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THERMODYNAMICS OF ANION EXCHANGE ON HYDROUS ZIRCONIA

IV. CALORIMETRIC DETERMINATION OF THE HEAT OF ANION EXCHANGE ON HYDROUS ZIRCONIA*

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ABSTRACT

Ion-exchange processes Cl^-/NO_3^- and SO_4^{2-}/NO_3^- were studied by calorimetric measurements. Experiments were so performed to obtain stoichiometric equilibrium concentration in order to calculate equilibrium constants, and the heat studied ion-exchange reaction. As a result -11.03 and -21.70 kJ mol^{-1} values were obtained for standard enthalpy changes of Cl^-/NO_3^- and SO_4^{2-}/NO_3^- ion exchange processes, respectively.

These values, together with these obtained from distribution measurements were used for calculation of free energy and standard entropy changes of investigated processes.

INTRODUCTION

Hydrous zirconia has been shown to have anionic ion-exchange properties in acid media[1-3]. For this reason, it is a very attractive anion exchanger especially at higher temperatures. Literature dealing with distribution measurements is abundant but that on thermodynamics is scarce. The data on thermodynamics obtained in the recent work indicate true thermodynamic exchange.

The aim of the present work was to determine the heat of the Cl^-/NO_3^- and SO_4^{2-}/NO_3^- ion-exchange reaction on hydrous zirconia by calorimetric measurements. Another aim of the present paper was to compare the values for enthalpy changes obtained by distribution data at various temperatures and by calorimetric measurements.

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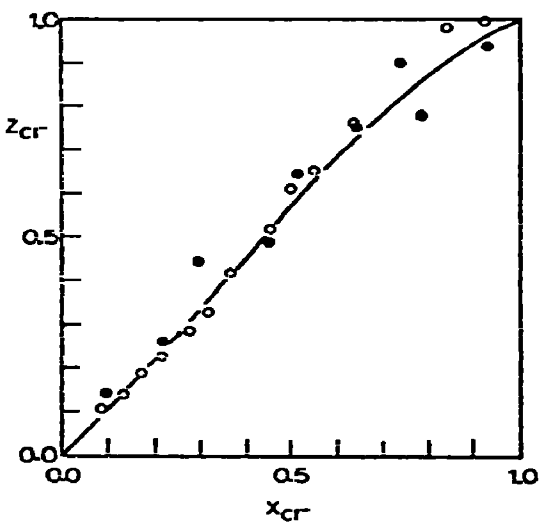
EXPERIMENTAL

Preparation of hydrous zirconia

The method used has been described earlier[8].

Calorimetric determination

An isothermal differential microcalorimeter was used for the determination of the heat of the ion-exchange reaction[7]. It was calibrated by determining the heats of KCl dissolution in water. The integral heat, obtained at infinite dilution in our runs, $\Delta H = 175.43 \pm 0.18$ kJ mol^{-1} (4190 ± 44 cal mol^{-1}), is in good agreement with literature values[9]. The heat of ion-exchange reactions was measured as follows: the calorimeter vessels were filled with 250 ml of the solution, which was a mixture of hydrochloric and nitric acid in the case of the Cl^-/NO_3^- ion-exchange reaction or sulphuric and nitric acid in case of the SO_4^{2-}/NO_3^- ion-exchange reaction, at the constant ionic strength ($I = 0.1M$). In order to avoid the heat of immersion in the solution 0.4–1.0 g of hydrous zirconia, together with 0.5 ml distilled water were measured and sealed in the glass ampoule. Calibration was performed by electric heating, after estabilishing temperature equilibrium in the calorimeter. The ampoule was then broken and hydrous zirconia poured in the solution where the heat was developed by the exchange reaction. The quantity of the exchanged ion was determined from the difference between the initial concentrations and concentrations of ions after the ion-exchange reaction in the calorimeter vessel. Chloride and nitrate were determined by Mohr's method[9] and spectrophotometrically[10], respectively. The concentration of sulphate ions was determined using the Perkin-Elmer 403 atomic absorption spectrophotometer.



