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Thermokinetic investigation of methanesulfonyl chloride–water system

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Abstract

Thermal analysis of the methanesulfonyl chloride (MSC)–water system reacting under both homogeneous and heterogeneous conditions has been performed by means of adiabatic calorimetry. The enthalpy of solution of methanesulfonyl chloride in water at 298 K (-112 cal mol^{-1}) and the enthalpy of the hydrolysis reaction ($\Delta H = -40.8$ kcal mol^{-1}) have been experimentally evaluated. A mathematical model describing the reactive behavior of the MSC–water system under heterogeneous conditions has been developed. The model gives rational criteria for assessment of the safe operating conditions in industrial applications.

Keywords: Adiabatic calorimetry; Heterogeneous reaction kinetics; Hydrolysis; Methanesulfonyl chloride–water

1. Introduction

Alkanesulfonyl chloride–water systems play a prominent role in industrial chemical processes for the production of alkanesulfonic acids by hydrolysis. Many studies on the mechanism of hydrolysis of different alkanesulfonyl chlorides are reported in the literature [1–3] whereas no information is available on the thermochemistry of the hydrolysis reaction, the exothermicity of which could affect both production yields and safe operating conditions.

In the present paper the results of a thermokinetic investigation, exploiting adiabatic calorimetry, of the methanesulfonyl chloride (MSC)–water system at different initial

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temperatures and/or feed ratios are reported. Attention is specifically focused on the reaction process occurring under heterogeneous conditions, such as those adopted in industrial applications. A mathematical model describing the behavior of the system under varying process conditions is presented, thus providing quantitative criteria for the assessment of safe operating procedures.

2. Experimental

Thermal analyses of the reacting MSC–water system were performed in a Sikarex 3 calorimeter (from Systag) used in the adiabatic mode [4] and equipped with a modified stirred glass reactor ($V = 70$ ml), as described elsewhere [5].

MSC–water feed molar ratios from 0.0032:0.67 to 0.14:0.17 and initial reactor temperatures from 298 to 313 K were adopted for the experiments. Each experiment was performed by adding the selected amount of MSC to the water inside the reactor, once both reactants had reached the thermal equilibrium at the initial oven temperature.

The thermal capacity of the reaction vessel (Q_R) was determined by means of an adiabatic experiment in which a known amount of water at a fixed temperature is added to a known volume of water contained in the reactor at a different temperature. The observed adiabatic temperature change enabled Q_R (6.72 cal K^{-1}) to be calculated, as the only unknown quantity in the corresponding heat-balance equation.

Q_R determination enabled the specific heat of MSC (0.30 cal g^{-1} K^{-1}) to be evaluated by means of a similar experiment employing MSC instead of water.

The enthalpy of solution of MSC in water was determined by measuring the adiabatic temperature increase following the rapid mixing of known amounts of MSC and water previously kept at the same temperature ($T = 298$ K). Mixing time and adopted temperature were such that no significant chemical change occurred in the MSC–water mixture.

Attempts were made to measure the solubility of MSC in water directly, but this did not give satisfactory results; the times required to achieve phase separation after mixing of MSC and water were not sufficiently short to prevent significant MSC hydrolysis. The actual solubility of MSC is, therefore, included as an adjustable parameter in the mathematical model describing the MSC–H_2O system behavior under heterogeneous conditions.

3. Results and discussion

The adiabatic thermal evolution observed at different initial temperatures for heterogeneous 0.039:0.60 and 0.14:0.17 molar ratio mixtures of MSC and H_2O are shown in Figs. 1 and 2, respectively. The diagrams show that system reactivity is strongly affected by the initial temperature. A marked influence of the initial MSC–H_2O molar ratio upon system behavior is also observed (Fig. 3).

