REACTION EQUILIBRIUM
OF POLYANHYDRIDE FORMATION. I.*
SOLUTION BASED ON BINARY SYSTEM EQUILIBRIA
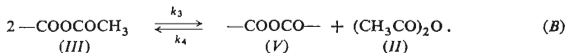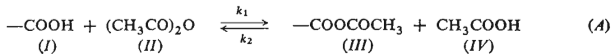
V.Zvonař and L.Mandík

Research Institute of Synthetic Resins and Lacquers, Pardubice

The method of determination of volatile phase composition at the liquid–vapour equilibrium as well as ebulliometry were used to determine the equilibrium constant for the reaction of an aliphatic dicarboxylic acid with acetanhydride. Both methods, although not requiring a direct determination of concentration of each component yield self-consistent results. The value of the equilibrium constant was found to be $1 \cdot 35 \pm 0 \cdot 29$.

The simplest and most advantageous method of linear polyanhydrides preparation is the reaction of acetanhydride with a dicarboxylic acid. Dicarboxylic acid containing less than four bonds between the two carboxyl groups (I), together with the acids having their carboxyls in *ortho*-position, yields exclusively low molecular derivatives possessing intramolecular anhydride bonds. A polymer is formed in other cases. In the first stage of reaction the acetanhydride (II) reacts with the acid forming a mixed anhydride (III) and acetic acid (IV); in the later stage the mixed anhydride decomposes to acetanhydride and original acid anhydride (V) (ref.[1])

$$-COOH + (CH_3CO)_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} -COOCOCH_3 + CH_3COOH \qquad (A)$$
$$\;\;(I) \qquad\quad (II) \qquad\qquad\qquad (III) \qquad\quad (IV)$$

$$2 -COOCOCH_3 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} -COOCO- + (CH_3CO)_2O \;. \qquad (B)$$
$$\quad (III) \qquad\qquad\quad (V) \qquad\quad (II)$$

The reaction scheme holds for polycarboxylic acids provided they contain equally reactive and sterically non-hindered carboxyl groups. This assumption is sufficiently fulfilled for case of polymethylenedicarboxylic acids and frequently employed in macromolecular chemistry[2].

Reaction equilibria of the processes (A) and (B) can be described by equilibrium constants

$$K_{12} = c_3 c_4 / c_1 c_2 \quad \text{and} \quad K_{34} = c_2 c_5 / c_3^2 \,;$$

the concentration of the original acid (c_1), acetanhydride (c_2), mixed anhydride (c_3), acetic acid (c_4) and polyanhydride (c_5) in the reaction mixture can be expressed as $c_1 = c_1^0 - q$, $c_2 = c_2^0 - q + r$, $c_3 = q - 2r$, $c_4 = c_4^0 + q$, $c_5 = r$; symbols q and r express the conversion of I to III and III to V respectively. Initial concentrations are denoted by an exponent 0 (for IV in the mixture with II). If the values of c_2 and c_4 are analytically attainable then it is possible to determine independently the values of equilibrium constants K_{12} and K_{34}. The concentration of polyanhydride units formed during the reaction is given by

$$c_5 = \frac{K_{12}^2 K_{34} (c_1^0 - q)^2 (c_2^0 - q)}{(c_4^0 + q)^2 - K_{12}^2 K_{34} (c_1^0 - q)^2} \,. \tag{1}$$

The determination of concentrations of reaction mixture components by conventional analytical methods is, however, not possible without disturbing the equilibrium[3-5]. This determination is possible under certain suitable conditions using spectroscopic methods[6-8].

The preparation of polyanhydrides from dicarboxylic acids and acetanhydride or by polycondensation of low molecular mixed anhydride formed in the reaction consists of shifting the reaction equilibrium towards polyanhydride[9] formation. The concentration changes in the reaction mixture can be unequivocally described if the values of equilibrium constants are known together with the time dependence of acetic acid and acetanhydride removal. A similar procedure has been selected to follow other types of polycondensations[10]. The method of determining the equilibrium data by measuring the liquid–vapour equilibrium and by using the principle of ebulliometry, respectively, was employed in this paper.

EXPERIMENTAL

Reagents

Adipic acid, pure (Rhône-Poulenc, Usine de Chalampé) and suberic acid (Loba-Chemie, Wien) did not contain any homologues, pimelic acid (Aldrick Chemical Co., Milwaukee, Wisc.) was 97%, azelaic acid (V/O Sojuzchimeksport, Moscow) 99% and sebacic acid (Grace Hatco Chem. Div., Fords N.Y.) 98% pure. The degree of purity and the homologues contents were determined by gas chromatography after quantitative esterification to dimethylesters[11]. Acetanhydride, pure (Chema, Prague) was analysed for acetic acid contents prior to each run.

