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STUDY OF THE ALCOHOLYSIS OF ETHYLENE-VINYL ACETATE COPOLYMERS WITH METHANOL IN THE EXTRUSION PROCESS

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ABSTRACT

We investigated the sodium methanolate (NaOMe) catalyzed transesterification of ethylene-vinyl acetate copolymers (EVA) of different compositions with the less compatible methanol (MeOH). The experiments were carried out in a twin-screw extruder with a specially designed reaction zone. The residence time was about 150 seconds. The influence of catalyst quantity on conversion yield was determined for different amounts of added alcohol. Increasing catalyst concentrations accelerated transesterification to such an extent that the state of equilibrium could be achieved during the residence time in the extruder. The dependence of equilibrium conversions on the starting molar ratio MeOH/VA were determined over a broad range, and the equilibrium constant of methanolysis was calculated for $K = 3.3$. Based on an overall reaction rate derived from the general reaction scheme and which considers a mass transfer for catalyst in the EVA melt, it is possible to calculate the rate constants $k_1 = 33.1$ and $k_{-1} = 8.0 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}$. The methanolysis of EVA in the extrusion process was shown to be a useful method suitable for industrial application. The results of our investigations allow for accurate modification of EVA products.

INTRODUCTION

A very economical procedure of acetoxy-hydroxide transformation by EVA copolymers is the alcoholate-catalyzed transesterification of pendant ester groups by alcohols in the molten state during extrusion. Previously, we reported on results of sodium methanolate-catalyzed alcoholysis of EVA with octanol-1 and butanol-1 which are compatible with the polymer under reactive extrusion conditions [1].

Methanol, despite its incompatibility with EVA, is a very attractive alcohol for EVA modification compared to its homologues. It has the following advantages for the acetoxy-hydroxide transformation:

- Good availability and low price
- High mobility and reactivity because of small molecular size
- Good solvent for sodium methanolate catalyst
- High volatility of both methanol and the reaction product methyl acetate, simplifying separation from the EVA melt
- Utilization of the reaction product, methyl acetate

There is still another reason for the use of methanol during the alcoholysis of EVA in extruders. The absorption capacity of liquids in extruders is limited. If a critical quantity of alcohol is exceeded, there will be pulsations, i.e., unstable states. Because of its small molar volume, a very high conversion can be achieved with methanol compared to other alcohols. However, the accessibility of the reaction partners is a precondition for this.

The purpose of this work was:

- To test the feasibility of the alcoholysis of EVA using methanol with sodium methanolate (NaOMe) as a catalyst during an extrusion process
- To describe the kinetics of this reaction in the melt
- To determine the equilibrium position of EVA methanolysis

EXPERIMENTAL

EVA types containing 21, 26, and 32 wt% vinyl acetate were supplied by Leuna-Werke AG, Germany.

Mixtures of purified methanol and sodium methanolate as reagents for the ester-alcohol transformation were prepared in our own laboratory by addition of determined quantities of sodium to methanol.

EVA methanolysis was carried out in a twin-screw extruder from Werner & Pfleiderer (ZSK 30). The pilot-plant scheme was described in a previous paper [1]. The degree of conversion was ascertained by pyrolytic determination of the amount of vinyl acetate not converted in the EVA reaction product [2].

RESULTS AND DISCUSSION

Influence of Catalyst Quantity on Conversion

The quantity of NaOMe catalyst was successively increased at constant initial molar ratios of MeOH and VA. The dependence of VA conversion, measured at the exit of the extruder, on the added catalyst amount is shown in Figs. 1-3 for three types of EVA with different compositions.

