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MOLAR MASS DISTRIBUTION OF HYDROXYETHYLATED ARALKYL ALCOHOLS

Péter SALLAY*, Mohamed H. M. AHMED**, Sándor BÉKÁSSY*, László FARKAS*, András VÍG***, and István RUSZNÁK*

* Department of Organic Chemical Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
** Department of Chemistry
Faculty of Science
Benha University, Benha, Egypt
*** Research Group of the Hungarian Academy of Sciences
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

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Abstract

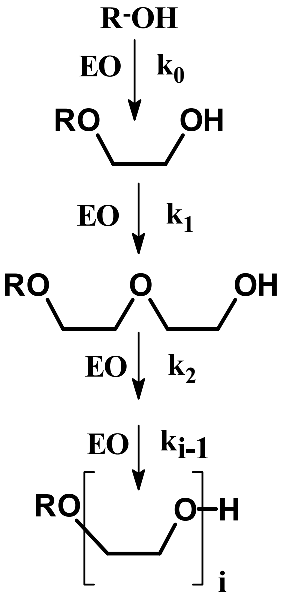
The molar mass distribution was investigated at the hydroxyethylation of aralkyl alcohols (benzyl-, β-phenylethyl- and γ-phenylpropyl) in the presence of conventional homogeneous and a heterogeneous catalyst, K10. While the widely used NaOH and $SnCl_4$ catalysts gave the expected results in molar mass distribution (with base it is of Weibull-Nycander-Gold type, with the Lewis acid of Flory type), the K10 caused a narrower Flory type distribution which is effected by the length of alkyl chain in the aralkyl alcohols and by the modification of the pure K10 with metal ions (Cu^{2+} and Fe^{3+}). By this way with a substrate- and MMD-friend hydroxyethylation can be achieved.

Keywords: aralkyl alcohols, hydroxyethylation, distribution constants.

1. Introduction

Hydroxyethylation, (ethoxylation) the reaction of ethylene oxide (EO) with a molecule having active hydrogen is an important reaction in the production of nonionic surfactants. This reaction, being a consecutive-competitive one, always results in a mixture of homologues of oligo hydroxyethylated molecules. (*Scheme 1*). These products can be characterized by the amount of ethylene oxide reacted per molecule of starting compound (average degree of hydroxyethylation, $ADE = \nu$) and by concentration of the individual homologues in the reaction mixture (molar mass distribution, MMD).
where k_i-s are rate constants of hydroxyethylation steps (k_0 of starting compound, k_i of homologue containing i ethylene glycol units)

The experimental data of composition of the product can be characterized by the comparison to various theoretical distributions based on kinetical assumptions. The most widely used theoretical distribution models are the FLORY [1], the WEIBULL–NYCANDER–GOLD (W-N-G) [2, 3, 4] and NATTA–MANTICA [5].



Scheme 1.

In the simplest case, when all rate constants are regarded to be equal, $k_0 = k_1 = \ldots = k_i$, (all hydroxyl groups have the same reactivity) the molar fractions of the individual compounds (x_i) are described by the FLORY's relationship [1] (*Eq.* 1)

$$x_i = e^{-v} \frac{v^i}{i!}. \tag{1}$$

Supposing that the reactivity of the hydroxyl group of the starting alcohol is different from the produced glycolic hydroxyl groups ($k_0 \neq k_1 = - \ldots - = k_i = k$), the molar fractions can be calculated using the WEIBULL–NYCANDER–GOLD (W-N-G) relationship [2, 3, 4] (*Eq.* (2), (3)):

$$x_i = \frac{c^{i-1}}{(c-1)^i} \left\{ x_0 - x_0^c \sum_{j=0}^{i-1} \frac{1}{j!} [(c-1) \ln x_0]^j \right\}, \tag{2}$$

$$c = \frac{x_0 + v - 1}{x_0 - \ln x_0 - 1}, \tag{3}$$

where (c) is the W-N-G distribution constant = k/k_0.

In the general case, all reaction rate constants are different ($k_0 \neq k_1 \neq \ldots \neq k_i$). Now, the relationship between the x_i values measured is given by the relationship described by NATTA and MANTICA [5] (*Eq. 4*):

$$x_i = (-1)^i \prod_{j=1}^{i-1} c_j \sum_{j=0}^{i} \frac{x_0^{c_j}}{\prod\limits_{\substack{k=0\\k\neq j}} (c_k - c_j)}, \tag{4}$$

where c_i is the Natta–Mantica distribution constant, $C_i = \frac{k_i}{k_0}$.

The aim of the work is the investigation of the difference between the product distributions of hydroxyethylated aralkyl alcohols (benzyl-, β-phenylethyl- and γ-phenyl-propyl-) produced by different catalysts (base /NaOH/, Lewis acid /$SnCl_4$/ and solid acid catalyst /K10/ and with its modified Cu^{2+}, Fe^{3+} forms) under various reaction conditions.

WEIBULL [6] found in the case of hydroxyethylation of γ-phenylpropyl alcohol that the MMD of products was of W-N-G's type and the observed Weibull–Törnquist effect (the dependence of C_i-s from the ADE [16]) could be eliminated by the use of complex forming agents during hydroxyethylation.