Determination of the Equilibrium Constant Employing Liquid–Vapour Equilibrium Data

A 1 000 ml round-bottom boiling flask with a still head to which a condenser was connected was used for the experiment. The angle between the still head and the end of the flask neck containing the thermometer was 68°. The condenser was slightly bent near the point where it was attached to the still head so that it was possible, by simple turning it over, to change its function from a reflux to a descending condenser. The flask contents (250 to 350 ml of the mixture) were

heated to the boiling point under the reflux. After the equilibrium had been established the condenser was turned over and a 10 ml sample was distilled off. Acetic acid and acetanhydride in the sample were determined by method of double titration *i.e.* by titration with a hydroxide solution after the reaction of the sample with water and methanol, respectively[3]. The liquid phase composition (*i.e.* reaction mixture composition) was then determined from the data on vapour phase composition using an equilibrium diagram.

Ebulliometric Determination of the Equilibrium Constant

The measurements were carried out using a specially designed ebulliometer whose main part was a wide-bore glass tube the end of which was adapted to a test tube placed into a heating element. A reflux condenser was sealed to the upper part of the tube. A Beckman thermometer (accuracy $\pm 0.002°C$) was inserted into the tube. The lower part of thermometer was in contact with the boiling solution in the test tube, the circulation being ensured by a Cottrell pump. The remaining part of thermometer was placed in the space heated by volatile components vapour. The tube was jacketed to eliminate heat loss.

50 ml of sample containing acetic acid and acetanhydride was pipetted into the ebulliometer test tube and the ebulliometer was, after inserting the thermometer, closed by a calcium chloride drying tube. The mixture was then heated to boil and after the equilibrium has been established the boiling point temperature T_0 was recorded. Because of easy hydrolysis of acetanhydride during weighing and other manipulations, the real initial composition of the acetic acid–acetanhydride mixture was calculated from the equation

$$x_4^0 = (T_0 - \alpha)/\beta \, , \qquad (2)$$

where x_4^0 is a molar fraction of acetic acid in the original mixture, T_0 is the measured temperature in °C, α and β are constants ($\alpha = 139.5°C$; $\beta = -21.2°C$).

After the equilibrium establishment and temperature T_0 reading, a known amount of dicarboxylic acid (*I*) was transferred into the ebulliometer. After several minutes when equilibrium was reached between the reaction mixture and vapours of acetanhydride (*II*) and acetic acid (*IV*) the boiling point T^+ was recorded. Both values of boiling points were corrected for barometric pressure.

Following, simplifying but in this case justified, assumptions have to be introduced in order to set up the equation for calculations of conversion of *I* to the mixed anhydride (*III*) from ebulliometric data: *1. I* and *III* are not, under mentioned experimental conditions, present in the vapour phase; *2.* with regard to the chemical behaviour of volatile components (*II* and *IV*) it is possible to assume, according to Ewell and coworkers[12], an ideal behaviour of their mixture in the vapour phase and thus to use partial pressures instead of activities, or fugacities of components in the vapour phase, for calculations; *3.* within the experimental temperature range there is no dependence of the activity coefficient on temperature, thus the coefficients obtained by measuring the isobaric equilibrium can be used; *4.* activity coefficients of volatile components in the liquid phase are not influenced by their interaction with non-volatile components and are dependent only on the ratio of components *II* and *IV*.

The vapour pressure changes of *II* and *IV* caused by changing the concentration of *IV* during the reaction (*A*) can be expressed by

$$\mathrm{d}p_2 = p_2^0(T_0) \, \frac{\partial a_2}{\partial x_4} \, \mathrm{d}x_4 + a_2(x_4^+) \, \frac{\partial p_2^0}{\partial T} \, \mathrm{d}T \qquad (3)$$

$$dp_4 = p_4^0(T_0) \frac{\partial a_4}{\partial x_4} dx_4 + a_4(x_4^+) \frac{\partial p_4^0}{\partial T} dT, \qquad (4)$$

where $p_2^0(T_0)$ and $p_4^0(T_0)$ are the vapour pressures of pure components II and IV respectively at initial temperature T_0; $a_2(x_4^+)$ and $a_4(x_4^+)$ are the activities of II and IV in the liquid phase at the final stage of reaction (A); x_4^+ is the concentration of acid IV after the reaction, expressed as a molar fraction.