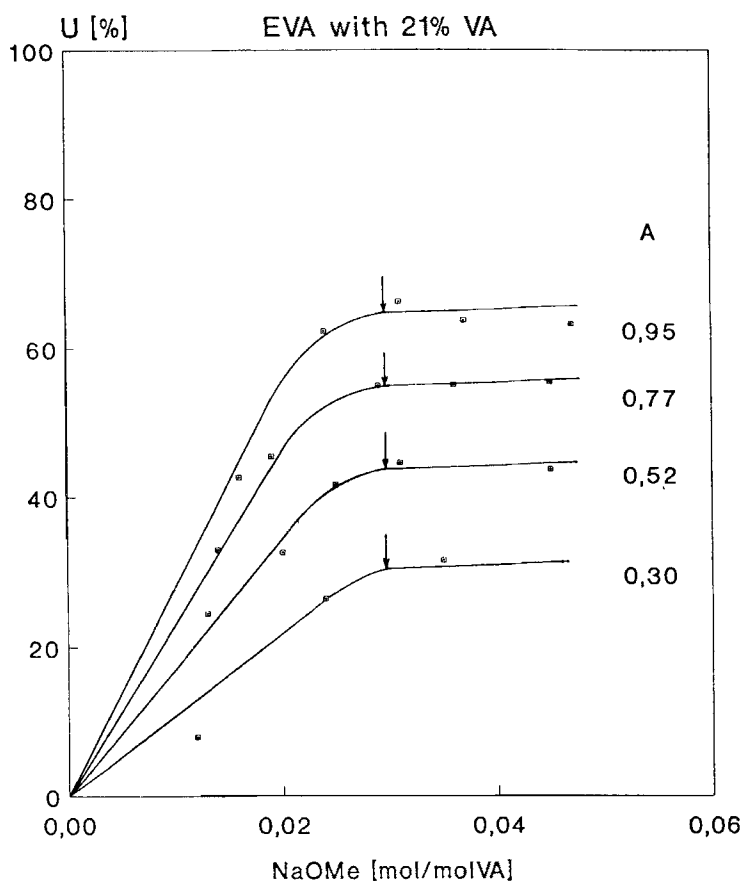


FIG. 1. Dependence of VA conversion (U) on the amount of added catalyst NaOMe at different molar ratios of MeOH/VA (A) for EVA with 21 wt% VA.

Contrary to results for EVA alcoholysis with butanol [1], the period of retardation caused by contaminants is much smaller and does not depend on the added amount of alcohol but on the type of EVA used. This points to pure NaOMe-MeOH solutions and few contaminants in the EVA products. It is known that EVA copolymers may contain residual monomer (VA). The appearance of a retardation period becomes quite apparent for the sample with 32 wt% VA in Fig. 3 compared to the 21 wt% VA sample in Fig. 1.

As alcoholysis proceeds, the curves appear to become similar. First, the degree of conversion rises rapidly with increasing NaOMe addition due to the growing catalytic acceleration of the alcoholysis reaction. The conversion approaches a limiting value which depends on the MeOH quantity. Further catalyst addition does not result in higher conversion in every case, a reliable indication that the equilibrium state of EVA methanolysis is reached.

From the similarity of the curves, which are based upon different EVA products, it can be assumed that EVA modification with methanol is only slightly influ-

