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CONFIDENTIAL

GENERAL FITS OF RATE CONSTANTS

FOR MUF RESINS

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Within DSM the chemistry of M(U)F resins has been studied extensively. Numerous experiments have been performed; each one at a constant temperature and at a constant pH. The experiments consist of four different types: melamine homocondensation by NMR and HPLC; urea homocondensation by NMR and cocondensation by HPLC. For each one of these different type of experiments we have concentration prophiles for different pH and temperature levels. The objective of this research is to use this data to perform a general fit of the kinetic rate constants of the reactions occurring in the experiments.

A set of differential equations has been derived in [3]. A first step in this research was a study of this set of equations. We had to make sure that the equations were correct since errors in these equations can have a very large (erroneous) effect on the fitting of the rate constants. Several corrections to the equations have been made and the latest version is included in this report.

The second step of the research involved a careful study of the experiments at $85°$ and pH 9. This particular temperature and pH level was chosen since it is the only one where we have experiments of all four types. This stage of the research was used to determine which rate constants we are able to identify from the data. Several rate constants could not be identified from the data. Either because there is insufficient data or because the reactions associated with these constants were not prominent enough in the performed experiments.

The third stage of the research was the actual estimation of the rate constants and their associated pH and temperature dependence. This was done first for the rate constants associated to the MF and UF homocondensation. These results were then used to obtain estimates of the rate constants for the HPLC cocondensation.

Besides a description of the above research this report will also include a conclusion where we try to give a final evaluation of the project.

1 Description of the model

The model we are using is a dynamic model describing the time-evolution of the concentration of 53 species. We will use y_i to denote the concentration of species number i. The following list shows the connection between the y_i and the different species. It also indicates whether the concentration of the specific species has been measured. Concentrations that have not been measured can be obtained directly from the model.

Table 1: List of species

Variable	Species	Measured by
y_1	[l]	HPLC
y_2	[lo]	HPLC
y_3	[structure]	HPLC
y_4	[structure]	HPLC
y_5	[structure]	HPLC
y_6	[structure]	HPLC
y_7	[lol]	HPLC
y_8	[lolo$_1$M]	HPLC
y_9	[lool]	HPLC
y_{10}	[loolo$_1$M]	HPLC
y_{11}	[lox]	HPLC
y_{12}	[loxo$_1$M]	HPLC
y_{13}	[loox]	HPLC
y_{14}	[looxo$_1$M]	HPLC
y_{15}	[x]	HPLC
y_{16}	[xo]	HPLC
y_{17}	[o]	NMR
y_{18}	[MNHCH$_2$OH]	NMR
y_{19}	[MN(CH$_2$OH)$_2$]	NMR
y_{20}	[MNH$_2$]	NMR
y_{21}	[MNH − CH$_2$ − NHM]	NMR
y_{22}	[MN(CH$_2$OH) − CH$_2$ − NHM]	NMR
y_{23}	[MNH − CH$_2$OCH$_2$ − NHM]	NMR
y_{24}	[MN(CH$_2$OH) − CH$_2$OCH$_2$ − NHM]	NMR
y_{25}	[UNH$_2$]	NMR
y_{26}	[UNHCH$_2$OH]	NMR
y_{27}	[UN(CH$_2$OH)$_2$]	NMR
y_{28}	[UNH − CH$_2$ − NHU]	NMR
y_{29}	[UN(CH$_2$OH) − CH$_2$ − NHU]	NMR
y_{30}	[UNH − CH$_2$OCH$_2$ − NHU]	NMR

Table 1: List of species

Variable	Species	Measured by
y_{31}	[UN(CH$_2$OH) $-$ CH$_2$OCH$_2$ $-$ NHU]	NMR
y_{32}	[lolo$_2$M]	
y_{33}	[structure]	
y_{34}	[structure]	
y_{35}	[structure]	
y_{36}	[structure]	
y_{37}	[loolo$_2$M]	
y_{38}	[loxo$_1$U]	
y_{39}	[loxo$_2$M]	
y_{40}	[loxo$_2$U]	
y_{41}	[looxo$_1$U]	
y_{42}	[looxo$_2$M]	
y_{43}	[looxo$_2$U]	
y_{44}	[lolo$_1$Mo$_2$M]	
y_{45}	[lolo$_1$Mo$_2$, M]	
y_{46}	[lol(o$_1$M)$_2$]	
y_{47}	[loolo$_1$Mo$_2$M]	
y_{48}	[loolo$_1$Mo$_2$, M]	
y_{49}	[lool(o$_1$M)$_2$]	
y_{50}	[all primary melamine NH]	
y_{51}	[all secondary melamine NH]	
y_{52}	[all primary urea NH]	
y_{53}	[all secondary urea NH]	

For species y_1 till y_{31} we have measurements. For species y_{32} till y_{49} we can obtain values from the algebraic equations described below. For species y_{50} till y_{53} we have a priori estimates:

$$[\text{all primary melamine NH}] = 2 * (3.9 \pm 0.4)$$
$$[\text{all secondary melamine NH}] = 2 * (3.8 \pm 0.2)$$
$$[\text{all primary urea NH}] = 2 * (2[x] + 1.11[xo])$$
$$[\text{all secondary urea NH}] = 2.67[xo]$$

3

The dynamical process is described by the following 8 differential equations:

$$\frac{d[\text{lol}]}{dt} = 6k_{\text{M,MB}}[\text{l}][\text{lo}] - 28k_{\text{M,-MB}}[\text{lol}]$$

$$- 8k_{\text{M,1}}[\text{lol}][\text{o}] + 28k_{\text{M,-1}}[\text{lolo}_1\text{M}]$$

$$- 2k_{\text{M,2}}[\text{lol}][\text{o}] + 28k_{\text{M,-2}}[\text{lolo}_2\text{M}]$$

$$- 8k_{\text{M,MB}}[\text{lol}][\text{all melamine primary methylols}] - 8 * 2.67 * k_{\text{co2,MB}}[\text{lol}][\text{xo}]$$

$$- 8ak_{\text{M,MB}}[\text{lol}][\text{all melamine secondary methylols}]$$

$$- 8 * 0.11 * bk_{\text{co2,MB}}[\text{lol}][\text{xo}]$$

$$- 2k_{\text{M,MB*}}[\text{lol}][\text{all melamine primary methylols}]$$

$$- 2 * 2.67 * k_{\text{co2,MB*}}[\text{lol}][\text{xo}] \qquad \text{(DV1)}$$

$$\frac{d[\text{lool}]}{dt} = k_{\text{M,EB}}[\text{lo}]^2 - 28k_{\text{M,-EB}}[\text{lool}]$$

$$- 8k_{\text{M,1}}[\text{lool}][\text{o}] + 28k_{\text{M,-1}}[\text{loolo}_1\text{M}]$$

$$- 2k_{\text{M,2}}[\text{lool}][\text{o}] + 28k_{\text{M,-2}}[\text{loolo}_2\text{M}]$$

$$- 8k_{\text{M,MB}}[\text{lool}][\text{all melamine primary methylols}]$$

$$- 8 * 2.67 * k_{\text{co2,MB}}[\text{lool}][\text{xo}]$$

$$- 8ak_{\text{M,MB}}[\text{lool}][\text{all melamine secondary methylols}]$$

$$- 8 * 0.11 * bk_{\text{co2,MB}}[\text{lool}][\text{xo}]$$

$$- 2k_{\text{M,MB*}}[\text{lool}][\text{all melamine primary methylols}]$$

$$- 2 * 2.67 * k_{\text{co2,MB*}}[\text{lool}][\text{xo}] \qquad \text{(DV2)}$$

$$\frac{d[\text{UNH} - \text{CH}_2 - \text{NHU}]}{dt} =$$

$$2k_{\text{U,MB}}[\text{UNH}_2][\text{UNHCH}_2\text{OH}] - 28k_{\text{U,-MB}}[\text{UNH} - \text{CH}_2 - \text{NHU}]$$

$$- 2k_{\text{U,2}}[\text{UNH} - \text{CH}_2 - \text{NHU}][\text{o}] + 28k_{\text{U,-2}}[\text{UN(CH}_2\text{OH)} - \text{CH}_2 - \text{NHU}]$$

$$- 2k_{\text{U,MB*}}[\text{UNH} - \text{CH}_2 - \text{NHU}][\text{UNHCH}_2\text{OH}] \qquad \text{(DV3)}$$

$$\frac{d[\text{UNH} - \text{CH}_2\text{OCH}_2 - \text{NHU}]}{dt} =$$

$$k_{\text{U,EB}}[\text{UNHCH}_2\text{OH}]^2 - 28k_{\text{U,-EB}}[\text{UNH} - \text{CH}_2\text{OCH}_2 - \text{NHU}]$$

$$- 2k_{\text{U,2}}[\text{UNH} - \text{CH}_2\text{OCH}_2 - \text{NHU}][\text{o}]$$

$$+ 28k_{\text{U,-2}}[\text{UN(CH}_2\text{OH)} - \text{CH}_2\text{OCH}_2 - \text{NHU}]$$

$$- 2k_{\text{U,MB*}}[\text{UNH} - \text{CH}_2\text{OCH}_2 - \text{NHU}][\text{UNHCH}_2\text{OH}] \qquad \text{(DV4)}$$

4

$$\frac{d[\text{lox}]}{dt} = 4k_{\text{co1,MB}}[\text{x}][\text{lo}] + 6k_{\text{co2,MB}}[\text{xo}][\text{l}]$$

$$- 28(k_{\text{co1,-MB}} + k_{\text{co2,-MB}})[\text{lox}]$$

$$- 4k_{\text{M,1}}[\text{lox}][\text{o}] + 28k_{\text{M,-1}}[\text{loxo}_1\text{M}]$$

$$- 2k_{\text{U,1}}[\text{lox}][\text{o}] + 28k_{\text{U,-1}}[\text{loxo}_1\text{U}]$$

$$- k_{\text{M,2}}[\text{lox}][\text{o}] + 28k_{\text{M,-2}}[\text{loxo}_2\text{M}]$$

$$- k_{\text{U,2}}[\text{lox}][\text{o}] + 28k_{\text{U,-2}}[\text{loxo}_2\text{U}]$$

$$- 4k_{\text{M,MB}}[\text{lox}][\text{all melamine primary methylols}]$$

$$- 2 * 2.67k_{\text{U,MB}}[\text{lox}][\text{xo}] - 4 * 2.67k_{\text{co2,MB}}[\text{lox}][\text{xo}]$$

$$- 2k_{\text{co1,MB}}[\text{lox}][\text{all melamine primary methylols}]$$

$$- 2ak_{\text{co1,MB}}[\text{lox}][\text{all melamine secondary methylols}]$$

$$- 4 * 0.11bk_{\text{co2,MB}}[\text{lox}][\text{xo}]$$

$$- 2 * 0.11bk_{\text{U,MB}}[\text{lox}][\text{xo}]$$

$$- 4ak_{\text{M,MB}}[\text{lox}][\text{all melamine secondary methylols}]$$

$$- k_{\text{co1,MB*}}[\text{lox}][\text{all melamine primary methylols}]$$

$$- 2.67k_{\text{co2,MB}} * [\text{lox}][\text{xo}]$$

$$- k_{\text{M,MB*}}[\text{lox}][\text{all melamine primary methylols}]$$

$$- 2.67k_{\text{U,MB*}}[\text{lox}][\text{xo}] \tag{DV5}$$
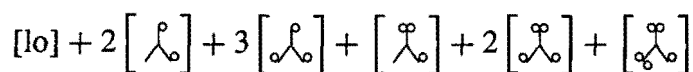
$$\frac{d[\text{loox}]}{dt} = k_{\text{co,EB}}[\text{lo}][\text{xo}] - 28k_{\text{co,-EB}}[\text{loox}]$$

$$- 4k_{\text{M,1}}[\text{loox}][\text{o}] + 28k_{\text{M,-1}}[\text{looxo}_1\text{M}]$$

$$- 2k_{\text{U,1}}[\text{loox}][\text{o}] + 28k_{\text{U,-1}}[\text{looxo}_1\text{U}]$$

$$- k_{\text{M,2}}[\text{loox}][\text{o}] + 28k_{\text{M,-2}}[\text{looxo}_2\text{M}]$$

$$- k_{\text{U,2}}[\text{loox}][\text{o}] + 28k_{\text{U,-2}}[\text{looxo}_2\text{U}]$$

$$- 4k_{\text{M,MB}}[\text{loox}][\text{all melamine primary methylols}]$$

$$- 2 * 2.67k_{\text{U,MB}}[\text{loox}][\text{xo}] - 4 * 2.67k_{\text{co2,MB}}[\text{loox}][\text{xo}]$$

$$- 2k_{\text{co1,MB}}[\text{loox}][\text{all melamine primary methylols}]$$

$$- 2ak_{\text{co1,MB}}[\text{loox}][\text{all melamine secondary methylols}]$$

$$- 4 * 0.11bk_{\text{co2,MB}}[\text{loox}][\text{xo}]$$

$$- 2 * 0.11bk_{\text{U,MB}}[\text{loox}][\text{xo}]$$

$$- 4ak_{\text{M,MB}}[\text{loox}][\text{all melamine secondary methylols}]$$

$$- k_{\text{co1,MB*}}[\text{loox}][\text{all melamine primary methylols}]$$

$$- 2.67k_{\text{co2,MB*}}[\text{loox}][\text{xo}]$$

$$- k_{\text{M,MB*}}[\text{loox}][\text{all melamine primary methylols}]$$

$$- 2.67k_{\text{U,MB*}}[\text{loox}][\text{xo}] \tag{DV6}$$

$$\frac{d[\text{MNH} - \text{CH}_2 - \text{NHM}]}{dt} =$$

$$2k_{\text{M,MB}}[\text{MNH}_2][\text{MNHCH}_2\text{OH}] - 28k_{\text{M,-MB}}[\text{MNH} - \text{CH}_2 - \text{NHM}]$$

$$- 2k_{\text{M,2}}[\text{MNH} - \text{CH}_2 - \text{NHM}][\text{o}] + 28k_{\text{M,-2}}[\text{MN(CH}_2\text{OH)} - \text{CH}_2 - \text{NHM}]$$

$$. - 2k_{\text{M,MB*}}[\text{MNH} - \text{CH}_2 - \text{NHM}][\text{MNHCH}_2\text{OH}] \tag{DV7}$$

$$\frac{d[\text{MNH} - \text{CH}_2\text{OCH}_2 - \text{NHM}]}{dt} =$$

$$k_{\text{M,EB}}[\text{MNHCH}_2\text{OH}]^2 - 28k_{\text{M,-EB}}[\text{MNH} - \text{CH}_2\text{OCH}_2 - \text{NHM}]$$

$$- 2k_{\text{M,2}}[\text{MNH} - \text{CH}_2\text{OCH}_2 - \text{NHM}][\text{o}]$$

$$+ 28k_{\text{M,-2}}[\text{MN(CH}_2\text{OH)} - \text{CH}_2\text{OCH}_2 - \text{NHM}]$$

$$- 2k_{\text{M,MB*}}[\text{MNH} - \text{CH}_2\text{OCH}_2 - \text{NHM}][\text{MNHCH}_2\text{OH}] \tag{DV8}$$

In the above equations "all melamine primary methylols" stands for

$$[\text{lo}] + 2\left[\begin{array}{c}\text{loox}\end{array}\right] + 3\left[\begin{array}{c}\text{loox}\end{array}\right] + \left[\begin{array}{c}\text{loox}\end{array}\right] + 2\left[\begin{array}{c}\text{loox}\end{array}\right] + \left[\begin{array}{c}\text{loox}\end{array}\right]$$

and "all melamine secondary methylols" stands for

$$2\left[\,\cdot\,\right] + 2\left[\,\cdot\,\right] + 4\left[\,\cdot\,\right] + 2\left[\,\cdot\,\right] + 4\left[\,\cdot\,\right] + 6\left[\,\cdot\,\right]$$
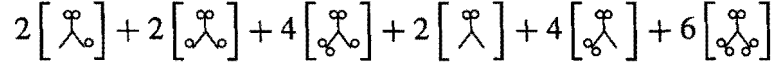
Besides the above 8 differential equations there are 39 algebraic equations

$$28 k_{M,-1}[\text{lo}] = 6 k_{M,1}[\text{l}][\text{o}] \tag{A1}$$

$$28 k_{M,-1}\left[\,\cdot\,\right] = 2 k_{M,1}[\text{lo}][\text{o}] \tag{A2}$$

$$3 * 28 k_{M,-1}\left[\,\cdot\,\right] = 2 k_{M,1}\left[\,\cdot\,\right][\text{o}] \tag{A3}$$

$$2 * 28 k_{M,-2}\left[\,\cdot\,\right] = k_{M,2}[\text{lo}][\text{o}] \tag{A4}$$

$$28 k_{M,-2}\left[\,\cdot\,\right] = k_{M,2}\left[\,\cdot\,\right][\text{o}] \tag{A5}$$

$$2 * 28 k_{M,-2}\left[\,\cdot\,\right] = 3 k_{M,2}\left[\,\cdot\,\right][\text{o}] \tag{A6}$$

$$4 * 28 k_{M,-2}\left[\,\cdot\,\right] = k_{M,2}\left[\,\cdot\,\right][\text{o}] \tag{A7}$$

$$2 * 28 k_{M,-2}\left[\,\cdot\,\right] = k_{M,2}\left[\,\cdot\,\right][\text{o}] \tag{A8}$$

$$6 * 28 k_{M,-2}\left[\,\cdot\,\right] = k_{M,2}\left[\,\cdot\,\right][\text{o}] \tag{A9}$$

$$4 * 28 k_{M,-1}\left[\,\cdot\,\right] = k_{M,1}\left[\,\cdot\,\right][\text{o}] \tag{A10}$$

$$2 * 28 k_{M,-1}\left[\,\cdot\,\right] = k_{M,1}\left[\,\cdot\,\right][\text{o}] \tag{A11}$$

