Line shape analysis of ^{129}Xe NMR spectra of xenon in zeolites

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Abstract

^{129}Xe NMR spectra of xenon in zinc-exchanged zeolites have been calculated assuming a macroscopic inhomogeneity resulting from a distribution of adsorption site concentrations. The experimentally observed characteristics of the lines such as line widths and shapes are qualitatively reproduced, as well as their dependence on xenon pressure.

1. Introduction

^{129}Xe NMR spectroscopy has proved to be a versatile tool for the investigation of physical and chemical properties of zeolite voids accessible to xenon [1-3]. One of its more recent applications is the study of cation concentrations and distributions in transition metal exchanged zeolites such as ZnY [4], AgY [5], and CdY [6].

In the majority of papers on the topic of ^{129}Xe NMR in zeolites, the interest has concentrated on the pressure dependence of the chemical shifts whereas the shapes and widths of the resonance lines have attracted much less attention. Thus, there is yet no satisfying explanation for two striking experimental observations, namely the influence of pressure on the line widths and the frequently observed asymmetry of the signals [7].

The present contribution explores the possibility that the shapes and widths of the ^{129}Xe NMR lines of xenon in diamagnetic cation exchanged zeolites are caused by a distribution of chemical shifts arising from sample inhomogeneities. The investigation refers to a partially zinc exchanged zeolite Y (ZnY) for which the ^{129}Xe NMR chemical shifts of ad-

sorbed xenon have been analyzed previously [4]. In this case, it has been observed [8] that the line widths are almost independent of the applied Zeeman field strength when measured on the ppm-scale, suggesting a magnetic shielding coupling to be operative.

2. Experimental

Zeolite ZnY (level of zinc-exchange: 74%) was prepared from NaY (LZ-Y 52, Union Carbide, Si : Al = 2.4 : 1) by a conventional ion-exchange procedure using a 0.1 mol dm^{-3} aqueous Zn(NO$_3$)$_2$ solution ($T = 353$ K, pH = 5.7–5.9). Dehydration was performed under high vacuum ($p < 10^{-5}$ hPa) at a maximum temperature of 673 K maintained for 16 h. Finally, at the same temperature, a 16 h oxygen treatment was performed. The results of the chemical characterization of the resulting material have been reported elsewhere [4]. The ^{129}Xe NMR measurements were performed at ambient temperature at the resonance frequency $\omega_0/2\pi = 21.4$ MHz using a Bruker (Karlsruhe, Germany) spectrometer type CXP 100.

3. Calculations

It has been shown [4] that for a given pressure p the isotropic chemical shift δ of ^{129}Xe adsorbed in a sample of ZnY can be calculated according to

$$\delta = \frac{1}{N_{Xe}}\left(\frac{n_1 k_1 p}{1 + k_1 p}\delta_1 + \frac{n_2 k_2 p}{1 + k_2 p}\delta_2 + K_H p\delta_H\right) + FN_{Xe}, \quad (1)$$

which is valid under the condition of rapid exchange of xenon atoms among the available adsorption sites. δ_j denotes the local chemical shift of a xenon atom accommodated on site i ($i = 1, 2$) whereas δ_H is the mean chemical shift of weakly adsorbed xenon; the influence of xenon–xenon interaction is taken into account by the additive term FN_{Xe}, with $F = 1.84$ ppm uc. The total amount of adsorbed xenon, N_{Xe}, is given by a superposition of Langmuir adsorption isotherms describing strong adsorption on sites 1 and 2 with concentrations n_i and adsorption constants k_i and the Henry term $K_H p$.

$$N_{Xe} = \frac{n_1 k_1 p}{1 + k_1 p} + \frac{n_2 k_2 p}{1 + k_2 p} + K_H p. \quad (2)$$

If we allow for macroscopic inhomogeneities of adsorption site concentrations our argumentation is no more applicable to the sample as a whole. It holds, however, for such domains, in which the xenon exchange is fast on the NMR time scale. As each domain is characterized by specific values of n_i it will contribute a chemical shift according to Eq. (1). In order to model the inhomogeneity of the sample mathematically we have to choose an appropriate distribution function $\Omega(n_1, n_2)$. Unfortunately, there is no reliable information on the actual nature of this function. For computational convenience, we assume $\Omega(n_1, n_2)$ to be composed of two statistically independent distribution functions $\omega(n_1)$ and $\omega(n_2)$, which represent the *individual* inhomogeneities of site 1 and 2, respectively, such that $\Omega(n_1, n_2) = \omega(n_1)\omega(n_2)$. Tentatively, Gaussian distribution functions $g(n_i)$ are chosen as a first approximation of the $\omega(n_i)$

$$\omega(n_i) = g(n_i) \propto \exp\left(-\frac{(n_i - \bar{n}_i)^2}{2\sigma_i^2}\right). \quad (3)$$

