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CALORIMETRIC MEASUREMENT OF IONEXCHANGE HEATS OF HOMOIONIC HEULANDITE AND MORDENITE

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The ionexchange heats of homoionic heulandite and mordenite were measured with a microcalorimeter. In the case of K, NH_4, Na, Mg and Ca, the selectivity of the zeolite is determined by the heat of hydration.

In an isothermal flow calorimeter where the heat evolved during ionexchange between a solution of ACl_{Z_A} and a homoionic *B*-zeolite is measured, the integral heat of ionexchange is approximately [1, 2] ($ZA+$ and $ZB+$ are the cation charges):

$$Q = \bar{n}_A(E_A - \bar{E}_A) - n_B(E_B - \bar{E}_B) \tag{1}$$

where: E_A and E_B are the internal molar energies of the cations A^{ZA+} and B^{ZB+} in solution, $\bar{E}_A$ and $\bar{E}_B$ are the internal molar energies of A and B in the zeolite, $\bar{n}_A$ is the amount of cations exchanged from the solution to the zeolite in moles and n_B is the amount of cations exchanged from the zeolite to the solution in moles. Clearly, relation (1) gives the heat released during the exchange of A, which was initially in solution and is finally in the zeolite, and that released by the exchange of B, which was initially in the zeolite and is finally in the solution. As $ZA^{\bar{n}_A} = Z_B n_B$, $Q = [\bar{E}_B - \bar{E}_A(Z_B/Z_A)/ - /E_B - E_A(Z_B/Z_A)]n_B$. The calorimeter used for the measurement was an LKB 2277 multichannel microcalorimetry system [3, 4]. The reaction vessel was a 3 ml glass ampoule carefully sealed with a teflon-covered rubber disc by means of an aluminium cap crimped onto the glass ring. The reaction vessel contained 1 g of homoionic zeolite (Na, K, Mg, Ca, NH_4, Ni heulandite: NaHC, KHC, MgHC, CaHC, NH_4HC, NiHC and Na, K, Mg, Ca mordenite: NaMP, KMP, where HC = heulandite and MP = mordenite) and 2 ml of 3 M NaCl, KCl, $CaCl_2$, $MgCl_2$, NH_4Cl or $NiCl_2$ (Table 1).

The ampoule with the exchange system $ACl_{Z_A} + B \rightarrow$Zeolite was transferred, after sealing, to the heat-exchange position, where it reached the temperature the

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Table 1 Description of the zeolites used

Phase composition			Elemental composition, %					
Sample	Mordenite	Heulandite	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	MgO
MP	80%	—	66.91	11.55	2.74	1.83	4.35	0.78
HC	—	85%	64.11	13.85	1.85	1.85	4.28	1.12

Table 2 Differential heats of ionexchange (Q_d) of homoionic heulandite and mordenite

ACl + B-zeolite	$Q_d = Q/n$, kJ/mol	n; mmol
NaCl + KMP	−2.73	0.82
NaCl + KMC	−3.35	0.51
$CaCl_2$ + KMP	−4.40	0.52
$CaCl_2$ + KHC	−3.85	0.62
$MgCl_2$ + NaMP	−3.81	0.54
$MgCl_2$ + NaHC	−3.88	0.50
$MgCl_2$ + KMP	−1.84	0.44
$MgCl_2$ + KHC	−2.86	0.36
$CaCl_2$ + NaMP	−2.03	0.60
$CaCl_2$ + NaHC	−2.12	0.60
NaCl + CaMP	5.30	0.53
NaCl + CaHC	5.60	0.47
NH_4Cl + CaMP	11.0	0.71
NaCl + MgHC	32	0.22
KCl + MgHC	35	0.46
$MgCl_2$ + CaMP	2.25	0.20
NH_4Cl + NaMP	0.2	1.39
NH_4Cl + KMP	−1.3	1.02
NH_4Cl + NiHC	34	0.34
$NiCl_2$ + NH_4HC	−3.61	0.20

Note: $Q_d > 0$ for exothermic process

water-bath (310 K) in 25 minutes. It was then lowered into the detecting position, where it was kept until the heat output was negligible (approximately 48 hours).

The results are reported in Table 2, in which it is seen that there is no appreciable difference between the differential heats of ionexchange of mordenite and heulandite. On the other hand, the selectivity sequence $K > NH_4 > Na > Ca$ is related with the hydration heats of the related cations (Table 3) with the exception of the pairs NH_4—K and Mg—Ca (in the exchanges NH_4 + KMP, $Q_d = -1.3$ kJ/mol, and $MgCl_2$ + CaMP, $Q_d = 2.25$ kJ/mol). The explanation of this behaviour comes from the relation

$$Q_d = Q/n_B = (\bar{E}_B - \bar{E}_A Z_B/Z_A) - (E_B - E_A Z_B/Z_A)$$

Table 3

Hydration heats

Cation	−Ha, kJ/mol
K^+	338.9
NH_4^+	326.4
Na^+	422.6
Mg^{2+}	1954.0
Ca^{2+}	1615.0
Ni^{2+}	2138.0

in which the sign of Q_d is determined as a rule by the difference between the hydration heats $(H_a^B - H_a^A Z_B/Z_A)$, which is approximately $(E_B - E_A Z_B/Z_A)$.

In conclusion, it is possible to state that in the case of mordenite and heulandite the selectivity is determined not by the interactions in the zeolite frame, but by the hydration heat, and it is possible to drive the system from outside.

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