7

$$28k_{M,-1}\left[\underset{o}{\overset{\infty}{\lambda}}\right] = k_{M,1}\left[\overset{\infty}{\lambda}\right][o] \tag{A12}$$

$$28k_{M,-1}[\text{lolo}_1\text{M}] = 8k_{M,1}[\text{lol}][o] \tag{A13}$$

$$28k_{M,-2}[\text{lolo}_2\text{M}] = 2k_{M,2}[\text{lol}][o] \tag{A14}$$

$$28k_{M,-1}[\text{loolo}_1\text{M}] = 8k_{M,1}[\text{lool}][o] \tag{A15}$$

$$28k_{M,-2}[\text{loolo}_2\text{M}] = 2k_{M,2}[\text{lool}][o] \tag{A16}$$

$$28k_{U,-1}[\text{UNHCH}_2\text{OH}] = 2k_{U,1}[\text{UNH}_2][o] \tag{A17}$$

$$2 * 28k_{U,-2}[\text{UN(CH}_2\text{OH)}_2] = k_{U,2}[\text{UNHCH}_2\text{OH}][o] \tag{A18}$$

$$28k_{U,-2}[\text{UN(CH}_2\text{OH)} - \text{CH}_2 - \text{NHU}] = 2k_{U,2}[\text{UNH} - \text{CH}_2 - \text{NHU}][o] \tag{A19}$$

$$28k_{U,-2}[\text{UN(CH}_2\text{OH)} - \text{CH}_2\text{OCH}_2 - \text{NHU}] = 2k_{U,2}[\text{UNH} - \text{CH}_2\text{OCH}_2 - \text{NHU}][o] \tag{A20}$$

$$28k_{M,-1}[\text{loxo}_1\text{M}] = 4k_{M,1}[\text{lox}][o] \tag{A21}$$

$$28k_{U,-1}[\text{loxo}_1\text{U}] = 2k_{U,1}[\text{lox}][o] \tag{A22}$$

$$28k_{M,-2}[\text{loxo}_2\text{M}] = k_{M,2}[\text{lox}][o] \tag{A23}$$

$$28k_{U,-2}[\text{loxo}_2\text{U}] = k_{U,2}[\text{lox}][o] \tag{A24}$$

$$28k_{M,-1}[\text{looxo}_1\text{M}] = 4k_{M,1}[\text{loox}][o] \tag{A25}$$

$$28k_{U,-1}[\text{looxo}_1\text{U}] = 2k_{U,1}[\text{loox}][o] \tag{A26}$$

$$28k_{M,-2}[\text{looxo}_2\text{M}] = k_{M,2}[\text{loox}][o] \tag{A27}$$

$$28k_{U,-2}[\text{looxo}_2\text{U}] = k_{U,2}[\text{loox}][o] \tag{A28}$$

$$28k_{M,-1}[\text{MNHCH}_2\text{OH}] = 2k_{M,1}[\text{MNH}_2][o] \qquad\qquad (A29)$$

$$2 * 28k_{M,-2}[\text{MN(CH}_2\text{OH)}_2] = k_{M,2}[\text{MNHCH}_2\text{OH}][o] \qquad\qquad (A30)$$

$$28k_{M,-2}[\text{MN(CH}_2\text{OH)} - \text{CH}_2 - \text{NHM}] = 2k_{M,2}[\text{MNH} - \text{CH}_2 - \text{NHM}][o] \qquad (A31)$$

$$28k_{M,-2}[\text{MN(CH}_2\text{OH)} - \text{CH}_2\text{OCH}_2 - \text{NHM}] = 2k_{M,2}[\text{MNH} - \text{CH}_2\text{OCH}_2 - \text{NHM}][o] \quad (A32)$$

$$2 * 28k_{M,-1}[\text{lol(o}_1\text{M)}_2] = 6 * k_{M,1}[\text{lolo}_1\text{M}][o] \qquad\qquad (A33)$$

$$28k_{M,-2}[\text{lolo}_1\text{Mo}_2\text{M}] = 2 * k_{M,2}[\text{lolo}_1\text{M}][o] \qquad\qquad (A34)$$

$$2 * 28k_{M,-2}[\text{lolo}_1\text{Mo}_2, \text{M}] = k_{M,2}[\text{lolo}_1\text{M}][o] \qquad\qquad (A35)$$

$$2 * 28k_{M,-1}[\text{lool(o}_1\text{M)}_2] = 6 * k_{M,1}[\text{loolo}_1\text{M}][o] \qquad\qquad (A36)$$

$$28k_{M,-2}[\text{loolo}_1\text{Mo}_2\text{M}] = 2 * k_{M,2}[\text{loolo}_1\text{M}][o] \qquad\qquad (A37)$$

$$2 * 28k_{M,-2}[\text{loolo}_1\text{Mo}_2, \text{M}] = k_{M,2}[\text{loolo}_1\text{M}][o] \qquad\qquad (A38)$$

$$14k_{U,-1}[\text{xo}] = 2k_{U,1}[\text{x}][o] \qquad\qquad (A39)$$

In the above equations, the following rate constants play a role (for the definition of the rate constants see [3]).

Table 2: Kinetic rate constants

Variable	Rate constants	Variable	Rate constants
a_1	$k_{M,MB}$	a_{16}	$k_{U,-MB}$
a_2	$k_{M,-MB}$	a_{17}	$k_{U,2}$
a_3	$k_{M,1}$	a_{18}	$k_{U,-2}$
a_4	$k_{M,-1}$	a_{19}	$k_{U,MB*}$
a_5	$k_{co2,MB}$	a_{20}	$k_{co1,MB*}$
a_6	$k_{co2,-MB}$	a_{21}	$k_{U,EB}$

Table 2: Kinetic rate constants

Variable	Rate constants	Variable	Rate constants
a_7	$k_{M,2}$	a_{22}	$k_{U,-EB}$
a_8	$k_{M,-2}$	a_{23}	$k_{col,MB}$
a_9	a	a_{24}	$k_{col,-MB}$
a_{10}	b	a_{25}	$k_{U,l}$
a_{11}	$k_{M,MB*}$	a_{26}	$k_{U,-l}$
a_{12}	$k_{co2,MB*}$	a_{27}	$k_{co,EB}$
a_{13}	$k_{M,EB}$	a_{28}	$k_{co,-EB}$
a_{14}	$k_{M,-EB}$	a_{29}	e
a_{15}	$k_{U,MB}$	a_{30}	f

All of the above constants of course depend on the temperature and pH. The temperature dependence is described by the Arrhenius law:

$$a_i = A_i e^{\left(\frac{-E_i}{RT}\right)}$$

where T is the temperature and R is the universal gas constant. The characteristic of the pH dependence is not explicitly described but is expected to be of either one of the following forms:
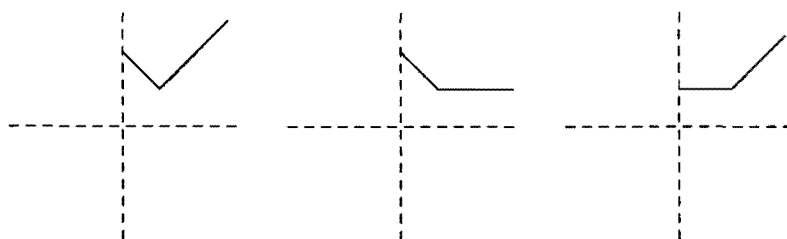
For constants a_9, a_{10}, a_{29} and a_{30} the Arrhenius law is still valid. On the other hand they depend differently on pH. This because they are quotients of rate constants.

1.1 Integration versus estimating the derivative

Given such a set of algebraic and differential equations, the traditional method is to compute the concentrations at time t_1 given the concentrations at time t_0. Then compare the computed concentrations with the measured concentrations and choose the parameters such that the computed concentrations are close to the measured concentrations. This method fails for the problem described above, because, given the concentrations at time t_0 and the values of the parameters, we can not compute the concentrations of the species at time t_1.

This problem occurs because of the way the model is constructed. In [3] a so-called *kinetically closed system* has been derived for the target molecules. This means that we take all reactions

into account with which a target molecule is created or removed. However, we do not derive **all** the equations for reactions how secondary molecules are created or removed. Therefore we can not predict the concentrations of these products in the future.

There is an obvious second method to approach this problem. We use the measurements at t_0, t_1, . . . to compute the derivative numerically in the obvious way. The problem is that the latter can be quite inaccurate if the time at which the different measurements are made are far away or if the signal varies strongly in time. In this problem we have only very sporadic measurements and hence this is a potential problem. It also complicates considerably any attempt to obtain error bounds for the estimates of the rate constants.

1.2 Algebraic versus differential equations

It is important to note that, although there are many algebraic equations, only 8 different rate constants occur in the algebraic equations. Even stronger, only the following four quotients play a role:

$$\frac{a_3}{a_4}, \qquad \frac{a_7}{a_8}, \qquad \frac{a_{17}}{a_{18}}, \qquad \frac{a_{25}}{a_{26}}$$

Moreover, there are good a priori estimates available for these four quotients:

$$\frac{a_3}{a_4} \approx 170, \qquad \frac{a_7}{a_8} \approx 100, \qquad \frac{a_{17}}{a_{18}} \approx 52, \qquad \frac{a_{25}}{a_{26}} \approx 390$$

These estimates can and will be used for all temperature and pH levels.

This implies that all further estimations are only concerned with the 8 differential equations. The algebraic equations have only been used to determine the concentrations $y_{32}, \ldots , y_{49}$.

1.3 Identifiability

We note that it is impossible to estimate $k_{co2,-MB}$ and $k_{co1,-MB}$ independently. They only occur together in DV5. Hence we can only estimate the sum of these two parameters.

2 Estimation for $85°$ and $pH\,9$

A first test at this temperature immediately reveals that $a_9, a_{10}, a_{11}, a_{12}, a_{19}, a_{20}, a_{25}, a_{29}, a_{30}$ can not be estimated from the data since changes in their value affect our fit more that a 1000 times less than any of the other variables. Hence we fix these parameters, as suggested by J.J. Nusselder (fax of April 3 and E-mail of January 31). His suggestion is based on the assumption that the rate of secondary bridge formation is slower or at the most equal to the rate of primary bridge formation. The probability that a secondary bridged trimer is formed is thus much less compared to the formation of primary bridged trimers. The data sets to be fitted include no information on any kind of trimers and is not extended enough to fit all 30 constants. Secondary

bridge formation is not taken into account to force progress in the parameter estimation and given the above consideration. Thereto:

$$a_9 = 0$$
$$a_{10} = 0$$
$$a_{11} = 0$$
$$a_{12} = 0$$
$$a_{19} = 0$$
$$a_{20} = 0$$
$$a_{25} = 5.9 * 10^{-4} * \exp\left(-6495 * \left(\tfrac{1}{273+T} - \tfrac{1}{358}\right)\right) \qquad \text{(see [1])}$$
$$a_{29} = 0$$
$$a_{30} = 0$$

where $\exp(1) = 2.7183\ldots$.

We first attempted the parameter estimation using weighting (a discussion what we mean by weighting is given in subsection 2.5). If we look carefully at the estimates for the different parameters and their sensitivity (low value: accurate estimation; high value: estimation difficult) we find:

Table 3: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_1	$k_{M,MB}$	7.3260e-10	2.8610e-05	
a_2	$k_{M,-MB}$	9.5133e-11	0.9248	
a_3	$k_{M,1}$	1.5427e-07	0.2705	
a_4	$k_{M,-1}$	9.0745e-10	0.0016	
a_5	$k_{co2,MB}$	2.3700e-09	0.0455	
a_6	$k_{co2,-MB}$	2.4751e-09	0.4894	
a_7	$k_{M,2}$	4.2395e-08	0.5810	
a_8	$k_{M,-2}$	4.2395e-10	0.0058	
a_9	a	0		Fixed
a_{10}	b	0		Fixed
a_{11}	$k_{M,MB*}$	0		Fixed
a_{12}	$k_{co2,MB*}$	0		Fixed
a_{13}	$k_{M,EB}$	1.8081e-06	4.7684e-05	
a_{14}	$k_{M,-EB}$	1.2982e-06	9.5367e-05	
a_{15}	$k_{U,MB}$	2.0940e-07	7.6294e-05	
a_{16}	$k_{U,-MB}$	3.1341e-09	0.1242	
a_{17}	$k_{U,2}$	8.2509e-04	2.7657e-04	

Table 3: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_{18}	$k_{U,-2}$	1.5867e-05	5.3186e-06	
a_{19}	k_{U,MB^*}	0		Fixed
a_{20}	k_{col,MB^*}	0		Fixed
a_{21}	$k_{U,EB}$	1.0995e-05	3.8147e-05	
a_{22}	$k_{U,-EB}$	8.2991e-06	6.6757e-05	
a_{23}	$k_{col,MB}$	7.7277e-07	1.7166e-04	
a_{24}	$k_{col,-MB}$	2.4751e-09	0.4894	
a_{25}	$k_{U,1}$	5.9000e-04		Fixed
a_{26}	$k_{U,-1}$	1.5128e-06		Fixed
a_{27}	$k_{co,EB}$	2.3256e-05	1.1444e-04	
a_{28}	$k_{co,-EB}$	6.8310e-06	1.3351e-04	
a_{29}	e	0		Fixed
a_{30}	f	0		Fixed

In a plot the pictures look as follows. For the hplc-coc experiment "p90t85e" we get:
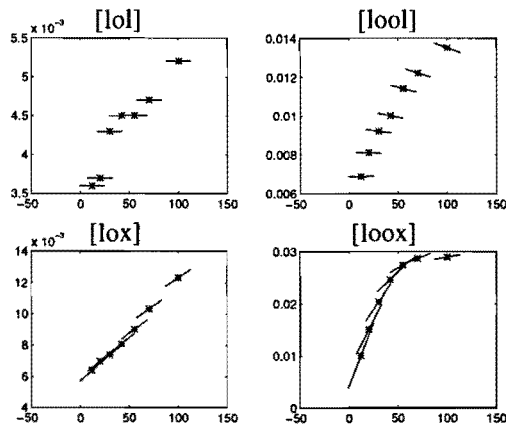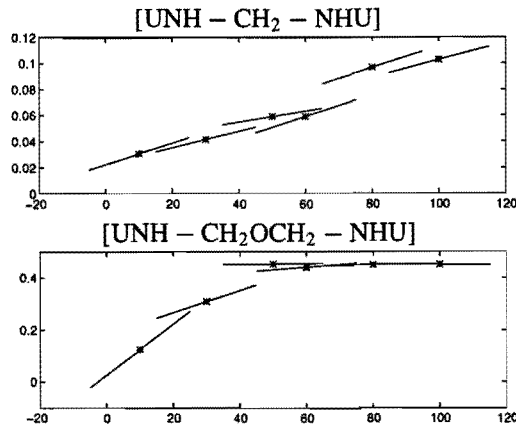
For the hplc-coc experiment "p90t85f3" we get:

[lol] [lool] [lox] [loox]

For the hplc-mf experiment "p90t85" we get:

[lol] [lool]

For the nmr-mf experiment "p90t85" we get:

$[MNH - CH_2 - NHM]$ $[MNH - CH_2OCH_2 - NHM]$

For the nmr-uf experiment "p90t85" we get:

$$[UNH - CH_2 - NHU]$$

$$[UNH - CH_2OCH_2 - NHU]$$
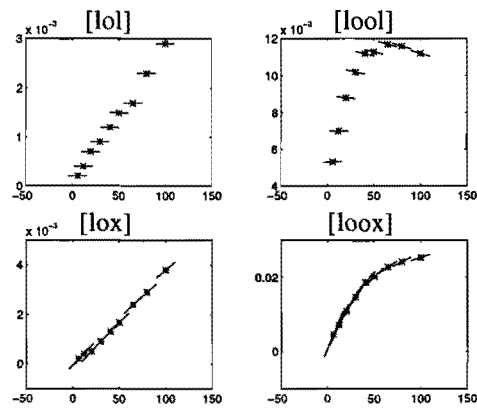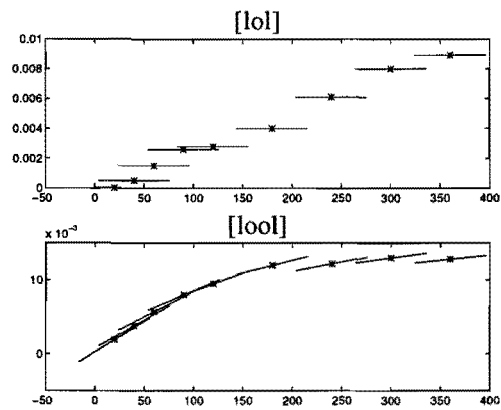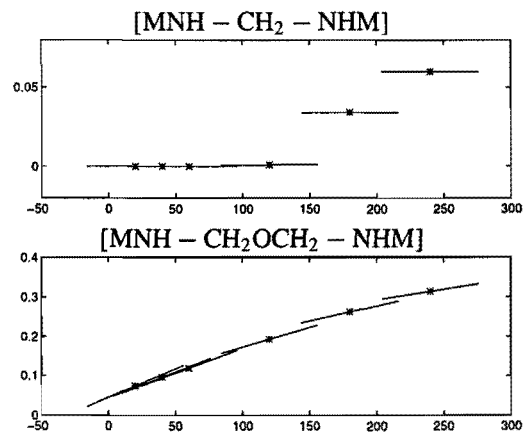
One of the key assumptions of this work is that the values of the rate constants do not depend on the resin system (MF UF homecondensation or cocondensation). In order to reduce ther complexity of the parameter estimation the problem was divided into three parts using this assumption (see E-mail by J.J. Nusselder of January 31):

- Estimation of a_1 and a_{13} from the MF experiments. If possible also the estimation of a_3, a_7, and a_{14}.

- Estimation of a_{15} and a_{21} from the UF experiments. If possible also the estimation of a_{17} and a_{22}.

- Finally the estimation of a_5, a_{23} and a_{27} from the HPLC-COC experiments. If possible also the estimation of a_{28}. In this phase we should make use of our estimates from the MF and UF experiments.

To decrease the number of parameters to be fitted even further it was decided (see fax by J.J. Nusselder of January 24) to use values for the rate constants of methylane bridge hydrolysis obtained from independent measurements [2]. It is assumed that the rate constants do not depend on the concentration of the resin. a_2, a_6, a_{16}, and a_{24} to the following values:

$$\log a_2 = \begin{cases} -\text{pH} + 0.6 - 4597.12 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 8.1 \\ -7.5 - 4597.12 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 8.1 \end{cases}$$

$$\log a_6 = \begin{cases} -\text{pH} - 0.5 - 5485.2 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 6.7 \\ -7.2 - 5485.2 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 6.7 \end{cases}$$

$$\log a_{16} = \begin{cases} -\text{pH} - 0.5 - 4283.68 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 6.5 \\ -7.0 - 4283.68 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 6.5 \end{cases}$$

$$\log a_{24} = \begin{cases} -\text{pH} - 0.5 - 5485.2 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 6.7 \\ -7.2 - 5485.2 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 6.7 \end{cases}$$
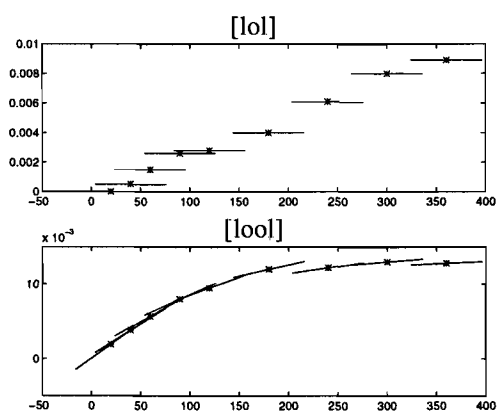
2.1   MF experiments

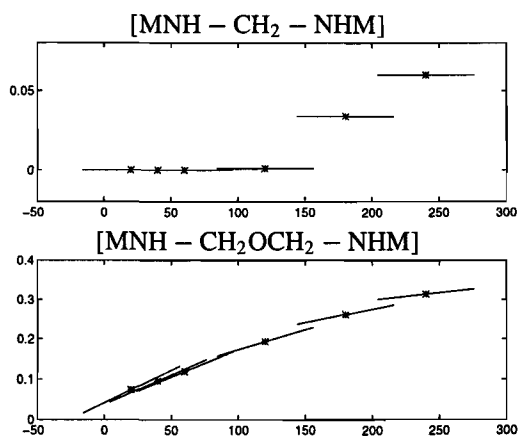We have applied this idea to the MF experiments. **With the use of weighting** we get the following results:

Table 4: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_1	$k_{M,MB}$	7.3178e-10	2.8610e-05	
a_3	$k_{M,1}$	7.9194e-08	0.5354	
a_7	$k_{M,2}$	1.8122e-08	1.3641	
a_{13}	$k_{M,EB}$	2.0685e-06	4.7684e-05	
a_{14}	$k_{M,-EB}$	1.9243e-06	7.6294e-05	

In a plot the pictures look as follows. For the hplc-mf experiment "p90t85" we get:
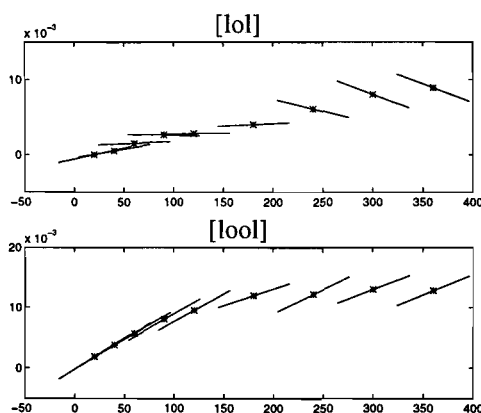

For the nmr-mf experiment "p90t85" we get:

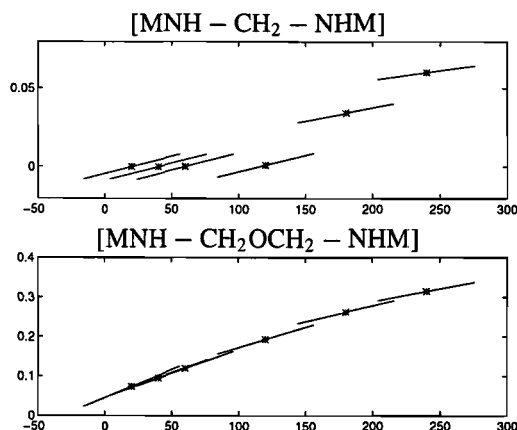**Without the use of weighting** we get the following results:

Table 5: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_1	$k_{M,MB}$	1.1631e-07	2.8610e-05	
a_3	$k_{M,1}$	8.0751e-04	3.4332e-04	
a_7	$k_{M,2}$	1.5871e-04	3.0518e-04	
a_{13}	$k_{M,EB}$	1.7727e-06	5.7220e-05	
a_{14}	$k_{M,-EB}$	7.9170e-07	2.2888e-04	

In a plot the pictures look as follows. For the hplc-mf experiment "p90t85" we get:

For the nmr-mf experiment "p90t85" we get:

Note that if we leave out any of the above parameters in the above estimation then the pictures look considerably worse. Moreover, we note that the unweighted case gives better and certainly more realistic results (see the discussion in subsection 2.5).