2. Experimental Procedures

Materials. Benzyl alcohol, β-phenylethanol and γ-phenylpropanol (Merck, purity under HPLC $> 98\%$). Ethylene oxide (Fluka, purity $> 99.9\%$), NaOH (Renal), $SnCl_4$ (Merck), K10 clay catalyst (Süd-Chemie, München) and its modification (K10 clay catalyst is manufactured by high temperature acidic treatment from a Bavarian bentonite). The high temperature acidic treatment destroys the originally layered structure of bentonite clay and results in a loss of crystallinity with a mesoporous pore system (average pore diameter: 56Å), and important Broensted acidity. Modification (Cu^{2+}-K10 and Fe^{3+}-K10) was prepared and characterized as reported in reference [7].

Hydroxyethylation. Hydroxyethylations were carried out in a semimicro apparatus [8] (*Fig. 1*) based on the measurement of the volumetric flow of EO before and after the reaction. The reactor has to be oxygen-free, because of safety and product requirements [9, 10].

Isothermal reaction conditions were ensured by a boiling liquid bath (the fluids of heating bath are xylene to 140 °C, water to 100 °C, chloroform to 60 °C, or with the help of a thermostat in the case of lower temperatures. The catalyst was added to the alcohols (0.02 mole) in the reactor tube. The reaction mixture was heated to the desired temperature. The system was purged with nitrogen to avoid oxygen (explosion concentration of EO with air is $3 - 10$ v %) [11] and to remove the water content of the reaction mixture in the case of alkali hydroxide catalyst. After 20 minutes the gas stream was changed to EO. The EO was added at a constant flow rate (7 cm^3/min., at which velocity of gas stream does not effect the EO uptake) to produce the desired average degree of hydroxyethylation. Finally, the stream of EO was changed to nitrogen to purge out the unreacted EO. The EO

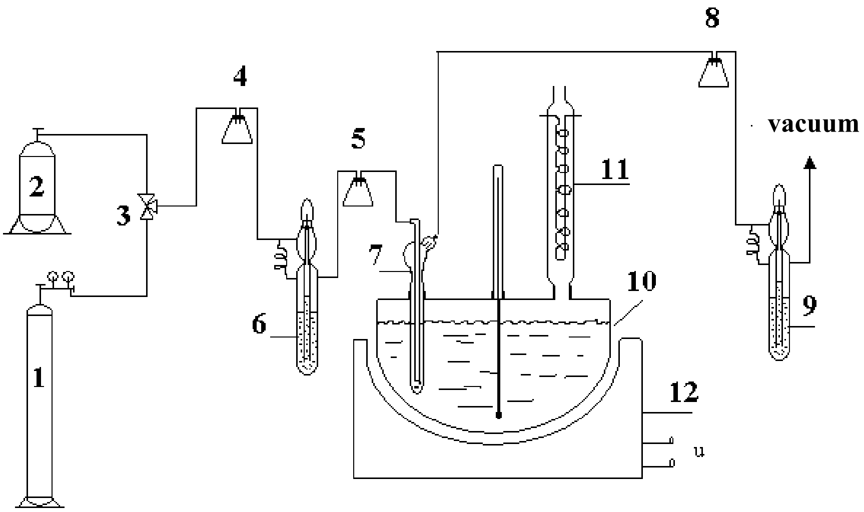


Fig. 1. Apparatus of the hydroxyethylation (1. N_2, 2. ethylene oxide, 3. valve, 4,5,8. buffers, 6,9. differential manometers, 7. semimicro reactor, 10. boiling bath, 11. cooler, 12. heater)

uptake (ADE) was determined from the increase of the mass of the reaction mixture and confirmed by IR, UV and refractive index [12]. Characteristic parameters of the hydroxyethylation reaction are given in *Table 1*.

Table 1. Hydroxyethylation parameters for aralkyl alcohols

Catalysts	Reaction conditions		Results
	Catalyst conc. [mol%]	Reaction temp. [°C]	ADE range
NaOH	1.96–9	100–180	0.75–14.00
$SnCl_4$	3.5–5.5	30–50	0.64–14.40
K10	1–30*	30–120	0.45–6.94

* g/mole

Purification of hydroxyethylated samples. Two types of impurities are formed in the reaction product, the catalyst and the polyethylene glycol (PEG).

Purification from the catalyst. The hydroxyethylated samples were purified according to the type of catalyst used.

The sodium hydroxide was removed by using cationic exchanger (Dowex-HCR-S, 20 – 50 mesh, in H^+ form).

The $SnCl_4$ was removed from samples by precipitation with Na_3PO_4 solution, (at 70 °C), and extracting with ethyl acetate.

The solid acid catalyst was removed simply with filtration.

Purification from glycols. The glycol content of the samples was removed by the Weibull's method (See estimation of PEG).

Estimation of polyethylene glycol content of reaction product. It was completed with the method described by WEIBULL [13]. 10 g was extracted (3 times) with equal amounts of 5 M NaCl solution and ethyl acetate (100 ml), the byproducts polyethylene glycol (PEG) were distributed into organic layer. Organic layer was distilled, washed with acetone. The pure hydroxyethylated sample was weighted (W_1). Aqueous layer was extracted with 50 ml chloroform (3 times), chloroform was distilled and PEG was weighted (W_2), the PEG percentage was calculated: $\text{PEG\%} = \frac{W_2}{10} \times 100$.

*Analysis of hydroxyethylated products.*The MMD of pure hydroxyethylated products were determined by HPLC (reversed-phase made 10C18), column length 250 × 4 mm, UV detection at 256 nm. *Table 2* shows the analysis conditions.

