

Co-operative Anion Exchange Mechanism of Layered Transition Metal Hydroxide Systems

Robert Schöllhorn* and Bernhard Otto

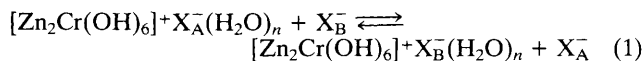
Technische Universität Berlin, Institut für Anorganische Chemie, Strasse des 17. Juni 135, D-1000 Berlin 12, West Germany

Discontinuous selectivity changes induced by co-operative structural transitions have been observed for anion exchange reactions of layered hydroxides with CdI₂-type lattice.

Layered host lattices with intercalated solvated ions provide most interesting models for the investigation of the behaviour of quasi-two-dimensional electrolyte systems.¹ It has been demonstrated recently that cation exchange reactions in these materials may lead to unusual structure induced selectivities based on co-operative transition mechanisms.^{1,2} We report in this study on results which show that similar processes can also be observed for corresponding layered phases with mobile solvated *anions* in the interlayer space. As the model system we selected the hydrotalcite related metal hydroxide [Zn₂Cr(OH)₆]+X⁻(H₂O)_n with CdI₂-type sheet elements (X⁻ = exchangeable anion).³

The reactions studied can be described by equation (1). In Figure 1(a) the structural changes are illustrated for the system NO₃⁻/ClO₄⁻ as a function of the composition of the equilibrium electrolyte. The interlayer spacings *d* of the pure phases are strongly different: the isometric tetrahedral ClO₄⁻ ions require a higher lattice spacing (*d* = 11.88 Å) as compared to the trigonal NO₃⁻ ions which are arranged parallel to the basal planes (*d* = 9.1 Å). It is clearly seen that in the range 0 ≤ γ(ClO₄)_L ≤ 0.77 the interlayer spacing remains constant and identical with that of the NO₃⁻ phase. At γ(ClO₄)_L = 0.77 a critical threshold point is reached and a transition to an interlayer spacing equal to that of the ClO₄⁻ phase occurs in a small two phase range 0.77 ≤ γ(ClO₄)_L ≤ 0.81. A similar discontinuous change is apparent from the ion exchange isotherm given in Figure 1(b). The latter transition is not as sharp as that found in the case of cation exchange reactions

with layered transition metal dichalcogenides.^{1,2} This is due to the small particle size of the layered hydroxides which results in measurable nonspecific anion absorption at the outer surface. These properties also present problems in the determination of the anion mobility as it is not possible to distinguish between the effect of bulk ions and adsorbed ions with respect to their proportional contribution to the total ionic conductivity.



The structure induced selectivity and the co-operative transition are obviously a consequence of the fact that (i) the formation of phases with mixed anions in the interlayer space

Table 1. Transition ranges for co-operative structural transformations in anion exchange reactions, *cf.* equation (1), of layered hydroxides [Zn₂Cr(OH)₆]+X⁻; starting phase = X_A⁻; *d* = interlayer spacing of pure phases; Ac⁻ = MeCOO⁻.

X _A ⁻	<i>d</i> _A (Å)	X _B ⁻	<i>d</i> _B (Å)	Transition range
NO ₃ ⁻	9.1	ClO ₄ ⁻	11.88	0.77 ≤ γ(X _B ⁻) ≤ 0.81
NO ₃ ⁻	9.1	Ac ⁻	12.9	0.41 ≤ γ(X _B ⁻) ≤ 0.43
Cl ⁻	7.7	Ac ⁻	12.9	0.88 ≤ γ(X _B ⁻) ≤ 0.93
Cl ⁻	7.7	MnO ₄ ⁻	10.4	0.15 ≤ γ(X _B ⁻) ≤ 0.20