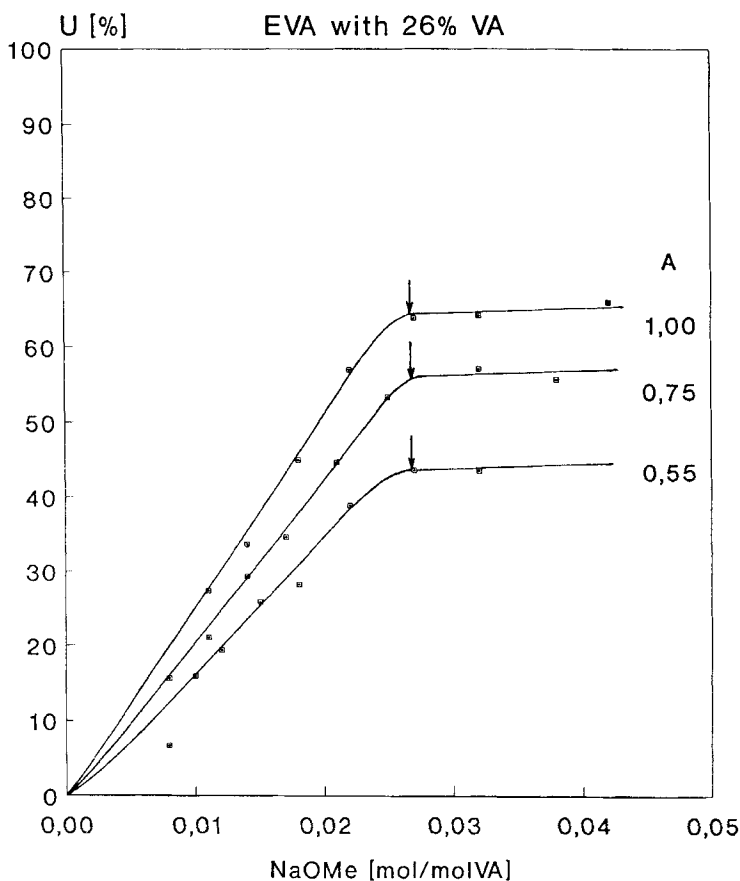


FIG. 2. Dependence of VA conversion (U) on the amount of added catalyst NaOMe at different molar ratios of MeOH/VA (A) for EVA with 26 wt% VA.

enced by the heterogeneity effects in the extruder. That means that the transport processes do not significantly influence the reaction rate of methanolysis.

With increasing VA content in the EVA copolymers employed, we found a decrease in the minimum catalyst quantity necessary to reach the conversion limits corresponding to the equilibrium conversions of methanolysis under the reaction conditions (see arrow markers in Figs. 1-3).

EVA with 21% VA: 0.030 mol NaOMe/mol VA₀

EVA with 26% VA: 0.027 mol NaOMe/mol VA₀

EVA with 32% VA: 0.025 mol NaOMe/mol VA₀

This was expected because an increase of VA and MeOH concentrations in the reaction mixture results in a higher rate of alcoholysis such that after the same reaction time (residence time in the extruder), less catalytic acceleration is required.

When carrying out EVA methanolysis, it is recommended that a NaOMe concentration above the ascertained minimum catalyst amount be used. Because of

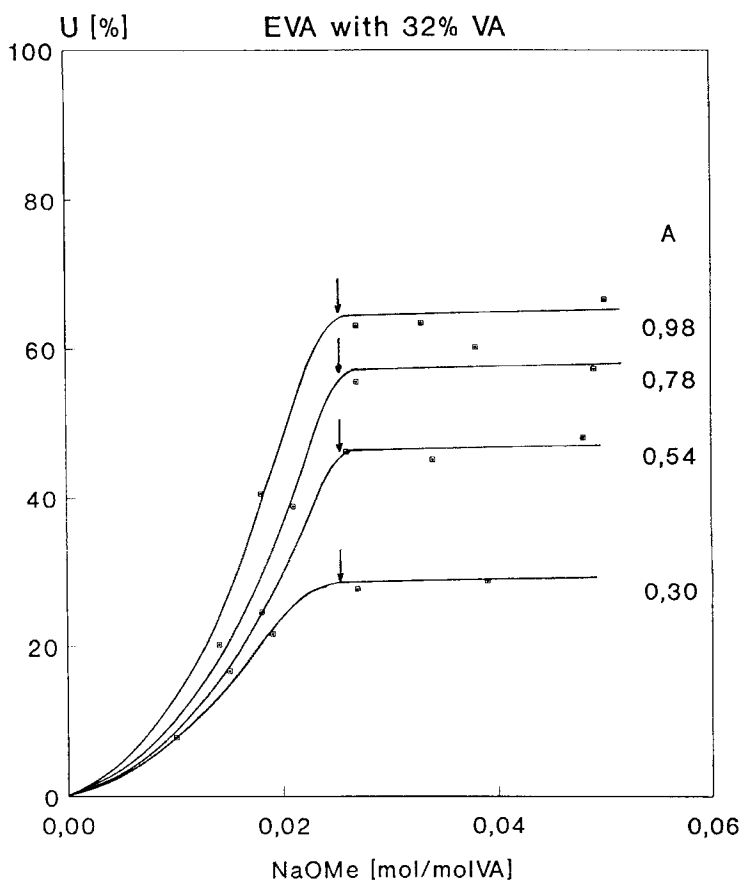


FIG. 3. Dependence of VA conversion (U) on the amount of added catalyst NaOMe at different molar ratios of MeOH/VA (A) for EVA with 32 wt% VA.

the precipitousness of the curves at lower catalyst quantities, the system responds very sensitively to small deviations from the composition due to the dosage of the NaOMe–MeOH mixture.

