

Relative activities of siloxane monomers toward the cation exchange resin-catalyst in the equilibration reactions

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The relative activities of a number of siloxane monomers, both cyclic and linear, toward the cation exchange resin-equilibration catalyst were determined. The determination was based on the fact that when a particular siloxane compound is added to an arbitrarily chosen equilibrate, it takes part in the equilibration process, provoking certain viscosity changes of the reaction mixture. Taking these viscosity changes as a measure of activities, the following order was obtained: hexamethylcyclotrisiloxane > hexamethyldisiloxane > octamethylcyclotetrasiloxane > one linear all-methyl oligosiloxane of number average molecular weight of approximately 800 > decamethylcyclopentasiloxane. The results obtained by using the described viscosimetric determination method were controlled by measuring the number average molecular weights of the reaction mixtures at the beginning and at the end of the equilibration process. The deviations of the experimentally measured from the calculated values were less than 20 %, as was found in one equilibration system. In most other systems the deviations were about 10 % which is a very good result which strengthens the validity of the applied determination method.

Keywords: cation exchange resin, catalyzed siloxane equilibration, activities of siloxane monomers, acidic equilibration catalyst.

INTRODUCTION

The problem of different activities of siloxane monomers toward the catalyst in equilibration processes was examined back in the early days of siloxane chemistry. More than forty years ago it was reported that in acid-catalyzed (by sulfuric acid) equilibrations the following order of activities exists¹: $D_3 > MM > MDM > MD_2M > D_4$ (where: M: $(CH_3)_3SiO_{1/2}$ and D: $(CH_3)_2SiO$). In the meantime new classes of acidic equilibration catalysts were introduced. Among others, cation exchange resins (CER) became very important, mostly because of their broad industrial application.^{2,3} Besides this, the use of CER-catalysts changes the nature of the catalytic process; instead of being homogeneous (if, for example, sulfuric acid is used) it becomes heterogeneous. For this reason it seemed to be opportune to (re)investigate the behavior of some commonly

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used siloxane monomers toward the acidic CER-catalysts. Finally, a new experimental approach to this problem, the principle of which was presented in a recently published article,⁴ gave an additional impetus to this investigation.

The activities of the following siloxane monomers were determined: hexamethylcyclotrisiloxane $[(\text{CH}_3)_2\text{SiO}]_3$, (D₃), octamethylcyclotetrasiloxane $[(\text{CH}_3)_2\text{SiO}]_4$, (D₄), decamethylcyclopentasiloxane $[(\text{CH}_3)_2\text{SiO}]_5$, (D₅), hexamethyldisiloxane $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$, (MM), and of one linear all-methyl oligosiloxane of number average degree of polymerization $\overline{DP}_n = 8.5$, $(\text{CH}_3)_3[(\text{CH}_3)_2\text{SiO}]_{8.5}\text{OSi}(\text{CH}_3)_3$, (MD_{8.5}M).

Elements of the determination procedure

The determination procedure was basically identical to that described in a previous communication.⁴ In brief, a series of equilibrations of an arbitrary chosen equilibrate (named the basic equilibrate, BE) and a siloxane compound, the activity of which was to be determined, was performed keeping the molal ratio (equilibrate)/(siloxane compound) constant throughout the entire series. The inherent viscosities of these equilibrating mixtures were registered at arbitrarily selected time intervals until the equilibria were attained. Then, taking the instantaneous viscosity changes as fractions of the total change, the "fractional viscosities" were calculated:

$$\eta_{\text{inh}}(\text{fractional}) = \frac{|\eta_{\text{inh}}^{(\text{initial})} - \eta_{\text{inh}}^{(\text{actual})}|}{|\eta_{\text{inh}}^{(\text{initial})} - \eta_{\text{inh}}^{(\text{final})}|} = \frac{\Delta\eta_{\text{inh}}^{(\text{actual})}}{\Delta\eta_{\text{inh}}^{(\text{total})}}$$

where $\eta_{\text{inh}}(\text{initial})$ is the viscosity of the starting reaction mixture; $\eta_{\text{inh}}(\text{actual})$ is the viscosity of the equilibrating reaction mixture at a specified reaction time; $\eta_{\text{inh}}(\text{final})$ is the viscosity of the equilibrate after completion of the reaction.

In the above formula, the viscosity changes $\Delta\eta_{\text{inh}}(\text{actual})$ and $\Delta\eta_{\text{inh}}(\text{total})$ were taken as absolute values of the corresponding differences, because these changes could be either positive or negative, depending on the nature of the reacting siloxane monomer. For example, MM would shorten the polymer chains and hence lower the viscosity, whereas D₄ would extend the chains and so increase the viscosity.

The obtained fractional viscosities as a function of reaction (equilibration) time are actually the measure of the activity of the examined siloxane compound toward the catalyst. A simple comparison made on a set of such viscosity–reaction time curves obtained for different siloxanes enables the determination of the order of the relative activities of these siloxanes toward the concrete equilibration catalyst.