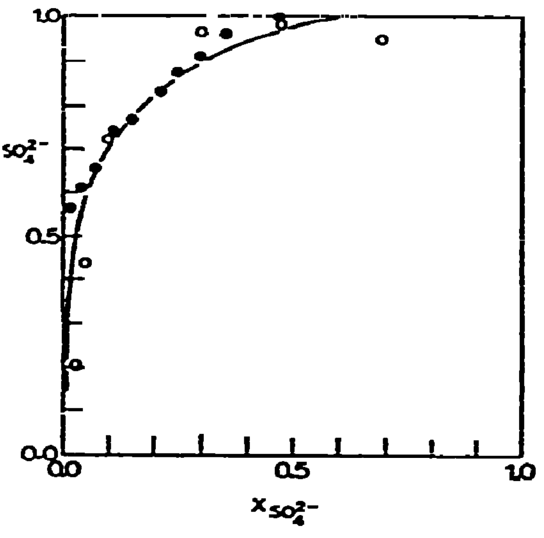


Fig. 1. Isotherms for the Cl^-/NO_3^- ion-exchange process on hydrous zirconia. (○) Data obtained by distribution measurements[8]; (●) data obtained by calorimetric measurements.

Fig. 2. Isotherms for the SO_4^{2-}/NO_3^- ion-exchange process on hydrous zirconia. (○) Data obtained by distribution measurements; (●) data obtained by calorimetric measurements.

TABLE 1

THE THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR INVESTIGATED ION-EXCHANGE PROCESSES

Reaction	*K*			*Reference*
	25°C	*50°C*	*80°C*	
Cl^-/NO_3^-	0.985	0.541	0.386	8
Cl^-/NO_3^-	0.985	—	—	this work
SO_4^{2-}/NO_3^-	1.789	—	—	this work

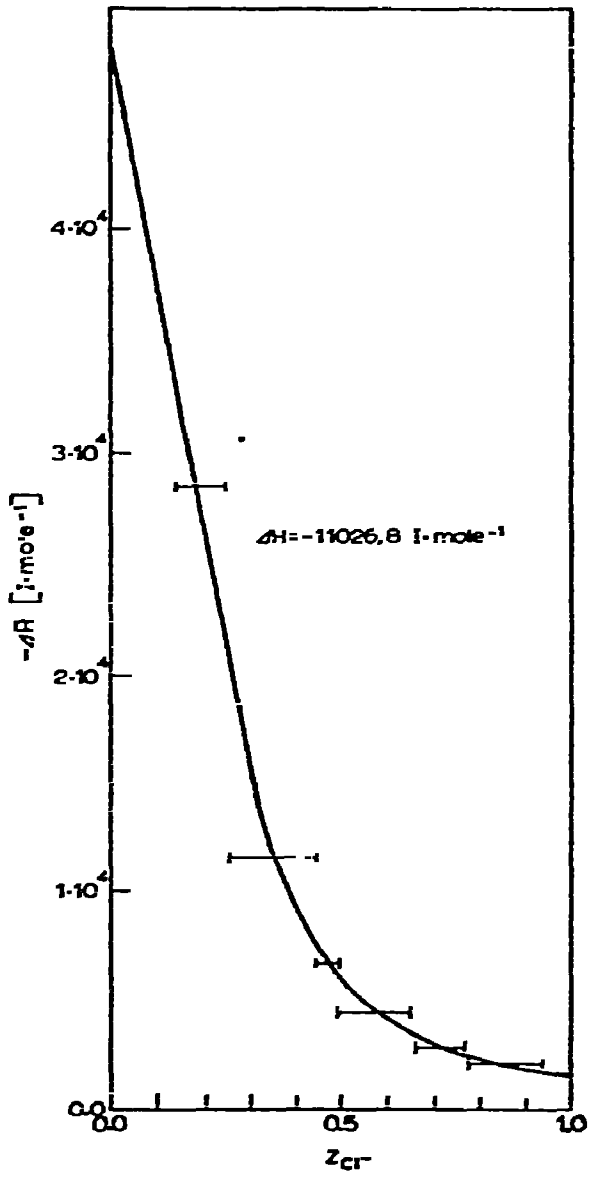


Fig. 3. Partial heat of the ion-exchange process studied as a function of Cl^- ion mole fraction in the exchanger.

