

REACTION EQUILIBRIUM OF POLYANHYDRIDE FORMATION. II.*

SOLUTION BASED ON THE VAPOUR-LIQUID EQUILIBRIUM OF A TERNARY SYSTEM

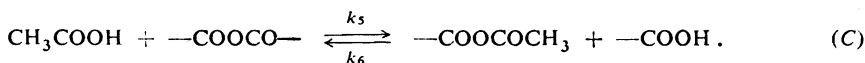
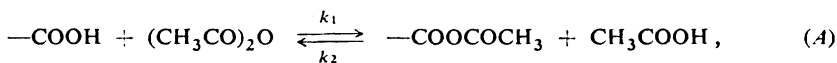
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The analysis of the vapour phase composition above the reaction mixture has made it possible, on the basis of the known vapour-liquid equilibrium for the ternary system chlorobenzene-acetic anhydride-acetic acid, to determine the content of components in the reaction mixture upon the formation of the mixed acetic and adipic acid anhydride and the corresponding polyanhydride from adipic acid and acetic anhydride. In this way we have succeeded in estimating the approximate values of equilibrium constants of partial reactions (A) and (B), $K_{12} = 1.34 \pm 0.11$ and $K_{34} = 0.16 \pm 0.045$, which define in an explicit way the total reaction equilibrium.

Linear polyanhydrides result from the reaction of non-volatile dicarboxylic acids with acetic anhydride. With this the primary reaction products are, besides the liberating acetic acid, low-molecular mixed anhydrides of the dicarboxylic acid and acetic acid. By the polycondensation of this product a polymer is formed. As a low-molecular by-product, acetic anhydride eliminates again and distills from the reaction mixture. On the contrary the acetic acid if present is able to degrade the originating polyanhydride. The total reaction can be represented by the following system of equations:



Both reactions are reversible so that for the characterization of the course of polycondensation and for the study of the reaction kinetics, it is important to know the values of equilibrium constants of single reactions:

$$K_{12} = c_3 c_4 / c_1 c_2, \quad (1)$$

$$K_{34} = c_2 c_5 / c_3^2, \quad (2)$$

$$K_{56} = c_1 c_3 / c_4 c_5 = 1 / K_{12} K_{34}. \quad (3)$$

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The constants depend on the concentration of carboxylic groups of the initial acid c_1 , acetic anhydride c_2 , mixed anhydride c_3 , acetic acid c_4 , and polyanhydride c_5 . Besides sporadic works dealing with an analogous reaction of monobasic acids¹, there are no necessary data available (at one's disposal) in the literature. With regard to a close chemical relationship of the substances involved it is next to impossible to estimate them by classic procedures and such efforts have been, for the time being, as a rule unsuccessful^{2,3}.

In the preceding paper⁴ an attempt was described to use physico-chemical methods for the determination of equilibrium constants. On the basis of the knowledge of vapour-liquid equilibrium for the given binary system, it is possible to determine the composition of a reaction mixture from the composition of the vapour phase above the reaction mixture or from the boiling point elevation. In this way we succeeded in obtaining the approximate value of the equilibrium constant for the first single reaction only, $K_{12} = 1.35 \pm 0.29$. Application of this procedure required to introduce a number of simplifying assumptions that eliminated the possibility of the independent determination of the equilibrium constants of further reactions.

The subject of this work is a modification of the original method which allows the independent determination of concentrations of all system components simultaneously and by that also the determination of both equilibrium constants from only one measurement of the vapour-liquid equilibrium above the reaction mixture. This is possible to do by adding a further component into the reaction mixture. This component must be a volatile non-reactive solvent which does not influence catalytically

