574 *J. Chem. Eng. Data* **1999,** *44,* 574−576

Solubility of Zeolite A and Its Amorphous Precursor under Synthesis Conditions

Tabassum Ejaz and Alan G. Jones*

Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, U.K.

Peter Graham

Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington L63 3JW, U.K.

Solubility measurements are reported for zeolite A crystals and amorphous zeolite precursor in aqueous sodium hydroxide solutions at conditions pertinent to industrial synthesis (3.02−4.39 M NaOH, 303−353 K). Zeolite crystal solubility is generally, but not always, found to increase with temperature and alkali concentration. Zeolite precursor has much higher solubility than the zeolite A crystals at similar conditions.

Introduction

Zeolites are three-dimensional, microporous crystalline solids comprising sodium aluminosilicates with well-defined structures containing aluminum, silicon, and oxygen in a regular framework (Barrer, 1982; Dyer, 1988). A hydrothermal synthesis route is normally employed industrially, using aqueous alkaline gels containing sources of silica, alumina, and cations. An amorphous gel phase results upon mixing of sodium silicate and sodium aluminate at high pH; subsequent transformation to the final product can take hours or days depending upon the synthesis conditions.

Industrial synthesis of zeolite A can involve solutions up to 4.0 M NaOH, where high caustic concentrations are essential to keep crystallization times short and allow effective recycling of the excess NaOH (Barrer, 1982). Previous studies, however, have investigated zeolite A solubilities at insufficiently high NaOH concentrations to be relevant to industrial zeolite synthesis (Caullet et al., 1979; Cizmek et al., 1991; Gasteiger et al., 1992). Similarly, Antonic et al. (1993, 1994) reported the dissolution of zeolite precursors but only at NaOH concentrations of 0.2 M. To rectify this deficiency, solubility measurements of zeolite A and its amorphous precursor are presented here at conditions pertinent to industrial synthesis.

Experimental Procedure

Precipitation. The synthesis recipe for sodium aluminosilicate (NAS) precipitation is listed in Table 1. The required mass of solid NaOH beads was dissolved in a known volume of deionized water in a 2 L stainless steel reactor, heated to 80 °C in a water bath and agitated at 300 rpm with a 7 cm diameter, six-bladed Rushton turbine. Sodium silicate and sodium aluminate solutions were then simultaneously added manually on a semibatch basis over a period of 15 min while a constant temperature was maintained.

The precipitation was allowed to proceed to completion over a further 15 min before the entire mixture was filtered hot under reduced pressure using a sintered glass filter. The resultant filter cake was resuspended in the reactor using 500 mL of deionized water (preadjusted to pH 9 using NaOH) before being refiltered. This washing/refiltering was repeated a total of five times. The washed filter cake was dried overnight in an oven at 50 °C, before being gently crushed and stored at 70% relative humidity in a desiccator (over saturated NaCl solution) for a period of 1 week. This was necessary to ensure constant water content within the pores of the precipitate over the course of the experiment, which could affect solubility measurements.

Table 1. Synthesis Recipe for NAS Precipitation

% dry solids	13
SiO_2/Al_2O_3 ratio	2
Na_2O/Al_2O_3 ratio	4
molecular weight	284
mass aluminate solution (g)	233.45
mass silicate solution (g)	183.10
mass NaOH pearls (g)	15.36
mass H_2O (g)	536.97
total mass	968.88

Analysis. A 15 mL aliquot of 3.02 M NaOH was measured and put into a polypropylene bottle, together with 1 g of the NAS precursor precipitate. A lid was placed upon the bottle that was sealed with Teflon tape, shaken vigorously, and placed in a water bath at 30 °C. Additional specimens were then made up using NaOH concentrations of 3.32 M, 3.89 M, and 4.39 M. The whole procedure was performed for temperatures of 30, 50, 65, and 80 °C for which samples were taken at 4, 3, 2, and 1 h, respectively. Each 0.5 g sample was filtered, using 0.1 μm pore size PVDF syringe filters to remove any suspended particles in the sample, and diluted with 25 g of deionized H_2O. Subsequent analysis of [Si] and [Al] in the samples was completed using inductively coupled plasma atomic emission spectroscopy (ICPAES).

Inductively coupled plasma (ICP) is an emission spectrometric technique in which a solution sample is introduced into hot argon plasma (at a temperature of approximately 8000 °C) as a fine mist. The interaction between the plasma and the sample results in stimulation of the elements in the sample to excited/ionized states. The atoms

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* To whom all correspondence should be addressed. E-mail: a.jones@ucl.ac.uk.