Table 2. Analytical condition for hydroxyethylation samples

Factors	Values	ADE range
Flow rate	0.9 ml/min.	For all range
Eluent	55:45 (MeOH: water) 60:40 (MeOH: water)	0.64-4 EO* 0.45-7 EO**
Concentration	0.5 wt % (in MeOH) 0.1 wt % (in MeOH)	Lower ADE Higher ADE

* For (benzyl and β-phenylethyl alcohols),

** For all γ-phenylpropyl alcohol and benzyl & β-phenylethyl alcohol derivatives (with 4 to 7 EO).

Quantitative analytical determination of molar mass distribution was done with the help of selected homogeneous member of the homologues series prepared by Williamson synthesis [14].

The accuracy of chromatographic determination of the molar fractions is ca. 3%. The error of the calculated distribution constants is determined by the chromatographic errors (the accuracy of computer calculation is below 0.1% [15]).

3. Results and Discussion

3.1. Poly(oligo)ethylene Glycol Content of Hydroxyethylated Compounds

In the first part of our investigations the production of the main byproduct, the glycol content was examined during the hydroxyethylation of aralkyl alcohols at different degrees of hydroxyethylation. It can be seen from the data of *Table3* that the amount of glycols is not considerable in this relative small range of average degree of hydroxyethylation investigated, its effect is negligible.

Table 3. Percentage of PEG in the hydroxyethylated samples

Starting alcohols	Catalysts	ADE	PEG [%]
Benzyl	NaOH	3.30	2.10
		13.87	2.47
	$SnCl_4$	4.60	2.08
		12.72	2.35
	K10	3.51	2.12
		6.90	2.26
β-phenylethyl	NaOH	4.80	2.06
		13.2	2.33
	$SnCl_4$	4.60	2.22
		12.72	2.52
	K10	3.99	2.02
		6.79	2.20
γ-phenylpropyl	NaOH	3.70	2.20
		9.50	2.43
	$SnCl_4$	3.68	2.34
		14.43	2.87
	K10	3.10	2.16
		6.80	2.32

3.2. *Molar Mass Distribution of Hydroxyethylated Materials*

In the first experiments the same catalysts are used as in our previous work in the hydroxyethylation of dodecyl alcohol [15], a basic one, sodium hydroxide and a Lewis acid, tin tetrachloride. All three aralkyl alcohols (benzyl-, β-phenylethyl-, and γ-phenylpropyl alcohol) were hydroxyethylated with these two catalysts and their molar mass distributions were determined by HPLC and compared with the two most important theoretical distribution models, with the Flory and the Weibull–Nycander–Gold distributions.

The type of all distributions catalyzed with NaOH were of WEIBULL–NYCANDER–GOLD type (e.g. *Fig.* 2) and with acid were of FLORY type (e.g. *Fig.* 3), therefore the effect of catalysts was the same found with dodecyl alcohol. This can well be seen from the values of NATTA–MANTICA's distribution constants (*Tables* 4, 5). The c_i values of products catalyzed with NaOH are higher than 2, the values of products catalyzed with $SnCl_4$ are lower than 2. The presence of phenyl group in the chain does not affect the hydroxyethylation process.

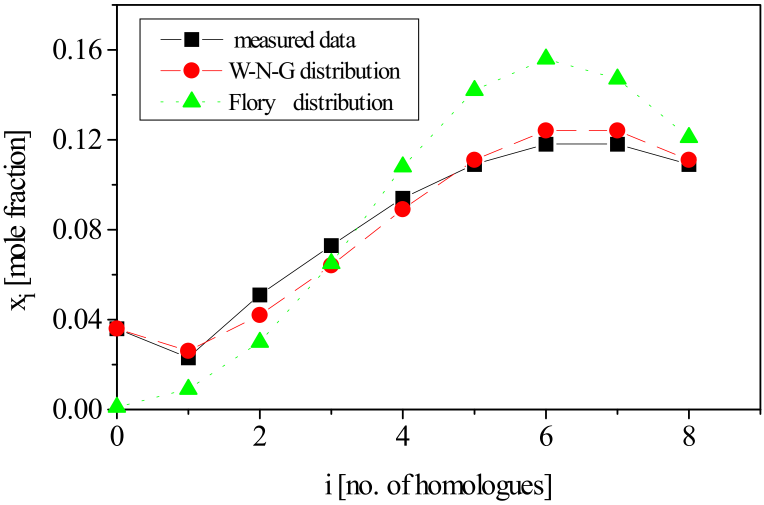


Fig. 2. Comparison of the measured MMD with the theoretical distribution for hydroxyethylated β-phenylethyl alcohol (NaOH, 4.76 mol %, 140 °C, ADE = 6.60)

Table 4. Distribution constants of some samples catalyzed with NaOH

Alcohol	ADE	c	c_1	c_2	c_3	c_4	c_5
benzyl	0.97	2.67	2.84	2.70	2.27	3.18	4.70
	1.63	1.98	2.19	1.93	1.89	1.61	1.86
	4.76	2.46	2.71	2.42	2.35	2.37	2.37
β-phenylethyl	1.03	2.24	1.96	2.33	3.08	6.55	2.24
	1.89	2.20	2.20	2.19	2.14	4.18	2.03
	4.76	2.41	2.04	2.36	2.32	2.38	2.36
γ-phenylpropyl	0.98	2.09	1.83	2.48	2.92	3.87	5.29
	1.71	2.28	2.11	2.09	2.46	2.47	3.16
	5.30	2.96	3.01	2.99	2.82	2.99	2.80