TABLE I

Equilibrium Contents (meq/g) of Acetic Anhydride y_2 and Acetic Acid y_4 in Vapour for Different Contents of Acetic Anhydride x_2 and Acetic Acid x_4 in Liquid in the Ternary System with Chlorobenzene

x_2	x_4	y_2	y_4	x_2	x_4	y_2	y_4
0.418	0.415	0.480	3.436	1.740	2.619	1.246	5.820
0.480	0.791	0.540	4.130	1.828	3.415	0.918	6.962
0.456	1.690	0.436	4.965	2.804	0.472	2.780	2.328
0.424	2.484	0.416	6.342	2.650	0.981	2.228	3.774
0.424	3.332	0.410	6.955	2.694	1.820	2.040	4.750
0.762	0.470	1.060	3.116	2.692	2.633	1.920	5.890
1.048	1.013	1.254	3.443	2.742	3.448	1.692	6.314
0.804	1.732	0.732	5.311	3.762	0.560	3.440	2.306
1.116	2.527	0.816	5.810	3.466	1.088	3.042	2.876
0.948	3.148	0.370	6.810	3.804	1.724	2.614	4.543
1.864	0.392	1.814	2.859	3.636	2.724	2.138	5.585
1.794	0.889	1.474	4.020	4.036	3.373	1.970	6.311
1.758	1.710	1.326	5.145				

the course of reaction but takes part in the establishing of the vapour-liquid equilibrium. In this work, chlorobenzene was chosen as one of few solvents common for all components of the reaction mixture. Its negligible catalytic activity may be assumed with respect to its nature. A disadvantage is the formation of azeotropic mixture containing 58.5 percent of acetic acid^{5,6} whose boiling point is 114.65°C.

EXPERIMENTAL

Materials Used

Adipic acid, a pure reagent (Leuna Werke, Merseburg), did not contain homologues. Adipic acid polyanhydride was prepared by the reaction of 1 mol of adipic acid with 5 mol of acetic anhydride followed by distilling off the mixture of acetic acid and excessive acetic anhydride at normal pressure. The last remainders of volatile components were removed in 5 Torr vacuum at temperatures up to 180°C. Its molecular weight was not determined, because all its anhydride bonds participate independently in the reactions studied and so the weight of segment equal to 128.12 is decisive. Chlorobenzene, a pure reagent (VChZ Synthesia, Pardubice Semtín) was dried with phosphorus pentoxide and distilled over. Acetic anhydride, a pure reagent (Chema, Prague) contained a various amount of acetic acid, which was included into calculations. Glacial acetic acid, an analytical grade reagent was not further purified.

Vapour-Liquid Equilibrium in the System Chlorobenzene-Acetic Anhydride-Acetic Acid

Experimental equipment for the determination of the equilibrium vapour phase composition was described in the preceding paper⁴. In the taken sample of the vapour phase (condensate) as well as of the liquid phase, the content of acetic acid and acetic anhydride was estimated by the method of double titration⁷. The found values (in meq/g) of the content of acetic anhydride x_2 and acetic acid x_4 in the liquid phase as well as of the content of acetic anhydride y_2 and acetic acid y_4 in the vapour phase are summarized in Table I. Weighed amounts were chosen so as to cover the concentration range from 2 to 20 percent in the liquid phase and from 2 to 20 percent of acetic anhydride or from 12 to 42 percent of acetic acid in the vapour phase.

Prior to the treatment of in this way obtained data, it was further to verify whether the presence of a non-volatile component did not influence the investigated vapour-liquid equilibrium. With regard to reactivities of components it was possible in principle to use to this purpose only the system adipic acid-chlorobenzene-acetic acid as a model mixture. The vapour-liquid equilibrium was determined in the same manner as in the preceding case. The found content of acetic acid y_4 (in meq/g) in the vapour phase is given in Table II. The dependence of the weight fraction of acetic acid in the vapour $w_{4(v)}$ on the weight fraction of acetic acid in the liquid phase $w_{4(1)}$ is not, according to the Fig. 1, influenced by the presence of the third non-volatile component. The volatile constituents of this ternary system behave as if adipic acid is not present. Besides, it is possible to approximate the initial part of the dependence up to $w_{4(1)} = 0.25$ very well by a linear relation between $1/w_{4(v)}$ and $1/w_{4(1)}$.