10.1021/je980164j CCC: $18.00

Table 2. Zeolite Precursor Solubility Data (This Work)[a]

t/°C	[NaOH]/(mol L^{-1})	[Al]/(10^{-3} mol L^{-1})	[Si]/(10^{-3} mol L^{-1})
80	3.02	28.95	38.60
80	3.32	33.32	45.18
80	3.89	41.14	57.14
80	4.39	22.03	29.56
65	3.02	41.43	56.67
65	3.32	35.07	46.38
65	3.89	47.06	67.53
65	4.39	32.87	45.28
50	3.02	38.70	52.53
50	3.32	42.59	59.73
50	3.89	50.78	70.84
50	4.39	43.30	60.08
30	3.02	34.50	46.53
30	3.32	41.46	56.45
30	3.89	49.82	67.25
30	4.39	54.34	74.28

[a] Composition: 0.93:1:2.32:5.15 Na_2O:Al_2O_3:H_2O.

reemit the exciting energy as light. Each element emits a characteristic spectrum of wavelengths. The intensity of light emitted at each wavelength varies with the concentration of the element. Measuring the intensities of the peaks in the emission spectrum of the sample allows determination of the concentration of elements present. This technique has a sensitivity of parts per million to parts per billion, a precision of 1−2% and an accuracy of about 5−10%. The values obtained from the spectroscopic analysis were corrected for the exact sample weights and diluent used.

A procedure similar to that for the precursor was employed to determine zeolite A solubility, using zeolite 4A powder from Crossfields Group Ltd., which had also been stored at 70% relative humidity for 1 week.

The exact composition of both solids (viz., amorphous and crystalline) was examined by a combination of total volatile matter (TVM) X-ray fluorescence analysis and X-ray diffraction (XRD). Furthermore, the exact water content by weight of samples of the two powders used was also examined via thermogravimetric analysis (TGA). This technique measures the amount and rate of change in the weight of a material as a function of temperature or time to determine composition, thermal stability, and related phenomena. TGAs using a Shimadzu TGA-50 instrument were undertaken upon both the amorphous phase and the zeolite A crystals to assess the water content of each powder (not shown). The equilibration at 70% relative humidity for 1 week was found to have been effective as both solids were found to lose approximately 17% weight upon heating to 222 °C, with the majority of the loss occurring around the boiling point of water. Consequently, differences in solubility evaluations caused by variations in water content within the pores of the solids could be assumed to be negligible.

Results and Discussion

Solubility results using ICPAES to analyze the liquid samples are shown in Tables 2 and 3 for NAS precursor and zeolite A, respectively, together with their compositions. Table 4 shows available literature data for the two solids for comparison. Figures 1 and 2 present the dissolved Si and Al concentrations for the series of caustic concentrations and range of temperatures studied for each phase.

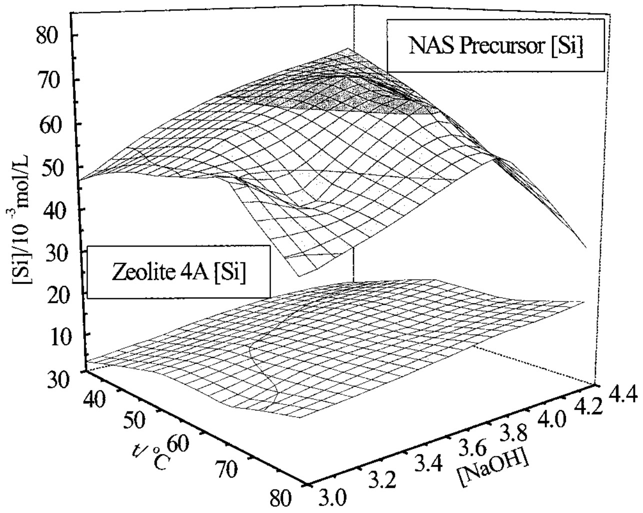

Figure 1. Si solubility as functions of temperature and [NaOH].

Table 3. Zeolite 4A Solubility Data (This Work)[a]

t/°C	[NaOH]/(mol L^{-1})	[Al]/(10^{-3} mol L^{-1})	[Si]/(10^{-3} mol L^{-1})
80	3.02	12.86	14.04
80	3.32	13.63	15.18
80	3.89	17.17	19.23
80	4.39	19.11	21.23
65	3.02	8.86	8.85
65	3.32	12.39	13.27
65	3.89	13.47	14.63
65	4.39	14.96	16.12
50	3.02	9.19	9.45
50	3.32	10.52	11.17
50	3.89	13.21	14.21
50	4.39	15.06	16.51
30	3.02	4.29	3.25
30	3.32	5.15	5.27
30	3.89	8.41	8.90
30	4.39	8.12	8.31

[a] Composition: 0.94:1:1.95:4.23 Na_2O:Al_2O_3:H_2O.

Table 4. Literature Data for Zeolite Solubility

t/°C	[NaOH]/(mol L^{-1})	[Al]/(10^{-3} mol L^{-1})	[Si]/(10^{-3} mol L^{-1})
Zeolite A Composition: 0.93:1:2.32:5.15 Na_2O:Al_2O_3:SiO_2:H_2O (Caullet et al., 1979)			
25	0.5	5.25	5.18
60	0.5	6.87	6.32
80	0.5	8.75	7.48
Zeolite A Composition: 3.8:1:2:311 Na_2O:Al_2O_3:SiO_2:H_2O (Cizmek et al., 1991)			
65	1	11.04	11.50
70	1	11.81	11.48
75	1	11.80	11.82
80	1	10.82	11.38
Zeolite A Composition: 6.6:1:2:314 Na_2O:Al_2O_3:SiO_2:H_2O (Cizmek et al., 1991)			
65	2	16.73	16.66
70	2	17.59	17.28
75	2	n/a	n/a
80	2	17.74	17.79

The precursor has much higher solubilities than the zeolite A crystals at similar conditions. The difference between the two phases ranges from the amorphous being 275% more soluble (at 80 °C and 3.02 M NaOH) to 900% more (at 30 °C and 4.39 M NaOH). The dissolved Si concentration is generally higher than the equivalent dissolved Al concentration. The difference between the two is greater for the precursor; up to 40% more silicon is dissolved than aluminum compared to 10% for the zeolite. This could be partly attributed to the approximately 16% higher Si content in the analyzed composition of the original amorphous solid compared to the zeolite A crystals.

