

REACTION EQUILIBRIUM OF POLYANHYDRIDE FORMATION. III.*
 COMPOSITION OF REACTION MIXTURE
 IN THE COURSE OF DISTILLATION

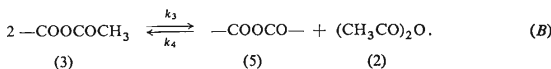
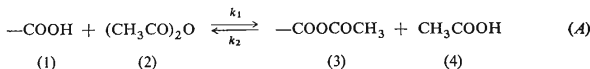
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The relations expressing the equilibrium composition of mixture upon the polyanhydride formation through mixed anhydride resulting from the reaction of adipic acid with acetic anhydride were derived on the assumption that the reaction rate is much higher than the rate of distillation. On using the previously determined values of equilibrium constants, the course of reaction was calculated during the distillation of liberated acetic acid with acetic anhydride for various reaction conditions. The optimum results are obtained if it is started with the mixture of 1 mol of adipic acid and only approximately 0.5 mol of acetic anhydride to which further 2.5 mol of acetic anhydride are dropped at a rate equal to the rate of distillation, whereupon the volatile constituents are distilled off. The yield of polyanhydride is then 92–93%, the quantity of unreacted adipic acid is 0.5–1.5%.

Non-volatile dicarboxylic acids react with acetic anhydride originating a low-molecular mixed polyanhydride. By the polycondensation of this intermediate product, the polyanhydride is formed. Both processes are reversible and can be represented by the following reaction schema:



Since in the reaction system acetic acid and acetic anhydride are the only volatile components, it is possible to control the equilibrium composition by distillation. The establishing of the reaction equilibrium is substantially quicker than the establishing of the vapour-liquid equilibrium. For a simplified description of the system, the knowledge of the initial concentrations, the total rate of distillation and both equilibrium constants is sufficient the determination of which was the subject of foregoing papers^{1,2}. The found values are as follows:

$$K_{12} = k_1/k_2 = c_3c_4/c_1c_2 = 1.34, \quad (1)$$

$$K_{34} = k_3/k_4 = c_2c_5/c_3^2 = 0.16, \quad (2)$$

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where c_1 denotes the equilibrium concentration of carboxyl groups of initial acid, c_2 the equilibrium concentration of acetic anhydride, c_3 that of mixed anhydride, c_4 that of acetic acid, and c_5 that of polyanhydride units.

The subject of this paper is the calculation of equilibrium composition of reaction mixture and its change in the course of distillation. As the distilling binary mixture contains acetic anhydride as a product of the reaction (B) but above all as the initial substance of the reaction (A), the main aim of this consideration was to minimize its consumption as a reagent. As a solution it offered a gradual adding of acetic anhydride in the course of distillation, *i.e.* the analogous principle which leads to an increase in the efficiency of extraction. Single variants were calculated and compared for each model and the reliability of the calculation was checked by an experiment.

THEORETICAL

The solution of the problem consists in the simultaneous expressing the dependence of concentrations of five components of the reaction system in accordance with the determinative reaction equilibria and the phase vapour-liquid equilibrium of the binary system formed by two volatile components of the mixture. Exact solution is rather troublesome. As an approximation, a numerical solution with sufficiently short steps was chosen. Every step consists of distilling off a small fraction of the binary acetic acid-acetic anhydride mixture and of restoring the reaction equilibrium.

If n_i^0 is an initial number of moles of the i -th component and q , r are conversions in the reaction (A) or (B), resp., then by substituting into Eqs (1) and (2) we obtain after rearranging

$$a_1 q^2 + (a_2 r - a_3) q + a_4 r + a_5 = 0, \quad (3)$$

$$b_1 q^2 + (b_2 r + b_3) q - b_2 r^2 - b_4 r - b_5 = 0, \quad (4)$$

where

$$\begin{aligned} a_1 &= K_{12} - 1, & a_2 &= 2 - K_{12}, & a_3 &= K_{12}(n_1^0 + n_2^0) + n_3^0 + n_4^0, \\ a_4 &= K_{12}n_1^0 + 2n_4^0, & a_5 &= K_{12}n_1^0n_2^0 - n_3^0n_4^0, & b_1 &= K_{34}, & b_2 &= 1 - 4K_{34}, \\ b_3 &= 2K_{34}n_3^0 + n_5^0, & b_4 &= 4K_{34}n_3^0 + n_2^0 + n_5^0, & b_5 &= n_2^0n_5^0 - K_{34}(n_3^0)^2. \end{aligned}$$