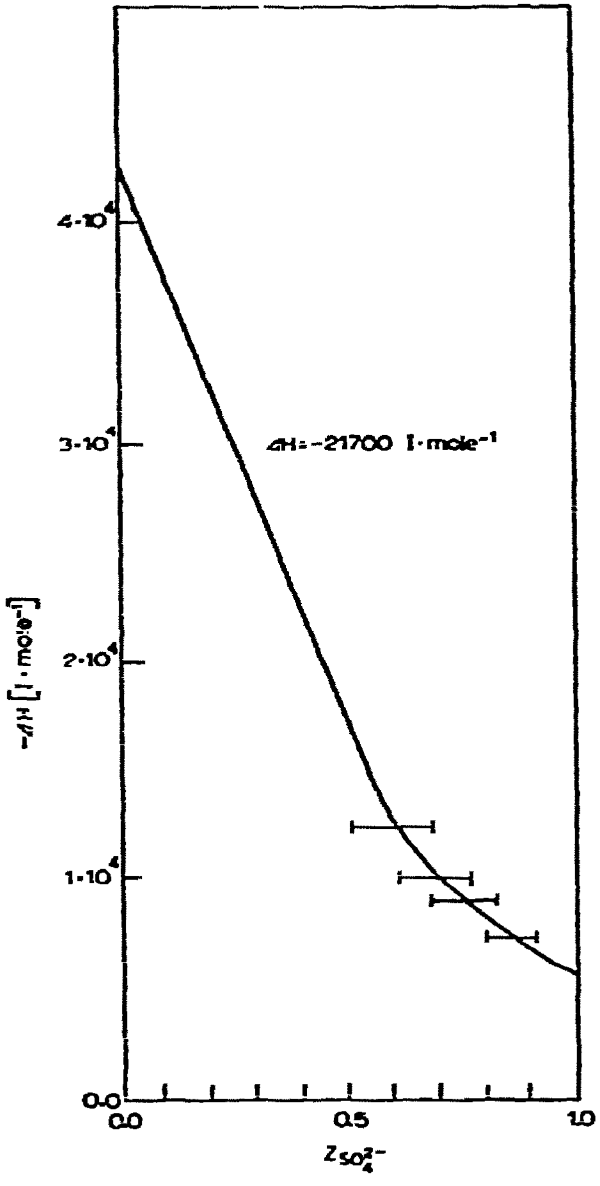


Fig. 4. The partial heat of the SO_4^{2-}/NO_3^- ion-exchange process as a function of a SO_4^{2-} mole fraction in the exchanger.

RESULTS AND DISCUSSION

Calculation of thermodynamic equilibrium constants

Changes of stoichiometric concentration during calorimetric measurements were calculated in order to obtain the quantity of exchanged anions. Along with the data for distribution measurements given in our earlier paper[8], the obtained values are presented in Figs. 1 and 2 as isotherms for Cl^-/NO_3^- and SO_4^{2-}/NO_3^- ion exchange.

It is evident that the results obtained in these two runs are in good agreement for Cl^-/NO_3^- ion-exchange process. However, there is discrepancy between the results obtained in the present and our previous work[8] in the case of the SO_4^{2-}/NO_3^-

ion-exchange process. Repeated calculation of experimental results from earlier work[8] has shown that mistakes were made in calculation of the uptakes of SO_4^{2-} ions on hydrous zirconia. Now calculation results fit very well with data obtained by calorimetric measurements.