2.2 UF experiments

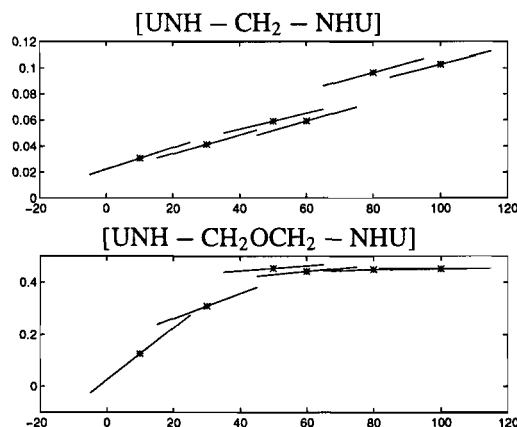Next we looked at the UF experiments. **With the use of weighting** we get the following results:

17

Table 6: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_{15}	$k_{M,-EB}$	2.2703e-07	5.7220e-05	
a_{21}	$k_{U,EB}$	1.1196e-05	2.8610e-05	
a_{22}	$k_{U,-EB}$	8.1613e-06	6.6757e-05	

It turned out that a_{17} could not be estimated from the data. Moreover after we fixed a_{17} as

$$\log a_{17} = -3.6 - 52.24 * 58 * \left(\frac{1}{273+T} - \frac{1}{358}\right)$$

according to the suggestion of J.J. Nusselder (fax of April 3) we still got good estimates. In a plot the pictures look as follows. For the nmr-uf experiment "p90t85" we get:
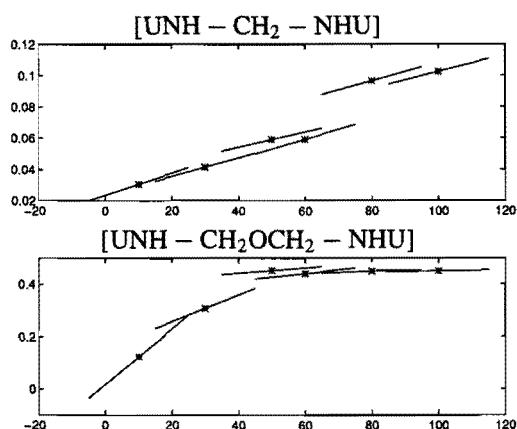

Without the use of weighting we get the following results:

Table 7: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_{15}	$k_{M,-EB}$	1.9019e-07	6.6757e-05	
a_{21}	$k_{U,EB}$	1.1759e-05	2.8610e-05	
a_{22}	$k_{U,-EB}$	8.4933e-06	6.6757e-05	

We again fixed a_{17}. In a plot the pictures look as follows. For the nmr-uf experiment "p90t85"

we get:

[UNH − CH$_2$ − NHU]

[UNH − CH$_2$OCH$_2$ − NHU]

2.3 Cocondensation experiments

In this subsection we will consider the estimation of the final set of rate constants. Given the fact that the weighted case yielded bad results, in particular for the MF experiments, I fixed all the other parameters to the values obtained in the unweighted case in the previous two subsections. In other words we have the following settings:

$$a_1 = 1.1631e - 07$$
$$a_3 = 8.0751e - 04$$
$$a_7 = 1.5871e - 04$$
$$a_{13} = 1.7727e - 06$$
$$a_{14} = 7.9170e - 07$$
$$a_{15} = 1.9019e - 07$$
$$a_{21} = 1.1759e - 05$$
$$a_{22} = 8.4933e - 06$$

**Without the use of weighting** we get the following results:

Table 8: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_5	$k_{co2,MB}$	1.2537e-07	0.0010	
a_{23}	$k_{co1,MB}$	2.8359e-07	5.5313e-04	
a_{27}	$k_{co,EB}$	1.9956e-05	2.1935e-04	
a_{28}	$k_{co,-EB}$	1.3640e-05	1.1444e-04	

19

In a plot the pictures look as follows. For the hplc-coc experiment "p90t85e" we get:
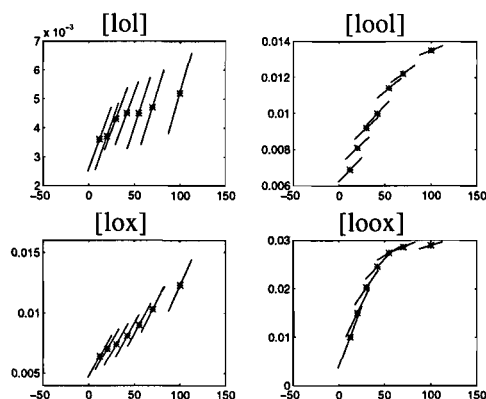
For the hplc-coc experiment "p90t85f3" we get:
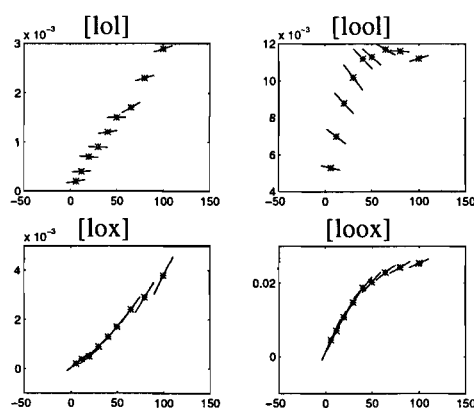
2.4 The HPLC-MF experiments

Especially in the unweighted case, we see that we have worse estimation results for differential equation (DV1) and, to a lesser degree, for differential equation(DV2), when compared with differential equations (DV7) and (DV8). These equations are the only two occurring in the HPLC-MF experiments. Hence it is of interest to see what happens if we estimate the parameters for the HPLC-MF experiments individually instead of in combination with the NMR-MF experiments.

Table 9: Kinetic rate constants

Variable	Rate constants	Estimate	Sensitivity	Comments
a_1	$k_{M,MB}$	3.8977e-07	1.7166e-04	
a_3	$k_{M,1}$	8.7447e-04	4.4823e-04	
a_{13}	$k_{M,EB}$	3.6973e-06	1.4305e-04	
a_{14}	$k_{M,-EB}$	7.8814e-06	2.7657e-04	

It turns out that a_7 can not be estimated from the HPLC-MF experiments. In a plot the pictures look as follows. For the hplc-mf experiment "p90t85" we get:
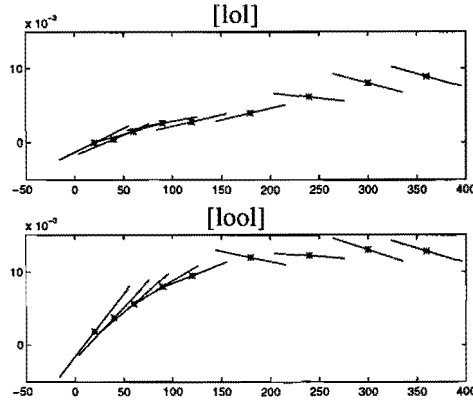
We see some improvement in the estimation (at the expense of a worse fit when looking at the NMR-MF data) but still the fit is far from perfect. The change in the values of the parameters is relatively smal: less than a factor of 2 for a_3, a_{13} and a_{14}. The value of a_1 depends more strongly on the type of experiments used. It seems that there are no values of the parameters for which the data of the NMR-MF experiment are well described by the model. In other words, it seems the data from the NMR-MF experiment at this temperature and pH is difficult to explain from our model. In my opinion from the data there is no evidence of a consistent difference between the HPLC and NMR data.

2.5 Discussion

We should discuss some of the issues related to the above results. First we have estimations with weightings and without weightings. For each measurement at a given time we have several differential equations which should be satisfied:

$$\dot{y}_{j_i}(t) = f_i(a, y(t)), i = 1, \ldots, p$$

where a is a vector consisting of the to be estimated parameters and y is a vector describing the concentrations at that particular point. y_j denotes the concentration of component number j. y_{j_i} denotes the concentration of the component whose dynamical behaviour is described by differential equation i. We then try to find a vector $\hat{a}$ such that

$$|\dot{\hat{y}}_{j_i}(t) - f_i(a, \hat{y}(t))|$$

is small. However, we want to choose a such that several of these equations and at several time instances are all small. The big question at that point is whether an estimate is better if the error in one equation is reduced by a factor 2 but at the expense of increasing the error in other equations. This decision is extremely ad hoc. The unweighted case minimizes the sum of squares

$$\sum_{\substack{i=1,\ldots,p \\ t \in T}} |\dot{\hat{y}}_{j_i}(t) - f_i(a, \hat{y}(t))|^2$$

This gives an equal importance to all equations. However, I have also considered a weighted case. That one was based on using the error bounds as supplied by DSM. We want to give more weight to equations where we have little noise, i.e. when the measurements are small. This is achieved by computing the maximal error we can get (under the assumption that our estimated parameters are correct) and minimizing the sum of squares of the misfit divided by the maximal error.

Beforehand, I believed the approach using weights to be the best method. However, if we study the estimates as presented in this section then we reach a different conclusion. Consider for instance the MF estimation problems. Then it is obvious from the plots that two equations (y_9 and y_{23}) are fitted very well but the other two (y_7 and y_{21}) are not estimated at all. Moreover, the estimated parameters are completely unrealistic (according to J.J. Nusselder). On the other hand, in the unweighted case, we see that all four equations are fitted. Of course, this involves a trade-off. Equations for y_7 and y_{21} are fitted better and the equations for y_9 and y_{23} are fitted worse.

This brings us to the problem of error bounds. Of course it is natural to ask for the accuracy of the estimation of the parameters. When we look at the statistical literature then nearly all the results are asymptotic. Hence these results are only valid if we have a large amount of data compared to the number of parameters we want to estimate. For the problem at hand these results are simply not applicable. Also from the previous discussion related to weighting it becomes obvious how difficult it is to get error bounds. Different weights have enormous effect on the estimates of our parameters. Moreover these weights are quite arbitrary. However, there are good reasons to "believe" the results for the unweighted case: the parameters are of the correct order of magnitude and all the equations are fitted (not in the weighted case where we have very good fits and very bad fits). But the essential problem remains: it is near impossible to give a precise errorbound. When I discuss sensitivity of the parameters then I am testing how much I have to perturb a parameter before it has a substantial effect on the error. A parameter I can make twice as big while the error (cost function) changes only very little is obviously very difficult to estimate. But again this only yields crude insight and can not be used to derive precise error bounds.

3   The overall estimation problem

There were originally 74 experiments. However several experiments were discarded after further analysis by J.J. Nusselder (see fax of April 3). In the table below we list the remaining experiments split over the four different types of experiments and indicating the different temperatures for which we have experiments for a given pH level. Between the parenthesis is indicated (in case there is more than 1) how many experiments we have for that specific pH/temperature.

Table 10: Experiments with pH versus temperature

pH	hplc-coc	hplc-mf	nmr-mf	nmr-uf
6				75
7	75			75 (2)
7	85 (2)			85

Table 10: Experiments with pH versus temperature

pH	hplc-coc	hplc-mf	nmr-mf	nmr-uf
7.5	75 (2)			
7.5	80			
7.5		85	85	
7.5		90	90	
7.5		95	95	
7.75		95		
7.82		85		
8	75 (2)			75
8	85 (4)	85	85	
8	90	90	90	
8	95	95	95	
8.25		95		
8.5				75
8.5		95		
9				65
9				75
9	**85 (2)**	**85**	**85**	**85**
9		90	90	
9		95	95	
9.25		85	85	
9.25		95	95	
9.4				75
9.5	70			
9.5	75			
9.5	85	85 (2)	85	
9.5	90	90	90	
9.5		95	95	

3.1 Estimation for homocondensation melamine

We have estimated the parameters a_1, a_3, a_7, a_{13}, and a_{14} for different pH and temperature. We have at each temperature a plot with our estimates of the parameter for different pH. We then try to fit a line through it to obtain the temperature and the pH dependence of the rate constants.

The lines in the figures are calculated by using the equations starting on 34. For a_1 we obtain the following three plots:

Estimates of a_1 for $T = 85$

Estimates of a_1 for $T = 90$

## Estimates of a_1 for $T = 95$
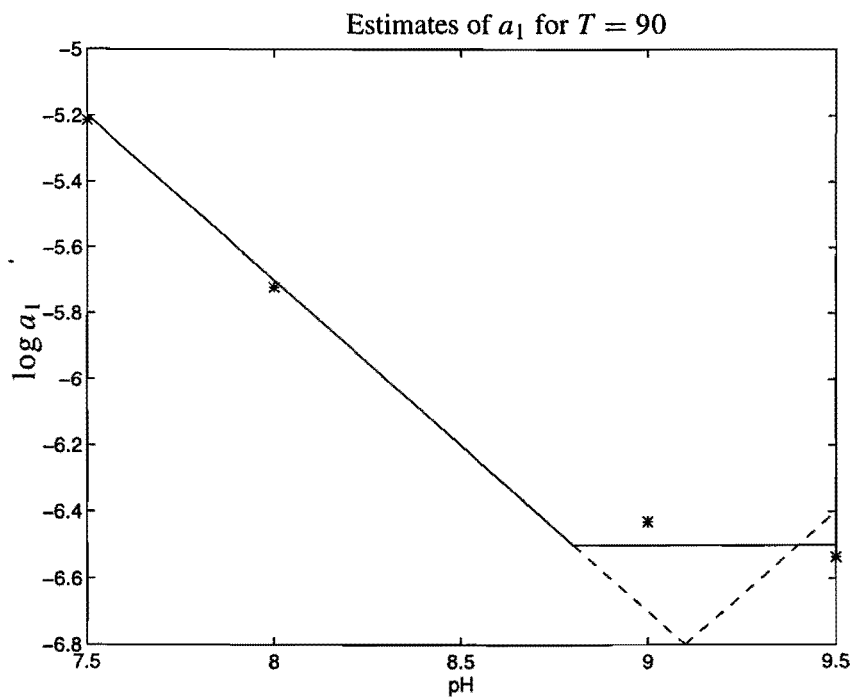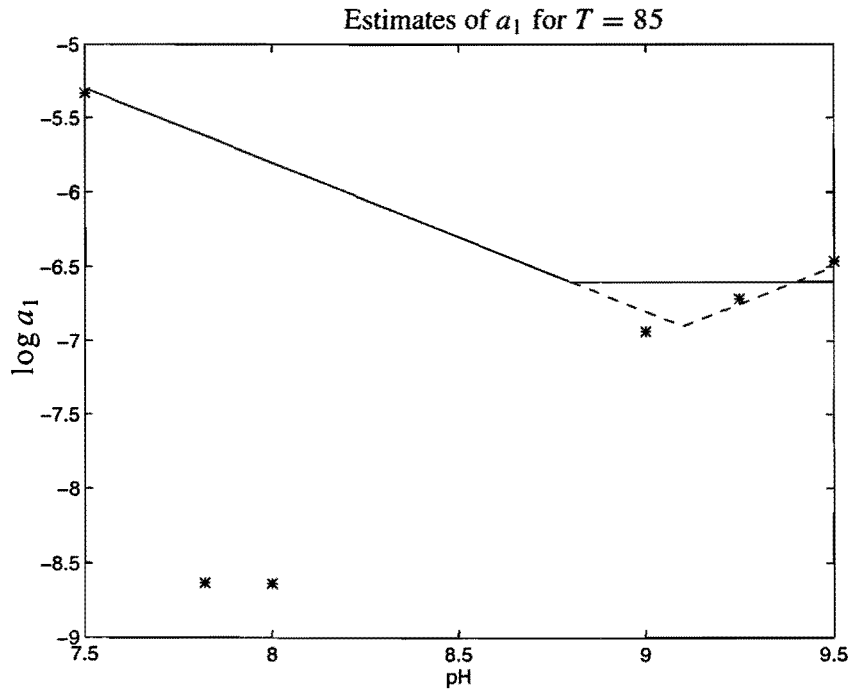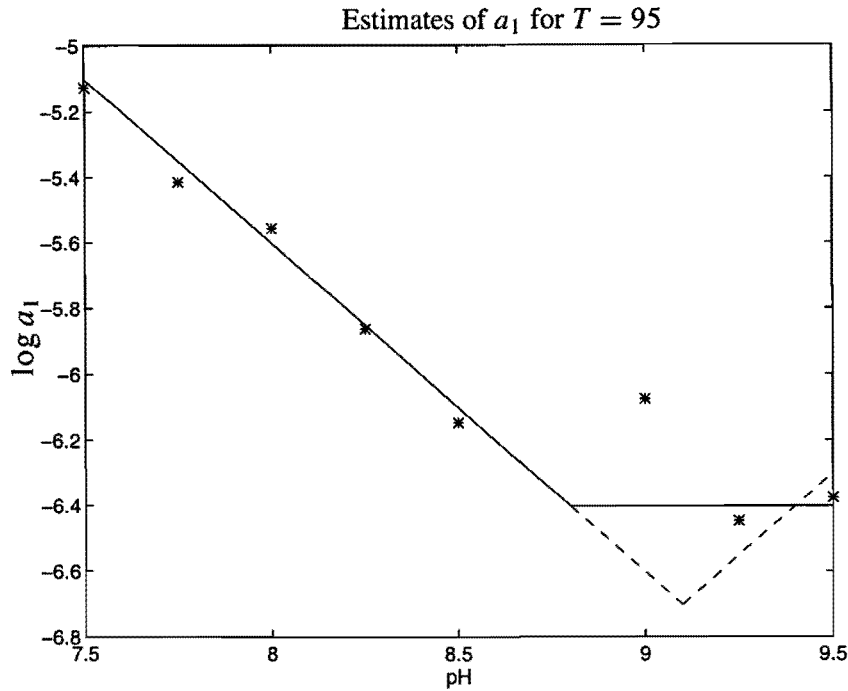
We see that in particular for temperature $T = 95$ and low pH we have a nice fit. It is however hard to see whether the rate constants stays constant or increases at high pH level. Both possibilities are shown in the plots. Finally we note that two estimates at $T = 85$ and pH equal to 7.82 and 8 are obviously wrong.

