Supplementary information for

Adsorption and HPLC of carbohydrates and related hydroxy compounds on zeolites

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Conversion of excess adsorption constants K_{ex} to absolute adsorption values K

The excess adsorption q_{ex} (in g solute per g zeolite) is defined by the concentration difference of the initial solute concentration c_o and its concentration in the equilibrium state c related to the mass of zeolite m_z per volume V_o and it is thus asimple expression of the mass balance

(1) $\qquad c_z = m_z / V_o$

(2) $\qquad q_{ex} = \dfrac{c_o - c}{c_z}$

Small adsorption values should obey Henry's law with K_{ex} being the excess adsorption constant

(3) $\qquad K_{ex} = q_{ex} / c$

Combination with the mass balance (eqn. (2)) yields

(4) $\qquad K_{ex} = \dfrac{c_o - c}{c\, c_z}$

When the volume of the micropore is known, e.g by measurement of the N_2-adsorption at 77K, this volume may be assumed to be filled with molecules of the solvent plus those of the adsorbed solute. The absolute adsorption q is given by the following equation ( )

(5) $\qquad q = \dfrac{c_o - (1 - \omega_o\, m_z / m_o)\, c}{m_z(1/V_o + c/m_o)}$

where ω_o is the amount of solvent (plus solute) in the micropore and m_o is the total mass of the solvent liquid. ω_o may be obtained by measuring the micropore volume by N_2 adsorption at 77K and assuming a density equal to the bulk phase. By defining the absolute henry constant via

(6) $\qquad K = q / c$

and by using the solvent density ρ according to

(7) $\qquad m_o = \rho\, V_o$

one obtains

(8) $\qquad K = \dfrac{c_o - (1 - \omega_o\, c_z / \rho)\, c}{c\, c_z (1 + c / \rho)}$

and after rearrangement

(9) $\qquad K = \dfrac{c_o - c}{c\, c_z (1 + c / \rho)} + \dfrac{\omega_o}{(\rho + c)}$

For the limit of small equilibrium concentrations that equation reduces to

(10) $\qquad \lim\limits_{c \to 0} K = \dfrac{c_o - c}{c\, c_z} + \omega_o / \rho$

Adsorption of a monobasic organic acid

The concentration of the monobasic acid in aqueous solution is given by the sum of its dissociated c_{A^-} and its non-dissociated part c_{AH}

(11) $\quad c_{AH,o} = c_{AH} + c_{A^-}$

The law of mass action

(12) $\quad (c_{A^-}\, c_{H^+}) / c_{AH} = K_a$

is modified by the condition of electro neutrality in a medium with the proton concentration c_{H^+} via

(13) $\quad c_{A^-} = c_{H^+}$

to

(14) $\quad c_{AH} = c_{H^+}^2 / K_a$

Due to the adsorption of the non-dissociated acid the initial concentration $c_{AH\,tot}$ is reduced to c_{AH} according to

(15) $\quad c_{AH,tot} - c_{AH\,o} = K_{ex}\, c_z\, c_{AH}$

where K_{ex} is the excess adsorption equilibrium constant for the non-dissociated acid and c_z is the zeolite concentration, and with eqn. (14) one obtains

(16) $\quad c_{AH\,tot} - c_{AH\,o} = K_{ex}\, c_z\, c_{H^+}^2 / K_a$

Formally the adsorption can also be described as the adsorption of the non-dissociated plus dissociated form by the constant K_{ex}' via

(17) $\quad c_{AH\,tot} - c_{AH,o} = K_{ex}'\, c_z\, c_{AH,o}$

and one obtains

(18) $\quad K_{ex}'\, c_{AH,o} = K_{ex}\, c_{H^+}^2 / K_a$

At last the substitution of $c_{AH,o}$ by the eqns. (11), (13), and (14) results in

(19) $\quad K_{ex}' = K_{ex}\, c_{H^+} / (c_{H^+} + K_a)$

Adsorption of a tribasic organic acid

The tribasic acid is composed of

(20) $c_{AH3,o} = c_{AH3} + c_{AH2^-} + c_{AH^{--}} + c_{A^{---}}$.