Since the pressure remains constant it must hold that

$$dp_2 + dp_4 = 0. \qquad (5)$$

From this condition, after rearrangement, follows that

$$p_2^0(T^+) \gamma_2^+ x_2^+ + p_4^0(T^+) \gamma_4^+ x_4^+ = P, \qquad (6)$$

where γ_2^+ and γ_4^+ are the activity coefficients of components II and IV respectively at temperature T^+, P being the overall pressure.

The terms in equation (6) must be expressed analytically in order to be able to use the equation for practical calculations. The activity coefficients can be computed using the known liquid–vapour relationship for the acetic acid–acetanhydride system which can be described by general equation

$$y_4 = ax_4 + bx_4^2 + cx_4^3, \qquad (7)$$

y_4 being a molar fraction of IV in the gas phase and a, b, c are constants ($a = 2.588$, $b = -2.810$, $c = 1.222$). If the assumptions 3) and 4) are valid, the activity coefficients may be expressed by the following equation:

$$\gamma_i^+ = Py_i/x_i p_i^0(T), \qquad \qquad (8)$$

where temperature T was calculated from equation (2). Therefore temperature T is not identical with the final temperature T^+.

The vapour pressures of pure components can be expressed by empirical relationships

$$p_2^0(T) = \exp(A + B/T), \qquad (9)$$

$$p_4^0(T) = \exp(C + D/T), \qquad (10)$$

the values of constants being $A = 18.42871$, $B = -4868.09$, $C = 18.46352$, $D = -4634.86$. Molar fractions of II and IV after the reaction (A) can be expressed in form

$$x_2^+ = [1 - (x_4^0 + Q)]/(1 + S) \qquad (11)$$

and

$$x_4^+ = (x_4^0 + Q)/(1 + S), \qquad (12)$$

where S is the number of mol of added acid I per one mol of the original mixture of II and IV, Q is the degree of conversion defined as a number of mol of reacted carboxylic groups of the component I per 1 mol of the original mixture II and IV.

Inserting (2), $(7)-(12)$ into (6) a final expression for calculation of Q is obtained

$$\frac{[1 + (x_4^0 + Q)]\,[1 + (b + c)\,(x_4^0 + Q) + c(x_4^0 + Q)^2]}{(1 + S)\exp\{A + B/[\alpha + \beta(x_4^0 + Q)]\}}\exp\left(A + B/T^+\right) +$$

$$+ \frac{(x_4^0 + Q)\,[a + b(x_4^0 + Q) + c(x_4^0 + Q)^2]}{(1 + S)\exp\{C + D/[\alpha + \beta(x_4^0 + Q)]\}}\exp\left(C + D/T^+\right) = 1 \,. \qquad (13)$$

The equilibrium constant for the reaction (A) can be expressed by means of these variables by the equation

$$K_{12} = Q(x_4^0 + Q)/(2S - Q)\,(x_2^0 - Q)\,. \qquad (14)$$

The degree of conversion Q was found by numerical iteration method within the interval $(0;\ 2S$ or $2x_2^0)$ employing an Elliott 4130 digital computer.

TABLE I

Equilibrium Concentration of Acetic Acid (molar fraction) in the Vapour Phase for the Mixture of Acetic Acid and Acetanhydride

The symbol x_4 means the concentration (in molar fractions) of the acetic acid in the liquid phase.

x_4	Ref.[13] (100 Torr)	Ref.[13] (160 Torr)	Ref.[14] (400 Torr)	Ref.[15]	Ref.[16]	Found in this work
0·00	0·00	0·00	0·00	0·00	0·00	0·00
0·05	0·12	0·10	0·11	0·13	0·11	0·11
0·10	0·20	0·18	0·20	0·23	0·21	0·20
0·20	0·36	0·33	0·37	0·42	0·37	0·36
0·30	0·50	0·46	0·48	0·56	0·51	0·50
0·40	0·61	0·57	0·58	0·65	0·61	0·61
0·50	0·70	0·66	0·68	0·72	0·70	0·70
0·60	0·78	0·74	0·76	0·79	0·78	0·77
0·70	0·85	0·82	0·83	0·84	0·85	0·83
0·80	0·90	0·88	0·89	0·90	0·91	0·90
0·90	0·95	0·94	0·95	0·95	0·96	0·95
1·00	1·00	1·00	1·00	1·00	1·00	1·00

TABLE II

Equilibrium Data for the Reaction of Dicarboxylic Acid (I) with Acetanhydride (II)

C_1^0 initial concentration of I in mol/2 mol II, C_4^0 initial concentration of acetic acid (IV) in mol/2 mol II, y_4' concentration of IV in the vapour phase in mass %, c_4 equilibrium contents of IV in the reaction mixture in mol, K_{12} equilibrium constant for reaction (A), $\overline{K}_{12}$ mean value of K_{12} (mean deviations are given).