The system of two general quadratic equations (3) and (4) of two unknown quantities has at most four solutions from which only the first non-negative roots make sense. The system represents a pair of hyperbolas whose axes include an angle of $\sim 62^\circ$, approximately in a symmetrical way round the axis x . Numerical solution by means of the classic iterative methods is rather laborious. A more advantageous way is the Meissner method³ in which for single iteration cycles, the independent

calculation of both consecutive equilibria considered isolated is taken. The iteration was finished if the roots of two successive steps already differ less than by $2 \cdot 10^{-10}$.

After establishing the equilibrium, the reaction mixture contains, in the j -th step, a binary mixture whose quantity is $L_{(j)} = n_{2(j)}M_2 + n_{4(j)}M_4$, where M_i denotes molecular weight. The initial concentration of the more volatile component is $x_{0(j)} = n_{4(j)}M_4/L_{(j)}$. By distilling off a small fraction of the volatile part of the mixture $\Delta D/L_0$, $x_{0(j)}$ changes to $x_{(j)}$ whose value can be determined from the Rayleigh equation. As the possibility of making up for the reacting and contingently distilling off acetic anhydride by its adding in the course of distillation was investigated, the balance equation of differential distillation was modified for this case^{4,5}. If the amount of the acetic anhydride added, containing if any a portion b of acetic acid, can be expressed as a portion c of the total amount of distillate D , then after integration, the following modified Rayleigh equations result for the case investigated:

$$\text{for } c < 1 \quad (1 - c) \Delta D/L_0 = 1 - [g(x_{0(j)})/g(x_{(j)})], \quad (5)$$

$$\text{for } c = 1 \quad \Delta D/L_0 = h(x_{0(j)}) - h(x_{(j)}). \quad (6)$$

The roots of the equation, $x_{(j)}$, are the searched solution from which a new equilibrium composition $n_{i(j+1)}$ can be determined again. Unlike these values, the quantities L , D , and x are in weight units.

The functions presented in Eqs (5) and (6) have the form

$$g(x) = \left(\frac{a + p - A_2x}{a - p - A_2x} \right)^{A_1} \cdot [(a + p - A_2x)(a - p - A_2x)]^{A_3}, \quad (7)$$

$$h(x) = A_4x + A_5 \ln |A_6x - b|, \quad (8)$$

$$\begin{aligned} \text{where} \quad a &= (\alpha - 1)(1 - bc) + c, & p &= \sqrt{(a^2 - 2A_2bc)}, \\ A_1 &= [2(1 - c) + a]/2p, & A_4 &= (\alpha - 1)/A_6, \\ A_2 &= 2(1 - c)(\alpha - 1), & A_5 &= \alpha/A_6^2, \\ A_3 &= 1/2, & A_6 &= (\alpha - 1)(1 - b) + 1. \end{aligned}$$

Vapour-liquid equilibrium is determined by the separation factor α . For $b \neq 0$, the functions (5) and (6) are discontinuous in the interval $0 < x < 1$. The position of discontinuity is determined by the relation

$$x_\infty = (a - p)/A_2. \quad (9)$$

This value is not defined for $c = 1$. By using the L'Hôpital rule, the relation results for $c = 1$

$$x_{\infty} = \lim_{c \rightarrow 1} x_{\infty} = b/A_6. \quad (10)$$

The number of reacting components in single successive steps of calculation is defined by the following relations

$$n_{1(j+1)} = n_{1(j)} - q_{(j+1)}, \quad (11)$$

$$n_{2(j+1)} = [n_{2(j)} + (n_{4(j)}M_4/M_2) - (1 - c) \Delta D_{(j)}M_2] (1 - x_{(j)}) - q_{(j+1)} + r_{(j+1)}, \quad (12)$$

$$n_{3(j+1)} = n_{3(j)} + q_{(j+1)} - 2r_{(j+1)}, \quad (13)$$

$$n_{4(j+1)} = [n_{4(j)} + (n_{2(j)}M_2/M_4) - (1 - c) \Delta D_{(j)}/M_4] x_{(j)} + q_{(j+1)}, \quad (14)$$

$$n_{5(j+1)} = n_{5(j)} + r_{(j+1)}. \quad (15)$$

For $\Delta D/L_0$, the value 0.05 was chosen. For this value of step, $\Delta x < 0.01$. Under these conditions it would be sufficient to integrate even the modified balance equation of differential distillation directly by means of the Simpson method but the calculation in this case is not substantially simplified in comparison with the use of the exact solution (7) and (8).