As only the behavior at lower pH is of interest, the concentration of $c_{A^{---}}$ is neglected here.

Instead of eqn. (12) the law of mass action is now represented by

(21) $(c_{AH2^-} \, c_{H^+}) / c_{AH3} = K_{a1}$

and

(22) $(c_{AH^{--}} \, c_{H^+}) / c_{AH2^-} = K_{a2}$

Instead of eqn. (13) the state of electro neutrality is defined by

(23) $c_{AH2^-} + (1/2) \, c_{AH^{--}} = c_{H^+}$

If the concentration of $c_{AH^{--}}$ is expressed by using the mass law action (21), eqn. (22) can be transformed to

(24) $c_{AH2^-} = c_{H^+}^2 / (c_{H^+} + (1/2) \, K_{a2})$

and by using eqn. (20) one obtains for the concentration of the non-dissociated acid

(25) $c_{AH3} = c_{H^+}^3 / \{(c_{H^+} + (1/2) \, K_{a2}) \, K_{a1}\}$

Again, it has to be implemented that the initial concentration $c_{AH3,tot}$ is reduced to $c_{AH3\,o}$ by the adsorption of the non-dissociated acid on the zeolite according to

(26) $c_{AH,tot} - c_{AH3\,o} = K_{ex} \, c_z \, c_{AH3}$

and by consideration of eqn. (25) one obtains

(27) $c_{AH,tot} - c_{AH3\,o} = K_{ex} \, c_z \, c_{H^+}^3 / \{(c_{H^+} + (1/2) \, K_{a2}) \, K_{a1}\}$

Alternatively the adsorption can also be described as the adsorption of the non-dissociated plus dissociated form by the constant K_{ex}' via

(28) $c_{AH\,tot} - c_{AH3,o} = K_{ex}' \, c_z \, c_{AH3,o}$

and one obtains

(29) $K_{ex}' \, c_{AH3,o} = K_{ex} \, c_{H^+}^3 / \{(c_{H^+} + (1/2) \, K_{a2}) \, K_{a1}\}$

$c_{AH3,o}$ can be expressed as a function of c_{H^+} by using the eqns. (21), (22), and (20) by canceling the $c_{A^{---}}$ term:

(30) $c_{AH3,o} = c_{H^+} (c_{H^+}^2 + c_{H^+} \, K_{a1} + K_{a1} \, K_{a2}) / \{ (c_{H^+} + (1/2) \, K_{a2}) \, K_{a1}\}$

At last the insertion of eqn. (30) into (29) yields

(31) $K_{ex}' = K_{ex} \, c_{H^+}^2 / (c_{H^+}^2 + c_{H^+} \, K_{a1} + K_{a1} \, K_{a2})$

Additional Tables and Figures

Table A1: Numerical data of Figure 7.

Retention times for a column filled with SC1011 and NH2P-50 4E both from Shodex company were taken from their website. In case of SC1011, which is a Ca++ exchanged sulfonic acid resin of 6 μm diameter, the temperature is 80°C, the eluent is water with 1 mL min^{-1}, and the column has a diameter of 8 mm and a length of 300 mm ; in case of NH2P-50 4E, which is functionalized with amino groups on porous silica of 5 μm diameter, the temperature is 30°C, the eluent is acetonitrile / water (75/25) with 1 ml min^{-1}, and the column has a diameter of 4.6 mm and a length of 250 mm. Data for the void volume (pullulan, D_2O) were disclosed by the company.