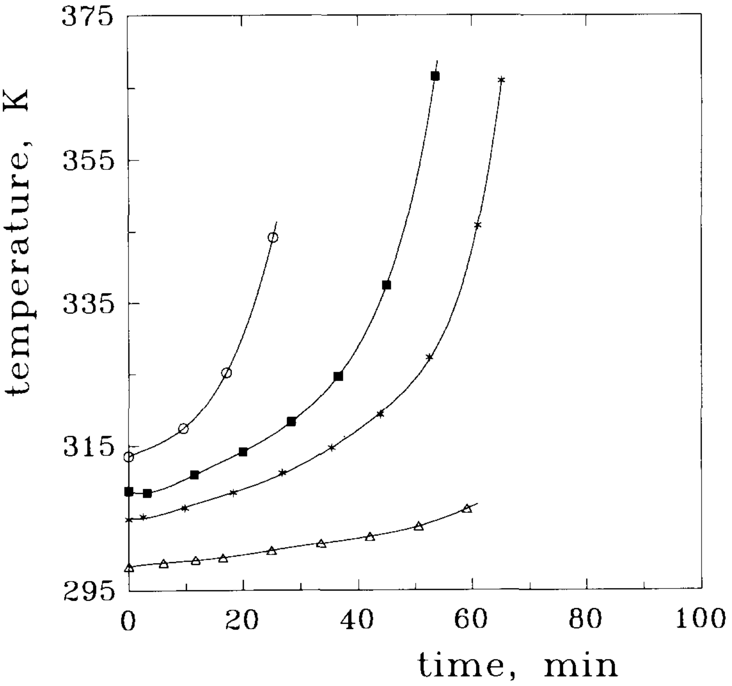

Fig. 1. Methanesulfonyl chloride–water system (at 0.039:0.60 molar ratio). Experimental and model results from Sikarex runs at different initial temperatures: ○, 313 K; ■, 308 K; *, 303K; Δ, 298 K.; —, model.

To develop a suitable mathematical model which simulates the behavior of the system reacting under heterogeneous conditions, knowledge of the reaction kinetics and of the mass-transfer phenomena involved was required.

First order reaction kinetics describing methanesulfonyl chloride hydrolysis:

$$CH_3SO_2Cl + H_2O \rightarrow CH_3SO_2OH + HCl$$

have already been reported [3]. The adequacy of these kinetic data ($k_0 = 5.6 \times 10^{12}$ min^{-1}, $E = 20.4$ kcal mol^{-1}) as modeling parameters of the adiabatic reaction process was checked by means of experiments performed under homogeneous conditions (Fig. 4) in which all the complications arising from mass-transfer phenomena were prevented.

The maximum temperature increases (ΔT_{ad}) recorded for each experiment, see Fig. 4, result from complete MSC conversion solely as a result of the hydrolysis reaction, as was confirmed by titrimetric analysis of the hydrogen ion content of the reacted mixtures. These results enabled the enthalpy of the reaction ($\Delta H = -40.8$ kcal mol^{-1}) to be evaluated according to the equation:

$$-\Delta H = \Delta T_{ad}(mC_p + Q_R)/n_S$$

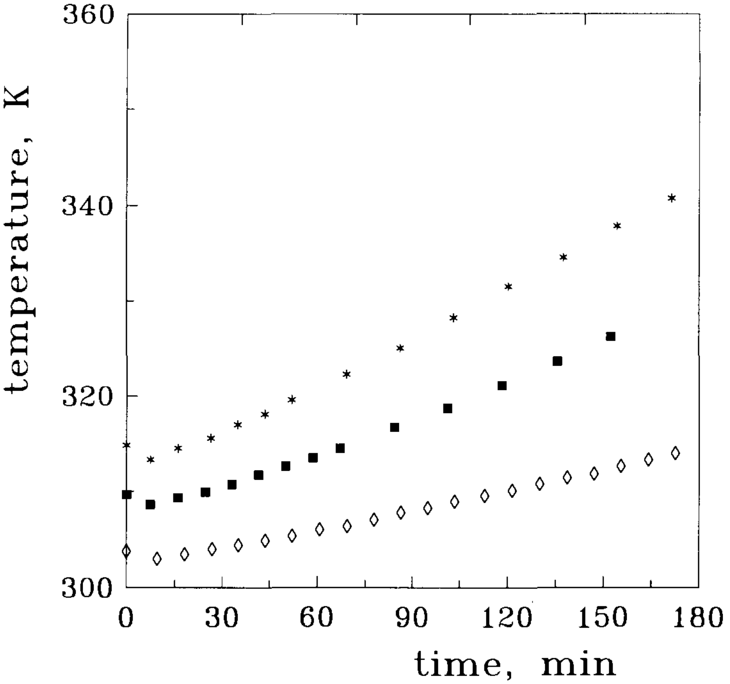

Fig. 2. Methanesulfonyl chloride–water system (at 0.14:0.17 molar ratio). Experimental results from Sikarex runs at different initial temperatures: ◇, 303 K; ■, 308 K; $*$, 313 K.

where n_S = moles of reacted MSC; m = mass of reacting mixture; and C_p = mean specific heat of reacting mixture.

The adoption of the kinetic data and of the experimentally evaluated reaction enthalpy led to satisfactory modeling of the homogeneous reaction process.

The evolution of heat was simulated by integration of the equations

$$\mathrm{d}T/\mathrm{d}t = V(mC_p + Q_R)^{-1}(-\mathrm{d}C_{\mathrm{MSC}}/\mathrm{d}t)(-\Delta H)$$

$$-\mathrm{d}C_{\mathrm{MSC}}/\mathrm{d}t = k_0 \mathrm{e}^{-E/RT} C_{\mathrm{MSC}}$$

is shown in Fig. 4 ($C^0_{\mathrm{MSC}} = 0.27$ and 0.39 M) by the solid lines; good correspondence was observed between experimental and calculated data.

Once the validity of the kinetic parameters had been ascertained, the mathematical modeling of the behavior of the heterogeneous MSC–water mixtures was performed according to the heat release rate equation:

$$(mc_p + Q_R)\,\mathrm{d}T/\mathrm{d}t = -\Delta H k_0 \mathrm{e}^{-E/RT} C^*_{\mathrm{MSC}} V$$

by assuming that methanesulfonyl chloride hydrolysis occurs only in the aqueous phase and that the reaction rate is adequately low to ensure the maintenance of the

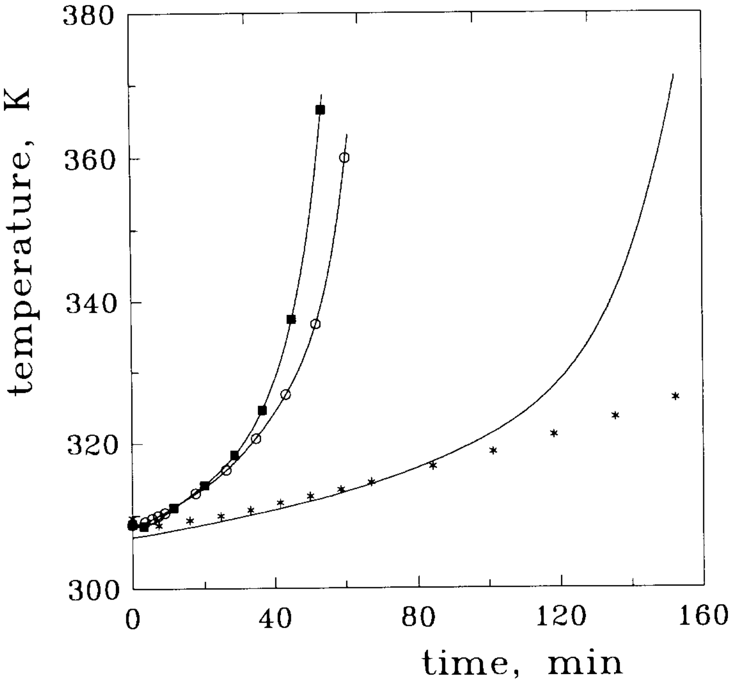

Fig. 3. Methanesulfonyl chloride–water system. Experimental and model results from Sikarex runs (at 309 K initial temperature) at different molar ratios: ■, MSC–water molar ratio = 0.039:0.60; ○, MSC–water molar ratio = 0.062:0.56; *, MSC–water molar ratio = 0.14:0.17; —, model.

