

ON THE THERMODYNAMIC TREATMENT FOR ANION EXCHANGE IN HYDROTALCITELIKE COMPOUNDS

Key Words—Anion exchange, Hydrotalcite, Layered compound, Thermodynamics.

Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ and the synthetic analogues substituted by different divalent metal ions have been extensively studied to determine their crystal structure (Allmann, 1968; Bish and Brindley, 1977; Brown and Gastuche, 1967; Gastuche *et al.*, 1967), thermal behavior (Brindley and Kikkawa, 1979, 1980), synthesis conditions (Brindley and Kikkawa, 1979; Kikkawa and Koizumi, 1982), ion exchange (Miyata, 1983), and gas adsorption (Miyata and Hirose, 1978). The thermodynamic quantities for anion exchanges have been cited in recent publication (Miyata, 1991).

Other metal silicates, e.g., clay compounds, zeolites, and Al^{3+} -substituted tobermorite with a 2:1 type layer structure, have been studied for ion-exchange selectivity toward cations. An analytical evaluation method of the chromatographic parameters (distribution coefficients and separation factors) has been derived using an ion-exchange isotherm and its conjugate expression, i.e., Kielland plot (Tsuji and Komarneni, 1989, 1991, 1992; Tsuji *et al.*, 1991). The method is also valid for anion exchange.

Recently, vivid contradictions were found in the thermodynamic treatment of the ion-exchange isotherms and the Kielland plot for anion exchange in reports on the hydrotalcites by Miyata (1983, 1991). The ion-exchange isotherm and the corresponding Kielland plot should be conjugate as mentioned above. However, the plot of the selectivity coefficients (K^{A/NO_3}) vs the equivalent fraction \bar{X}_A in the exchanger given for A^-/NO_3^- exchange can never be derived from the corresponding isotherms. They can be exemplified by the Kielland plots for OH^- and F^-/NO_3^- exchanges (Figure 1), which still contain errors that will be described below. The contribution of the activity ratio of anions in the solution phase is negligible. They were calculated using the data points in Figure 1 of the Miyata paper (1983), assuming that the hydrotalcite is in the pure NO_3^- form ($\bar{X}_{NO_3} = 1$). The author also gives the isotherms for divalent anions A^{2-}/NO_3^- exchange in the total normality of 0.1N, where the equivalent fraction is used. The selectivity coefficients K_e (Figures 3 to 9 in his report) are given as a function of the mole fraction, but the equation of the K_e is expressed in terms of the equivalent fraction in the text. For the 2:1 exchanges, e.g., the CO_3^{2-}/NO_3^- and SO_4^{2-}/NO_3^- exchanges, the selectivity coefficients must include a term of the total normality and cannot be expressed only by the equivalent fractions of ions in the solution and the

solid phases (Gaines and Thomas, 1953; Barrer and Klinowski, 1974; Tsuji and Komarneni, 1991, 1992). The expressions of the thermodynamic quantities have been derived in terms of the equivalent fraction. Thus, the Miyata paper should be revised using the expressions in terms of the equivalent fraction as long as the Gaines-Thomas equation is used for evaluation of the equilibrium constant. The use of the equivalent fraction also has the following advantages. Prediction of the ion exchange isotherm at various total normalities is possible using the Kielland plot at a total normality when the Kielland plot was determined in terms of the equivalent fraction of the exchanging ions. Moreover, the distribution coefficients can be calculated using the Kielland plot as a continuous function of the concentration of exchanging ions (Tsuji and Komarneni, 1992). The use of the mole fraction in the thermodynamic treatment for the 2:1 or n:1 exchange does not permit such prediction or calculation.

Other weak points are the use of mixed ionic form and ambiguity in the definition of the standard state. Anions A^{n-} in the interlayer of the hydrotalcite $[Mg_{1-x}Al_x(OH)_2]^{x+}[(x/n)A^{n-} \cdot nH_2O]$ are believed to

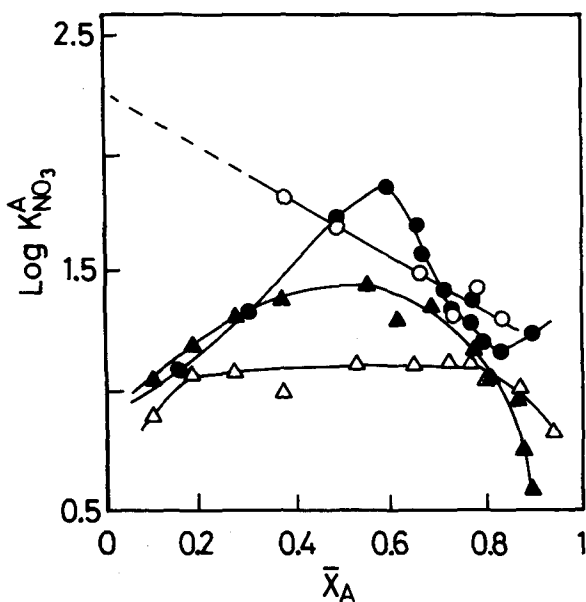


Figure 1. Kielland plot for OH^- or F^-/NO_3^- exchange on hydrotalcite. OH^-/NO_3^- exchange: ● by Miyata, ○ recalculated, F^-/NO_3^- exchange: ▲ by Miyata, △ recalculated.