|	retention		capacity factors			selectivity		
	Ca^{++}	NH_2	Ca^{++}	NH_2	DAY	Ca^{++}	NH_2	DAY
void marker	**5.30**	**2.53**						
glucose	**7.30**	**6.75**	**0.38**	**1.67**	**1.73**	**1.00**	**1.00**	**1.00**
galactose	7.98	8.10	0.51	2.20	2.04	1.34	1.32	1.18
sorbose	8.03	7.35	0.52	1.91	2.71	1.37	1.14	1.57
mannose	8.17	7.84	0.54	2.10	2.88	1.44	1.26	1.66
fructose	8.85	6.79	0.67	1.68	3.40	1.78	1.01	1.97
gentiobiose	6.08	16.36	0.15	5.47	0.97	0.75	1.18	0.83
maltose	**6.34**	**14.24**	**0.20**	**4.63**	**1.17**	**1.00**	**1.00**	**1.00**
lactose	6.51	13.27	0.23	4.25	1.61	1.16	0.92	1.38
trehalose	6.27	13.25	0.18	4.24	1.69	0.93	0.92	1.44
melibiose	6.45	14.70	0.22	4.81	2.69	1.11	1.04	2.30
lactulose	6.99	10.72	0.32	3.24	3.15	1.63	0.70	2.69
