CCA-722

541.24
Note

The Ion-Exchange between Zn^{++} and Cd^{++} on Synthetic Zeolite of Type A

S. Lomić and I. J. Gal

Faculty of Technology, The University, 21000 Novi Sad, and »Boris Kidrič« Institute, 11000 Belgrade, Serbia, Yugoslavia

Received March 27, 1972

From ion-exchange isotherm at 10 and 25° C the following thermodynamic data for the reaction Cd^{++} (aq) + ZnZ (s) ⇆ CdZ (s) + + Zn^{++} (aq), have been obtained: $\log K_{283} = 0.35_4$; $\log K_{298} = 0.33_3$; $\Delta H^0_{298} = -0.57 \pm 0.15$ kcal/mol and $\Delta S^0_{298} = -0.4 \pm 0.2$ cal/mol K. The results are consistent with the data on Cd^{++} — Na^+ and Zn^{++} — Na^+ exchanges and confirm that the three counter-ions Na^+, Cd^{++} and Zn^{++} exchange reversibly, independently of the initial composition of the A-zeolite.

In a previous work[1] on ion-exchange equilibria between some divalent cations and the sodium form of synthetic zeolite 4A it has been shown that Zn^{++} and Cd^{++} ions displace practically completely the sodium ions from the crystalline framework of the zeolite. In the present paper we report data on the thermodynamics of ion — exchange between Zn^{++} and Cd^{++} on zeolite A, starting with the pure ZnA and CdA forms of the exchanger. The thermodynamic equilibrium constant of the heterogenous ion-exchange reaction is compared with the corresponding values for Cd^{++}—NaA and Zn^{++}—NaA exchange, and it is shown that the experimental data are consistent with a reversible ion-exchange for the three types of counter-ions at whatever composition of the solid phase.

EXPERIMENTAL

Cadmium and zinc forms of A-zeolite have been prepared and analysed as described previously[1]. To keep the water content of the zeolites constant, samples were stored in a dessicator over a saturated NH_4Cl solution at ambient temperature (22—24° C). The results of chemical analysis and the composition of the crystallographic unit cell are presented in Table I. The latter data are based on the assumption that the silica content corresponds exactly to 12 SiO_2 groups per unit cell[2].

TABLE I

Chemical Composition of Zeolites

Zeolite	Wt %					Atoms and H_2O molecules per unit cell				
	Na^+	M^{++}	AlO_2^-	SiO_2	H_2O	Na	M	Al	Si	H_2O
NaA	12.15	—	32.80	33.30	22.7	11.5	—	12.0	12.0	27.3
CdA	< 0.02	25.60	26.50	27.45	20.6	0.0	6.0	11.8	12.0	30.0
ZnA	0.11	16.20	29.40	30.40	22.1	0.1	5.9	11.8	12.0	29.1

The ion-exchange isotherms at 25 and 10° C were obtained by equilibrating in a thermostat 0.1 g of pure CdA or ZnA with 10 ml of a 0.05 isomolar solution of $CdCl_2 + ZnCl_2$, in which the molar ratio of $ZnCl_2/CdCl_2$ varied from 0 to 1. When the initial solid phase was pure ZnA, the solution was labelled with radioactive ^{115}Cd, while in the case of CdA, the isotope was ^{65}Zn. The equilibration time was 3 days[1], and the equilibrium concentrations of Zn and Cd in the liquid phase were deduced from the decrease of radioactivity of liquid samples relative to the corresponding samples before equilibration.

RESULTS AND DISCUSSION

The isotherms are presented in Fig. 1, where $n_{Zn} \equiv (Zn^{++})/0.05$ is the fraction of zinc in solution and $\bar{n}_{Zn} \equiv (ZnZ)/(ZnZ + CdZ)$ the fraction of zinc in the solid zeolite phase. Thus, for the reaction

$$Cd^{++}\,(aq) + ZnZ\,(s) \rightleftharpoons CdZ\,(s) + Zn^{++}\,(aq)$$

the thermodynamic equilibrium constant is defined by

$$K = \frac{n_{Zn}\,(1 - \bar{n}_{Zn})}{(1 - n_{Zn})\,\bar{n}_{Zn}} \cdot \frac{\gamma_{Zn^{++}}\, f_{CdZ}}{\gamma_{Cd^{++}}\, f_{ZnZ}} \tag{1}$$