The experiments are not designed to give information about a_3 and a_7. The plots, describing the limited information we have obtained, can be found in the appendix.

Estimates of a_{13} for $T = 85$

Estimates of a_{13} for $T = 90$

Estimates of a_{13} for $T = 95$
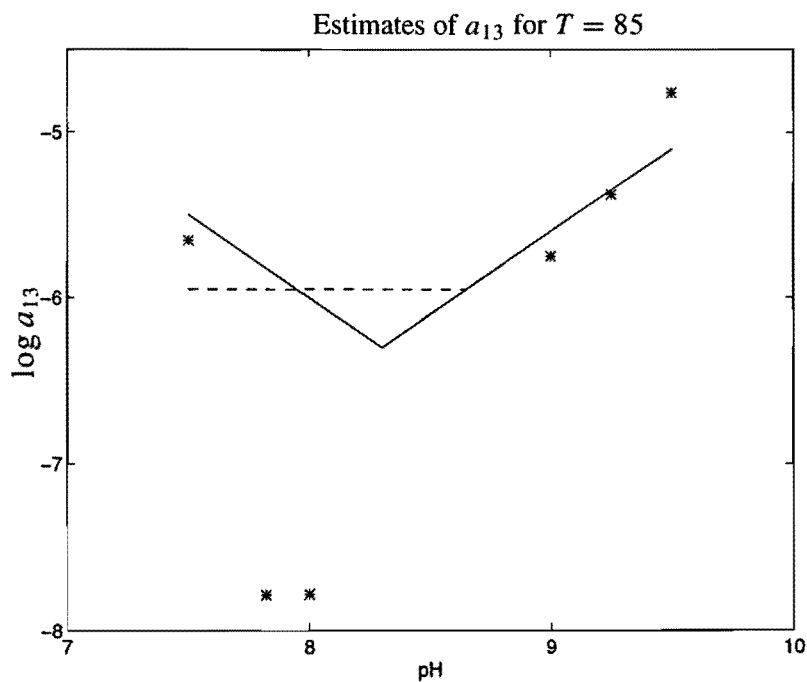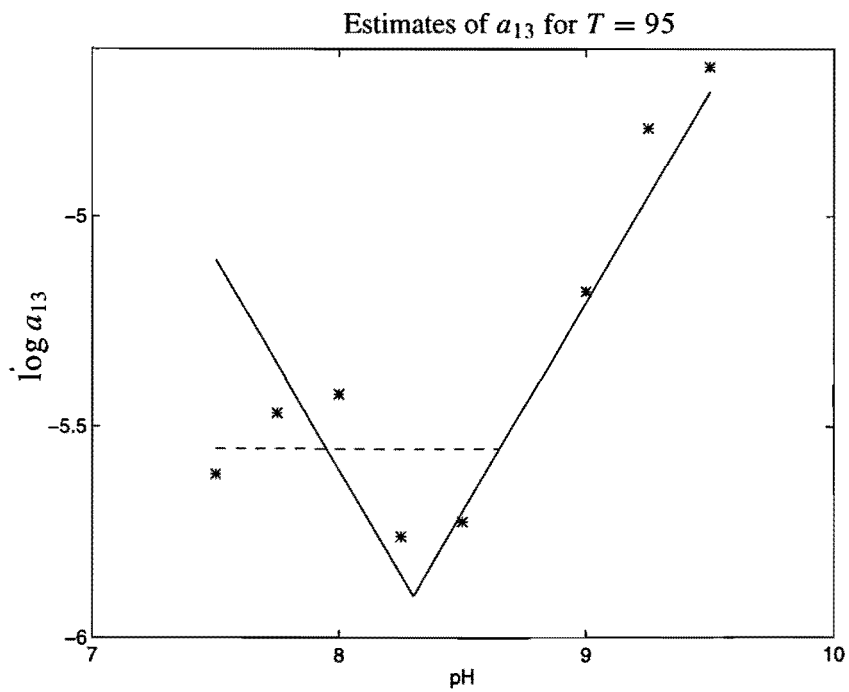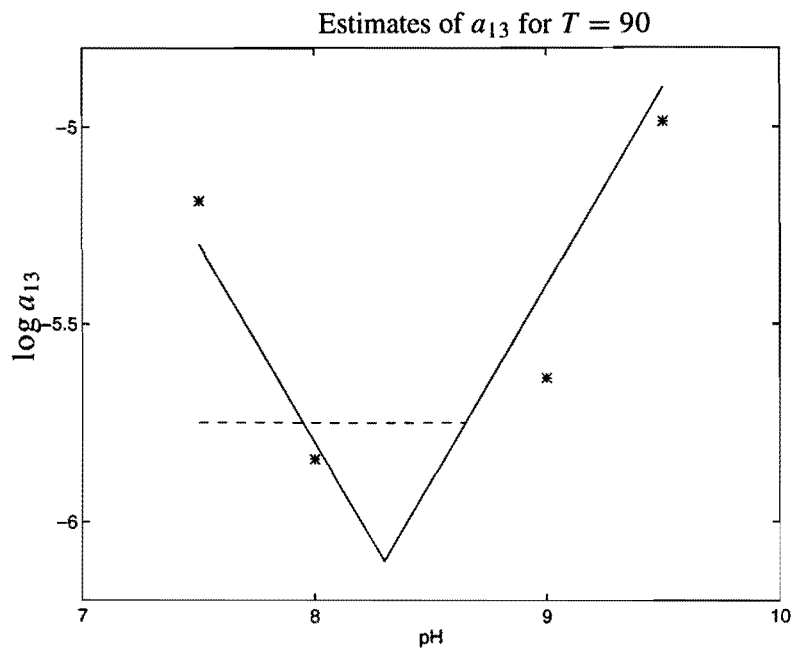
a_{13} can be estimated reasonably well but it is not really clear from the estimates whether the a_{13}

is constant or decreasing at low pH levels. The solid line probably gives the best estimate.

Estimates of a_{14} for $T = 85$

Estimates of a_{14} for $T = 90$

Estimates of a_{14} for $T = 95$
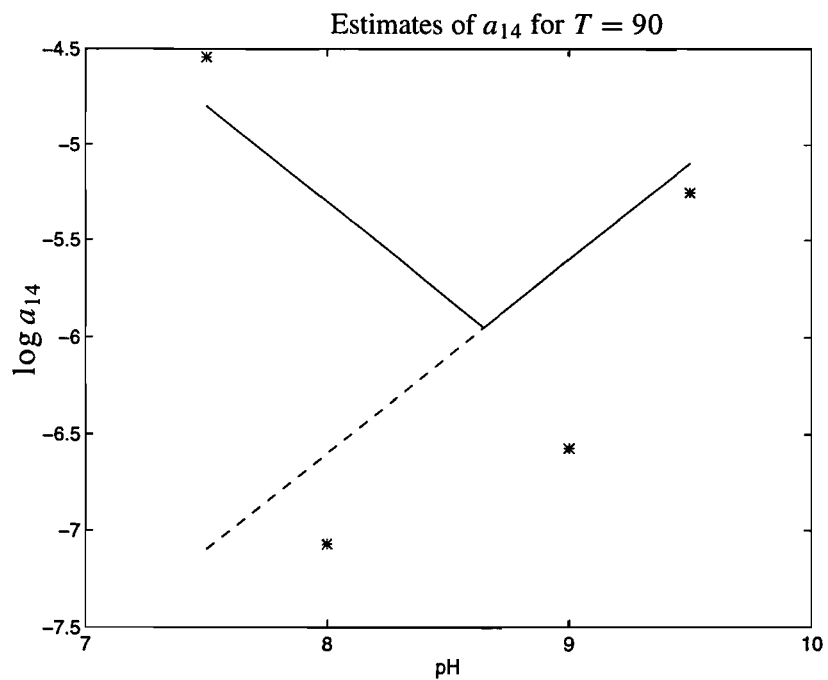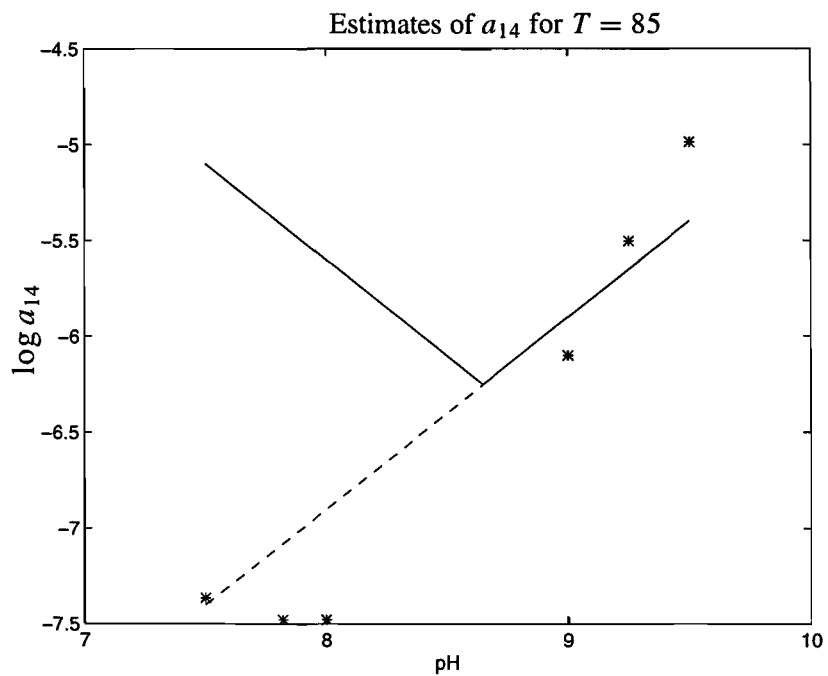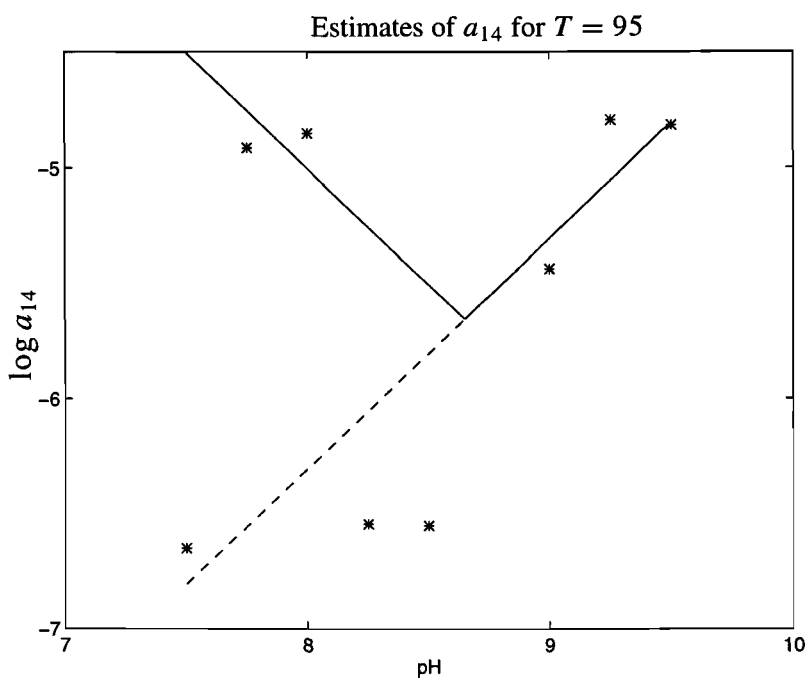
For a_{14} the behaviour for low pH is not really clear. There are contradictory estimates for the behaviour at low pH levels.

Finally note that the above is not taking into account any insight into the chemistry these rate constants are representing.

Finally we summarize the estimates in the following tables

Table 11: Estimates for mf experiments at $T = 85$

Temperature	a_1	a_3	a_7	a_{13}	a_{14}
7.5	4.6340e-06	2.9574e-04	7.1988e-04	2.2040e-06	4.3242e-08
7.82	2.3312e-09	5.6046e-04	0.0026	1.6414e-08	3.3250e-08
8.0	2.3202e-09	7.7489e-04	0.0026	1.6469e-08	3.3224e-08
9.0	1.1631e-07	8.0751e-04	1.5871e-04	1.7727e-06	7.9170e-07
9.25	1.9380e-07	4.4219e-04	5.2304e-05	4.1908e-06	3.1423e-06
9.5	3.4454e-07	1.0847e-04	0.0027	1.7358e-05	1.0272e-05

Table 12: Estimates for mf experiments at $T = 90$

Temperature	a_1	a_3	a_7	a_{13}	a_{14}
7.5	6.0978e-06	4.4445e-04	2.1904e-05	6.4708e-06	2.8668e-05
8.0	1.8992e-06	5.0653e-04	9.1845e-04	1.4453e-06	8.4999e-08

Table 12: Estimates for mf experiments at $T = 90$

Temperature	a_1	a_3	a_7	a_{13}	a_{14}
9.0	3.7190e-07	5.3132e-04	6.5143e-04	2.3129e-06	2.6800e-07
9.5	2.9120e-07	9.4255e-04	3.2477e-04	1.0316e-05	5.5831e-06

Table 13: Estimates for mf experiments at $T = 95$

Temperature	a_1	a_3	a_7	a_{13}	a_{14}
7.5	7.4598e-06	3.6852e-04	6.3882e-06	2.4324e-06	2.2419e-07
7.75	3.8361e-06	3.6668e-04	2.2759e-05	3.4046e-06	1.2157e-05
8.0	2.7738e-06	5.0059e-04	2.2759e-05	3.7834e-06	1.3990e-05
8.25	1.3700e-06	4.1284e-04	6.5143e-04	1.7299e-06	2.8535e-07
8.5	7.1332e-07	4.3669e-04	6.5143e-04	1.8739e-06	2.8005e-07
9.0	8.4005e-07	4.1866e-04	5.6395e-04	6.6451e-06	3.6669e-06
9.25	3.5668e-07	6.4346e-04	4.1495e-04	1.6232e-05	1.5965e-05
9.5	4.2104e-07	0.0019	1.8486e-05	2.2698e-05	1.5230e-05

3.2   Estimation for homocondensation ureum

We have estimated the parameters a_{15}, a_{21}, and a_{22} for different pH and temperature. We have at each temperature a plot with our estimates of the parameter for different pH. We then try to fit a line through it to obtain the temperature and the pH dependence of the rate constants.

The experiments are not designed to give information about a_{15}. The plots, describing the limited information we have obtained, can be found in the appendix.

We continue with a_{21}:

Estimates of a_{21} for $T = 65$

Estimates of a_{21} for $T = 75$

Estimates of a_{21} for $T = 85$
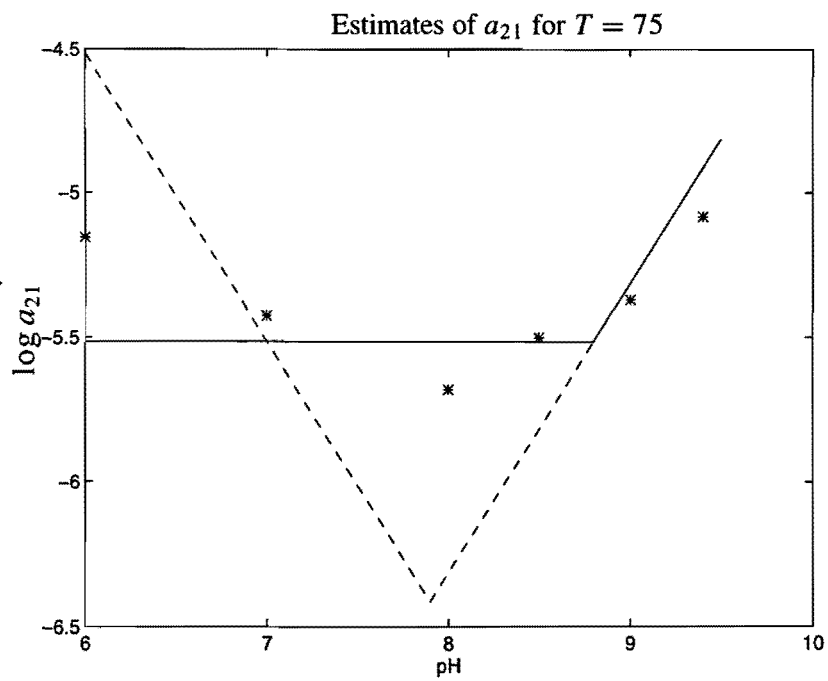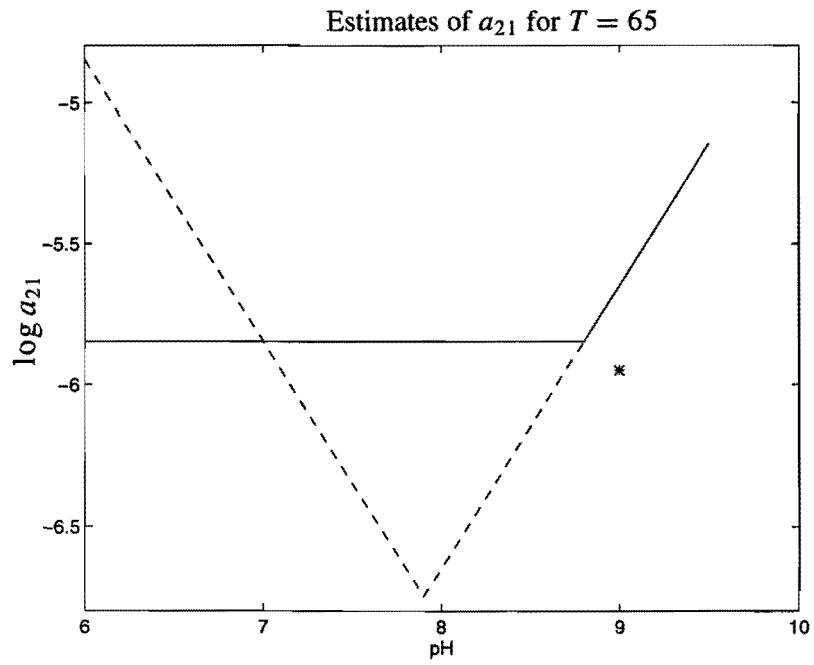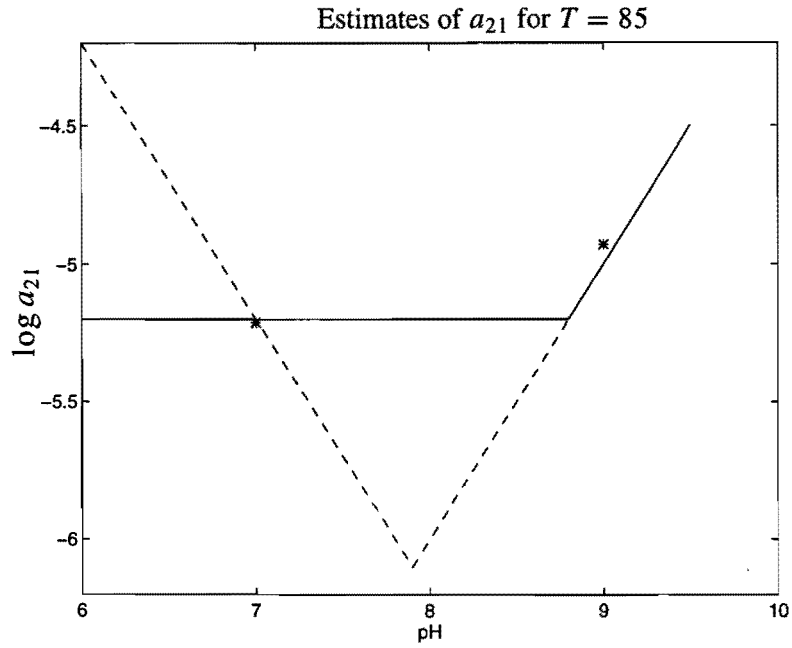
The estimates again look pretty consistent except for the behaviour at low pH. It is from our estimates not really clear what the behaviour for low pH is like. Based on other experiments described in [2] we conclude that the dotted line describes the behaviour best.