EXPERIMENTAL

The calculation was carried out by means of a cyclic program on the table computer Hewlett-Packard Calculator 9100 A in the system with an external HP Extended Memory 9101 A, an HP Calculator Printer 9120 A and an HP Calculator Plotter 9125 A. In this way, the tables of values and at the same time the graphical representation were obtained of searched functions of the instantaneous content of acetic acid y in the distilling mixture and of the average content of acetic anhydride in distillate, $1 - \bar{y} = \Sigma \Delta D_2 / \Sigma \Delta D$, where $\Delta D_2 = M_2 n_{2(j-1)} - M_2 n_{2(j)} + (1 - b) \cdot c \Delta D_{(j)}$. The reliability of the calculation was verified with one typical example by changing the value of step. When changing $\Delta D/L_0$ from 0.05 to 0.025 or 0.10, the instantaneous content of acetic acid in the distilling mixture y and further n_1 appeared as the most sensitive quantities. Their final deviation grows gradually by the error propagation up to 10–20% relative. The other values are far less sensitive to the changes of the step. When increasing the step to 0.20, the error increases approximately to double and the recorded curves deviate evidently from those calculated with smaller $\Delta D/L_0$. In all model calculations, only adipic acid was considered as a dicarboxylic acid and for it, too, the constant K_{12} and particularly K_{34} was determined. The found relations and calculated functional dependences hold qualitatively without substantial deviations for the other comparable aliphatic dicarboxylic acids, too.

The reliability of calculations was tested by means of the experiment. Into the previously described apparatus¹ 876 g of pure adipic acid (Rhône-Poulenc) and 318 g of acetic anhydride (Chema, Prague), containing 4% acetic acid, were weighed. The mixture was brought into boiling under a reflux condenser, after the establishing of equilibrium the condenser was tilted to a descendent condenser position and further acetic anhydride was dropped at the same rate at which the mixture distilled. After adding 1272 g of acetic anhydride, the dropping was finished and the distillation was completed. During the whole experiment, samples were taken and as the only analytically accessible data, the content of acetic acid and acetic anhydride in the distillate was determined by the method of double titration. Owing to the sufficiently large weighed amount it was possible to determine in this way without substantial error on the one hand the instantaneous composition of distilling mixture and on the other hand the total average composition of distillate. The results of measurements are compared with the calculations in Fig. 3.

RESULTS AND DISCUSSION

As the essential characteristics of the reaction system, the equilibrium composition was calculated at different molar ratios of initial components under static conditions, *i.e.* without removing the volatile components. The course of functions $N_i = f[n_2^0 : (n_1^0 + n_2^0)]$ is represented in Fig. 1. The highest equilibrium content of the polyanhydride units is 6 mol % at the initial molar ratio of acetic anhydride and adipic acid equal approximately 1 : 2. At the same time it is evident that the conversion of acetic anhydride increases quickly with its decreasing initial content. The equilibrium content of polyanhydride is relatively low because the value of K_{34} is much smaller than that of K_{12} . The amount of polyanhydride can be further increased

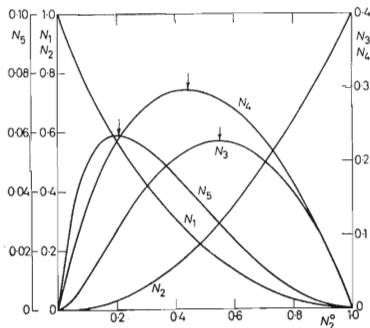


FIG. 1

Dependence of Equilibrium Mole Fraction of Carboxyl Groups of Dicarboxylic Acid N_1 , Acetic Anhydride N_2 , Mixed Anhydride N_3 , Acetic Acid N_4 and Polyanhydride Units N_5 on the Initial Content of Acetic Anhydride N_2^0 in Reaction Mixture

only by disturbing the established equilibrium, *e.g.* by distilling off the formed acetic acid. The usual hitherto used methods recommended as a rule to use an excess of acetic anhydride⁶ and, if need be, to face its losses during distillation of the binary mixture by efficient rectification^{7,8}. With respect to the character of the relations found it is, however, much more advantageous to use on the contrary an initial excess