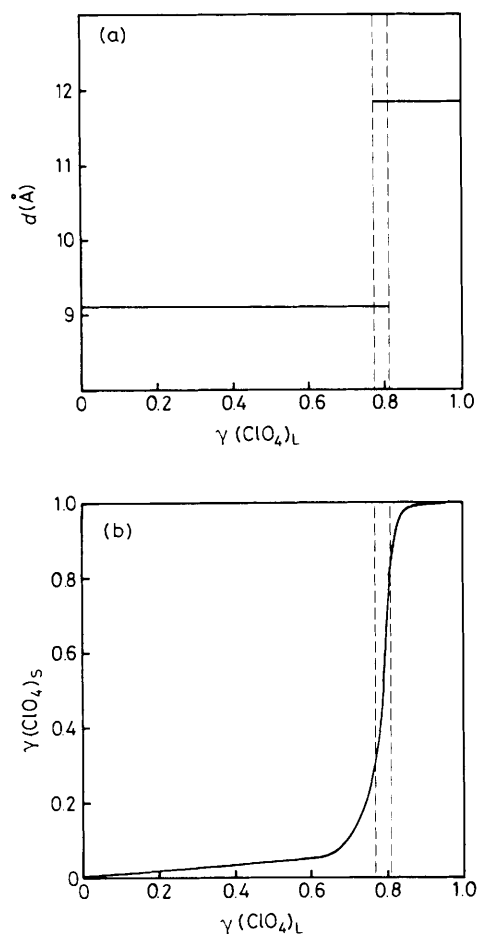


Figure 1. Ion exchange equilibria $\text{NO}_3^-/\text{ClO}_4^-$ for the layered oxide system $[\text{Zn}_2\text{Cr}(\text{OH})_6]^+\text{X}^-(\text{H}_2\text{O})_n$. (a) Dependence of interlayer spacing d upon the mole fraction $\gamma(\text{ClO}_4)_L$ in the equilibrium electrolyte phase; (b) ion exchange isotherm. $T = 300\text{ K}$; total ionic concentration 1 mol/l ; equilibration time 48 h , starting material nitrate phase.

is energetically unfavourable and (ii) a high activation energy is required for the transition. The position of the transition range is dependent upon the type of competing anions as shown in Table 1. In all cases hysteresis effects were observed:

the transition indicated in Figure 1 moves to $\gamma(\text{ClO}_4)_L = 0.70-0.67$, if the pure ClO_4^- phase is used instead of the NO_3^- phase as the starting material for equilibration. With decreasing difference in interlayer spacing X_A^-/X_B^- the transition width was found to increase strongly (e.g. Cl^-/Br^-); simultaneously strong X -ray line broadening occurs which is attributed to the appearance of statistical layer sequences X_A^-/X_B^- and the formation of either mixed anion layers or small domains X_A^- and X_B^- within one interlayer space leading to aperiodic elastic deformation (buckling) of the layers.

By far the most selective anion found is carbonate CO_3^{2-} . In a study on the related system reevesite $[\text{Ni}_{3/4}\text{Fe}_{1/4}(\text{OH})_2]^{1/4+}\text{X}^{-1/4}(\text{H}_2\text{O})_n$ we observed that exchange reactions in the presence of air (CO_2) can only be performed in electrolytes with $\text{pH} \leq 5$ because of the extreme carbonate selectivity. The latter can be understood in terms of a particularly strong Coulomb interaction host layer/guest ions in the case of planar trigonal CO_3^{2-} ions resulting from low interlayer spacing and high effective ionic charge.⁴

Layered double hydroxides of the type described have recently found increasing interest as fast proton conductors⁵ and heterogeneous catalysts with novel properties.⁶ There is a rather wide potential of 'tailoring' these solids by choice of the intralayer transition metal components as well as the choice of mobile lattice anions and co-operative processes and structure induced selectivities may be of interest in optimizing and reversibly monitoring the properties of these materials.

Received, 21st March 1986; Com. 370

References

- 1 R. Schöllhorn, 'Intercalation Chemistry,' eds. M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1982, p. 315; A. Lorf and R. Schöllhorn, *Inorg. Chem.*, 1977, **16**, 2950.
- 2 R. Schöllhorn, 'Chemical Reactions in Organic and Inorganic Constrained Systems,' ed. R. Setton, D. Reidel Publishing Co., Dordrecht/Boston, 1986, p. 323.
- 3 U. P. Boehm, J. Steinle, and C. Viehweger, *Angew. Chem.*, 1977, **89**, 259.
- 4 A. Mendiboure, B. Otto, and R. Schöllhorn, manuscript in preparation.
- 5 A. De Roy, J. P. Besse, and P. Boudot, *Mater. Res. Bull.*, 1985, **20**, 1091; M. Lal and A. T. Howe, *J. Chem. Soc., Chem. Commun.*, 1980, 737.
- 6 K. J. Martin and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1986, **108**, 541; W. T. Reichle, *J. Catal.*, 1985, **94**, 547; W. T. Reichle and N. J. Warren, U.S. Patent 4 458 026, 1984.