Estimates of a_{22} for $T = 65$

Estimates of a_{22} for $T = 75$

Estimates of a_{22} for $T = 85$
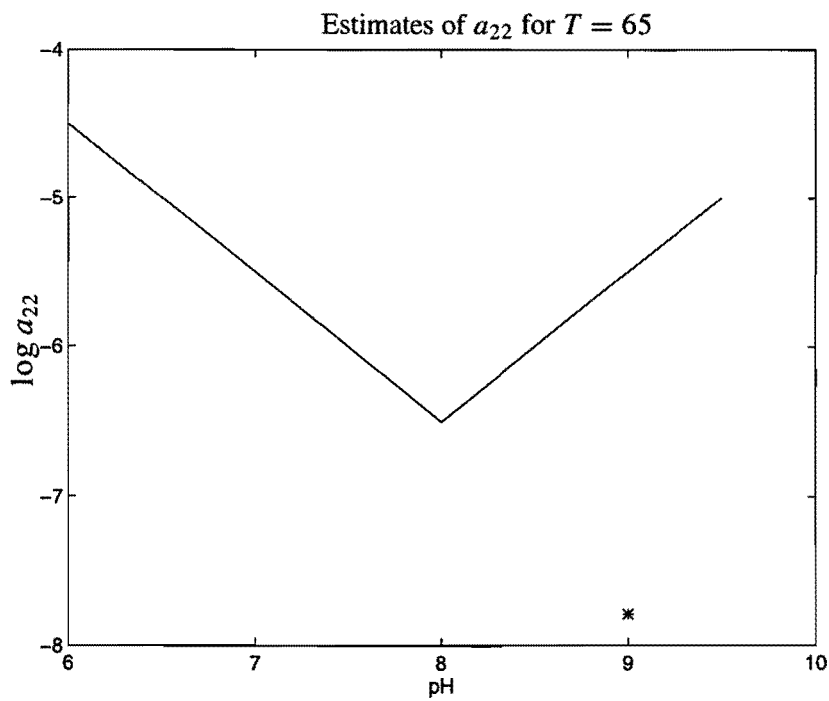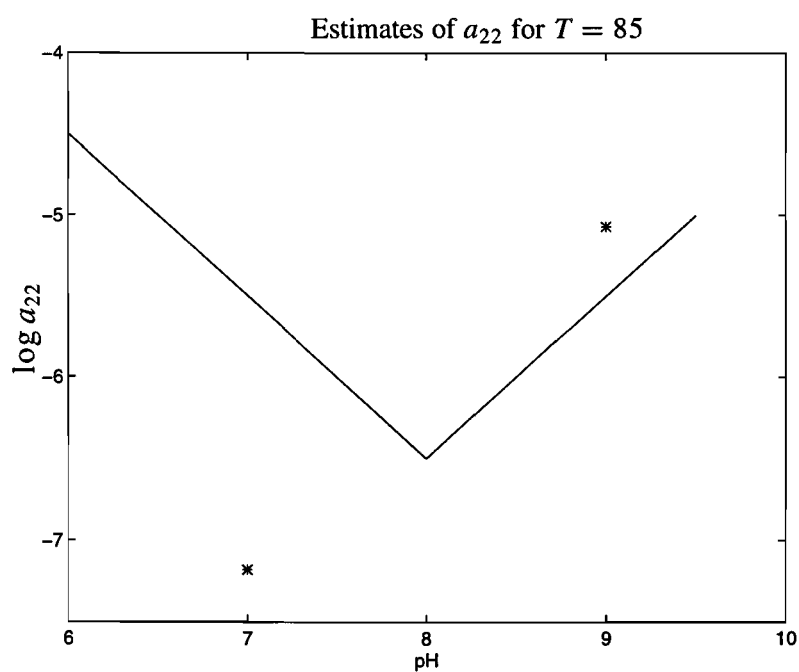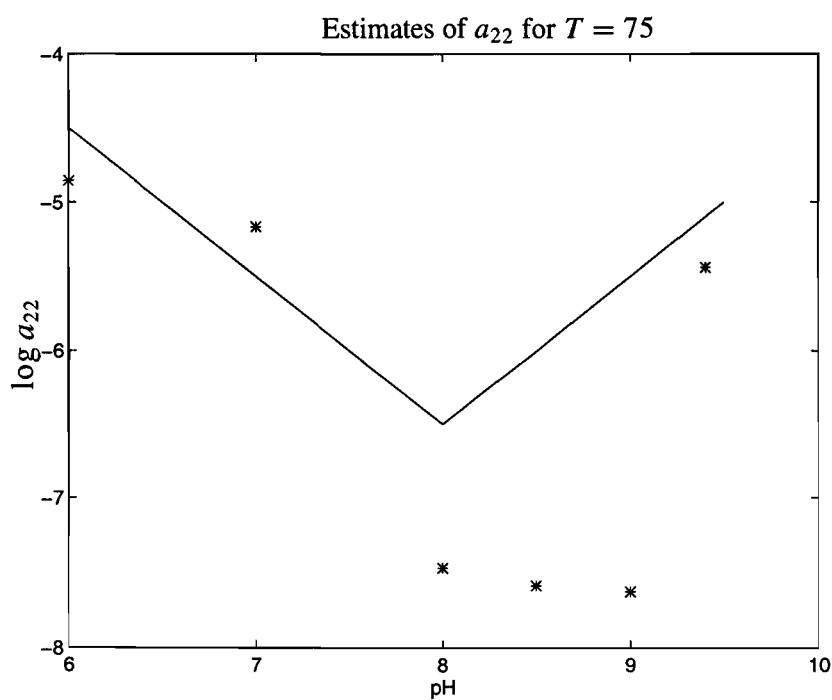
There are four estimates which are rather large and five estimates are relatively large. It is impossible to find a fit which describes both the large and the small values. Based on initial estimates we have concluded that the large values are probably more realistic. Note that a_{21} and a_{22} shoud have the same temperature profile. We have therefore used the same profile as we had chosen earlier for a_{21}.

Finally we summarize the estimates in the following tables

Table 14: Estimates for uf experiments at $T = 65$

Temperature	a_{15}	a_{21}	a_{22}
7.0	2.2273e-06	6.1384e-06	6.6075e-08
9.0	1.9019e-07	1.1759e-05	8.4933e-06

Table 15: Estimates for uf experiments at $T = 75$

Temperature	a_{15}	a_{21}	a_{22}
6.0	1.6679e-05	6.9623e-06	1.3952e-05
7.0	1.2861e-06	3.7398e-06	6.8136e-06
8.0	1.4106e-07	2.0922e-06	3.4009e-08
8.5	1.1828e-07	3.1650e-06	2.6036e-08
9.0	4.9823e-08	4.2506e-06	2.3549e-08
9.4	1.0222e-07	8.2249e-06	3.6510e-06

Table 16: Estimates for uf experiments at $T = 85$

Temperature	a_{15}	a_{21}	a_{22}
7.0	2.2273e-06	6.1384e-06	6.6075e-08
9.0	1.9019e-07	1.1759e-05	8.4933e-06

3.3 Estimation for cocondensation

We are going to estimate the remaining rate constants a_5, a_{23}, a_{27} and a_{28}. In the estimation the other rate constants are fixed to the following values. For a_1 we use our estimate (the dotted line) from the melamine homocondensation experiments:

$$\log a_1 = \begin{cases} -\text{pH} + 2.2 - 52.24 * 50 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 9.1 \\ \text{pH} - 16 - 52.24 * 50 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 9.1 \end{cases}$$

a_2 was fixed (see page 15):

$$\log a_2 = \begin{cases} -\text{pH} + 0.6 - 52.24 * 88 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 8.1 \\ -7.5 - 52.24 * 88 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 8.1 \end{cases}$$

For a_3 we have a (bad) fit from the melamine homocondensation experiments:

$$\log a_3 = \begin{cases} -3.2 + 52.24 * 50 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH < 9.1 \\ pH - 12.3 + 52.24 * 50 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH \geqslant 9.1 \end{cases}$$

An alternative estimate for a_3 was given by J.J. Nusselder (fax of April 3):

$$\log a_3 = -2.76 - 52.24 * 100 * \left(\frac{1}{273+T} - \frac{1}{358}\right)$$

The latter estimate was used in the estimations for the cocondensation experiments. For a_4 we use the relation described in subsection 1.2:

$$a_4 = a_3/170$$

a_6 was fixed (see page 15):

$$\log a_6 = \begin{cases} -pH - 0.5 - 52.24 * 105 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH < 6.7 \\ -7.2 - 52.24 * 105 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH \geqslant 6.7 \end{cases}$$

For a_7 we choose the dotted line based on our estimates from the melamine homocondensation experiments. This is very close to an estimate for a_7 as given by J.J. Nusselder (fax of April 3):

$$\log a_7 = -3.0 + 52.24 * 150 * \left(\frac{1}{273+T} - \frac{1}{358}\right)$$

For a_8 we use the relation described in subsection 1.2:

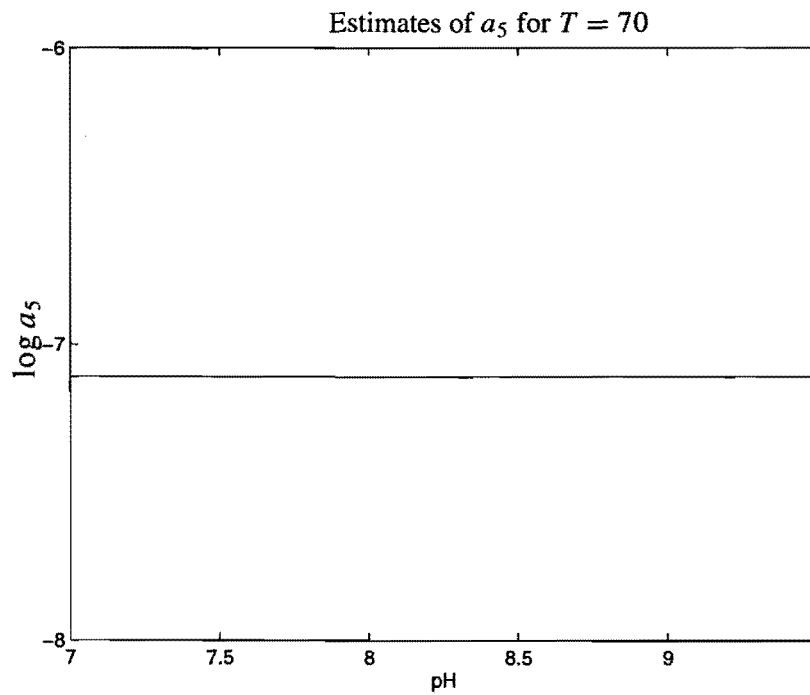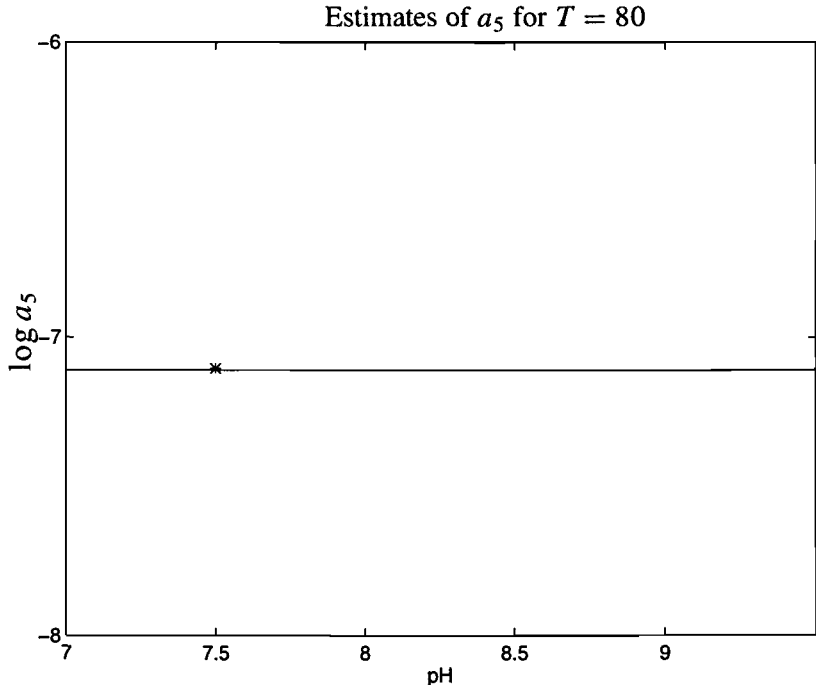$$a_8 = a_7/100$$

a_9, a_{10}, a_{11}, and a_{12} are fixed (see 12):

$$a_9 = 0$$
$$a_{10} = 0$$
$$a_{11} = 0$$
$$a_{12} = 0$$

a_{13} and a_{14} were estimated (solid lines) from the melamine homocondensation experiments:

$$\log a_{13} = \begin{cases} -pH + 2.0 - 52.24 * 100 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH < 8.3 \\ pH - 14.6 - 52.24 * 100 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH \geqslant 8.3 \end{cases}$$

$$\log a_{14} = \begin{cases} -pH + 2.4 - 52.24 * 150 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH < 8.65 \\ pH - 14.9 - 52.24 * 150 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if } pH \geqslant 8.65 \end{cases}$$

a_{15} was estimated from the ureum homocondensation experiments:

$$\log a_{15} = \begin{cases} -\text{pH} + 1.5 - 52.24 * 50 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 8.8 \\ \text{pH} - 16.1 - 52.24 * 50 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 8.8 \end{cases}$$

a_{16} was fixed (see page 15):

$$\log a_{16} = \begin{cases} -\text{pH} - 0.5 - 52.24 * 82 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 6.5 \\ -7.0 - 52.24 * 82 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 6.5 \end{cases}$$

a_{17} was fixed (see page 18):

$$\log a_{17} = -3.6 - 52.24 * 58 * \left(\frac{1}{273+T} - \frac{1}{358}\right)$$

For a_{18} we use the relation described in subsection 1.2:

$$a_{18} = a_{17}/52$$

a_{19} and a_{20} are fixed (see 12):

$$a_{19} = 0$$
$$a_{20} = 0$$

a_{21} (dotted line) and a_{22} (solid line) have been estimated from the ureum homocondensation experiments:

$$\log a_{21} = \begin{cases} -\text{pH} + 1.8 - 52.24 * 75 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 7.9 \\ \text{pH} - 14.0 - 52.24 * 75 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 7.9 \end{cases}$$

$$\log a_{22} = \begin{cases} -\text{pH} + 1.5 - 52.24 * 200 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 8.0 \\ \text{pH} - 14.5 - 52.24 * 200 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 8.0 \end{cases}$$

a_{24} was fixed (see page 15):

$$\log a_{24} = \begin{cases} -\text{pH} - 0.5 - 52.24 * 105 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} < 6.7 \\ -7.2 - 52.24 * 105 * \left(\frac{1}{273+T} - \frac{1}{358}\right) & \text{if pH} \geqslant 6.7 \end{cases}$$

a_{25} is fixed (see 12):

$$\log a_{25} = -3.2 - 52.24 * 54 * \left(\frac{1}{273+T} - \frac{1}{358}\right)$$

For a_{26} we use the relation described in subsection 1.2:

$$a_{26} = a_{25}/390$$

a_{29} and a_{30} are fixed (see 12):
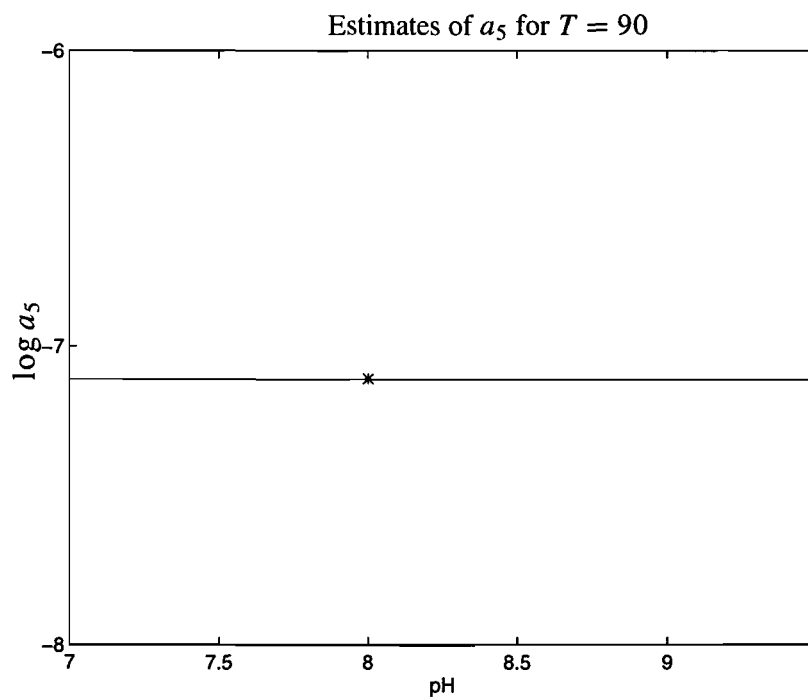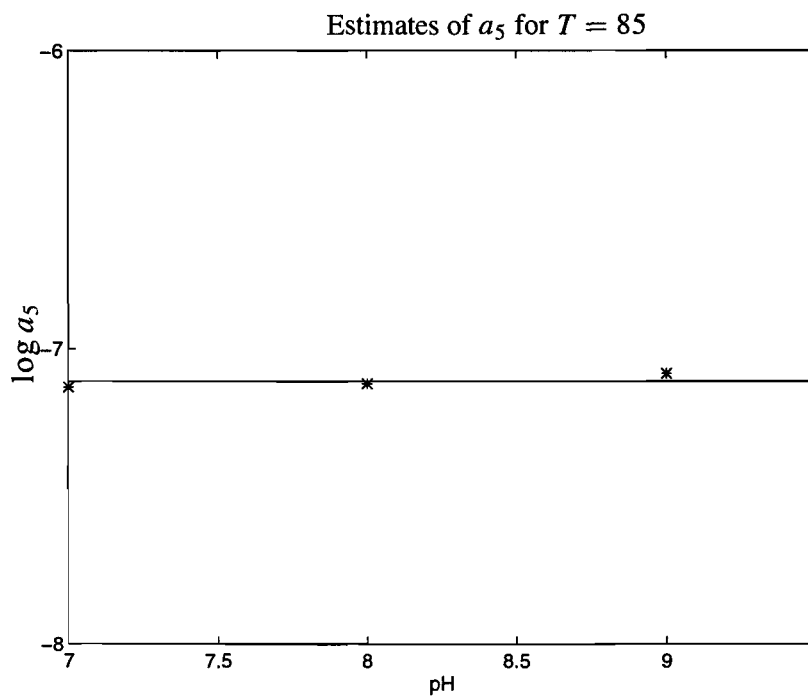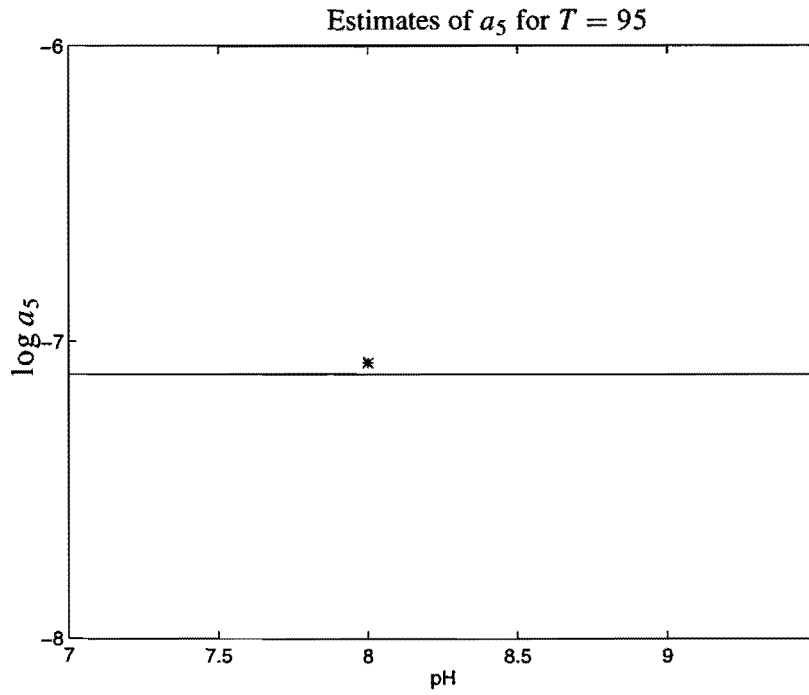
$$a_{29} = 0$$
$$a_{30} = 0$$