In Eq. (3) $\bar{n}_i$ denotes the sample's mean value of n_i and σ_i the standard deviation of the distribution. A spectrum can then easily be determined using the following algorithm: Both n_1 and n_2 are varied independently while the chemical shift δ is calculated according to Eq. (1) and sorted into a histogram where bins are of small but finite width $\Delta\delta$. Each combination n_1, n_2 is weighted by $N_{Xe}(n_1, n_2) \times \Omega(n_1, n_2)$. By this procedure we directly obtain the relative intensity I as a function of the chemical shift.

In the general case of a multiple distribution, numerical methods have to be applied. For the sake of simplicity we restrict the present study to the case of a distribution of n_1 only, for which an analytical expression of $I(\delta)$ can be easily derived (vide infra). Computer calculations were performed to ensure that an additional distribution of the weaker adsorption site concentration n_2 has only minor influence on the shapes and widths of the spectra and does not change the qualitative features which will be discussed in Section 4.

As a starting point for the analytical treatment of a single distribution of n_1 we use the relation

$$\int_{\delta_1}^{\delta_2} I(\delta)\,d\delta = \int_{[\delta_1, \delta_2]} N_{Xe}(n_1)\omega(n_1)\,dn_1, \quad (4)$$

which is a consequence of the proportionality between the integral NMR signal intensity and the spin concentration. In the case of single-valued functions $\delta(n_1)$ and $n_1(\delta)$ Eq. (4) can be transformed to give

$$I(\delta) = N_{Xe}(n_1)\omega(n_1)\left|\frac{d\delta}{dn_1}\right|^{-1}. \quad (5)$$

Conveniently, Eq. (1) may be written in shorthand notation as

$$\delta = c_1 n_1 + \frac{c_2}{c_3 n_1 + 1} + c_4, \quad (6)$$

where the constants c_j abbreviate somewhat cumbersome algebraic terms, which arise on insertion of Eq. (2) into Eq. (1). Substituting Eq. (6) into Eq. (5) we obtain

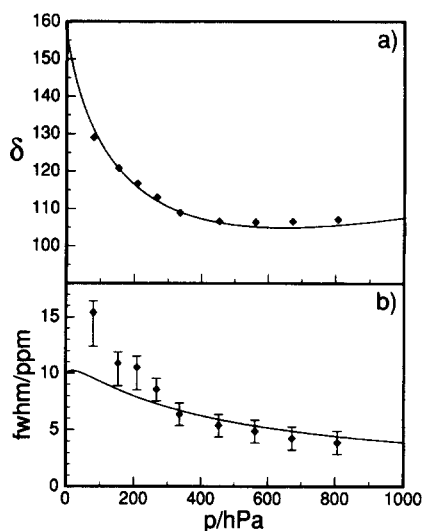$$I(\delta) = \frac{N_{Xe}(n_1)\omega(n_1)}{|c_1 - c_2 c_3/(c_3 n_1 + 1)^2|}, \quad (7)$$

Fig. 1. Ambient temperature ^{129}Xe NMR chemical shifts (a) and signal halfwidths fwhm (b) of Xe in zeolite ZnY. Symbols: experiment; solid lines: results according to the model discussed in the text.
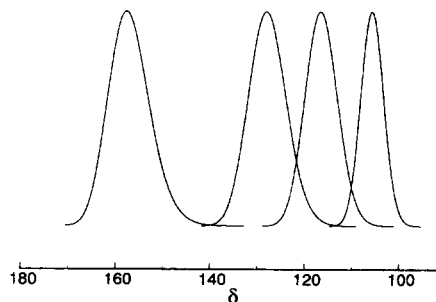

Fig. 2. ^{129}Xe NMR spectra of xenon adsorbed in zeolite ZnY, calculated via Eq. (7) (see text). Xenon pressures are, from left to right, 0.1, 100, 200 and 500 hPa, respectively.

which is the implicit mathematical description of the NMR spectrum (note, that $n_1 = n_1(\delta)$).