As in the previous paper[8], thermodynamic equilibrium constants were calculated from the isotherms shown in Figs. 1 and 2, by both the Högfeldt[12] method and the method developed by Ruvarac and Vesely[14]. These values and the results obtained in the previous work[8] are given in Table 1.

Measurement of the heat investigated ion-exchange reaction

Enthalpy changes of Cl^-/NO_3^- and SO_4^{2-}/NO_3^- ion-exchange reactions were measured directly, at 25°C, using a differential microcalorimeter. The plots of directly measured heats of partial change of Cl^- and SO_4^{2-} ions with NO_3^- ions as a function of the mole fraction of Cl^- (or SO_4^{2-}) ion in the ion exchanger are shown in Figs. 3 and 4.

Differential heats of exchange:

$$\Delta H = \delta(\Delta H)/\delta \bar{X}_M \text{ (Where M is } Cl^- \text{ or } SO_4^{2-})$$

can be obtained from such plots by applying the Chord–area method[13]. Integral heats of exchange per mole of exchanging ion are defined by the relationship:

$$\Delta H = \int_0^1 \Delta \bar{H}\, d\bar{X}_M$$

In this work, no correction was made due to relative apparent molal heat contents because of small value of the corrections in comparison with the integral heats of the exchange per mole of the exchanging ions[15]. The values of the relative apparent molal heat contents are estimated to be about 50 J mol⁻¹, which is approximately 2% of the heats of the ion-exchange processes studied[15].

Calculation of thermodynamic functions

Other thermodynamic functions were calculated by calculating the standard free energy change, ΔG^0, from distribution data according to equation:

$$\Delta G^0 = -RT \ln K$$

In order to obtain values for standard entropy changes, ΔS^0, the values for ΔG^0 were combined with those obtained by calorimetric measurements for ΔH^0, by using the equation:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

The data obtained in the same way for the thermodynamic function are presented in Table 2 together with other literature values for investigated systems.

TABLE 2

THERMODYNAMIC FUNCTION FOR ANION EXCHANGE PROCESSES STUDIED ON HYDROUS ZIRCONIA

Reaction	*ΔH^0 (kJ mol^{-1})*	*ΔG^0 (kJ mol^{-1})*	*ΔS^0 (J mol^{-1} deg^{-1})*	*Reference*
Cl^-/NO_3^-	—	0.02	—	4
Cl^-/NO_3^-	−16.97	0.01	−13.61	8
Cl^-/NO_3^-	−11.03	0.04	−33.12	this work
SO_4^{2-}/NO_3^-	−21.70	−0.34	−67.70	this work

It is obvious from Table 2, that the examined processes are exothermic. The same conclusion has been drawn in our previous paper[8] from distribution data for the Cl^-/NO_3^- ion-exchange reaction. There are differences between the values for the heats of examined reactions obtained in these two ways.

The indirect way for calculation of the heat of ion-exchange reaction from distribution measurements produces considerable errors of the final value for ΔH^0. Errors could be made in two steps of the procedure. First, as it has been mentioned above in the method used for calculation of the equilibrium constants, K, when by using graphical integration over the whole range of the exchanger composition[12], their values were affected by relatively low precision of the experimental data in the ranges of $X_M < 0.1$ and $X_M > 0.9$, where the curves of the functions to be integrated often have asymptotic character and require limiting values of the function at $X_M = 0$ and $X_M = 1$ are sometimes hard to obtain. The second source of the error would be graphical determination of ΔH^0 where the function of $\ln K$ is presented versus temperatures. In the calorimetric measurements performed in this work, experimental errors were calculated to be 5% and 8% for Cl^-/NO_3^- and SO_4^{2-}/NO_3^- ion-exchange processes, respectively. These values are in good agreement with those given by the calorimeter producer[7].

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