Reaction Equilibrium

The equilibrium composition of the vapour phase above the reaction mixture solution was determined by using the same apparatus⁴ and in the same way as it was done when the vapour-liquid equilibrium was investigated in the ternary system. The mixture of initial substances was

TABLE II

Acetic Acid Content y_4 (meq/g) in the Vapour Phase above the System Adipic Acid–Chlorobenzene–Acetic Acid

Chlorobenzene g	Acetic acid g	Adipic acid, g				
		0	25	50	100	150
40	160	11.78	11.28	11.21	10.98	10.76
80	120	10.21	9.40	9.12	8.68	8.46
120	80	8.47	7.78	7.63	6.75	6.70
160	40	7.19	5.87	5.61	4.43	4.25

TABLE III

Initial Composition of Reaction Mixture, Composition after Establishing Reaction Equilibrium and Values of Equilibrium Constants Corresponding to Composition Changes

Experiment	1	2	3	4	5
Adipic acid, g	—	—	—	—	37
Adipic acid polyanhydride, g	135	135	135	222	—
Acetic anhydride, g	99	99	99	—	189
Acetic acid, g	1	1	1	60	11
Chlorobenzene, g	400	400	400	300	300
Heating period, h	2	4	10	2	2
y_2 , meq/g	2.54	2.65	2.57	0.84	4.35
y_4 , meq/g	0.30	0.45	0.44	2.66	2.67
x_2 , meq/g	1.85	2.00	1.90	0.67	6.00
x_4 , meq/g	0.04	0.06	0.05	0.36	1.20
n_1^0 , mol	0	0	0	0	0.5
n_2^0 , mol	0.97	0.97	0.97	0	1.85
n_4^0 , mol	0.03	0.03	0.03	1.0	0.17
n_5^0 , mol	1.05	1.05	1.05	1.73	0
n_1 , mol	0.02	0.02	0.02	0.88	0.09
n_2 , mol	0.41	0.45	0.42	0.10	1.45
n_3 , mol	1.14	1.06	1.12	0.68	0.40
n_4 , mol	0.01	0.01	0.01	0.12	0.58
n_5 , mol	0.47	0.51	0.48	0.95	0.01
K_{12}	1.40	1.20	1.35	0.95	1.78
K_{34}	0.15	0.20	0.16	0.20	0.09

heated to the boiling point under reflux and after the establishing of equilibrium, the condenser was tilted to a descendent condenser position. Subsequently, the sample was taken and analyzed by double titration method. The weight, heating period, and the found composition of the vapour phase samples (condensate) are given in Table III. The composition of the reaction mixture was chosen so that the establishing of the resulting equilibrium might be reached along different paths, *i.e.* either according to the reaction (A) in the fifth experiment or the reaction (B) in the opposite direction for the first to third experiments, of the reaction (C) for the fourth experiment.

For estimating the temperature effect on the reaction equilibrium, the approximate value of the heat change of the total reaction of 2 mol of acetic anhydride with 1 mol of adipic acid after mixing the components in the form of approximately 40 percent solutions in chlorobenzene or dimethylformamide was determined at 25 and 85°C in a calorimetric vessel. The enthalpy change of this moderately exothermic reaction is, however, very low and attains the approximate value of at most 1 : 0.2 kcal/mol.

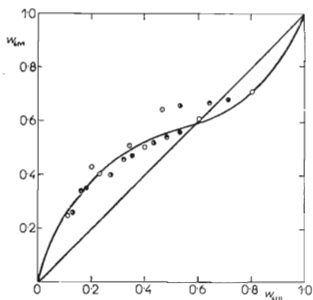


FIG. 1

Dependence of the Acetic Acid Weight Fraction in Vapour $w_{4(v)}$ on the Acetic Acid Weight Fraction in Liquid $w_{4(l)}$ in the Ternary System Adipic Acid-Acetic Acid-Chlorobenzene

Adipic acid content: ○ 0%, ● 11%,
⊙ 20%, ⊚ 33%, ⊕ 43%.

RESULTS AND DISCUSSION

To determine the composition of the liquid from the known composition of the vapour it is necessary to know the function $x_i = f(y_1, y_2, \dots, y_i)$ considering that for y_i values it is not possible to realize equidistant steps. The obtained equilibrium data for the ternary system refer to a limited concentration interval and for their treatment the relations for ideal mixtures may be used. The vapour-liquid equilibrium of an ideal p -component system with a contingently present non-volatile component N is given⁸ by the system of equations:

$$y_i = \alpha_{ip} x_i / \left[1 - x_N + \sum_{i=1}^{p-1} x_i (\alpha_{ip} - 1) \right] \quad (4)$$

The values x_i , y_i may be expressed both in mole fractions and in weight ones. The constants α_{ip} represent the relative volatility of the i th component with respect to the component p .