sulfonyl chloride concentration (C^*_{MSC}) in the aqueous phase volume (V) at its saturation value during the entire reaction process, as pointed out by the comparison between characteristic diffusion times reported for the industrial heterogeneous reactors [6] and reaction times. The small value of the enthalpy of solution of methanesulfonyl chloride in water (-112 cal mol^{-1})—as experimentally evaluated—enables the assumption for modeling purposes of constant reactant solubility in water at varying reaction temperatures.

The actual MSC solubility value ($C^*_{MSC} = 0.5$ mol l^{-1}) was determined by means of a computerized best fitting procedure exploiting data from experimental runs.

Satisfactory modeling is achieved for all the experiments reported in Figs. 1 and 3 with the exclusion of the runs with feed molar ratio MSC–H_2O = 0.14:0.17, the evolution of heat from which at different initial temperatures is reported in Fig. 2. The observed discrepancy between model and experiments with relatively small amounts of water is likely to be because of the high concentrations of hydrogen ion produced in the system which has been reported to affect the reaction kinetics negatively [1].

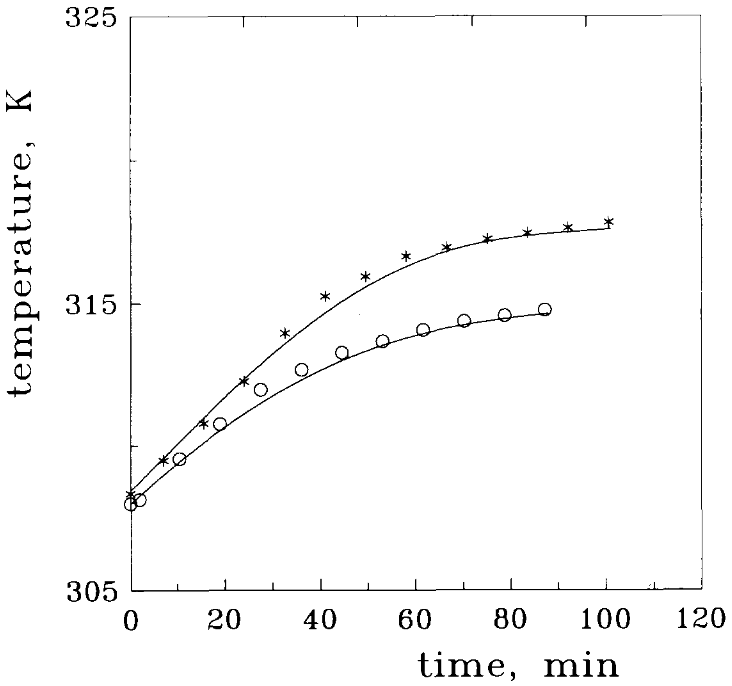

Fig. 4. Methanesulfonyl chloride-water homogeneous system. Experimental and model results from Sikarex runs (at 308 K initial temperature) at different initial MSC concentration: ○, $C^0_{MSC} = 0.27$ M; *, $C^0_{MSC} = 0.39$ M; —, model.

4. Conclusion

The enthalpies of the MSC hydrolysis and solution in water, and the MSC specific heat, have been evaluated on the basis of appropriate calorimetric measurements.

The thermokinetic analysis of the MSC-water system by adiabatic calorimetry enables the initial reactants feed ratios and temperature to be considered as the process parameters mainly affecting system reactivity.

A mathematical model of the MSC-water system reacting under heterogeneous conditions has been developed.

Comparison between simulated and experimental behavior gave evidence of the applicability of the elaborated model for heterogeneous mixtures provided the initial MSC-water molar ratio was such as to make the kinetic influence of hydrogen ions negligible.

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