Equilibrium of EVA Methanolysis

The maximum practical conversions which can be reached are determined by the dependence of the equilibrium conversion of the alcoholysis reaction on the starting molar ratio of the reaction partners VA and MeOH. All tests in which limit conversions were reached are recorded in Fig. 4, i.e., experiments in which the NaOMe-additions were above the minimum catalyst quantity. The degree of conversion of VA is shown to depend on the starting molar ratio of MeOH to VA (MeOH/VA). The experimental points of all three EVA products can be described by a curve, as expected for equilibrium conversions as well. According to the law of mass action, the equilibrium constant for the methanolysis of EVA can be calcu-

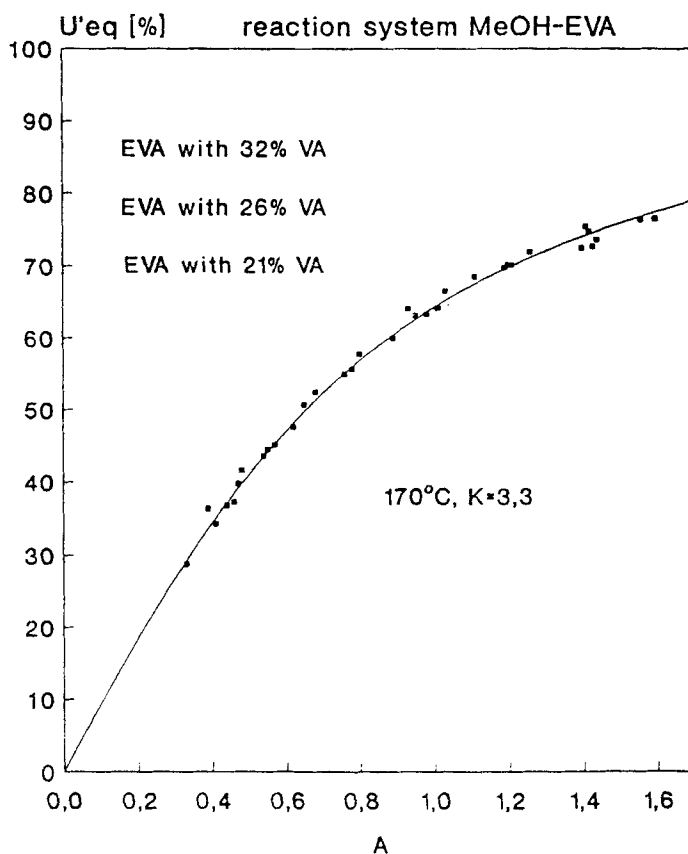


FIG. 4. Equilibrium conversions U'_{eq} versus the initial molar ratios used ($A = \text{MeOH}/\text{VA}$) and the calculated equilibrium curve for $K = 3.3$. The values of the three starting EVA products are given within the figure.

for each point according to

$$K = \frac{[\text{PVOH}]_{eq}[\text{MeAc}]_{eq}}{[\text{PVAc}]_{eq}[\text{MeOH}]_{eq}} = \frac{U_{eq}^2}{(1-U_{eq})(A - U_{eq})} \quad (1)$$

where K is the equilibrium constant, U_{eq} is the equilibrium conversion, and A is the starting molar ratio MeOH/VA .

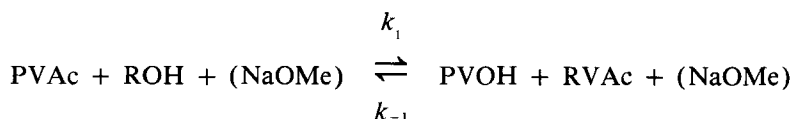
The average value of K is 3.3 with a standard deviation of 0.35. The curve in Fig. 4 represents the calculated equilibrium.