We first investigate our estimates for parameter a_5 at different temperature and pH levels:

Estimates of a_5 for $T = 70$
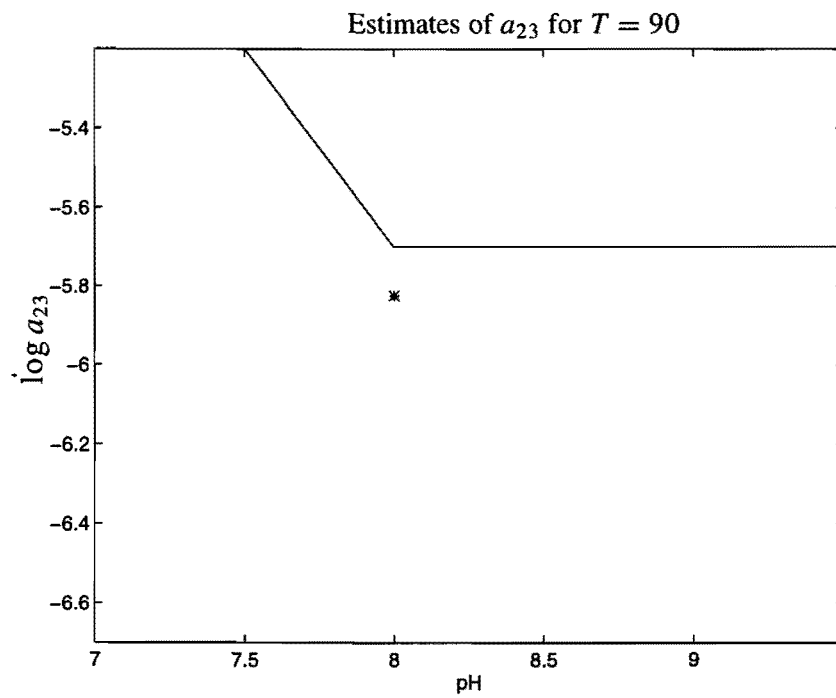
Estimates of a_5 for $T = 75$

Estimates of a_5 for $T = 80$

Estimates of a_5 for $T = 85$

Estimates of a_5 for $T = 90$

Estimates of a_5 for $T = 95$
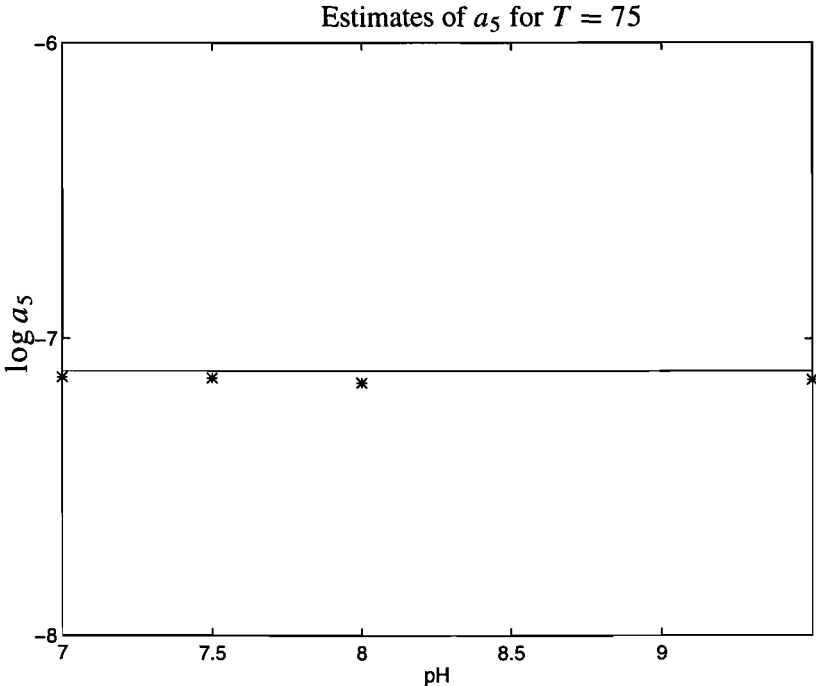
We see that a_5 is quite consistent with a constant fit. However we have seen earlier that the sensitivity in our estimates of a_5 was quite low which makes us a bit skeptical regarding these estimates. The next to look at is a_{23}:
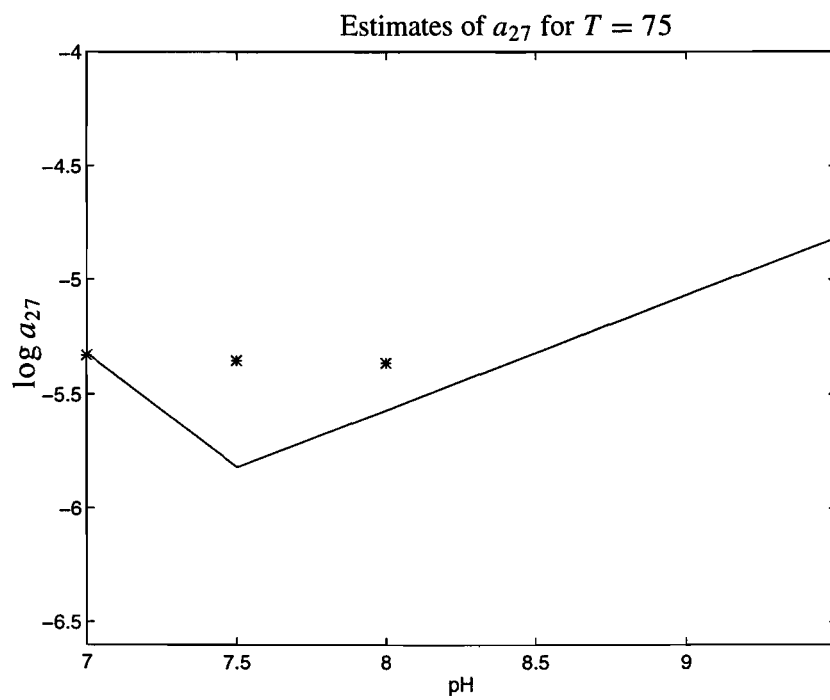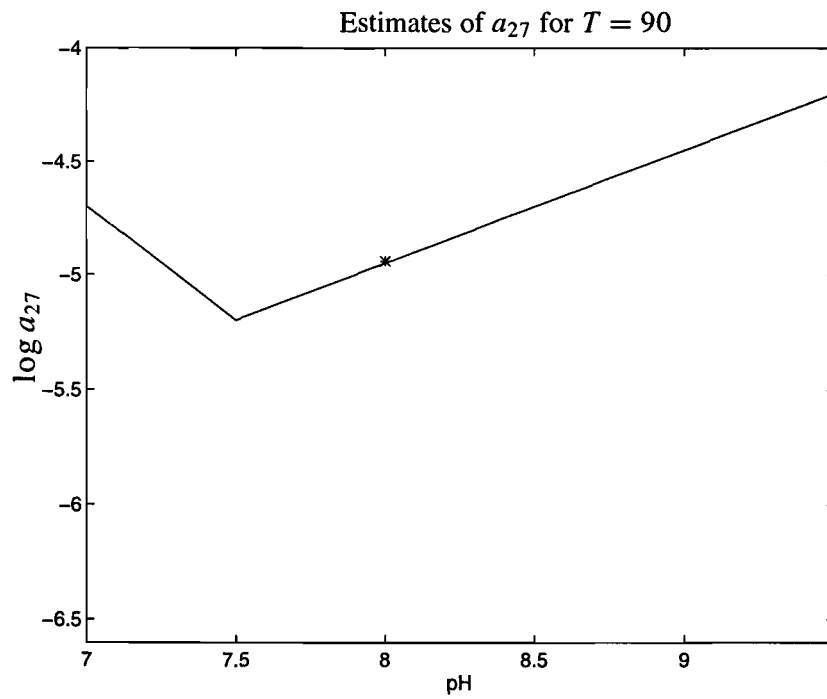
Estimates of a_{23} for $T = 70$

Estimates of a_{23} for $T = 75$

Estimates of a_{23} for $T = 80$

41

Estimates of a_{23} for $T = 85$

Estimates of a_{23} for $T = 90$

Estimates of a_{23} for $T = 95$
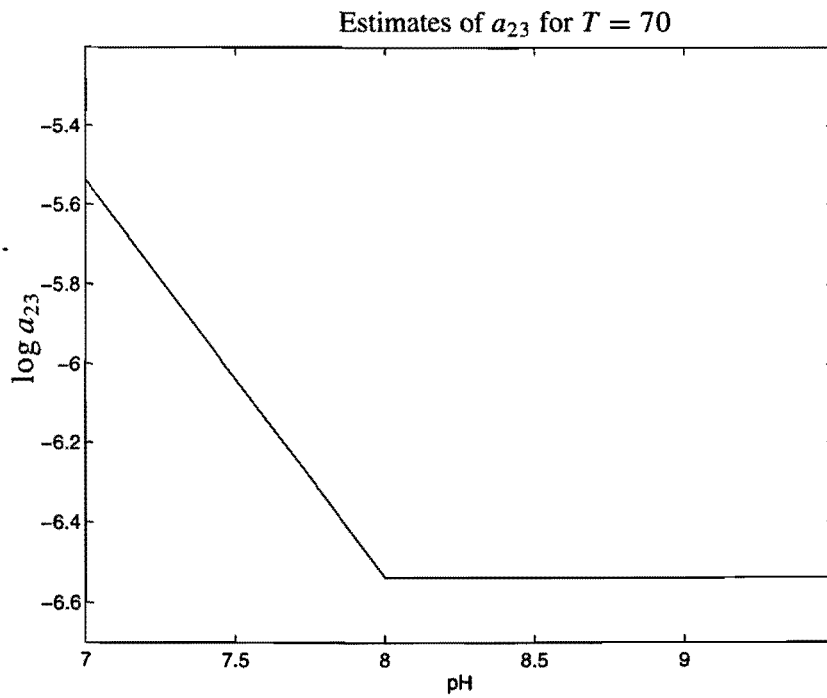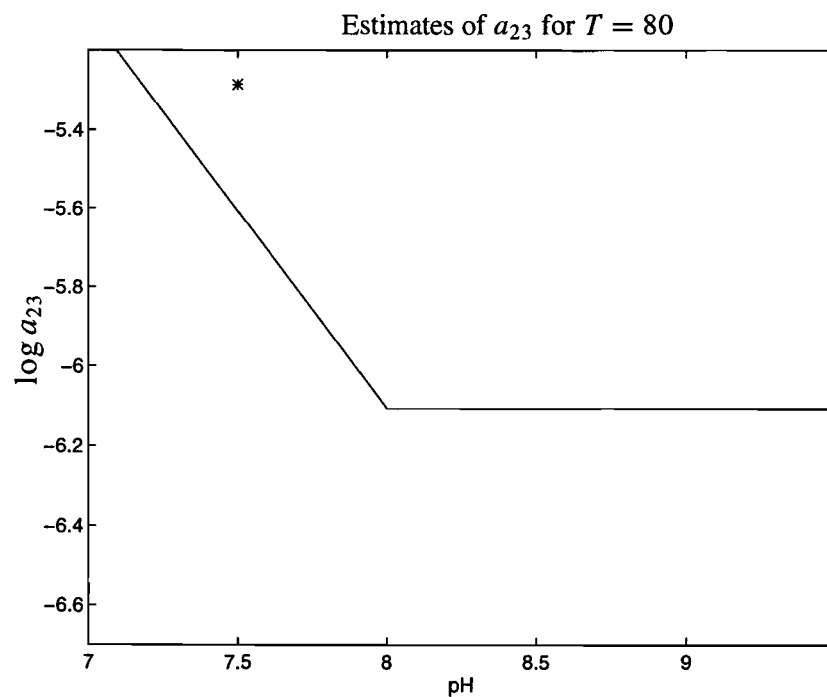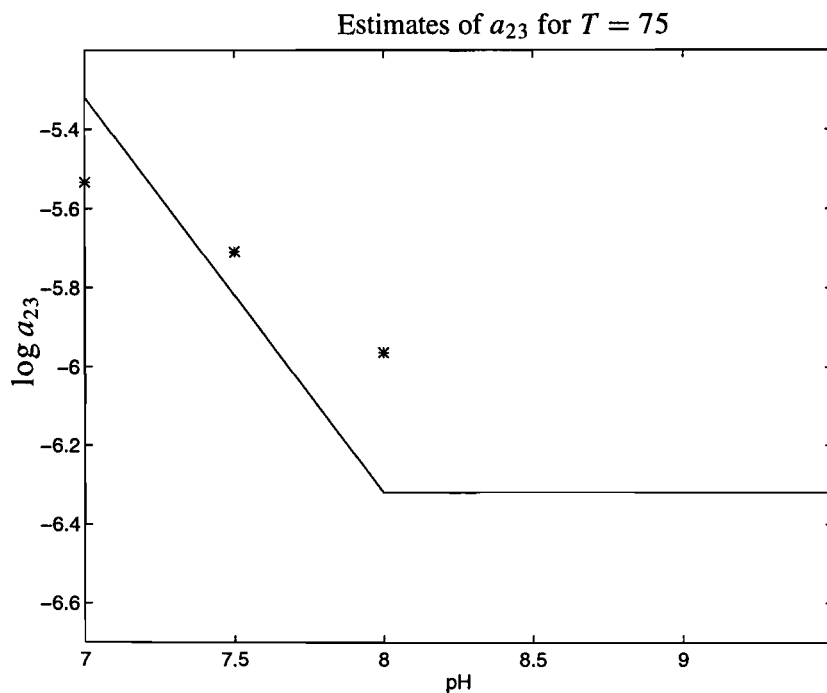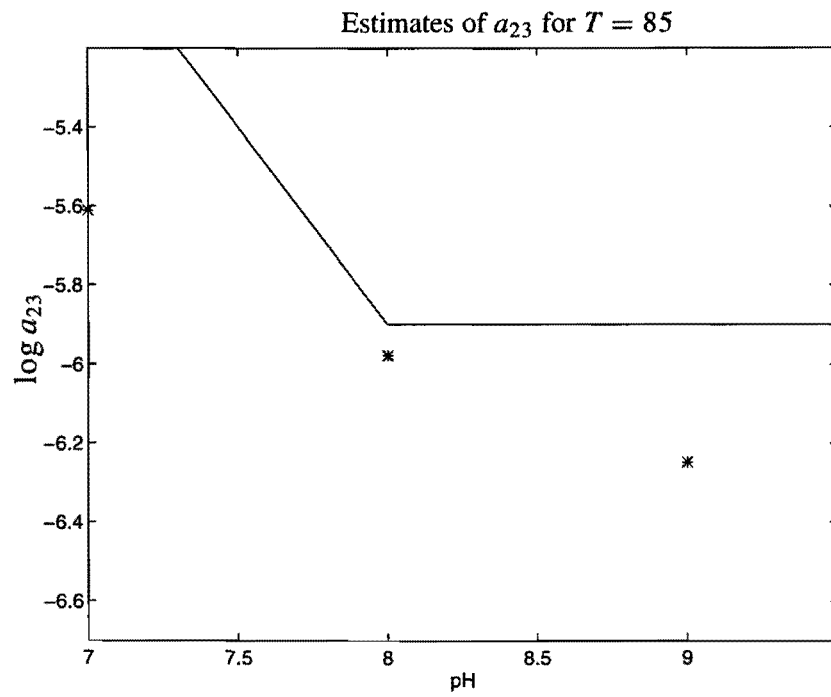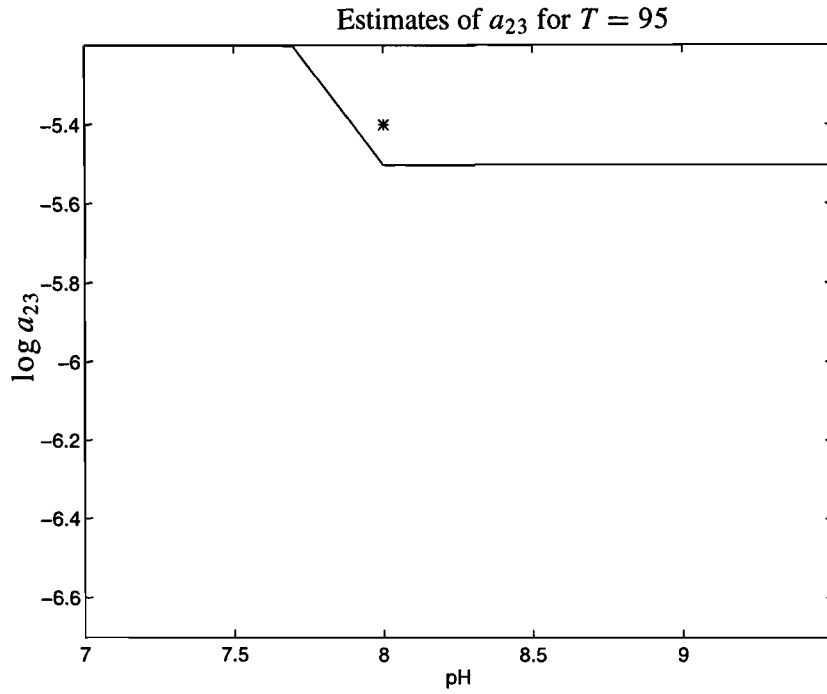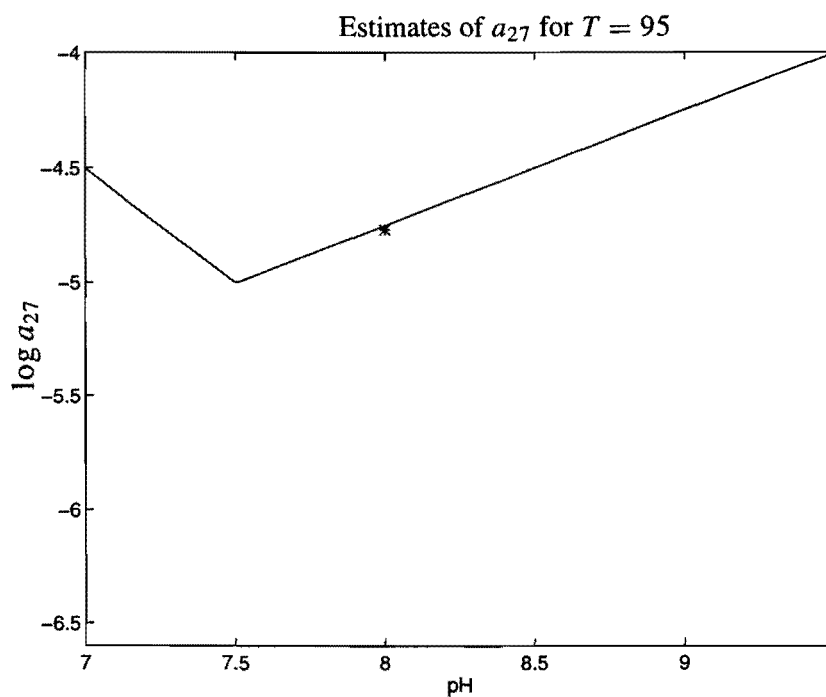