4. Results and discussion

In Fig. 1a experimentally observed ^{129}Xe NMR chemical shifts of xenon in zeolite Zn(74)Y at ambient temperature and various pressures are compared with results of Eq. (1). The underlying set of parameters (Table 1) was determined using a fitting algorithm. It is necessary to be aware of the fact that the obtained parameters are strictly valid only in the case of a perfectly homogeneous sample. As a consequence, the maximum intensities of the calculated

Table 1
Site concentrations and site characteristic parameters obtained from the analysis of experimental ambient temperature adsorption and ^{129}Xe NMR data of xenon in zeolite ZnY

Adsorption site	n_i (uc^{-1})	k_i (hPa^{-1})	K_3 (10^{-2} uc^{-1} hPa^{-1})	δ_i
1	1.2	0.023	–	220
2	1.8	0.008	–	135
3	–	–	1.44	58

spectra are observed at values of δ which are not necessarily the same as predicted by Eq. (1). The deviations, however, turn out to be negligible within the accuracy of measurement (≤ 0.5 ppm), so that a large-scale iterative determination of the exact set of parameters can be avoided.

In Fig. 1b, the corresponding line halfwidths which we define as the signals' full width at half maximum height (fwhm) are displayed in units of ppm. The original values of fwhm have been corrected by the contribution of the inhomogeneity of the magnetic field which gives rise to an extra line broadening of 2 ppm. Assuming a value of the standard deviation $\sigma_1 = 0.02$ sc^{-1} the pressure dependence of fwhm as predicted by the present model has been calculated by application of Eq. (7). Actually a series of calculations with standard deviations between 0.01 and 0.05 sc^{-1} was performed and the aforementioned value of σ_1 turned out to be the most suitable one for a comparison with the experimental results. Some representative spectra in the pressure range between 0.1 and 500 hPa are shown in Figs. 2 (calculation) and 3 (experiment). It can be seen that the calculated as well as the experimental signals exhibit asymmetric line shapes. This asymmetry is especially pronounced in the case of the lowest pressure investigated. As a tendency the asymmetry diminishes as p increases.

The assumption of a macroscopic inhomogeneity of the sample and its mathematical treatment are capable of substantiating a variety of experimental observations. First of all, the systematic decrease of the line widths with increasing equilibrium pressure p is reproduced. At medium and high xenon pres-
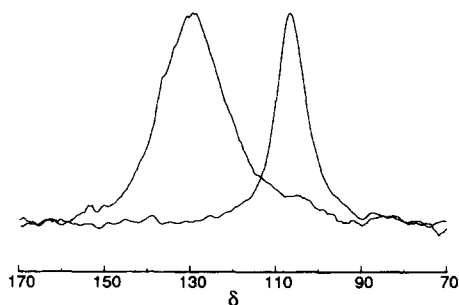
Fig. 3. Experimental ambient temperature ^{129}Xe NMR spectra of xenon adsorbed in zeolite ZnY at xenon pressures 80 hPa (left) and 450 hPa (right).

sures the experimental data are compatible with the assumption of a single-distribution of n_1 as the dominating line-broadening effect, whereas in the low pressure region additional influences, probably distributions of δ_i and/or relaxational broadening, yield a significant contribution [8]. The quality of the correspondence between calculated and measured values of fwhm could be improved if these effects were taken into account. However, such a procedure would drastically increase the number of parameters which have to be optimized and give little additional insight. The calculated curve fwhm versus p should therefore not be understood as an optimum fit but as a systematic *trend* for one single, reasonable value of σ_1.

Remarkably, the calculated asymmetry of the lines is less distinct than in the case of experiment. This is probably due to actually asymmetric distribution functions $\omega(n_i)$ instead of the symmetric normal distribution, which was used in our present calculation. Nevertheless, even a symmetric distribution function produces asymmetric lines. In this context, we like to emphasize that within the previously discussed restrictions the applicability of Eq. (7) is not limited to $\omega(n_1) = g(n_1)$ but can be extended to virtually any type of physically significant distribution function.

5. Conclusion

^{129}Xe NMR signal line shape analysis allows the investigation of sample heterogeneities in zeolites Y exchanged with diamagnetic multi-valent cations. In the special case of a zinc-exchanged zeolite NaY line shapes have been shown to reflect a distribution of averaged isotropic chemical shifts due to heterogeneities in supercage zinc cation concentrations. The quantitative analysis is based on a well-established multi-site adsorption model and yields information on the nature of the distribution function of zinc-site concentrations. General features of ^{129}Xe NMR lines such as line widths and their pressure dependence as well as signal asymmetries can be explained on a semiquantitative basis by this approach.

Acknowledgement

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