Accordingly it was not a surprise that the WEIBULL–TÖRNQUIST effect [16] (the NATTA–MANTICA's distribution constants are functions of the average degree of hydroxyethylation due to the complex formation of alkali ions with oligo ethylene glycol ethers formed) observed in the sodium hydroxide catalyzed reactions of dodecyl alcohol was proven in the case of hydroxyethylation of aralkyl alcohols too (*Fig. 4*). Whereas the molecules of aralkyl alcohols are less flexible than the linear aliphatic molecules, the complex forming effect of their oligomers is different, the values of distributions constants decrease faster and arrive at a limit value at smaller

Table 5. Distribution constants of some samples catalyzed with $SnCl_4$

Alcohol	ADE	c	c_1	c_2	c_3	c_4	c_5
benzyl	1.78	1.15	1.13	1.15	1.12	1.20	1.57
	1.96	1.17	1.16	1.38	1.35	1.33	1.86
	4.60	1.58	1.93	1.59	1.41	1.44	1.43
β-phenylethyl	1.82	1.82	1.47	1.86	2.16	2.72	2.94
	3.30	1.54	1.92	1.47	1.42	1.50	1.58
	4.60	1.61	1.59	1.86	1.68	1.61	1.67
γ-phenylpropyl	1.00	1.09	1.08	1.04	1.06	1.08	1.57
	2.02	1.43	1.35	1.29	1.58	1.58	1.21
	3.68	1.53	1.82	1.43	1.39	1.37	1.36

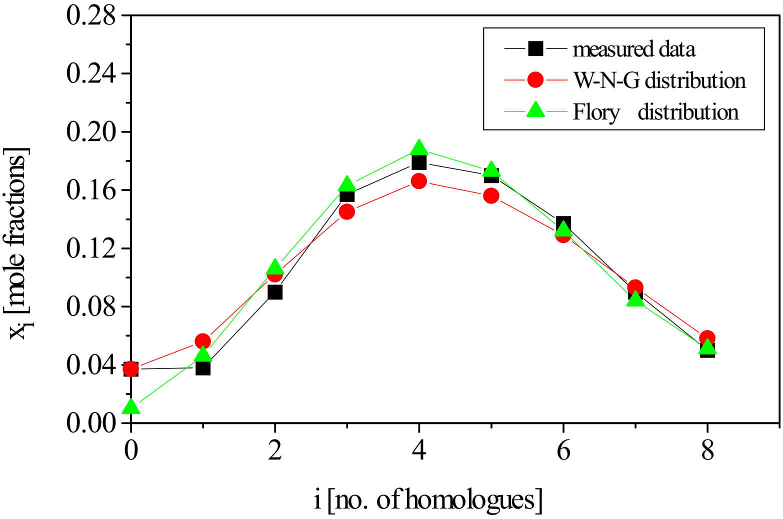


Fig. 3. Comparison of the measured MMD with the theoretical distributions for hydroxyethylated benzyl alcohol ($SnCl_4$, 4.5 mol %, 30 °C, ADE = 4.64)

ADE (near to 2, while in the case aliphatic alcohols this value is above 3.5 [15]). (The WEIBULL–TÖRNQUIST effect was recently noticed [6] in the case of γ-phenyl propyl alcohol. This effect was abolished using a strong complex-forming material, crown ether.)

The MMD is independent of the temperature in the case of aralkyl alcohols too (*Figs.* 5, 6). That means that the activation energies of the competitive-consecutive reactions of hydroxyethylation are near the same.

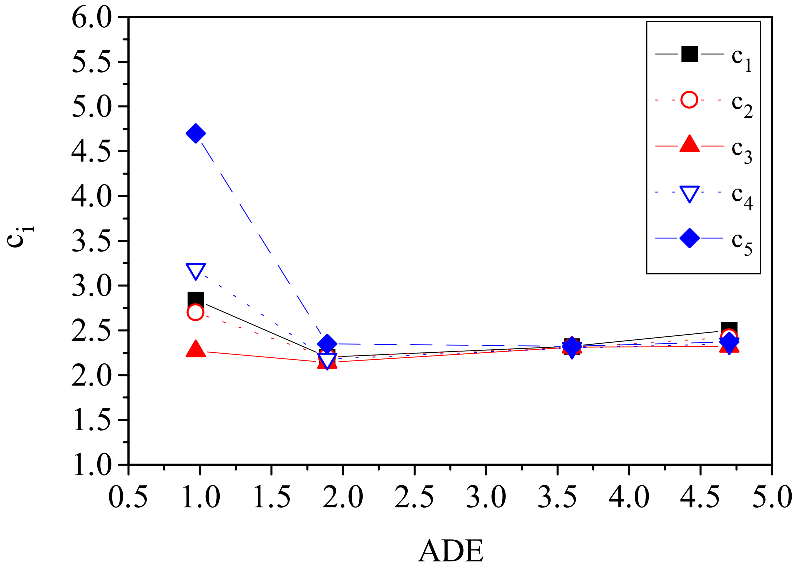


Fig. 4. Dependence of the distribution coefficients on ADE of hydroxyethylated benzyl alcohol (140 °C, NaOH 4.76 mol %)

The concentration of catalysts has no considerable effect on MMD, either in the case of base or in the case acid catalysis (*Figs.* 7, 8). It means that the mechanisms of the reaction does not change with the change of activity of catalyst's ions or molecules.