isomaltose	6.26	15.18	0.18	5.00	5.14	0.92	1.08	4.39
trehalulose	6.95	11.68	0.31	3.62	13.80	1.59	0.78	11.79
isomaltulose	6.45	12.14	0.22	3.80	16.25	1.11	0.82	13.89
sucrose	6.29	11.87	0.19	3.69	32.05	0.95	0.80	27.39
melezitose	5.79	19.27	0.09	6.62	0.02	0.83	0.75	0.05
maltotriose	**5.89**	**24.96**	**0.11**	**8.87**	**0.44**	**1.00**	**1.00**	**1.00**
panose	5.78	25.60	0.09	9.12	2.61	0.81	1.03	5.92
raffinose	5.78	20.25	0.09	7.00	17.90	0.81	0.79	40.68
isomaltotriose	5.80	27.60	0.09	9.91	51.00	0.85	1.12	115.91
stachyose	5.60	36.20						
nystose	5.50	31.90						
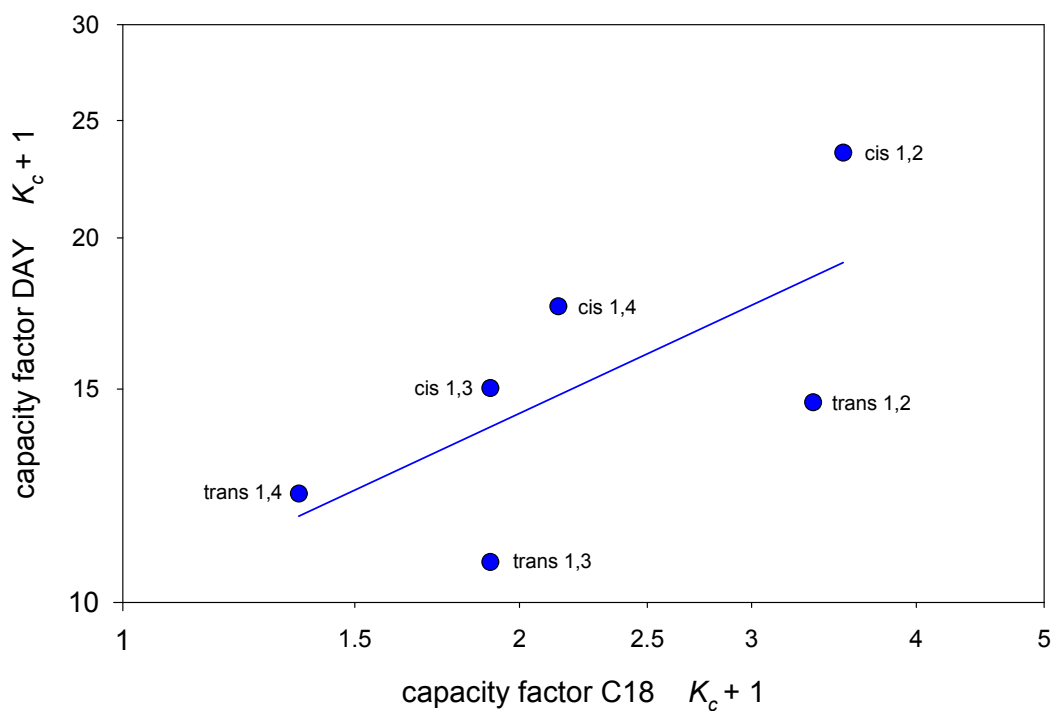
Figure A1: Correlation of the HPLC on the DAY zeolite at 25°C and the hydrophobicity at the C18 surface for isomeric cyclohexanediols at 60°C.
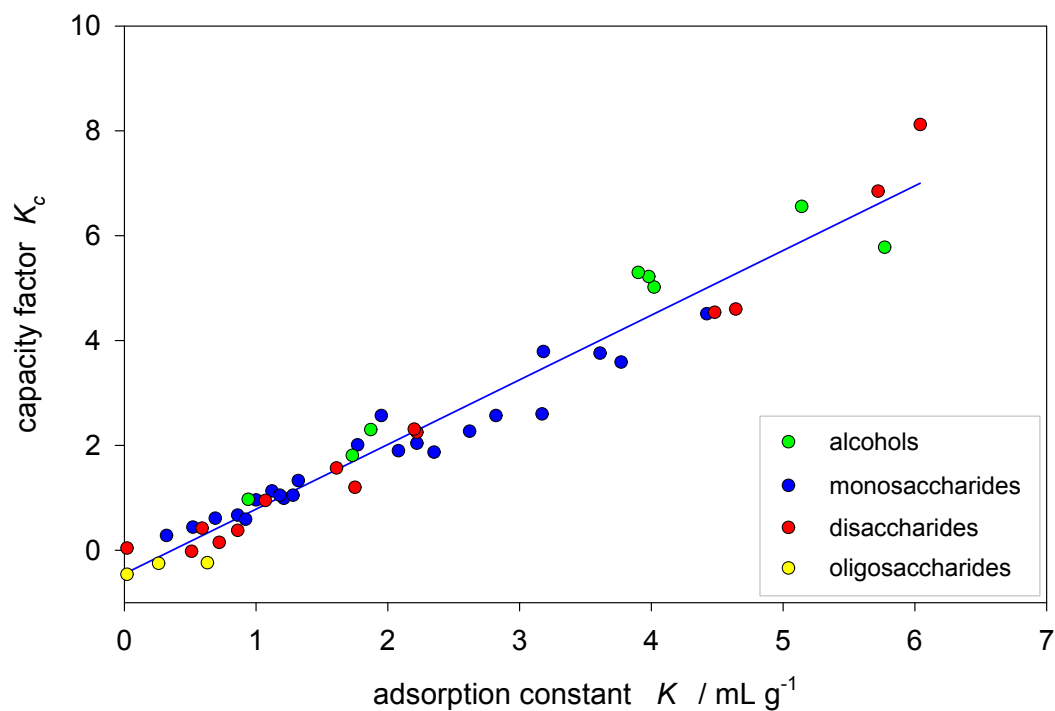