The system of equations (4) can be expressed in a matrix form (5):

$$\begin{pmatrix} y_1 & 0 & 0 & \dots & 0 \\ 0 & y_2 & 0 & \dots & 0 \\ 0 & 0 & y_3 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & y_{p-1} \end{pmatrix} \cdot \begin{pmatrix} \alpha_{1p} - 1 - \frac{\alpha_{1p}}{y_1} \alpha_{2p} - 1 & \dots & \alpha_{p-1,p} - 1 \\ \alpha_{1p} - 1 & \alpha_{2p} - 1 - \frac{\alpha_{2p}}{y_2} & \dots & \alpha_{p-1,p} - 1 \\ \vdots & \vdots & \ddots & \vdots \\ \alpha_{1p} - 1 & \alpha_{2p} - 1 & \dots & \alpha_{p-1,p} - 1 - \frac{\alpha_{p-1,p}}{y_{p-1}} \end{pmatrix} \cdot \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{p-1} \end{pmatrix} = \begin{pmatrix} -y_1 \\ -y_2 \\ \vdots \\ -y_{p-1} \end{pmatrix} \quad (5)$$

Since the determinant of the system (6) has a non-zero value

$$D = \left(\prod_{i=1}^{p-1} \alpha_{ip} \right) \left[1 - \sum_{i=1}^{p-1} y_i (1 - 1/\alpha_{ip}) \right], \quad (6)$$

it is possible to find $(p - 1)$ independent solutions:

$$x_i = \frac{(1 - x_N) y_i / \alpha_{ip}}{1 - \sum_{i=1}^{p-1} y_i [1 - (1/\alpha_{ip})]} \quad (7)$$

By using a program for multiple regressions⁹ and the data from Table I, the searched functions (8) and (9) of the dependence of acetic anhydride content x_2 and acetic acid content x_4 in the volatile part of the liquid phase on the corresponding concentrations y_2 and y_4 in the vapour phase (expressed in meq/g) were evaluated by means of the

digital computer Elliott 4130 as follows

$$x_2 = y_2/[1.79 - 0.15(y_2 + y_4)], \quad (8)$$

$$x_4 = y_4/[12.3 - 1.47y_2 - 1.39y_4]. \quad (9)$$

The correlation coefficient $r = 0.94$ is identical for both equations. The scattering of experimental values about the calculated function is illustrated in Figs 2 and 3. The equations are not to be used for extrapolating outside the concentration range investigated.

From the obtained values x_2 and x_4 the number of mol n_i of respective component in the reaction mixture was calculated using the relations (10) and (11):

$$n_2 = Gx_2/(2000 - M_2x_2 - 2M_4x_4), \quad (10)$$

$$n_4 = 2Gx_4/(2000 - M_2x_2 - 2M_4x_4), \quad (11)$$

where G is the weight of chlorobenzene (g) and M are molecular weights of corresponding components. By means of n_2 and n_4 and on the basis of the known initial values of n_i^0 of single components, the number of mol of remaining components present in the reaction mixture after establishing of equilibrium was calculated from

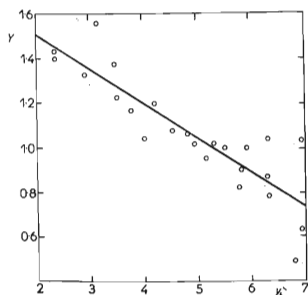


FIG. 2

Correlation of Experimental Data by Eq. (8) in the Form of Linear Dependence of $Y = (y_2/x_2) + 0.15y_2$ on the Acetic Acid Content in Vapour Phase y_4

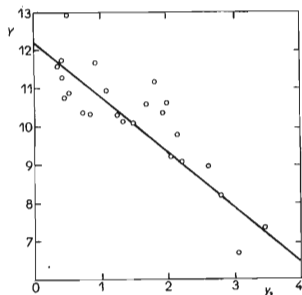


FIG. 3

Correlation of Experimental Data by Eq. (9) in the Form of Linear Dependence of $Y = (y_4/x_4) + 1.39y_4$ on the Acetic Anhydride Content in Vapour Phase y_2

these balance relations:

$$n_1 = n_1^0 + n_4^0 - n_4, \quad (12)$$

$$n_3 = 2n_2^0 + n_4^0 - 2n_2 - n_4, \quad (13)$$

$$n_5 = n_5^0 - n_2^0 - n_4^0 + n_2 + n_4. \quad (14)$$

In this way obtained values and equilibrium constants calculated after substituting into Eqs (1) and (2) are given in Table III as well.