It was observed that the length of the alkyl chain in the aralkyl alcohols does not play any role in the development of distribution in the base and acid catalyzed processes (*Fig.* 8).

Possessing the results of homogeneous hydroxyethylation we dealt with the hydroxyethylation of aralkyl alcohol in the presence of a heterogeneous catalyst. A bentonite based acidic clay was used, K10, which has Brönsted and Lewis acid sites. It was used at a relative low concentration range because of stirring problems in the given apparatus.

The clay catalyst was effective in a wide range of temperature (30 to 140˚C) and could be easily removed from the reaction mixture after hydroxyethylation.

The MMD of hydroxyethylated products achieved with K10 was of Flory type with all three aralkyl alcohols (*Figs.* 9, 10, 11) corresponding to the acid character of the catalyst. This can be seen from the low values of NATTA–MANTICA's distribution constants (*Table* 6) too and from the distribution curves which have only one extreme value.

In contrast to the MMD's achieved with conventional homogeneous catalysts

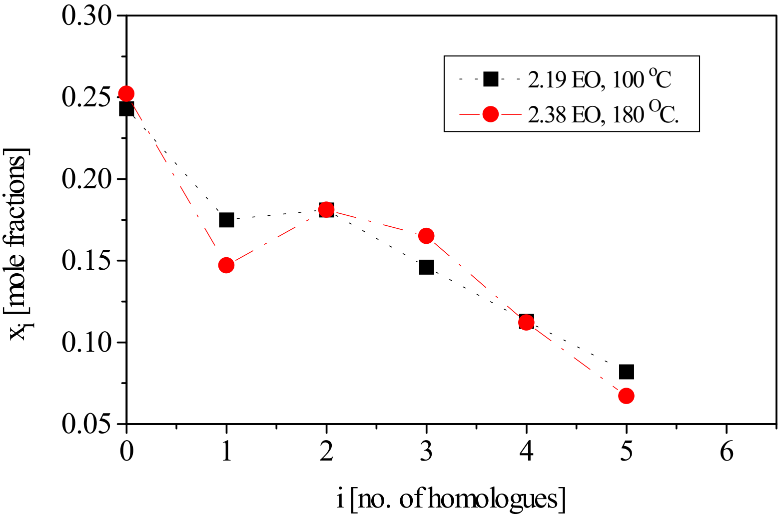


Fig. 5. Effect of temperature on the MMD of hydroxyethylated γ-phenylpropyl alcohol (NaOH 9 mol %)

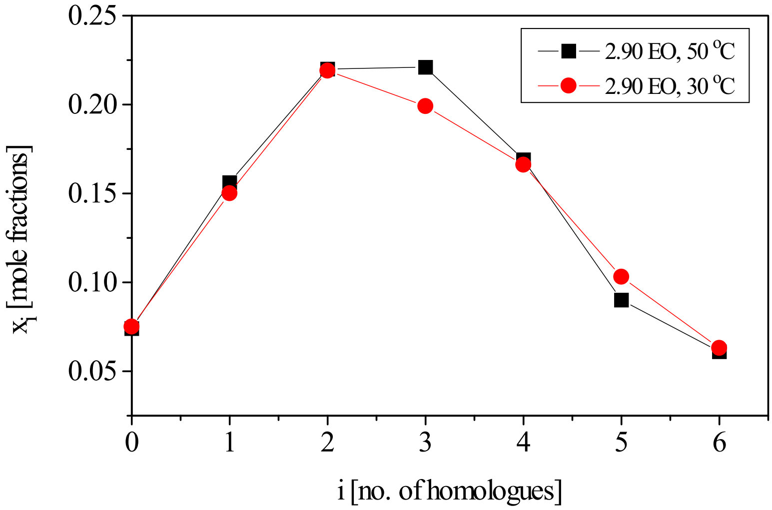


Fig. 6. Effect of temperature on the MMD of hydroxyethylated benzyl alcohol, ($SnCl_4$ 5.5 mol %)

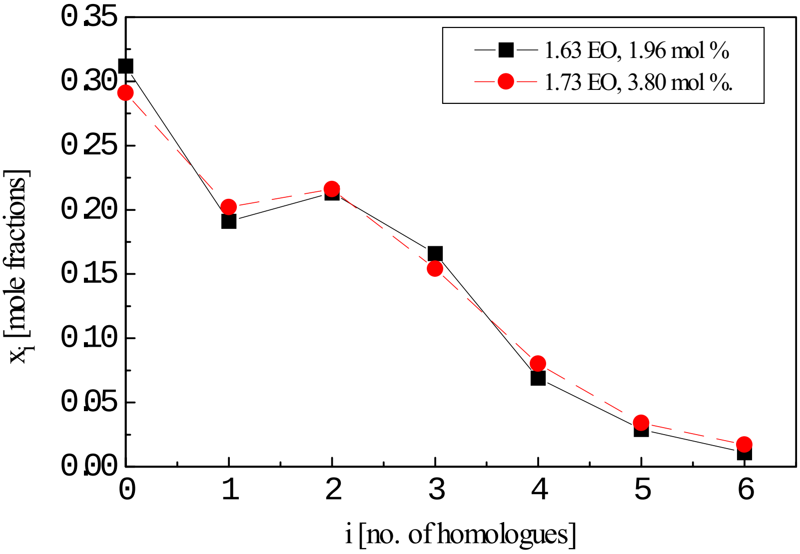


Fig. 7. Effect of catalyst concentration on the MMD of hydroxyethylated benzyl alcohol (NaOH 140 °C)