Figure A2: Correlation of the original capacity K_c factors as related to dextran and the absolute adsorption equilibrium constant K.
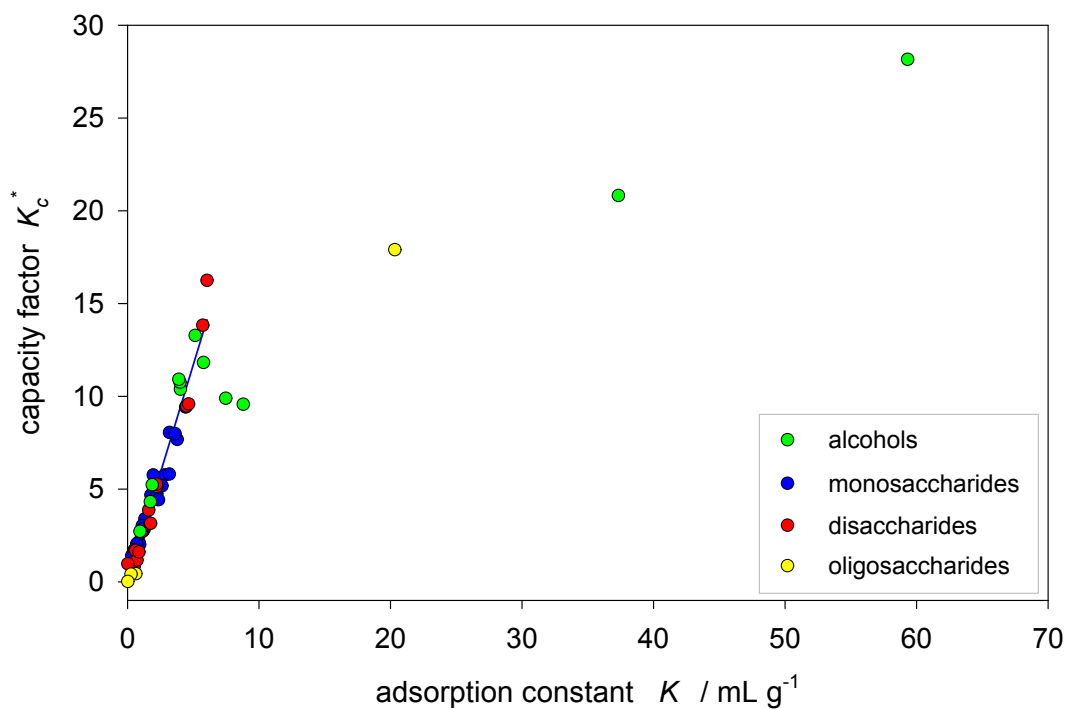
Figure A3: Full-range correlation of the HPLC capacity factors (corrected values) K_c^* and the absolute adsorption equilibrium constants K for the DAY zeolite.
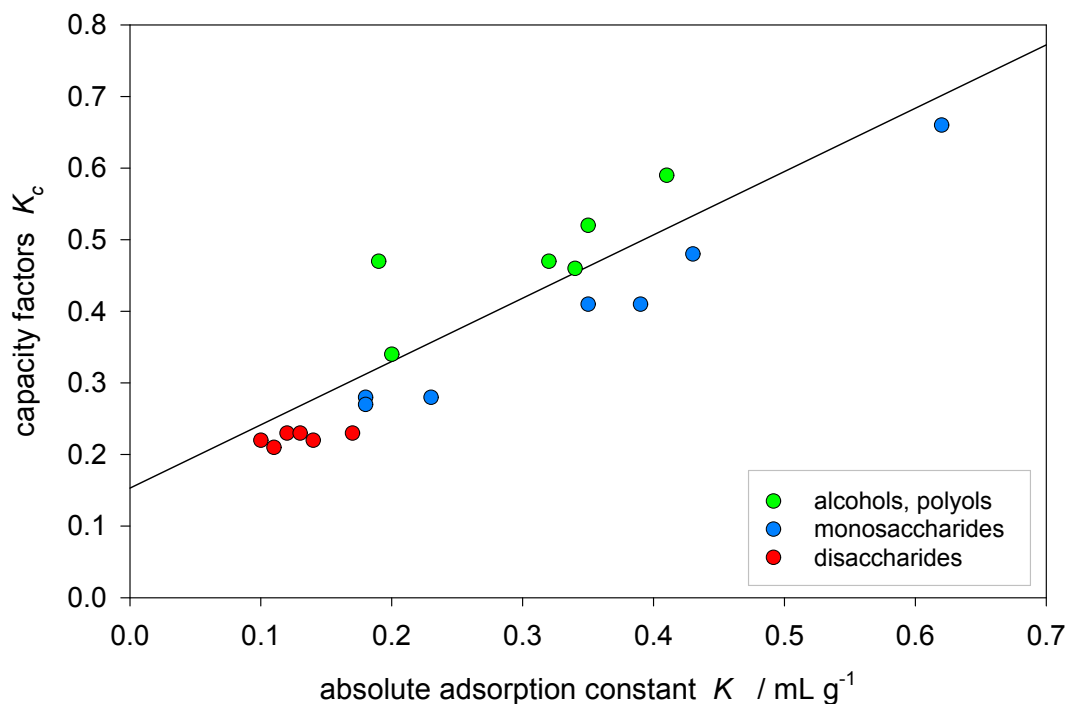