It is clearly more difficult to estimate a_{23}. The general structure is not too bad but it is difficult to obtain hard results. The next estimates are for a_{27}
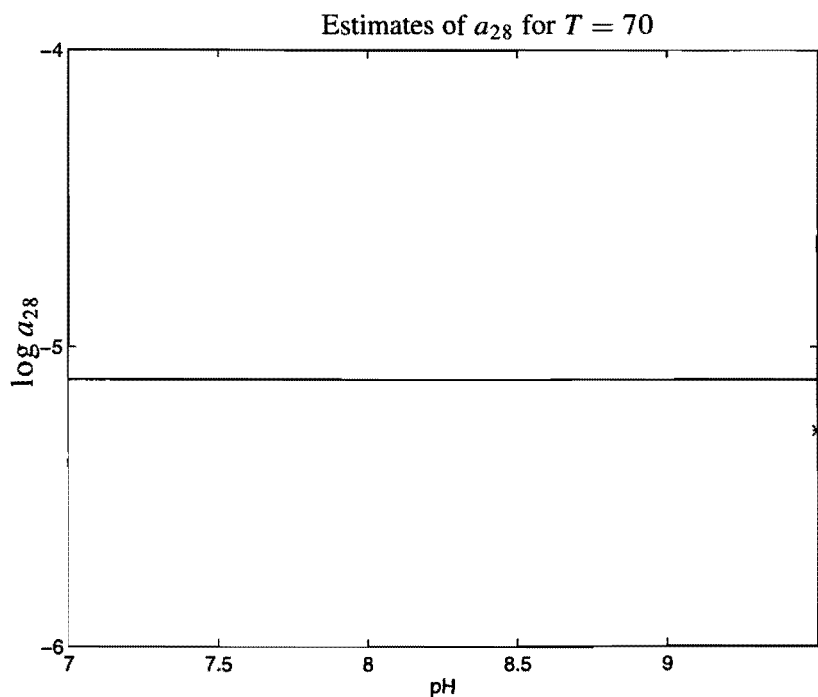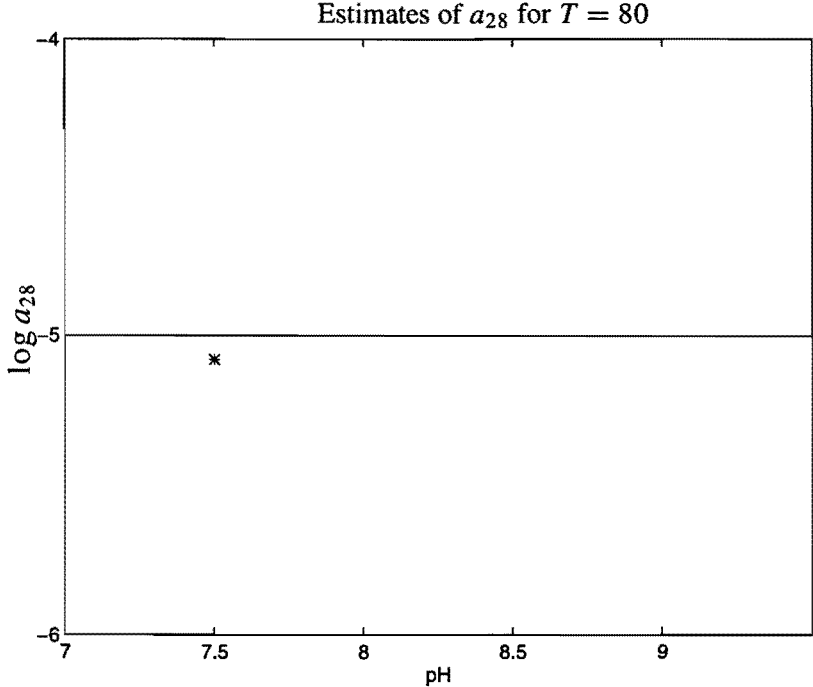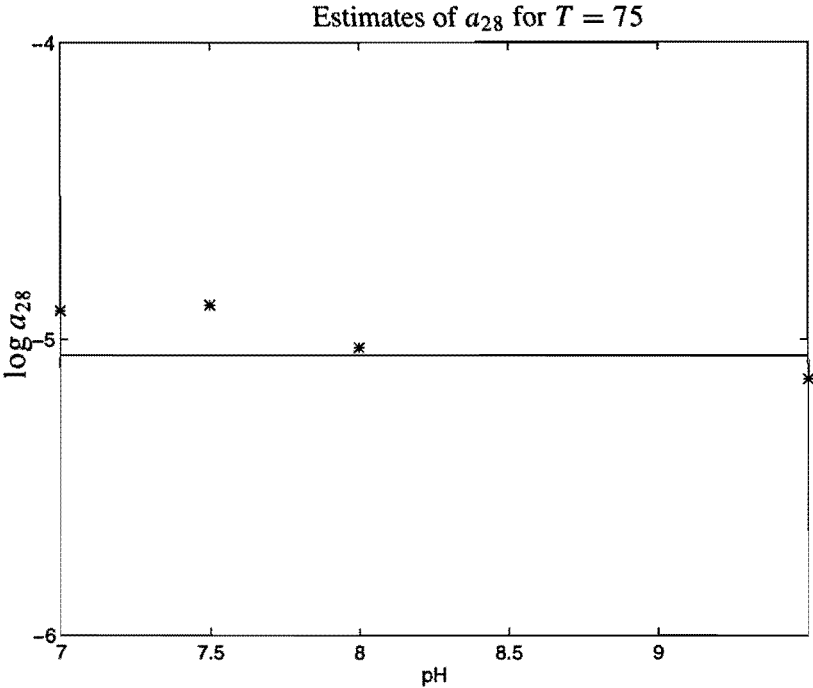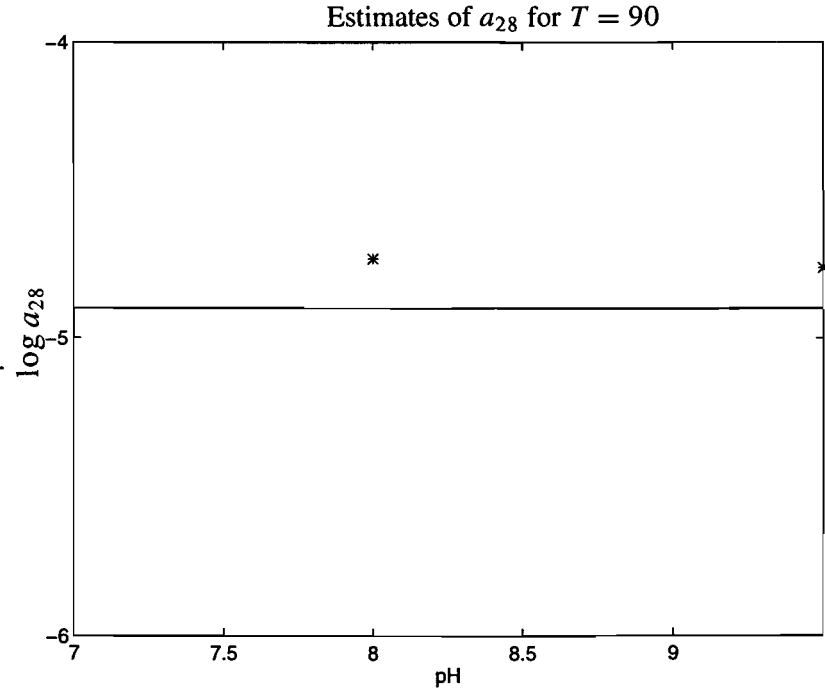
Estimates of a_{27} for $T = 70$

Estimates of a_{27} for $T = 75$

Estimates of a_{27} for $T = 80$

Estimates of a_{27} for $T = 85$

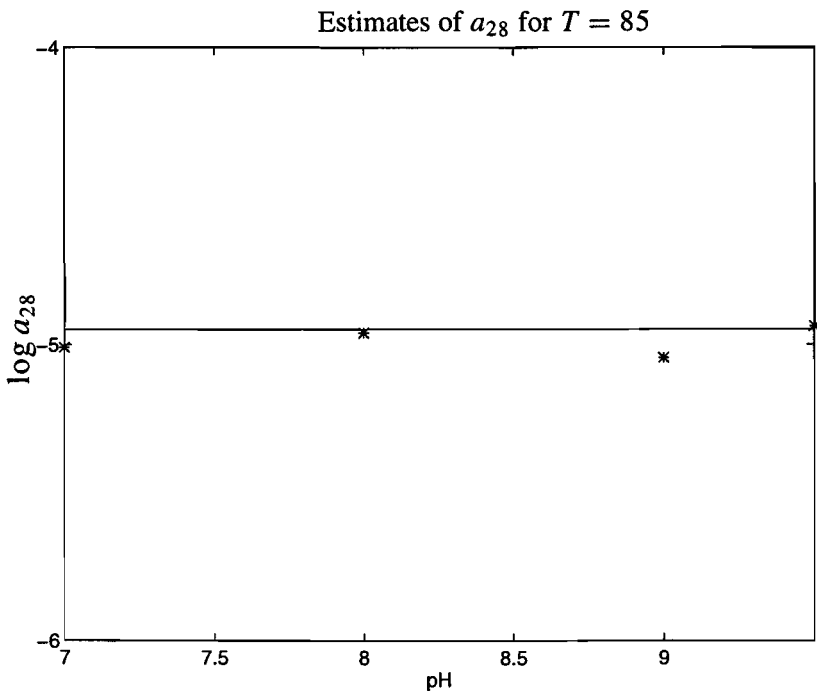## Estimates of a_{27} for $T = 90$

45

Estimates of a_{27} for $T = 95$
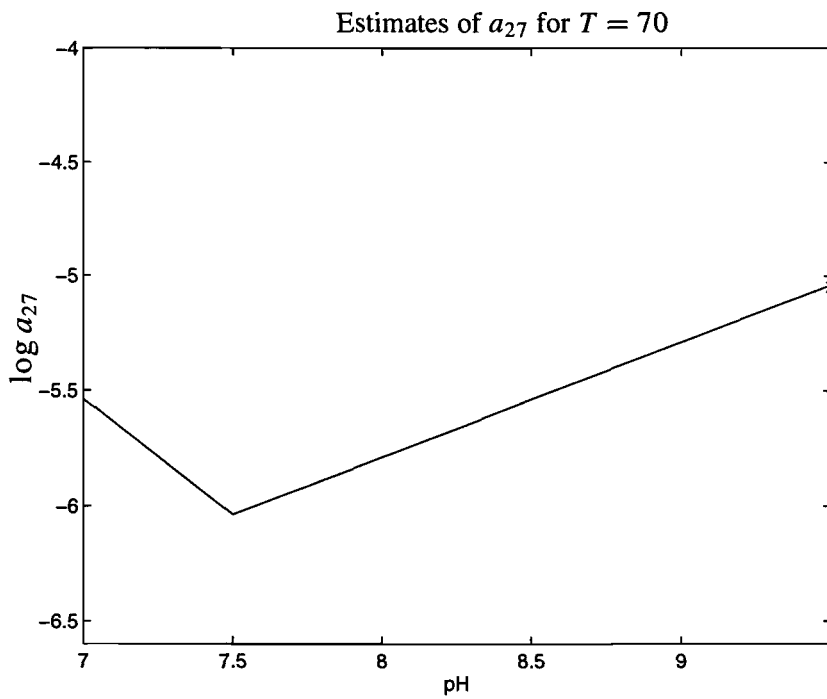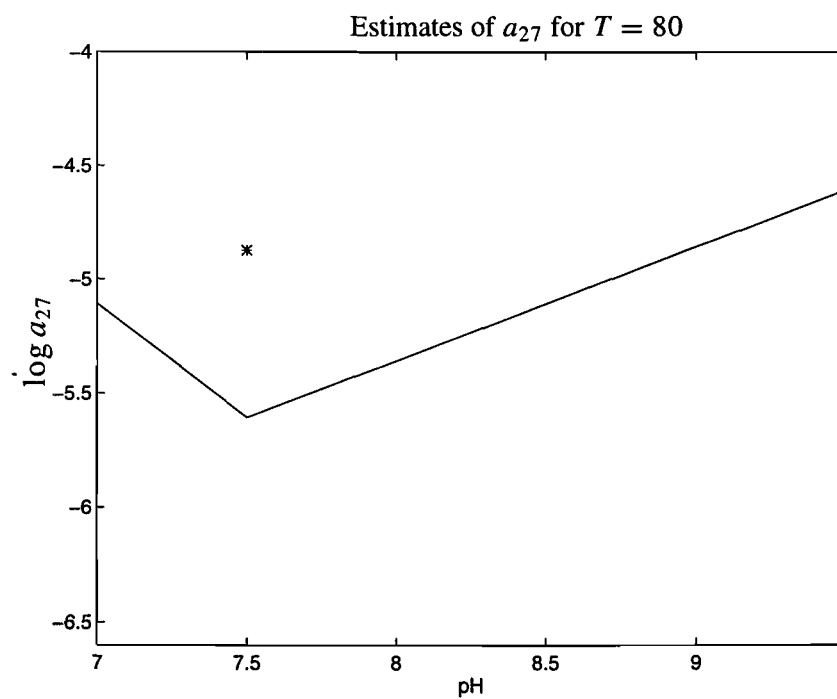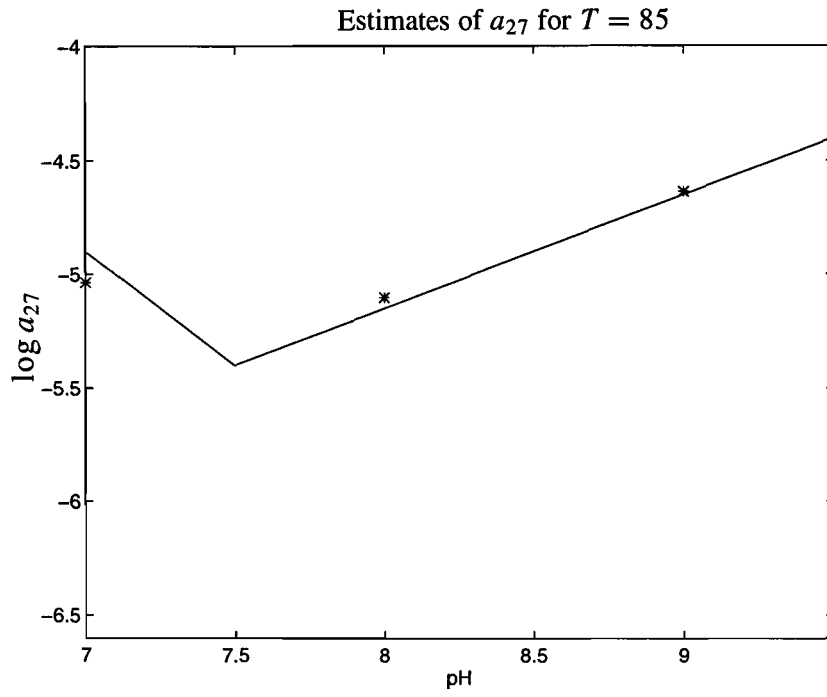
Frmo the plot for a_{27} at temperature $75°$ and $85°$ it seems that a_{27} increases slowly as function of pH. My plot which gives a reasonable fit uses:
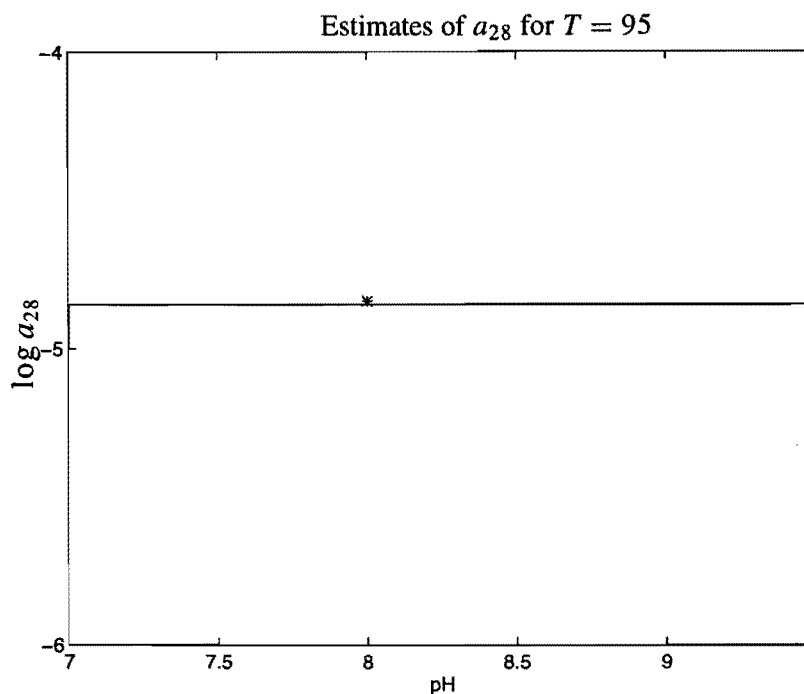
$$\log a_{27} = 0.5\,\mathrm{pH} + \cdots$$

for larger pH levels. Also it is not clear from the estimates whether a_{27} is constant or decreasing for low pH. The final parameter to estimate is a_{28}:

Estimates of a_{28} for $T = 70$

Estimates of a_{28} for $T = 75$

Estimates of a_{28} for $T = 80$

Estimates of a_{28} for $T = 85$

Estimates of a_{28} for $T = 90$

Estimates of a_{28} for $T = 95$

It seems quite consistent to estimate this parameter as constant although like a_5 the sensitivity is quite low which should make us cautious in relying too much on the obtained estimates. Finally we summarize the estimates in the following tables

Table 17: Estimates for coc experiments at $T = 70$

Temperature	a_5	a_{23}	a_{27}	a_{28}
9.5	6.8117e-08	4.2909e-07	8.9575e-06	5.2182e-06

Table 18: Estimates for coc experiments at $T = 75$

Temperature	a_5	a_{23}	a_{27}	a_{28}
7.0	7.3878e-08	2.9291e-06	4.6810e-06	1.2512e-05
7.5	7.3576e-08	1.9547e-06	4.4524e-06	1.3068e-05
8.0	7.0880e-08	1.0864e-06	4.3350e-06	9.3865e-06
9.5	7.2612e-08	6.3784e-07	1.6447e-05	7.3211e-06

Table 19: Estimates for coc experiments at $T = 80$

Temperature	a_5	a_{23}	a_{27}	a_{28}
7.5	7.8654e-08	5.1705e-06	1.3400e-05	8.2791e-06

Table 20: Estimates for coc experiments at $T = 85$

Temperature	a_5	a_{23}	a_{27}	a_{28}
7.0	7.4162e-08	2.4494e-06	9.1858e-06	9.7708e-06
8.0	7.6232e-08	1.0506e-06	7.8981e-06	1.0963e-05
9.0	8.2480e-08	5.6355e-07	2.3108e-05	9.0126e-06
9.5	7.6043e-08	8.7257e-07	3.1238e-05	1.1495e-05

Table 21: Estimates for coc experiments at $T = 90$

Temperature	a_5	a_{23}	a_{27}	a_{28}
8.0	7.8042e-08	1.5003e-06	1.1484e-05	1.8559e-05
9.5	7.5392e-08	1.5342e-06	1.9285e-05	1.7254e-05

Table 22: Estimates for coc experiments at $T = 95$

| Temperature	a_5	a_{23}	a_{27}	a_{28}
8.0	8.5222e-08	3.9689e-06	1.6944e-05	1.4488e-05

4 Conclusion

We have fitted several parameters in this setup. There is unfortunately very little theoretical foundation to obtain good errorbounds. But the important feature is that each estimate at different pH and temperature level is made independent and if we then still obtain a very clear structure of the parameter as a function of pH and temperature then it seems reasonable to expect that we could estimate these parameters quite well. But on the other hand, one could counter this argument by saying that the estimates are made independent but the method to get the estimate is the same in each case and hence the weighting and relative importance given to a particular equation is roughly the same in each case. This could yield a consistent error. But again there is very little theory to prevent this.