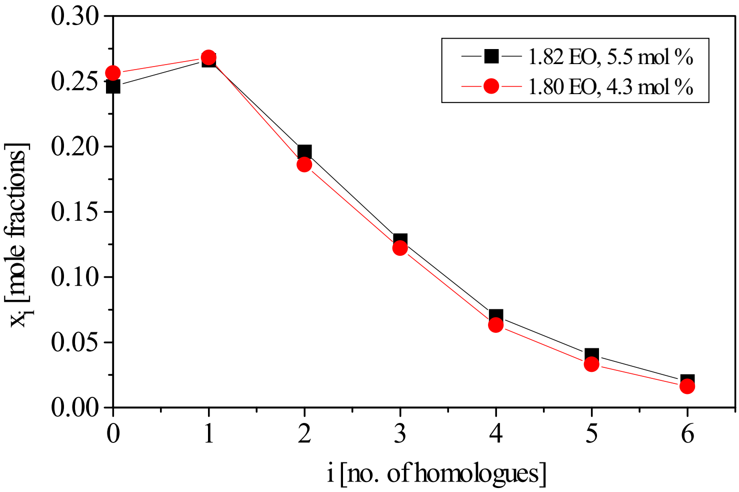


Fig. 8. Effect of catalyst concentration on the MMD of hydroxyethylated β-phenylethyl alcohol ($SnCl_4$ 30 °C)

Table 6. Distribution constants of some samples catalyzed with K10

Alcohol	ADE	c	c_1	c_2	c_3	c_4	c_5
benzyl	0.74	0.45	0.16	1.12	1.96	2.74	
	1.94	0.88	0.28	1.33	1.77	1.05	0.89
	3.51	1.14	0.10	1.04	1.03	1.15	1.25
	5.34	1.30	0.05	0.79	0.81	0.88	0.57
β-phenylethyl	1.83	1.03	1.22	1.59	2.40	2.67	
	2.64	1.88	1.03	1.20	1.46	1.84	1.96
	3.99	0.70	0.45	0.45	0.39	0.41	0.42
γ-phenylpropyl	1.82	1.07	0.88	1.27	3.49	6.95	13.35
	3.12	1.37	1.55	1.14	1.06	0.96	5.51
	5.20	1.69	1.89	1.27	1.50	1.31	0.97

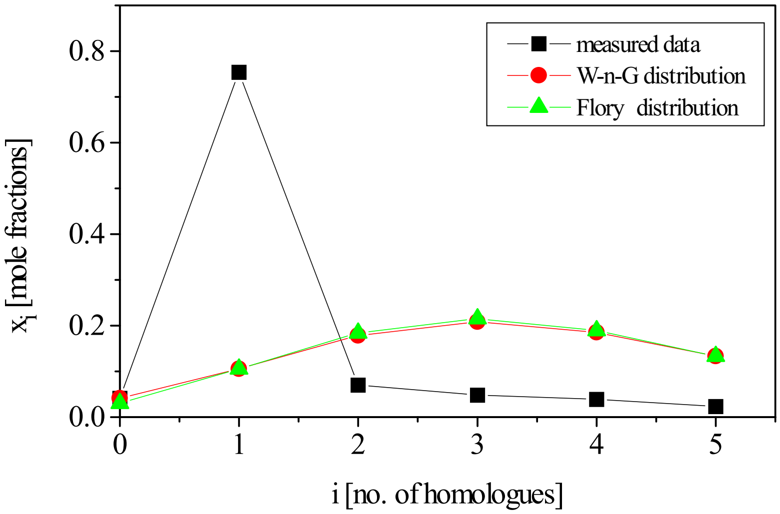


Fig. 9. Comparison of the measured MMD with the theoretical distribution for hydroxyethylated benzyl alcohol (K10, 8.35 g/mol alcohol, 30 °C, ADE = 3.51)

the length of the alkyl chain in the aralkyl alcohols affects the distribution (*Fig.12*) especially in the case of benzyl alcohol presuming a favoring sorption of ethylene oxide and substrate on the active sites. In this way a narrower distribution is available. The place of the distribution maximum (if ADE ≈ 2) is near to 1 for all the three aralkyl alcohols, and the amount of the first homologue of benzyl alcohol is extremely high.

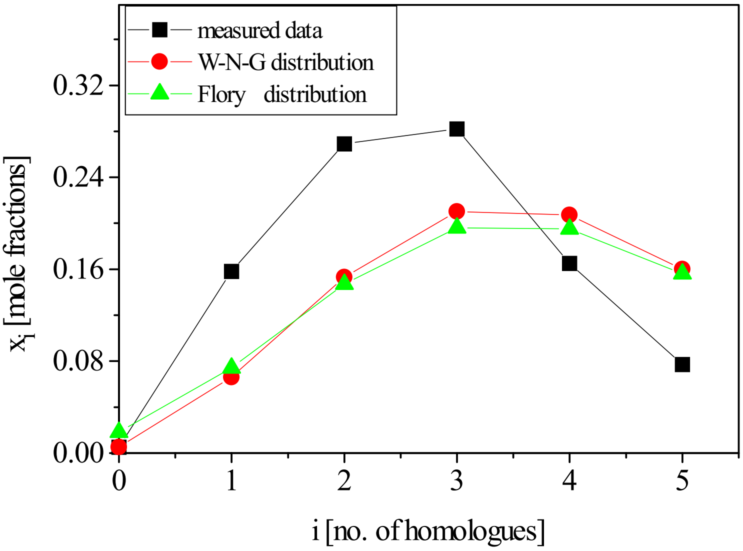


Fig. 10. Comparison of the measured MMD with the theoretical distribution for hydroxyethylated β-phenylethyl alcohol (K10, 8.35 g/mol alcohol, 30 °C, ADE = 3.99)