Figure A4: Correlation of the original capacity factors K_c and the absolute adsorption equilibrium constants K for the MOR type zeolite (Si/Al = 73.5)
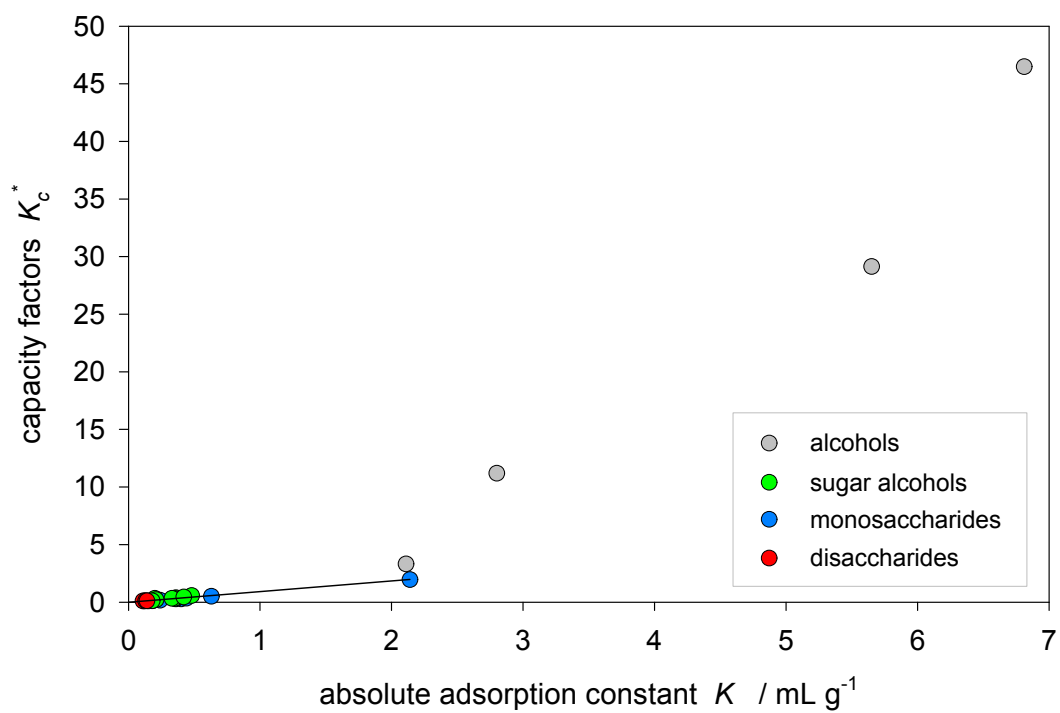
Figure A.5: Correlation between the corrected capacity factors K_c^* and the absolute adsorption equilibrium constants