where γ and f are the activity coefficients of the ionic species in the liquid and solid phase, respectively. The ratio of $\gamma_{Zn^{++}}/\gamma_{Cd^{++}}$ can be expressed in terms of the mean molal activity coefficients of $CdCl_2$ and $ZnCl_2$[3] as

$$G = \gamma_{Zn^{++}}/\gamma_{Cd^{++}} = \left(\frac{\gamma_{\pm}\,(ZnCl_2)}{\gamma'_{\pm}\,(CdCl_2)}\right)^3 \tag{2}$$

where $\gamma_{\pm}$ refer to the mean molal activity coefficients of the 1—2 salts in the »mixed« 0.05 molal solution of the two electrolytes. The latter values have been obtained from the data of mean molal activity coefficients of the pure salts at the corresponding ionic strength[3] using the well-known equation of Glueckauf[4]. As f_{CdZ}/f_{ZnZ} is not known, the thermodynamic equilibrium constant was calculated according to the method of Gaines and Thomas[5]. In the present case, when the two cations have the same charge and the two zeolites (ZnA and CdA) have practically the same water content per unit cell (see Table I), the equation of Gaines and Thomas[5] is reduced to

$$\ln K = \int_0^1 \ln\, Q_{ZnZ}^{CdZ}\; G\; d\bar{n}_{Cd} \tag{3}$$

where $Q_{ZnZ}^{CdZ} \equiv (n_{Zn}\,\bar{n}_{Cd}/n_{Cd}\,\bar{n}_{Zn})$. Thus, the thermodynamic equilibrium constant can be obtained by graphical integration of the curve $\log\,(Q_{ZnZ}^{CdZ}\,G)$ *vs.* $\bar{n}_{Cd}$. These curves are shown in Fig. 2. (To facilitate the determination of area under these curves, smoothed lines are drawn). From the two equilibrium constants, thermodynamic data are calculated in the usual way:

$$\Delta G_T^{\circ} = -RT \ln K_T$$

$$\Delta H^{\circ} = -R\left[(\ln K_2 - \ln K_1)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}\right]$$

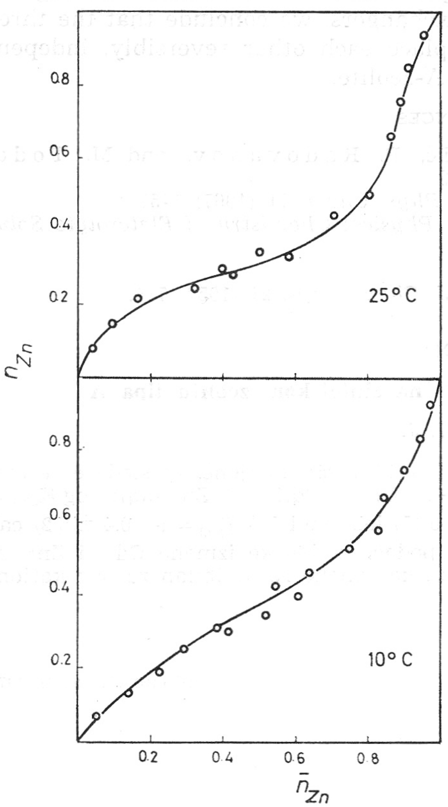

Fig. 1. Ion-exchange isotherms n_{Zn} *vs.* $\bar{n}_{Zn}$.