exchange with other anions. The reported contents of NO_3^- and CO_3^{2-} were used to calculate the total ion-exchange capacity. The “ NO_3^- form” yielded the total capacity of 3.09 meq/g as the sum of 2.74 meq NO_3^- /g and 0.35 meq CO_3^{2-} /g. These give the equivalent fractions of $\bar{X}(\text{NO}_3^-) = 0.887$ and $\bar{X}(\text{CO}_3^{2-}) = 0.113$ for the initial composition, where the overbar on the character denotes the solid phase. The ionic composition of the “ Cl^- form” is calculated to be $\bar{X}(\text{Cl}) = 0.936$ and $\bar{X}(\text{CO}_3^{2-}) = 0.073$. However, these deviations from the “ideal” composition or $\bar{X}_A = 1.00$ do not seem to be taken into account in the ionic composition. These major revisions will be only possible using the original data and are not made in this report. The similar situation can be found on other ionic forms where the “pure” ionic form is not used. Thus, major corrections are needed for these figures and tables so as to remove these confusions on the ion-exchange data of hydrotalcites and the thermodynamic treatment.

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REFERENCES

- Allmann, R. (1968) The crystal structure of pyroaurite: *Acta Crystallogr.* **24**, 972–977.
- Barrer, R. M. and Klinowski, J. (1974) Ion exchange selectivity and electrolyte concentration: *J. Chem. Soc., Faraday Trans. 1* **70**, 2080–2091.
- Bish, L. and Brindley, G. W. (1977) A reinvestigation of takovite, a nickel aluminum hydroxy-carbonate of pyroaurite group: *Amer. Mineral.* **62**, 458–464.
- Brindley, G. W. and Kikkawa, S. (1979) A crystal-chemical study of Mg, Al and Ni, Al hydroxy-perchlorates and hydroxy-carbonates: *Amer. Mineral.* **64**, 836–843.
- Brindley, G. W. and Kikkawa, S. (1980) Thermal behavior of hydrotalcite and of anion-exchanged forms of hydrotalcite: *Clays & Clay Minerals* **28**, 87–91.
- Brown, G. and Gastuche, M. C. (1967) Mixed magnesium-aluminium hydroxides. II. Structure and structural chemistry of synthetic hydroxycarbonates and related minerals and compounds: *Clay Miner.* **7**, 193–201.
- Gaines Jr., G. L. and Thomas, H. C. (1953) Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption: *J. Chem. Phys.* **21**, 714–717.
- Gastuche, M. C., Brown, B., and Mortland, M. M. (1967) Mixed magnesium-aluminium hydroxides. I. Preparation and characterization of compounds formed in dialysed systems: *Clay Miner.* **7**, 177–192.
- Kikkawa, S. and Koizumi, M. (1982) Ferrocyanide anion bearing Mg-Al hydroxide: *Mater. Res. Bull.* **17**, 191–198.
- Miyata, S. (1983) Anion-exchange properties of hydrotalcite-like compounds: *Clays & Clay Minerals* **31**, 305–311.
- Miyata, S. (1991) Application and properties of hydrotalcite-like compounds: *ZEORAITO* (in Japanese) **8**, 7–16.
- Miyata, S. and Hirose, T. (1978) Adsorption of N_2 , O_2 , CO_2 and H_2 on hydrotalcite-like system: Mg^{2+} - Al^{3+} - $(\text{Fe}(\text{CN})_6)^{4-}$: *Clays & Clay Minerals* **26**, 441–447.
- Tsuji, M. and Komarneni, S. (1989) Alkali metal ion exchange selectivity of Al-substituted tobermorite: *J. Mater. Res.* **4**, 698–703.
- Tsuji, M., Komarneni, S., and Malla, P. (1991) Substituted tobermorites: ^{27}Al and ^{29}Si MASNMR, cation exchange, and water sorption studies: *J. Am. Ceram. Soc.* **74**, 274–279.
- Tsuji, M. and Komarneni, S. (1991) An evaluation method of chromatographic parameters from the ion-exchange isotherm of Al^{3+} -substituted tobermorite cation exchanger: *Sep. Sci. Technol.* **26**, 647–659.
- Tsuji, M. and Komarneni, S. (1992) An extended method for analytical evaluation of distribution coefficients on selective inorganic ion exchangers: *Sep. Sci. Technol.* **27**, 813–821.

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