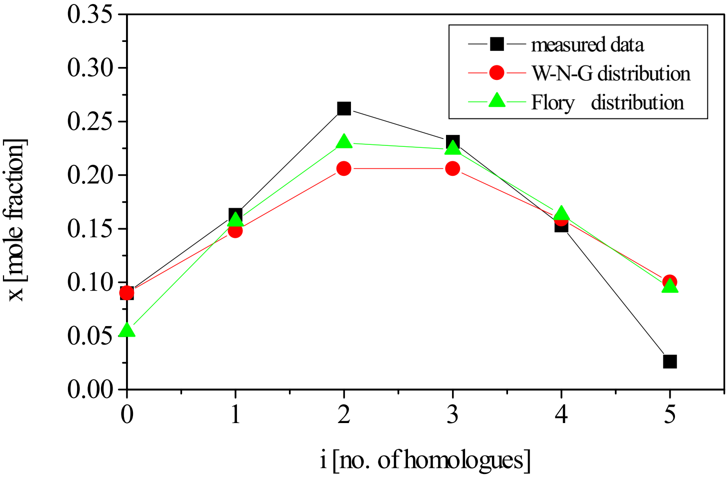


Fig. 11. Comparison of the measured MMD with the theoretical distribution for hydroxyethylated γ-phenylpropyl alcohol (K10, 8.35 g/mol alcohol, 120 °C, ADE = 2.92)

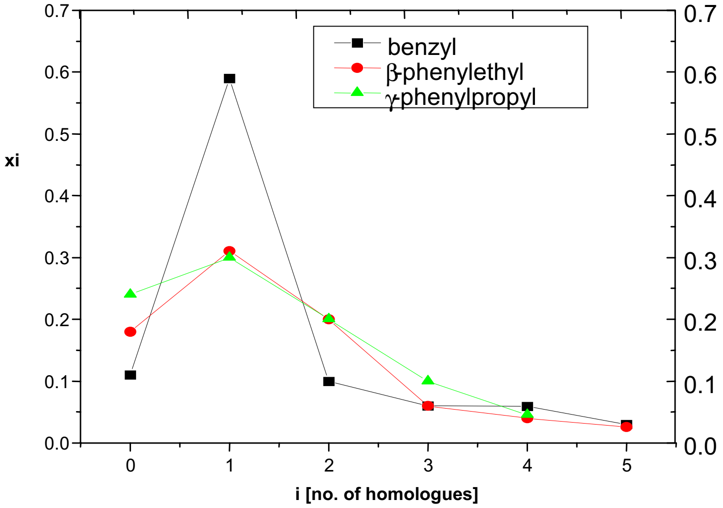


Fig. 12. Effect of the aralkyl alcohol on the MMD (K10 ≈ 8 g/mol, 30 °C, ADE ≈ 2)

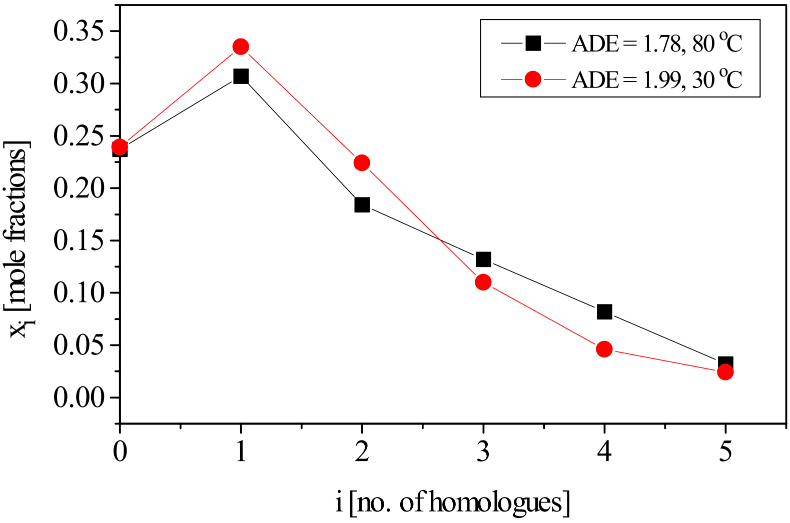


Fig. 13. Effect of temperature on the MMD of hydroxyethylated β-phenylethyl alcohol (K10, 8.35 g/mol)

The other parameters (temperature and concentration of catalyst) have no effect on the distribution as in the case of homogeneous catalysts (*Figs.13*, *14*).