K for the MOR type zeolite (Si/Al = 73.5) - full data range.
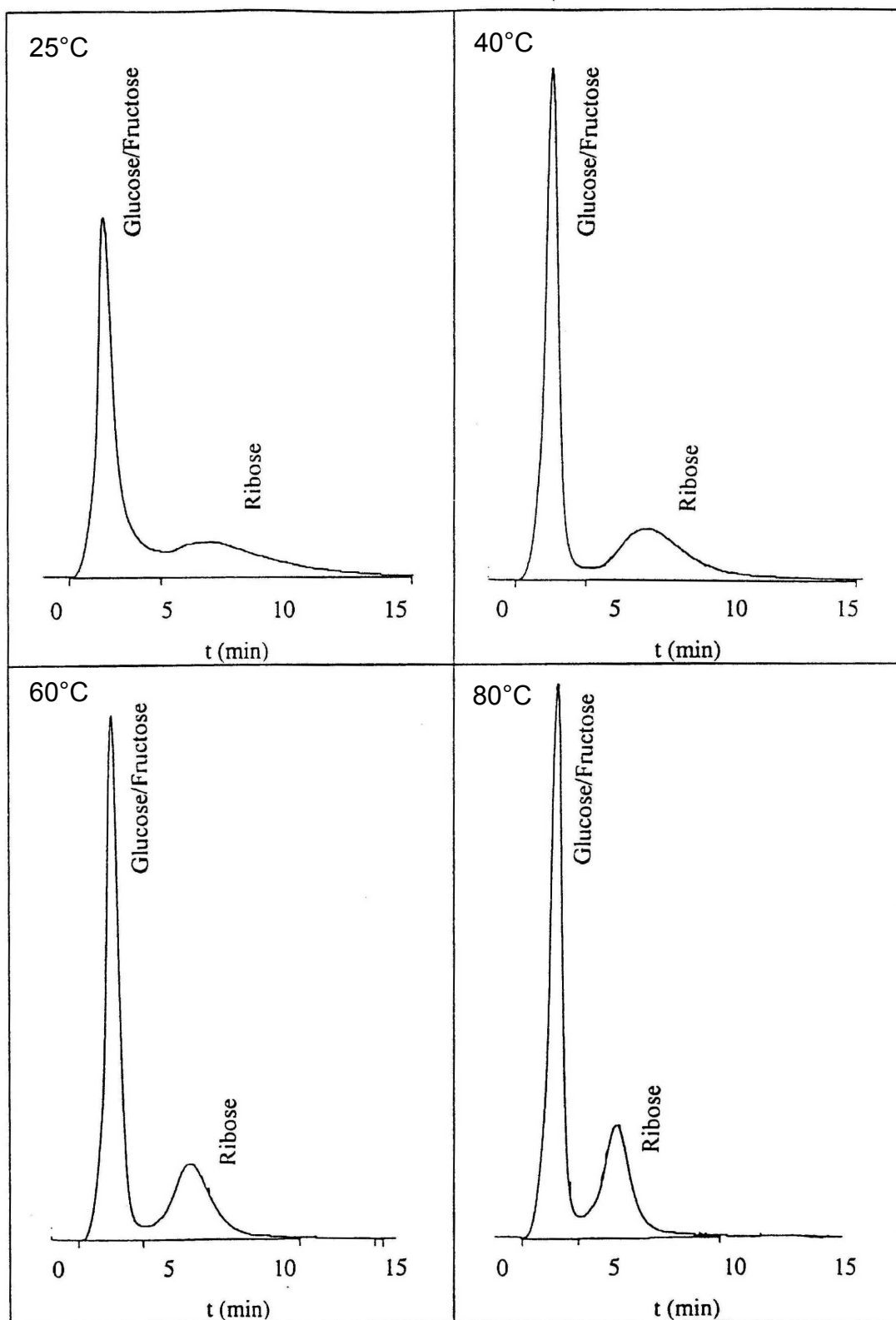
Figure A.6: HPLC of a solution of ribose, fructose, and glucose (each 10 gL^{-1}) at different temperatures on the column filled with MOR zeolite (Si/Al = 73.5), 125 x 4 mm, flow 0.5 mL min^{-1}, injection 20 µL