We have shown that by a suitable choice of the amount of catalyst, it is possible to reach thermodynamic equilibrium during the residence time in the extruder. Thus, methanolysis can be used for the specific production of EVA modification products with a defined composition of VA, VOH, and E. Of the alcohols examined, MeOH proved to be the most reactive with the highest equilibrium constant of 3.3 (K is 2.35 with butanol-1 and 2.18 with octanol-1).

Kinetic Studies

The preceding experimental examinations demonstrated the sensitivity of alcoholysis reactions to trace contaminants. To discover the kinetics of the technically relevant reaction of EVA with methanol, it is necessary to exclude any influences by side reactions of the contaminants. Therefore, an intensive vacuum devolatilization was used to purify the EVA polymers. The result of our efforts can be seen in Fig. 2. The recorded dependences are not influenced by contaminants; retardation does not appear. We next adapt the general rate equation to the experimental data by parameter optimization of the rate constants k_1 and k_{-1} .

The rate equation is derived from the general reaction scheme



$$\frac{d[\text{PVOH}]}{dt} = k_1[\text{NaOMe}][\text{PVAc}][\text{ROH}] - k_{-1}[\text{NaOMe}][\text{PVOH}][\text{RVAc}] \quad (2)$$

where at initial state $t = 0$: $[\text{PVOH}] = 0$, $[\text{RVAc}] = 0$.

To simplify, Eq. (2) is transformed into the conversion rate:

$$\frac{dU}{dt} = [k_1(1 - U)(A - U) - k_{-1}U^2]C \quad (3)$$

where U = PVAc conversion (degree of alcoholysis)

A = initial molar ratio ROH/PVAc

C = $[\text{NaOMe}][\text{PVAc}]_0 = \text{constant}$

$[\text{NaOMe}]$ = catalyst concentration used

$[\text{PVAc}]_0$ = initial concentration of vinyl acetate groups in the reaction mixture

k_1, k_{-1} = rate constants in $(\text{L}^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1})$

Integration of Eq. (3) for the conversion rate leads to the conversion-time dependence of the alcoholysis:

$$U = \frac{2k_1A}{\sqrt{-\Delta} \frac{(e^{\sqrt{-\Delta}t} + 1)}{(e^{\sqrt{-\Delta}t} - 1)} + k_1(1+A)}$$

$$\Delta = 4k_1(k_1 - k_{-1})A - k_1^2(1 + A)^2$$

$$= 4k_1^2(1 - 1/K)A - k_1^2(1 + A)^2 \quad (4)$$

In the case of reactive extrusion, t is the average residence time of the reaction zone (152 seconds).

It should be mentioned that this model assumes a homogeneous reaction system, i.e., the reaction partners have to be completely miscible under the conditions of reactive extrusion. Heterogeneity effects must not superimpose on the alcoholysis. Another precondition is the constancy of the alcoholate concentration and

complete catalytic activity during the reaction. This means that the side reactions which lead to the destruction of the alcoholysis catalyst are negligible.

In Fig. 5 the fitted model curves are shown as dashed lines. Considerable deviations between the experimental points and model curves can be seen. Obviously the proposed kinetic model is not able to describe the methanolysis of EVA copolymers as carried out under extrusion conditions. Thus, the hypotheses and simplifications inherent in the derivation of the rate equation are not completely justified.

The defect in the model originates from the quantity of catalyst used. The assumption that the NaOMe–MeOH solution is absorbed by the EVA melt and that a homogeneous reaction occurs is questionable. Surely the conditions of extrusion favor the solution process, but in reality we must start from a multiphase system in which mass transfer and mass transport occur. To begin with, we conclude that the MeOH of the dosed NaOMe–MeOH solution is absorbed almost completely and very rapidly by the EVA melt and is available for methanolysis. Otherwise the determination of the limiting conversion of the starting molar ratios MeOH/VA would not show such good correlation with the law of mass action (see Fig. 4). NaOMe is much less compatible with EVA. Therefore, only a small amount of catalyst is initially transferred from the NaOMe–MeOH solution to the EVA melt. Due to the fast sorption of MeOH after injection of the NaOMe–MeOH solution into the extruder, only a small quantity of solution with a high concentration of NaOMe remains. If the methanolysis is to proceed at a high rate, as much catalyst as possible has to be transferred into the polymer. The NaOMe transfer is essentially dependent on the mixing quality of the extruder. It is important to reach a fine dispersion of the NaOMe–MeOH solution in the EVA melt with a large transfer surface.