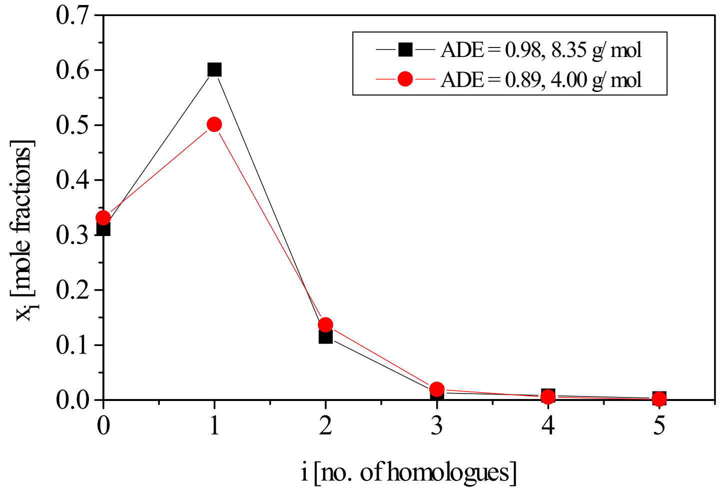


Fig. 14. Effect of catalyst concentration on the distribution of hydroxyethylated γ-phenylpropyl alcohol (K10, 80 °C)

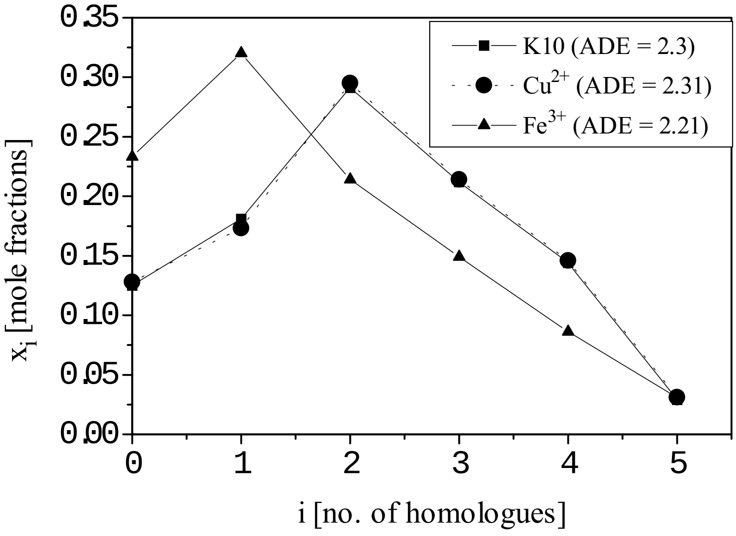


Fig. 15. Effect of various clay catalysts on the MMD of hydroxyethylated γ-phenylpropanol (at 80 °C)

The increase of the number of Lewis acid sites can affect the distribution. In the case of γ-phenyl propyl alcohol the modification of K10 with Cu^{2+} ions does not modify the distribution achieved with pure K10 but in the presence of Fe^{+3} ions the distribution becomes narrower (and the place of maximum shifts to the lower homologues) (*Fig. 15*).

It can be established that aralkyl alcohols can be easily hydroxyethylated using the heterogeneous clay catalyst (K10). The MMD of the products will be narrow and with the modification of the K10 by metal ions a substrate- and MMD-friend hydroxyethylation can be achieved.

Acknowledgement

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References

[1] Flory, P. J., *J. Am. Chem. Soc.*, **62** (1940), p. 1561.
[2] Weibull, B. – Nycander, B. *Acta Chem. Scand.*, **8** (1954), p. 847.
[3] Gold, L., *J. Chem. Phys.*, **20** (1952), p. 1651.
[4] Gold, L., *J. Chem. Phys.*, **28** (1958), p. 91.
[5] Natta, G. – Mantica, E., *J. Am. Chem. Soc.*, **84** (1952), p. 3152.
[6] Weibull, B., *Acta Chem. Scand.* **49** (1995), p. 207.
[7] Cseri, T. – Békássy, S. – Figueras, F. – Cseke, E. – de Ménorval, L. C. – Dutartre, R., *Applied Catal. A.: General*, **132** (1995), p. 141.
[8] Morgós, J. – Sallay, P. – Farkas, L. – Rusznák, I., *J. Am. Oil Chem. Soc.*, **60** (1983), p. 1905.
[9] Hess, G. L. – Tilton, V. V., *Ind. Eng. Chem.*, **42** (1950), p. 1251.
[10] Pogány, G. A., *Chem. Ind.*, (1979), p. 16.
[11] Bailey, F. E. Koleske, J. V., *Polyethylene Oxide*, Academic Press, New York, (1976) p. 9.
[12] Ahmed, M. M. H. – Sallay, P. – Rusznák, I. – Farkas, L., *Tenside Surf. Det.*, **33** (1996), p. 410.
[13] Weibull, B., *Proceedings of C.I.D. Congress*, München, (1960). p. 121.
[14] Sallay, P. – Ahmed, M. M. H. – Rusznák, I. – Farkas, L. – Tungler, A., *ACH Models in Chem.*, **133** (1996), p. 21.
[15] Farkas, L. – Morgós, J. – Sallay, P. – Rusznák, I. – Bartha, B. – Veress, G., *J. Am. Oil Chem. Soc.*, **58** (1981), p. 650.
[16] Sallay, P. – Morgós, J. – Farkas, L. – Rusznák, I. – Veress, G. – Bartha, B., *Tenside Surf. Det.*, **17** (1980), p. 6.