Okayama University, Tsushima, Okayama*

(Received December 16, 1968)

The extractions of alkali metals reported to date have almost all been based upon the ion-association principle. For example, polyiodide,[1] tetraphenylborate,[2,3] hexafluorophosphate,[4] and phenols[5,6] have been investigated. The extraction of alkali metals into nitrobenzene using Hexyl[7,8] is also related to the ion association. However, the mechanism for the extraction with Hexyl has not yet been extensively studied. In our previous paper,[9] the mechanism for the extraction of alkali metals using Hexyl was discussed, and the association constants of Hexyl salts in an aqueous solution and in a nitrobenzene solution, the partition coefficients of ion-pairs, and the extraction constants were reported.

In this paper, the separation factor of two alkali metals will be discussed and an equation for the extraction separation of alkali metals with Hexyl will be given theoretically and examined in the cases of sodium and potassium.

Calculations

The Separation Factor of Two Alkali Metals. The general equation for the separation factor, α, is given hereafter by using the extraction and the association constants.

The separation factors for alkali metals, M_1 and M_2, are written as:

$$\alpha^{M_1}_{M_2} = \frac{q_{M_1}}{q_{M_2}} = \left(\frac{[M_1R]_o + [M_1^+]_o}{[M_1R]_a + [M_1^+]_a}\right)\left(\frac{[M_2R]_o + [M_2^+]_o}{[M_2R]_a + [M_2^+]_a}\right)^{-1} \quad (1)$$

where q_{M1} and q_{M2} are the distribution ratios of M_1 and M_2 respectively, and where the subscripts o and a refer to the organic and aqueous phases respectively. $[MR]$, $[M^+]$, and $[R^-]$ are the concentrations of the ion-pair, the metal ion, and the Hexyl anion respectively. $[M_1R]_o$ and $[M_2R]_o$ can be neglected compared with $[M_1^+]_o$ and $[M_2^+]_o$ respectively, because the association constants for M_1R and M_2R are very small. When $[R^-]_a$ is relatively small compared with the concentration of the alkali metal in the aqueous phase, $[M_1R]_a$ and $[M_2R]_a$ can also be neglected compared with $[M_1^+]_a$ and $[M_2^+]_a$ respectively. Therefore, Eq. (1) can be rearranged to Eq. (2):

$$\alpha^{M_1}_{M_2} = \frac{[M_1^+]_o}{[M_2^+]_o} \times \frac{[M_2^+]_a}{[M_1^+]_a} \quad (2)$$

The combination of the two association constants, $K_o^{M_1R}$ and $K_o^{M_2R}$, leads to Eq. (3):

$$\frac{[M_1^+]_o}{[M_2^+]_o} = \frac{K_o^{M_2R}}{K_o^{M_1R}} \times \frac{[M_1R]_o}{[M_2R]_o} \quad (3)$$

The combination of Eqs. (2) and (3) leads to Eq. (4):

---

[1] M. Kyrš and S. Podesva, *Anal. Chim. Acta*, **27**, 183 (1962).

[2] K. Haruyama and T. Ashizawa, *Japan Analyst*, **14**, 120 (1965).

[3] R. C. Fix and J. W. Irvine, Jr., MIT Lab. Nuclear Science, Annual Progress Report (Nov. 30, 1955).

[4] *Idem*, *ibid*., Progress Report (May 31, 1955).

[5] K. B. Brown, Oak Ridge National Laboratory Rept. ORNL-TM-449 (1963).

[6] W. J. Ross and J. C. White, *Anal. Chem.*, **36**, 1998 (1964).

[7] M. Kyrš, *Collection Czechoslov. Chem. Commun.*, **27**, 2380 (1962).

[8] T. Iwachido and K. Tôei, This Bulletin, **37**, 1276 (1964).

[9] K. Tôei, T. Iwachido and S. Motomizu, *ibid*., **42**, 1006 (1969).

$$\alpha^{M_1}_{M_2} = \frac{K_o^{M_2R}}{K_o^{M_1R}} \times \frac{[M_1R]_o[M_2^+]_a}{[M_2R]_o[M_1^+]_a} = \frac{K_o^{M_2R} \cdot E_{M_1R}}{K_o^{M_1R} \cdot E_{M_2R}} \quad (4)$$

where E_{M_1R} and E_{M_2R} are the extraction constants of M_1R and M_2R respectively and are defined as:

$$E_{M_1R} = \frac{[M_1R]_o}{[M_1^+]_a[R^-]_a f_a^2} \quad (5)$$

$$E_{M_2R} = \frac{[M_2R]_o}{[M_2^+]_a[R^-]_a f_a^2} \quad (6)$$

where f_a indicates the activity coefficient.

Equation (4) is rearranged to Eq. (7):

$$[M_1^+]_a = \frac{1}{1+(q_{M_2} \cdot \alpha^{M_1}_{M_2})} \times T_{M_1} \quad (7)$$

where T_{M1} is the total concentration of metal, M_1.