The mass flow of NaOMe into the polymer phase can be calculated by means of Nernst's diffusion layer (see Fig. 6) [3]. The concentration within the phases is equalized largely by turbulent flows. Quite near to the interface, laminar flow layers in which the mass transport is due to diffusion are formed. It is assumed that the thermodynamic equilibrium of NaOMe distribution is adjusted at the interface. The difference between the actual NaOMe concentration (c_2) inside the polymer phase and the equilibrium concentration at the interface ($c_{2,s}$) causes mass transfer (\dot{n}):

$$\dot{n} = V \frac{dc_2}{dt} = DO \frac{c_{2,s} - c_2}{d}$$

After converting and integrating this equation, the time-dependent increase of the concentration of NaOMe in the polymer phase is found.

$$c_2 = c_{2,s} (1 - e^{-k_u t}) \quad (5)$$

$c_{2,s}$ is the maximum NaOMe concentration in the polymer phase which results from thermodynamic equilibrium. Unfortunately, the distribution coefficient of NaOMe in the EVA–MeOH system is not known. If it is supposed that in the final state the rest of the NaOMe–MeOH solution is totally absorbed by the polymer, then

$$c_{2,s} \approx \frac{n_{\text{NaOMe}}}{V_{\text{MeOH}} + V_{\text{EVA}}}$$

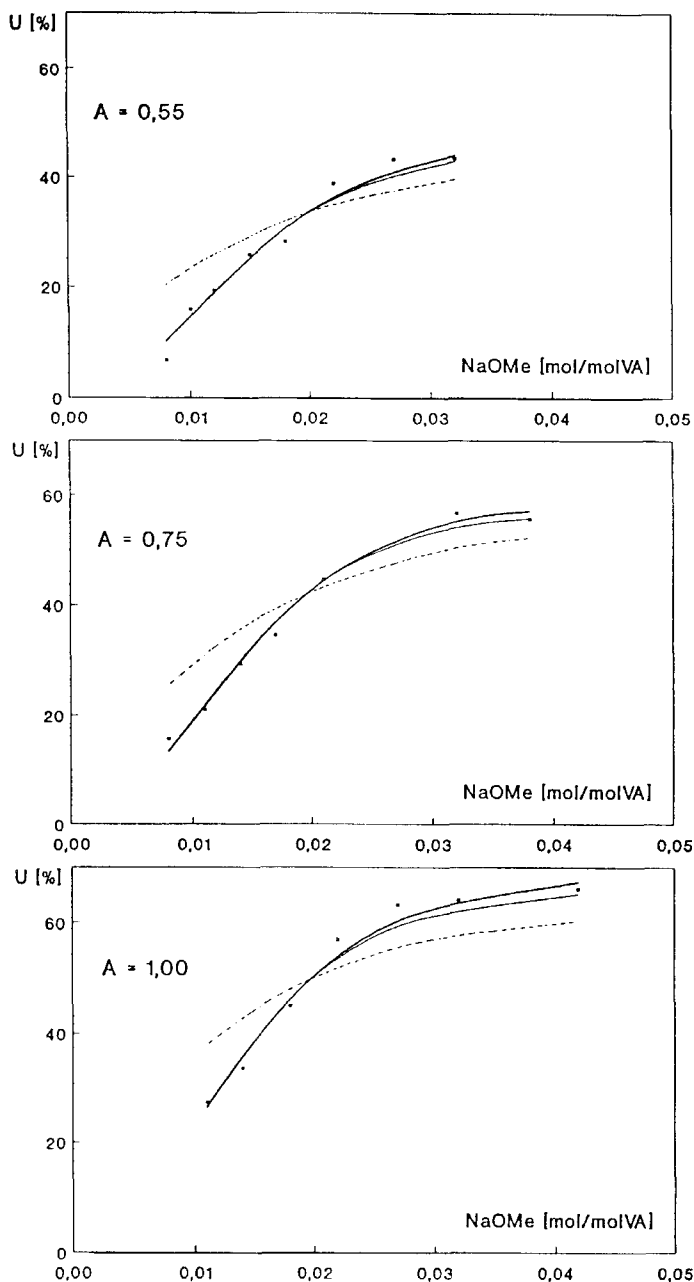


FIG. 5. Model curves found by parameter optimization: dependence of the conversion (U) on the quantity of added catalyst (NaOMe) at three different initial molar ratios of MeOH/VA (A). Model curves of Eq. (4) for a homogeneous system: (---) optimization of k_1 and k_{-1} . Model curves of Eq. (4) after taking into account the mass transfer of the catalyst in the EVA phase by Eq. (5): (—) optimization of k_1 and k_0 and $K = 3.3$; (—) optimization of k_1 , k_{-1} , and k_0 .

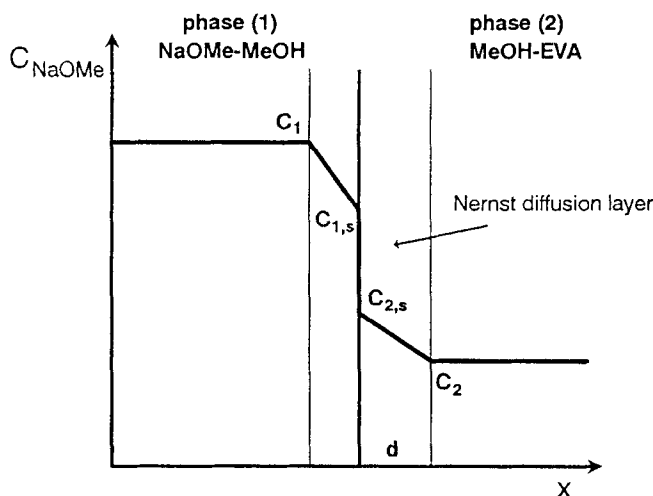


FIG. 6. Mass transfer of NaOMe catalyst in the reaction phase of MeOH-EVA.