Zeolite solubility increased with temperature (Table 3), except for a slight decrease from 50 °C to 65 °C at both the

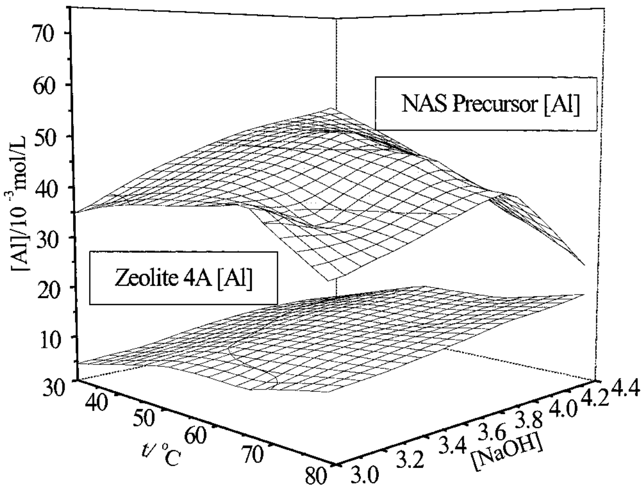

Figure 2. Al solubility as functions of temperature and [NaOH].

lowest and highest [NaOH]. Similarly, it increased with NaOH concentration, except for a small drop on going from 3.89 to 4.39 M NaOH at 30 °C.

Zeolite precursor solubility (Table 2) was much higher, as noted above. It also increased with increasing [NaOH] at 30 °C, but at the higher temperatures there was a considerable drop on going from 3.89 to 4.39 M NaOH (and a questionably lower value at 65 °C and 3.32 M NaOH). These changes of the solubility trend could reflect incomplete dissolution due to a shorter equilibrium time used at the higher temperature or to significant synthesis of the crystalline phase (or to both). Thus, these results provide tentative evidence of a possible dynamic equilibrium between the two phases.

Although a direct comparison cannot be made, due to the different conditions used, the solubility results compare favorably with values quoted in the literature. For example for zeolite A at 80 °C, results from this study of 21.23×10^{-3} mol/L at 4.39 M NaOH compare well with 11.50×10^{-3} mol/L at 1.00 M NaOH recorded by Cizmek et al. (1991)—particularly in view of the trends with caustic concentration already noted.

The greater scatter in the precursor results than in those for the zeolite could be attributed to the difficulties in equilibrating the solutions with a metastable phase that could easily transform into a mass of less soluble material. These results, however, proved to be a sufficiently accurate basis for the subsequent investigation into the zeolite synthesis mechanism (Ejaz, 1997).

Acknowledgment

The authors are indebted to Unilever Research Ltd. for permission to publish this work.

Literature Cited

Antonic, T.; Cizmek, A.; Subotic, B. Dissolution of amorphous aluminosilicate zeolite precursors in alkaline solutions. Part 1-Kinetics of the dissolution. *J. Chem. Soc., Faraday Trans.* **1993**, *89* (11), 1817−1822.

Antonic, T.; Cizmek, A.; Subotic, B. Dissolution of amorphous aluminosilicate zeolite precursors in alkaline solutions. Part 2-Mechanism of the dissolution. *J. Chem. Soc., Faraday Trans.* **1994**, *90* (13), 1973−1977.

Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982.

Caullet, P.; Guth, J. L.; Wey, R. Solubility of zeolites 4A and 13X in the aqueous basic solutions and thermodynamics of dissolution. *C. R. Seances Acad. Sci., Ser. D* **1979**, *288*, 1059−1062.

Cizmek, A.; Komunjer, L.; Subotic, B.; Siroki, M.; Roncevic, S. Kinetics of zeolite dissolution: Part 1. Dissolution of Zeolite A in hot Sodium Hydroxide. *Zeolites* **1991**, *11*, 258−264.

Dyer, A. *An Introduction to Zeolite Molecular Sieves*; J. Wiley: New York, 1988.

Ejaz, T. Hydrothermal precipitation of zeolite A crystals. Ph.D. Thesis, University of London, 1997.

Gasteiger, H.; Frederick, W. J.; Streisel, R. C. Solubility of aluminosilicates in alkaline solutions and a thermodynamic model. *Ind. Eng. Chem. Res.* **1992**, *31*, 1183−1190.

Received for review July 15, 1998. Accepted February 18, 1999. T.E. was supported by an EPSRC studentship.

JE980164J