EXPERIMENTAL

Materials. The monomeric siloxane compounds: D₃, D₄, D₅ and MM were purchased from ABCR GmbH + Co.KG (Germany) and used as received. The linear all-methyl oligosiloxane, MD_{8.5}M, was prepared in our laboratory. A commercial grade macroreticular cation exchange resin, MCER, Doulite C 26, obtained from Diamond Shamrock, USA, and having a total capacity of 1.85 eq/L, was used as the equilibration catalyst after overnight warming at 50 °C.

Equilibrations. All equilibrations, including that used for the preparation of the basic equilibrate, were carried out in a three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser and a thermometer. The flask was placed into a constant temperature oil bath.

The amount of MCER-catalyst was in all cases 2.2 meq/10 g of reaction mixture. The reaction temperature was held constant at 70 °C, whereas the basic equilibrate was obtained by equilibrating at 95 °C for 24 h. A detailed description of the equilibration procedure can be found elsewhere.⁵

Determination of inherent viscosities. The viscosities were determined using an Ubbelohde-type viscosimeter in toluene at 30 °C. The concentrations of solutions amounted to approximately 0.15 g/cm³.

Determination of molecular weights. The number average molecular weights were determined on a Knauer vapor pressure osmometer at 30 °C. The instrument was calibrated with benzil (dibenzoyl) and the samples were dissolved in methylene chloride.

RESULTS AND DISCUSSION

Relative activities. The equilibrate used in the equilibrations aimed at the determination of the relative activities (BE) was obtained by equilibrating a mixture of 99 wt% of D₄ and 1 wt% of MM, which was an arbitrary choice, as any other composition could also have been used as long as it represents a real equilibrate. The main characteristics of the chosen equilibrate were: inherent viscosity $\eta_{inh} = 11.4 \text{ cm}^3/\text{g}$, bulk viscosity $\eta_{bulk} = 0.402 \text{ Pa s}$ and number average molecular weight $\bar{M}_n = 2613$.

Table I lists the compositions of the starting reaction mixtures and the measured inherent viscosities after different reaction time intervals. Using these viscosity data, the fractional viscosities were calculated and the results are presented as a function of reaction time in Fig. 1.

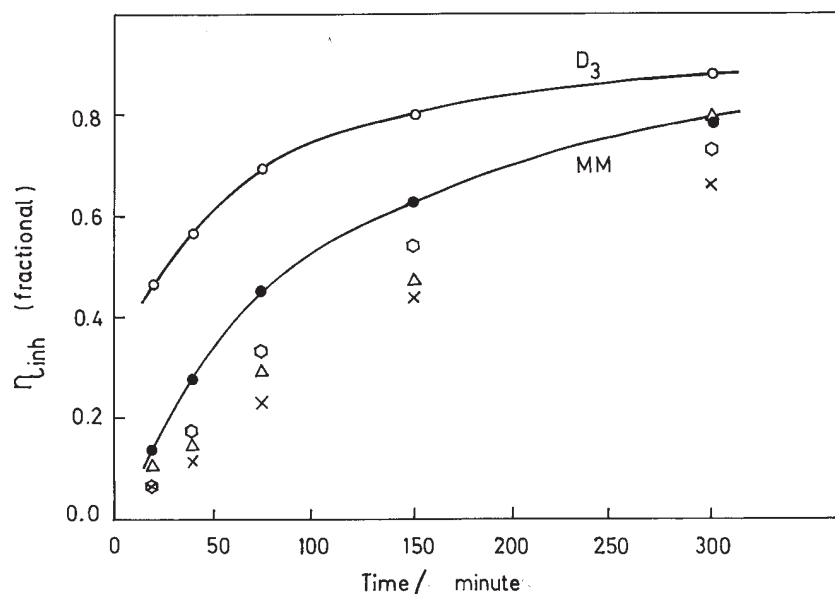


Fig. 1. η_{inh} (fractional) as a function of reaction time (siloxane compounds: D₃ - o; D₄ - \circ ; D₅ - x; MM - \bullet ; MD_{8.5}M - Δ).

It can be seen that the activities of D₃ and MM only are clearly distinguishable; D₃ is the most active siloxane monomer followed by MM. The position of the other ex-

perimental points did not permit the construction of unambiguous and hence quite distinguishable curves. It is clear, however, that all the other examined siloxanes are less active than the first two, *i.e.*, D₃ and MM. Therefore, in a somewhat speculative way, the following order of activities might be adopted: D₃>MM>(D₄≥MD_{8.5}M≥D₅).