This assumption might be permissible because the affinity between catalyst and polymer increases because methanolysis is proceeding simultaneously. From the literature [4] it is well known that the mass transfer of OH ions considerably increases with conversion during the heterogeneous saponification of EVA.

The coefficient $k_{\bar{u}}$ is a complex term:

$$k_{\bar{u}} = DO/(dV) \quad (6)$$

It includes the diffusion coefficient D , the thickness d of the laminar flow layer, the volume V of the polymer phase, and the interface O which is dependent on the quantity of NaOMe used, $O = f n_{\text{NaOMe}}$ (f = proportionality factor).

In addition to Eq. (4), the mass transfer of the catalyst into the polymer phase is taken into account in the kinetic model. In this case the fitting of the model curves to the experimental dependences is reached by optimization of the coefficient $k_{\bar{u}}$ for the mass transfer of NaOMe and the rate constant k_1 of the methanolysis toward reaction. The equilibrium constant K , which has already been determined, is given. The dependences of Fig. 2 were analyzed separately in each case. The results are included in Fig. 5. A satisfying adaption of the model curves (thin lines) to the experimental data is obtained. In the initial stages, in which the mass transfer of the catalyst influences the curves decisively, a good correlation can be observed between the experimental data and the calculated curves.

In another variant of curve fitting including the already determined transition coefficients, the two rate constants of the methanolysis forward and back reactions, k_1 and k_{-1} , are calculated next. The resultant curves are shown in Fig. 5 (heavy lines). An additional improvement of the adaption of the model curves to the measured series is reached.