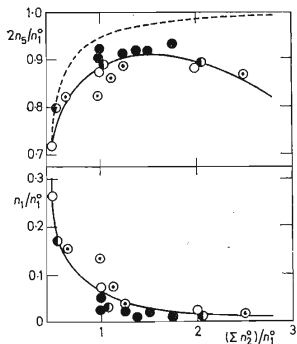


FIG. 2

Dependence of Conversion, as the Portion of Unreacted Carboxyl Groups of Adipic Acid n_1/n_1^0 and the Portion of Polyanhydride Units Formed $2n_5/n_1^0$, on the Molar Ratio of Totally Consumed Acetic Anhydride to the Initial Amount of Carboxyl Groups of Adipic Acid

○ $c = 0$, ○ $c = 0.2$, ◐ $c = 0.5$, ● $c = 1.0$.
Dashed curve in upper part is the mirror image of the curve in lower part of the graph.

TABLE I

Dependence of Equilibrium Composition on Starting Concentration of Initial Components and on the Conditions of Distillation at $c < 1$, $b = 0$, and $\Delta D/L_0 = 0.05$

n_1^0	Σn_2^0	c	n_1	n_2	n_3	n_4	n_5
0.333	0.667	0.0	0.0076	0.0010	0.031	0.00034	0.147
0.333	0.835	0.2	0.0033	0.0018	0.040	0.00020	0.145
0.500	0.500	0.0	0.038	0.00049	0.026	0.00097	0.218
0.500	0.630	0.2	0.018	0.0011	0.039	0.00071	0.221
0.500	0.565	0.2 ^a	0.038	0.00075	0.032	0.0012	0.215
0.500	0.500	0.2 ^b	0.066	0.00037	0.022	0.0015	0.206
0.500	1.014	0.5	0.0020	0.0023	0.056	0.00011	0.221
0.667	0.333	0.0	0.178	0.00005	0.0084	0.0013	0.240
0.667	0.427	0.2	0.102	0.00015	0.016	0.0013	0.274
0.667	0.694	0.5	0.020	0.0017	0.056	0.00080	0.296
0.800	0.445	0.5	0.137	0.00027	0.023	0.0021	0.320

^a $b = 0.5$; ^b $b = 1.0$.

of dicarboxylic acid and to add acetic anhydride into the reaction mixture only during distillation. The course of such way of preparation was calculated for various conditions and the main results of calculation are summarized in Table I. It is unambiguously evident that any decrease in the acetic anhydride content ($b \neq 0$) leads to a fall of yield of mixed anhydride and polyanhydride.

The yield of polyanhydride or unreacted adipic acid is influenced in a decisive way by the total ratio of acetic anhydride to the initial amount of adipic acid. If the initial amount of the latter was n_1^0 and the amount of acetic anhydride $n_2^0 = 1 - n_1^0$ and if acetic anhydride was dropped during distillation at a rate c , then its overall consumption is $\sum n_2^0 = n_2^0 + c \sum \Delta D$. The dependence of the polyanhydride yield and of the unreacted adipic acid residue (related to n_1^0) on the value of $(\sum n_2^0)/n_1^0$ is represented in Fig. 2. The scattering of points round the curves plotted is not a consequence of experimental errors or numerical inaccuracies but it resulted from the comparison of the values valid for different c or b . From Fig. 2 it is evident that the amount of unreacted adipic acid decreases quickly and monotonously with increasing excess of totally consumed acetic anhydride whereas the yield of polyanhydride increases and reaches the maximum at $(\sum n_2^0)/n_1^0$ lying in the region about 1.5. As the calcula-

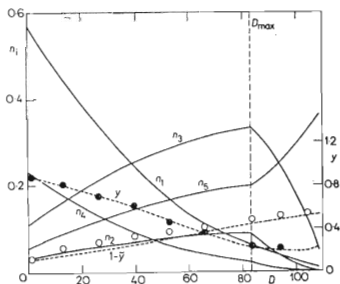


Fig. 3

Dependence of the Content of Single Components n_i in Reaction Mixture (solid lines), of the Instantaneous Content of Acetic Acid y in Distilling Mixture and of the Average Content of Acetic Anhydride ($1 - \bar{y}$) in Distillate (dotted lines) on the Amount of Distillate $D(g)$