TABLE I. Starting equilibration compositions and inherent viscosities at different reaction time intervals

Reaction times, minutes	Inherent viscosities*, cm ³ /g, at given starting compositions**, g				
	D ₃	D ₄	D ₅	MM	MD _{8.5} M
	4.50	6.00	7.50	3.28	16.00
Initial state	9.48	9.21	8.14	10.84	6.34
20	11.87	9.58	8.63	9.85	5.94
40	12.37	10.26	8.99	8.82	5.79
75	13.02	11.23	9.79	7.49	5.25
150	13.59	12.51	11.38	6.21	4.57
300	14.00	13.67	13.00	5.06	3.40
Final state	14.61	15.28	15.53	3.39	2.63
Δη _{inh} (total)	5.13	6.06	7.39	7.45	3.71

*These values are averages obtained from 4–5 individual runs, none of them differed by more than ±5% from the average value.

**In all equilibrations the amount of BE was 15 g and the concentration of CER-catalyst was 0.45 g (corresponding to 2.2 meq)/10 g of the reaction mixture.

D₃ is the most active siloxane monomer probably due to the relative instability introduced by the strain energy of its six-membered planar ring. Higher membered siloxane rings are nonplanar (and hence more or less unstrained) and the energies of their Si–O bonds, as well as of siloxane bonds in linear siloxanes, are very similar to each other.⁶ Furthermore, the effect of CH₃ electron-donating groups on the Si–O bond(s), *i.e.*, on the basicity of the oxygen atom of the Si–O bond(s) and, in this way, on its(their) activity(ies) toward the acidic catalysts in linear siloxanes, must be much more pronounced in MM than in higher homologues. This means that, with the exceptions of D₃ and MM, the activities of all higher siloxane homologues, both cyclic and linear, should become more and more similar.

Molecular weights. The above outline and hence the results obtained by its application too, were additionally substantiated in the following way.

The base of the procedure is the equilibration reaction between BE and a particular siloxane monomer. The number average molecular weights of both the starting mixtures, as well as of these mixtures in final state can be easily experimentally determined. However, the same molecular weight values can also be calculated using the following assumptions and approximations: a) the compositions of all equilibria – regarding the (linear polymer)/(cyclics) ratio – were adopted from literature data,^{7,8} and they ranged, when expressed as weight fractions of cyclics in the equilibria, between approximately 4 % and 14 %, depending on the molecular weight of the linear polymer present in the equilibria; b) the average molecular weight of the cyclosiloxane mixture at equilibria

was taken to amount to 300, as the main constituent of this mixture, D₄, has a molecular weight of 296, and c) all the final states were assumed to be real equilibria.

TABLE II. Number average molecular weights of initial and final equilibration mixtures

Sample composition (g)	$M_n(\text{initial})$		$M_n(\text{final})$	
	Calc.	Exp.	Calc.	Exp.
BE* + D ₃ (15 + 4.50)	730	–	2415	2590
BE* + D ₄ (15 + 6.00)	787	822	2437	2957
BE* + D ₅ (15 + 7.50)	843	905	2454	2839
BE* + MM (15 + 3.28)	685	750	754	850
BE* + MD _{8.5} M (15 + 16.00)	1163	1025	1027	909

*The calculated and experimentally determined number average molecular weights of BE were 2334 and 2613, respectively.

The comparison of the calculated and corresponding experimentally determined (by vapor pressure osmometry) average molecular weights, given in Table II, shows a fair agreement and supports the validity of the applied procedure used for the determination of the relative activities.

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ИЗВОД

РЕЛАТИВНЕ АКТИВНОСТИ СИЛОКСАНСКИХ МОНОМЕРА ПРЕМА КАТЈОНСКОЈ ЈОНОИЗМЕЊИВАЧКОЈ СМОЛИ – КАТАЛИЗАТОРУ РЕАКЦИЈЕ ЕКВИЛИБРАЦИЈЕ

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Одређене су релативне активности неких силоксанских мономера, како цикличних тако и линеарних, према катјонској јоноизмењивачкој смоли, катализатору реакције еквилибрације. Одређивање базира на чињеници да када се неко силоксанско једињење дода произвољно одабраном еквилибрату, оно тада учествује у еквилибрацији изазивајући одређене промене вискозитета реакционе смеше. Узимајући ове промене вискозитета за меру активности, добијен је следећи редослед: хексаметилциклотрисилоксан > хексаметилдисилоксан > октаметилциклотетрасилоксан > један линеарни метил супституисани олигосилоксан средње бројне моларне масе од око 800 > декаметилциклопентасилоксан. Резултати добијени применом описане вискозиметријске методе су проверени тако што су одређене средње бројне моларне масе реакционих смеша на почетку и на крају еквилибрације. Одступање експериментално одређених од израчунатих вредности је било мање од 20 %, и то само у једном случају, у већини осталих еквилибрационих система одступање је било око 10 %, што је веома добар резултат који потврђује исправност примењеног метода одређивања активности.

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