Experimental

Reagents. The Hexyl sodium salt was prepared and purified by the method reported in the previous paper.[9] The Hexyl-Na nitrobenzene solution was prepared by dissolving the Hexyl-Na in nitrobenzene to give 1.0×10^{-3} M. All the other chemicals used were of a guaranteed reagent grade. Aqueous solutions were prepared by dissolving the sodium hydroxyde, the sodium, and the potassium chloride to give 0.001 M, 0.1 M, and $2 \times 10^{-5} - 1 \times 10^{-3}$ M respectively.

Apparatus. The concentration of potassium in the aqueous phase after the extraction was determined flame-photometrically by using a Hitachi Flamephotometer, FPF-2.

Extraction Procedures. The extractions were all carried out at 25°C. Twenty milliliters of an aqueous solution containing sodium and potassium were placed into a 50-m*l* separatory funnel and shaken moderately for about thirty minutes with an equal volume of a nitrobenzene solution of Hexyl-Na (1.0×10^{-3} M) so as not to form an emulsion. The final equilibrated pH of the aqueous phase was 10—11. The potassium and Hexyl in the aqueous phase separated from the organic phase were determined flamephotometrically and spectrophotometrically respectively.

TABLE 1. THE CONSTANTS FOR HEXYL SALTS

MR	K_o^{MR} *1	K_a^{MR} *2	D_{MR} *3	E_{MR}
Hexyl-Li	3.3	8.9	0.5	4.5
Hexyl-Na	4.0	9.4	3.4	3.2×10
Hexyl-K	4.6	174	20.4	3.5×10^3
Hexyl-Rb	4.7	365	22.2	8.1×10^3
Hexyl-Cs	2.3			

*1 The association constant in nitrobenzene saturated with water:

$$K_o^{MR} = [MR]_o/[M^+]_o[R^-]_o f_a^2$$

*2 The association constant in the aqueous solution:

$$K_a^{MR} = [MR]_a/[M^+]_a[R^-]_a f_a^2$$

*3 The partition coefficient:

$$D_{MR} = [MR]_o/[MR]_a$$

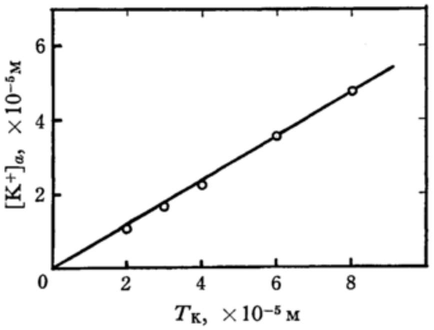

Fig. 1. The plot of $[K^+]_a$ *vs.* T_K.
Original concentration of sodium chloride in the aqueous phase: 1.0×10^{-1}M.
Original concentration of Hexyl-Na in the organic phase: 1.0×10^{-3}M.
In all extractions, the concentration of Hexyl salt in the aqueous phase was less than about 10^{-5}M.

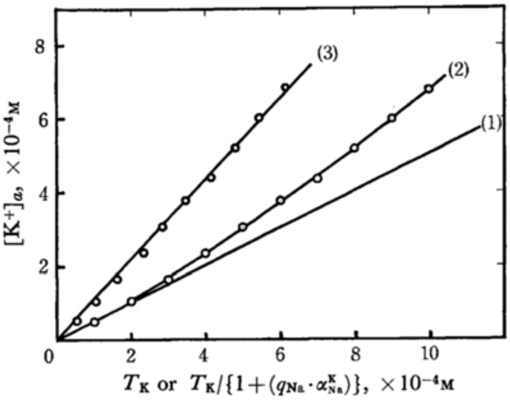

Fig. 2. The plot of $[K^+]_a$ *vs.* T_K or $T_K/\{1+(q_{Na} \cdot \alpha^K_{Na})\}$.
(1): the line with a slope of 0.5.
(2): the plot of $[K^+]_a$ *vs.* T_K.
(3): the plot of $[K^+]_a$ *vs.* $T_K/\{1+(q_{Na} \cdot \alpha^K_{Na})\}$.

Results and Discussion

As is shown in Table 1, which is reprinted from our previous report,[9] the association constants of Hexyl alkali metal salts in an organic phase are very small, so the theoretical equation (4) is useful. For example, if M_1 and M_2 are potassium and sodium respectively, the value of α^K_{Na} is calculated from the extraction constants and the association constants to be 9.5×10.

Figures 1 and 2 show the plot of $[K^+]_a$ against T_K. In the region where the concentration of potassium can be neglected in the organic phase, compared with the concentration of sodium, q_{Na} is thought to be kept at 0.01 and α^K_{Na} is 9.5×10, as has been mentioned above, so the slope may be expected to be about 0.5 ($1/(1+0.95)$). In Fig. 1 the slope is about 0.5, as expected. When q_{Na} seems to vary, the plot of $[K^+]_a$ against T_K gradually deviates from the line of the 0.5 slope (Fig. 2). Figure 2 also shows the plot of $[K^+]_a$ against $T_K/\{1+(q_{Na}\cdot\alpha_{Na}^K)\}$. This plot shows a good linearity, and the slope is 1.1.

Equation (7) has thus been found to be in good agreement with the experimental data. Therefore, Eq. (4) will be very useful in estimating the separation of alkali metals.