The statistics literature for a very large part is concerned with asymptotic results and for this problem all these results are completely useless. But one has to admit that it is also to be expected since probability only predicts about the average. If you only very few measurements then you can simply not guarantee that you are close to the average.

In any case it is obvious that it is hard to get the temperature and pH dependence from this amount of measurements. More measurements are needed. But this is easier said than done.

# A   Estimation of a_3, a_4, a_7, a_8 and a_{15}

From the estimation for homocondensation melamine we have obtained some information about a_3 (and hence also about a_4):

Estimates of a(3) for T=85

Estimates of a(3) for T=90

Estimates of a(3) for T=95
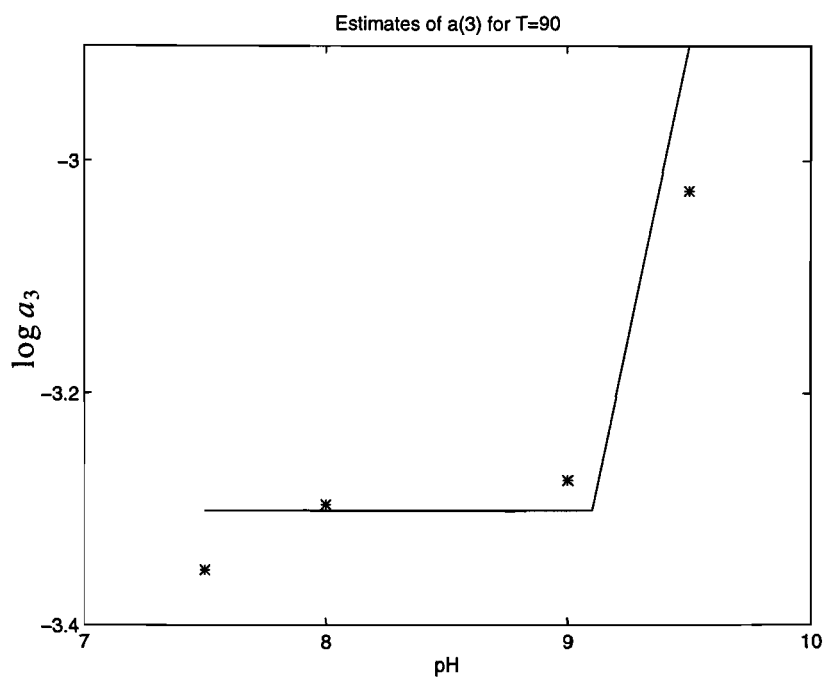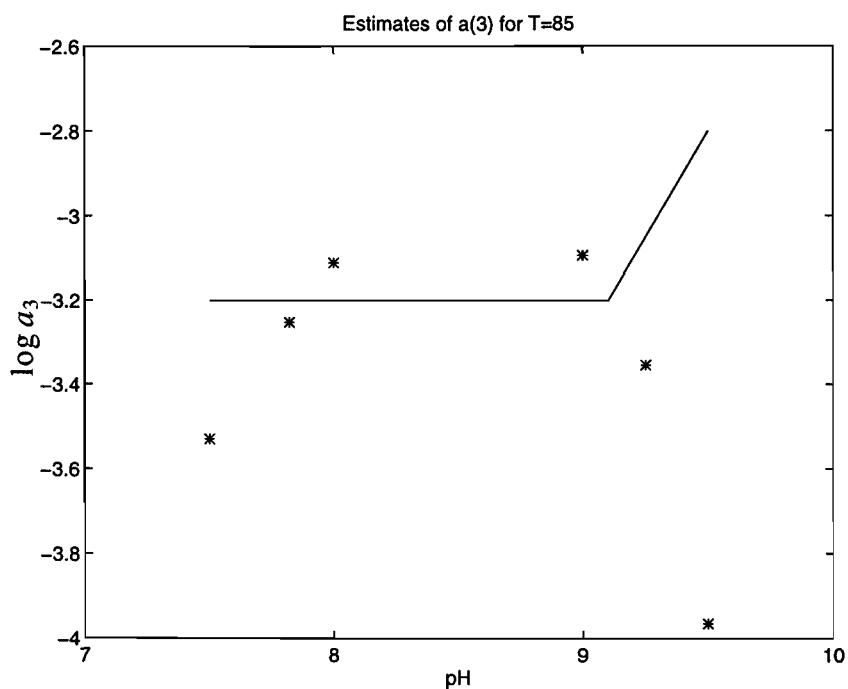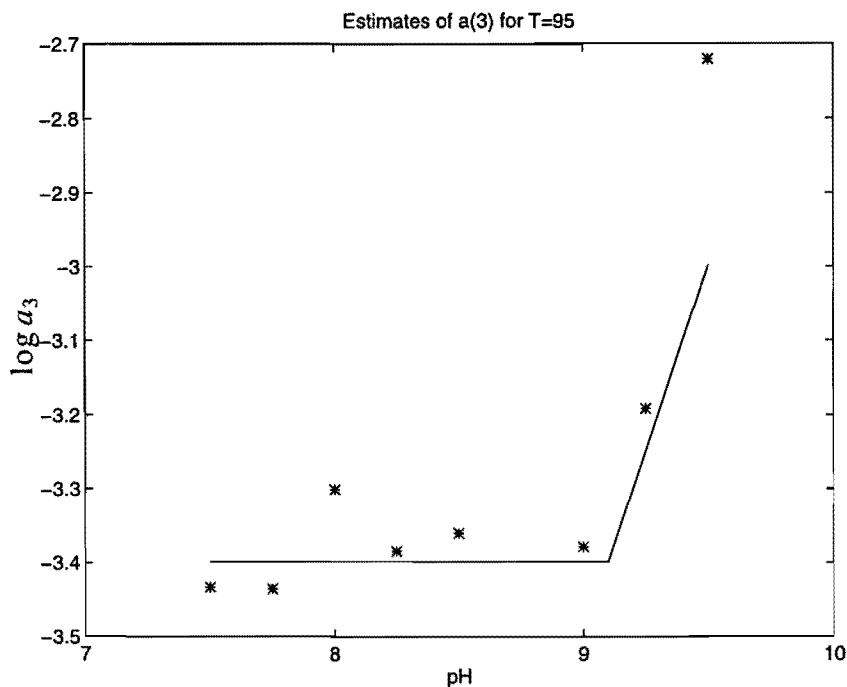
Obviously the pH and temperature dependece of of a_3 is much harder to estimate. The main problem is at $85°$. Our estimates are very small at both low and high pH. The current plot fits that very badly but does a pretty good job at the other temperature levels. Another problem is that it seems that the rate constants are actually decreasing with increasing temperature. My estimation of the activation energy is -50.

We have also obtained some information about a_7 (and hence also about a_8):

Estimates of a_7 for $T = 85$

Estimates of a_7 for $T = 90$


Estimates of a_7 for $T = 95$
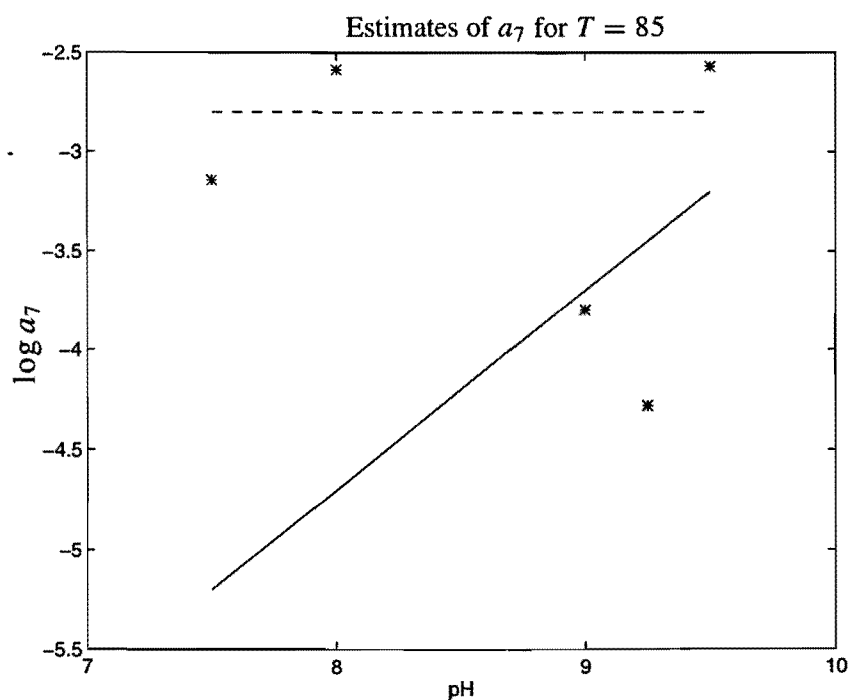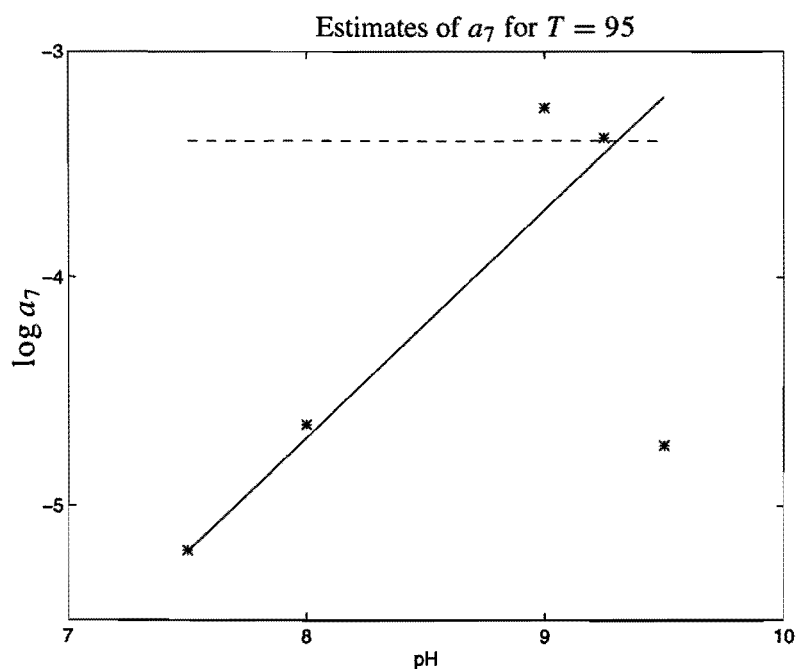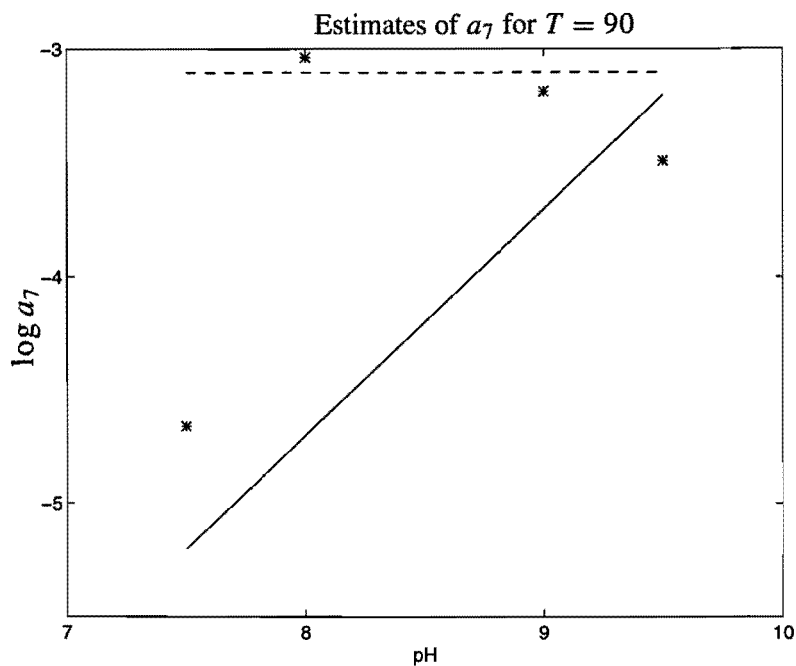
Clearly it is near impossible to say anything regarding a_7 from the above plots. From subsection 2.4 we know that it is very difficult to estomate a_7 from the hplc-mf experiments and hence we have basically fewer data points. Whether we choose the straight line or the dashed line is mathematically impossible to decide. In either case some points are well interpolated and others very badly.

From the estimation for homocondensation ureum we have obtained some information about a_{15}:

Estimates of a_{15} for $T = 65$

Estimates of a_{15} for $T = 75$

Estimates of a_{15} for $T = 85$
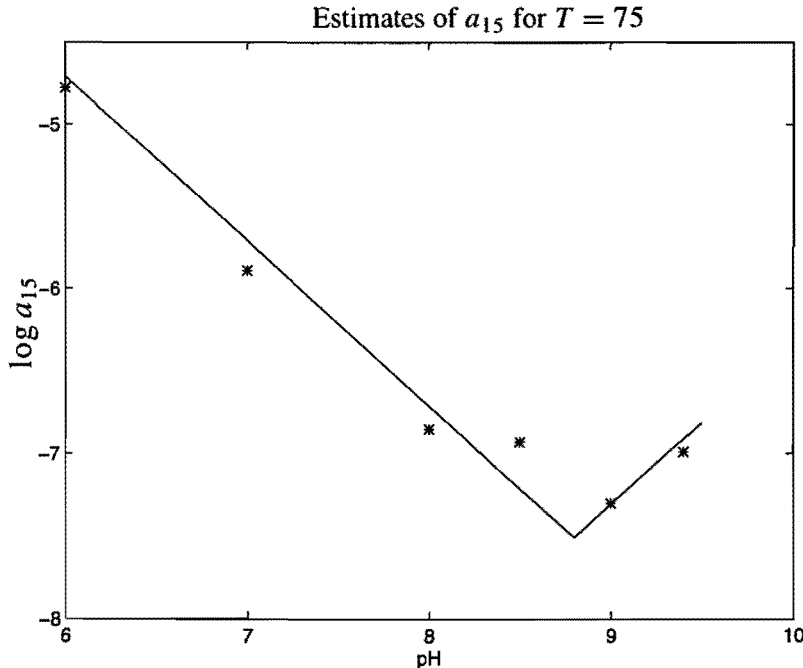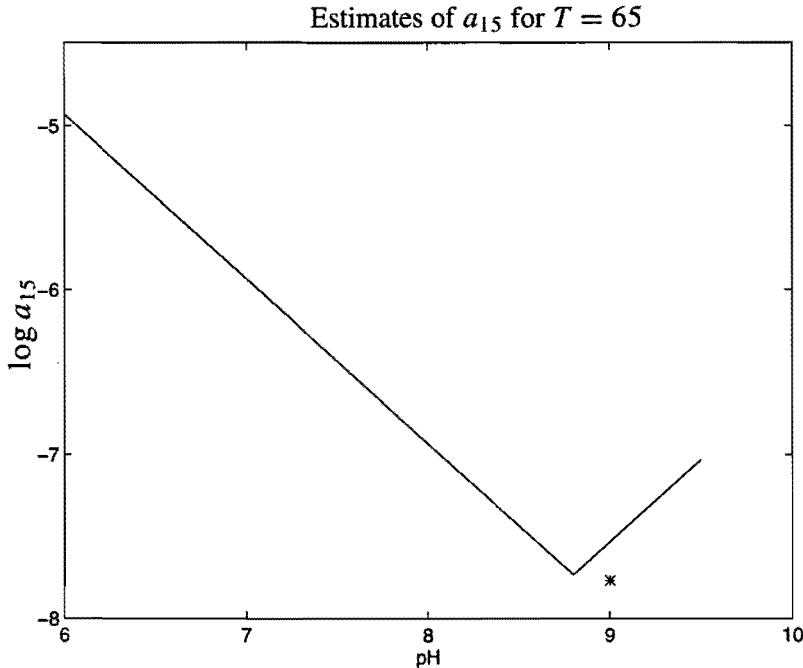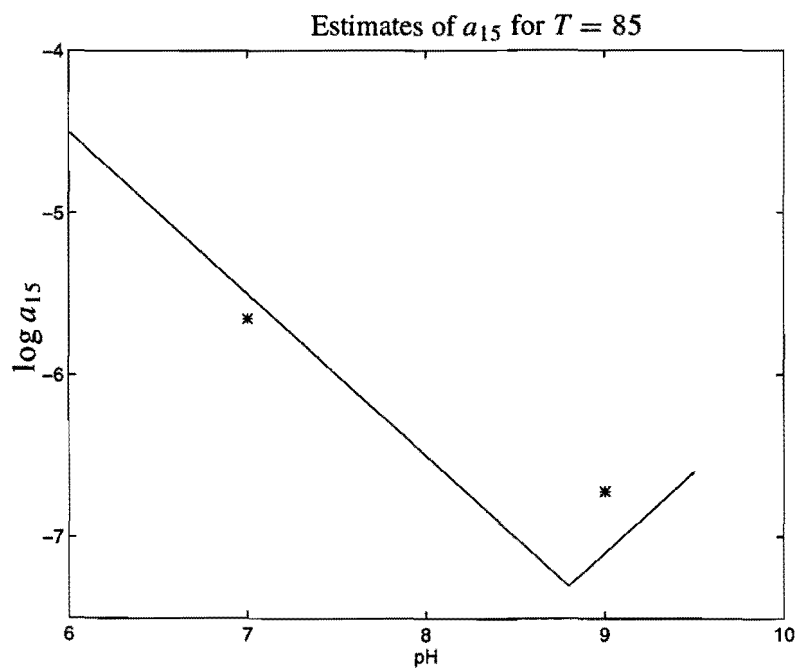
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