These calculations supply slightly higher values of the equilibrium constant in comparison with that already determined from the limiting conversions (Fig. 4). This was expected because, on the one hand, the latter was determined from conversion data which had been approximated to the equilibrium states, and, on the other

hand, in the case of a heterogeneous reaction system, not all of the added MeOH takes part in the alcoholysis. Really, the degrees of conversion are reached with less MeOH, from which an increase of the equilibrium constant results.

It is satisfying that the parameters determined from all three measured series have about the same values (see Table 1). This shows that the validity of our kinetic model is confirmed for a wide composition.

In addition to the mass transfer process, the characteristics of alcoholates are also noted. With a large surplus of MeOH, NaOMe exists as totally dissociated, solvated ions. As the concentration of MeOH decreases, ion pairs or aggregates are formed [5]. Analogous to the association behavior of sodium iodide in a series of aliphatic alcohols [6], a similar increase in association with increasing temperature and the existence of alcohols with a higher molecular weight and a higher degree of branching can also be expected for NaOMe. Therefore, in our reaction system, in which separation of the alcoholate can be expected and in which the low molecular weight primary alcohol MeOH is replaced by polymer alcohol with a secondary structure, alterations in the catalyst activity must occur.

TABLE 1. Results of the Parameter Calculation by Two-Dimensional Simplex Optimization for Different Kinetic Models

Measured series, MeOH/VA (A)	k_1 k_{-1}		K	ESS	Model	
	$L^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}$					
0.55	3.60	1.10	3.3 ^a	0.0493	Homogeneous system	
0.75	3.72	1.13	3.3 ^a	0.0574		
1.00	4.13	1.25	3.3 ^a	0.0673		
Total	3.75	1.14	3.3 ^a	0.0101		
				k_{ii}, min^{-1}		
0.55	34.07	10.32	3.3 ^a	4.75	0.0037	Heterogeneous system with NaOMe transfer
0.75	32.31	9.79	3.3 ^a	5.30	0.0031	
1.00	31.43	9.52	3.3 ^a	5.52	0.0028	
Total	34.08	10.33	3.3 ^a	4.97	0.0101	
0.55	33.56	7.63	4.40	4.75 ^a	0.0033	Homogeneous system, order $n \neq 1$
0.75	31.55	7.91	3.99	5.30 ^a	0.0027	
1.00	30.81	7.53	4.09	5.52 ^a	0.0020	
Total	33.11	7.96	4.16	4.97 ^a	0.0083	
				NaOMe order		
0.55	41.00	12.42	3.3 ^a	1.84	0.0045	Homogeneous system, order $n \neq 1$
0.75	58.63	17.76	3.3 ^a	1.93	0.0030	
1.00	58.10	17.60	3.3 ^a	1.93	0.0030	
Total	60.17	18.23	3.3 ^a	1.95	0.0112	

^aThe value of the parameter was given.

A complete modeling of the reaction system seems impossible because of the complexity and lack of knowledge of all the processes which occur. Typically, a general reaction rate equation with adapted reaction order, which reflects the course of reaction, is formally used in such cases. In the derived kinetic model which starts from a homogeneous system, a reaction order differing from 1 for the catalyst is assumed. This parameter is also included in the optimization. The results (Table 1) show that a description of the experimental dependences also turns out well, but only formally. The system which takes into account the heterogeneity of the reaction system and the mass transfer of the catalyst is surely more realistic and more functional.

CONCLUSION

The methanolysis of EVA copolymers in an extrusion process is a useful industrial procedure. The reactive extrusion of the alcoholysis system EVA/NaOMe/MeOH is easy to master. Increasing the addition of catalyst causes an increase in the degree of alcoholysis. Limiting conversions which depend on the starting molar ratio MeOH/VA are achieved. The equilibrium of methanolysis can be reached during residence time in the extruder. The law of mass action is confirmed, and the position of equilibrium of alcoholysis EVA/MeOH is determined. The kinetic modeling of the reaction process was successful. The rate equation based upon the general reaction scheme is applicable if the mass transfer of catalyst in the EVA melt is taken into account. The production of well-defined modification products with desired chemical compositions is possible.

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