In this manner for the reaction (A) at the boiling temperature of reaction mixture, *i.e.* about 140°C, the value of the equilibrium constant $K_{12} = 1.34 \pm 0.11$ was determined which is identical with the result of measurements described in preceding paper⁴. Owing to the low heat change of the total reaction the boiling point differences of the reaction mixture for various concentrations of components are insignificant and do not influence practically the result of measurement. Likewise the heating period of the reaction mixture plays no essential part, which is proved by the observation that the reaction equilibrium is established very quickly. Heating time used was necessary only for the reliable establishing of the equilibrium between the liquid and vapour and for the equalization of temperatures. As the reaction is weakly exothermic the equilibrium constant decreases with increasing temperature. The constant K_{12} would attain the value about 4 at room temperature and under given conditions. From this follows that a more favourable conversion in preparation of anhydrides is reached at a lower temperature, *i.e.* at reduced pressure, which is also utilized in practice¹⁰. Further this fact does not allow to assume that the tendency to an increase in K_{12} when the initial concentration of dicarboxylic acid is rising, which was found when using the simplified calculation in preceding paper⁴, is caused by an effect of increasing boiling point of the mixture, because then the reaction would have to be at least moderately endothermic.

The value of the equilibrium constant K_{34} of the reaction (B) found in this work is 0.16 ± 0.045 . By using the known values of constants K_{12} and K_{34} , Eqs (12)–(14) can be substituted into the relations (1) and (2). As a result two general quadratic equations with two unknown quantities are obtained whose solution gives the equilibrium composition of the mixture. In comparison with the constant K_{12} , the constant K_{34} is, in keeping with the assumption expressed in preceding paper⁴, really relatively low so that the reaction comes to a standstill practically in the reaction stage of mixed anhydride. The correctness of the found value as for its order is also confirmed by the values of K_{34} for propionic and butyric acid¹ (0.22 and 0.50, resp.). Owing to this fact that parallel to the reaction (A) the reaction (B) takes place, too, the equilibrium concentrations of acetic acid and mixed anhydride do not attain a maximum at the equimolar ratio of carboxylic groups and acetic anhydride but they are somewhat displaced against it. The equilibrium content of mixed anhydride does not exceed

at the same time 23 mol percent. Analogously it is possible to determine the maximum for the dependence of the polyanhydride content in reaction mixture on the initial ratio of starting components. From rather complicated expressions for concentrations of single components results, by using successive approximations, the value 6 mol percent for the ratio of mole fractions of acetic anhydride and adipic acid equal to 1 : 2. Conversion of acetic anhydride is under these conditions about 85 %. Further increase of the polyanhydride content is to be attained by distilling off acetic acid.

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REFERENCES

1. Mironov D. P., Žarkov V. V.: *Ž. Org. Chim.* *1*, 1731 (1965).
2. Gault H., El-Kik E.: *Compt. Rend.* *232*, 2225 (1951).
3. El-Kik E., Gault H.: *Compt. Rend.* *238*, 2428 (1954).
4. Zvonař V., Mandík L.: *This Journal* *36*, 1397 (1971).
5. Horsley L. H.: *Advan. Chem. Ser.* *6*, 3 (1952).
6. Venkateswarlu K., Sriraman S.: *Bull. Chem. Soc. Japan* *31*, 211 (1958).
7. Zvonař V., Klaban J., Krejcar E.: *Chem. průmysl* *18*, 407 (1968).
8. Hála E., Pick J., Fried V., Vilím O.: *Rovnováha kapalina-pára*. Published by NČSAV, Prague 1955.
9. Carolly O.: *Regress Program*, British Petroleum Co.
10. Henkel GmbH: D.B.R. Pat. 955 143 (1956).

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