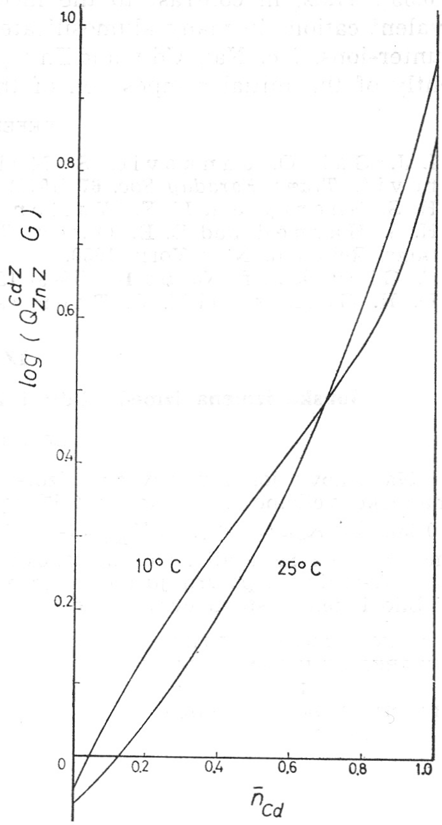

Fig. 2. Plots of log (Q^{CdZ}_{ZnZ} G) *vs.* $\bar{n}_{Cd}$ (Eq. 3).

$$\Delta S^{o}_{T} = (\Delta H^{o} - \Delta G^{o}_{T})/T$$

The following results are obtained:

$$\log K_{283} = 0.35_4$$
$$\log K_{298} = 0.33_3$$
$$\Delta G^{o}_{298} = (-0.45 \pm 0.01)\ \text{kcal/mol}$$
$$\Delta H^{o} = (-0.57 \pm 0.15)\ \text{kcal/mol}$$
$$\Delta S^{o}_{298} = (-0.4 \pm 0.2)\ \text{cal/(mol K)}$$

It is interesting to compare the equilibrium constant at 298 K with our previously published values[1] for the Cd^{++}—Na^{+} and Zn^{++}—Na^{+} exchanges on the same zeolite:

$$Cd^{++}\,(aq) + 2\,NaZ\,(s) \rightleftharpoons CdZ\,(s) + 2\,Na^{+}\,(aq); \quad \log K_{298} = 1.58_6$$
$$Zn^{++}\,(aq) + 2\,NaZ\,(s) \rightleftharpoons ZnZ\,(s) + 2\,Na^{+}\,(aq); \quad \log K_{298} = 1.26_9$$

The difference between the above two $\log K_{298}$ values is 0.31_7, in fairly good agreement with the directly determined value of the present work, $\log K_{298}$ =

$= 0.33_3$. Thus, in contrast to the incomplete and/or irreversible exchange of divalent cations in many alumosilicate exchangers, we conclude that the three counter-ions, *i. e.* Na^+, Cd^{++} and Zn^{++} replace each other reversibly, independently of the initial composition of the A-zeolite.

REFERENCES

1. I. J. Gal, O. Janković, S. Malčić, P. Radovanov, and M. Todorović, *Trans. Faraday Soc.* **67** (1971) 999.
2. H. S. Sherry and H. F. Walton, *J. Phys. Chem.* **71** (1967) 1457.
3. H. S. Harned and B. B. Owen, *The Physical Chemistry of Eletcrolyte Solutions,* Reinhold, New York, 1950.
4. E. Glueckauf, *Nature* **163** (1949) 1223.
5. G. H. Gaines and H. C. Thomas, *J. Chem. Phys.* **21** (1953) 714.

IZVOD

Jonska izmena između Cd^{++} i Zn^{++} na sintetskom zeolitu tipa A

S. Lomić i I. J. Gal

Na osnovu jonoizmenjivačkih izotermi na 10 i 25⁰ dobijene su sledeće termodinamičke veličine za reakciju: $Cd^{++}(aq) + ZnZ(s) \leftrightharpoons CdZ(s) + Zn^{2+}(aq)$: $\log K_{283} = 0.35_4$, $\log K_{298} = 0.33_3$, $\Delta H^{\circ}_{298} = (-0.57 \pm 0.15)$ kcal/mol i $\Delta S^{\circ}_{298} = (-0.4 \pm 0.2)$ cal/ /(mol K). Ovi rezultati su u saglasnosti sa podacima jonske izmene Cd^{++} i Zn^{++} sa Na^+ u A-zeolitu, i potvrđuju da je proces jonske izmene reversibilan za ove katjone pri bilo kojem sastavu čvrste faze.

TEHNOLOŠKI FAKULTET
UNIVERZITET U NOVOM SADU
I
INSTITUT »BORIS KIDRIČ«
11000 BEOGRAD

Primljeno 27. marta 1972.