Broken vertical line at D_{max} corresponds to finishing the dropping of acetic anhydride. Input data: $n_1^0 = 0.790$, $n_2^0 = 0.197$, $n_4^0 = 0.013$, $c_1 = 1.0$, $c_2 = 0$, $b = 0.04$, $\Delta D/L_0 = 0.05$, $\Sigma \Delta D_{max} = 83.42$, and $\Sigma n_2^0 = 0.982$. Curves represent theoretical calculation, experimental values are marked by points: \circ ($1 - \bar{y}$), \bullet y .

TABLE II
Equilibrium Composition of Reaction Mixture at the Stage A after Finishing the Dropping of Acetic Anhydride ($c = 1$, $b = 0$) and at the Stage B at the End of Distillation ($c = 0$) for $\Delta D/L_0 = 0.05$

n_1^0	Σn_2^0	Stage	n_1	n_2	n_3	n_4	n_5
	0.669	A	0.186	0.152	0.296	0.128	0.092
		B	0.035	0.00057	0.033	0.00082	0.299
0.667	0.843	A	0.115	0.168	0.336	0.077	0.107
		B	0.016	0.00091	0.042	0.00048	0.304
	1.004	A	0.071	0.178	0.361	0.047	0.117
		B	0.0085	0.0012	0.047	0.00028	0.306
	0.805	A	0.111	0.082	0.311	0.039	0.189
		B	0.022	0.00091	0.045	0.00059	0.366
0.800	1.095	A	0.032	0.089	0.344	0.011	0.212
		B	0.0049	0.0013	0.055	0.00015	0.370
	1.401	A	0.0073	0.091	0.354	0.0025	0.219
		B	0.0010	0.0014	0.056	0.00003	0.371

tion is finished by the program as a rule at the content of volatile binary mixture in the reaction system from 0.3 to 0.5%, this amount may be neglected and the complement to 100%, according to Fig. 2, represents the yield of mixed anhydride which under the conditions investigated, grows from 1 to 18%. This is represented in Fig. 2 in the upper part of the graph by the mirror reversal of the lower curve for n_1/n_1^0 . Vertical distance between the solid and dashed curves in the upper part of the graph represents the quantity of resulting mixed anhydride of adipic and acetic acid. The content of mixed anhydride increases monotone with increasing $(\Sigma n_2^0)/n_1^0$ and at $(\Sigma n_2^0)/n_1^0 > 1.5$ it takes place then to the prejudice of the polyanhydride content. Consequently, the minimum consumption of acetic anhydride for obtaining the optimum yield is 3 mol for 1 mol of adipic acid. Larger consumption has no sense, smaller consumption results in an increase of the portion of unreacted adipic acid.

It is significant that the way of adding acetic anhydride into the reaction mixture (all at once at the beginning or gradually during distillation) is not an important and decisive factor from the point of view of the final results (Table II). An evidence of it gives on the whole a random and rather small scattering of points round generalizing

curves with the exception of the points for $c = 1$ which show an expressive tendency to deviate systematically from the plotted curves towards a smaller amount of unreacted adipic acid, or other words, towards a higher portion of polyanhydride. From this point of view it is therefore more advantageous for preparation of polyanhydride to start with the reaction mixture *e.g.* at $N_2^0 = 0.2$ (Fig. 1) and to use dropping acetic anhydride at a rate equal to the rate of distillation ($c = 1$, *i.e.* full exchange of the volatile phase) than only a partial dropping ($c < 1$) for all the time of distillation which is besides even slower. With the minimum consumption of acetic anhydride found it is possible in this arrangement to lower the portion of unreacted adipic acid to 0.5–1.5% and to obtain simultaneously the yield of polyanhydride of 92–93%. The correctness of the calculation was checked by experiment. Fig. 3 gives the illustration of the record of calculated values. Directly into this graph, the experimental points for y and $(1 - \bar{y})$ were plotted as the only analytically accessible data. The agreement of the experiment with calculation is very good and proves the adequacy of the approximation chosen.

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