C_1^0	C_4^0	Adipic acid			Pimelic acid			Suberic acid			Azelaic acid			Sebacic acid		
		y_4'	c_4	K_{12}	y_4'	c_4	K_{12}	y_4'	c_4	K_{12}	y_4'	c_4	K_{12}	y_4'	c_4	K_{12}
0·25	0·3	34·3	0·65	0·92	34·8	0·65	0·92	35·0	0·67	1·17	35·9	0·69	1·52	34·3	0·66	1·03
0·5	0·3	47·7	0·92	1·09	48·8	0·94	1·23	47·6	0·92	1·09	47·8	0·92	1·09	50·9	0·98	1·58
0·5	0·2	44·3	0·81	0·91	45·2	0·84	1·10	45·2	0·83	1·03	45·9	0·85	1·16	45·0ᵃ	0·80ᵃ	1·22ᵃ
0·5	0·15	43·7	0·78	0·97	—	—	—	—	—	—	—	—	—	—	—	—
0·66	0·2	51·9	0·95	0·98	52·5	0·98	1·14	53·0	0·99	1·20	54·1	1·01	1·32	52·3ᵃ	0·95ᵃ	1·29ᵃ
0·66	0·15	50·3	0·92	1·03	—	—	—	—	—	—	—	—	—	—	—	—
1	0·2	62·2	1·20	1·20	62·4	1·21	1·25	63·4	1·22	1·30	62·1	1·18	1·11	61·8ᵃ	1·14ᵃ	1·18ᵃ
1	0·15	62·3	1·17	1·23	65·4	1·24	1·64	62·0	1·16	1·20	63·2	1·15	1·15	62·9	1·18	1·29
1	0·15	63·3	1·20	1·40	—	—	—	—	—	—	—	—	—	—	—	—
2	0·2	78·5	1·63	1·59	80·1	1·68	1·89	81·0	1·70	2·04	79·6	1·66	1·76	80·0ᵃ	1·62ᵃ	1·95ᵃ
2	0·15	76·8	1·54	1·35	—	—	—	—	—	—	—	—	—	—	—	—
		$\overline{K}_{12}$			$\overline{K}_{12}$			$\overline{K}_{12}$			$\overline{K}_{12}$			$\overline{K}_{12}$		
		1·15 ± 0·21			1·31 ± 0·31			1·29 ± 0·32			1·30 ± 0·23			1·36 ± 0·28		

[a] The values at $C_4^0 = 0.13$.

RESULTS AND DISCUSSION

The equilibrium composition of the vapour phase above the reaction mixture was measured for various initial concentrations of dicarboxylic acid (I). The reaction mixture contains only acetanhydride (II) and acetic acid (IV) as volatile compounds The volatility of dicarboxylic acids can be neglected because in case of adipic acid only 0·01% of this acid was found in the distillate by gas chromatography. The liquid–vapour equilibrium for the mixture of acetic acid–acetanhydride was measured first. The experimental results are compared with the literature data[13–16] and are presented in Table I. By determining the equilibrium composition of vapour above the reaction mixture it is possible to express the ratio of volatile components but not their absolute amount in the reaction mixture; that is why it is not possible to determine the equilibrium constant K_{34} for the reaction (B) but only the constant K_{12} for the reaction (A) assuming that $K_{34} = 0$. The constants found experimentally

TABLE III

Ebulliometric Determination of the Equilibrium Data for the Reaction of Dicarboxylic Acid (IV) with Acetanhydride (III)

x_4^0 Initial concentration of acetic acid (IV) in the mixture with II, T_0 boiling point of the initial mixture of II and IV in °K, S initial concentration of I in mol/mol of original mixture II and IV, Q carboxylic groups of I that reacted in mol/mol of the original mixture of II and IV, K_{12} equilibrium constant for the reaction A, $\overline{K}_{12}$ mean value of K_{12} (mean deviations given).

Acid	x_4^0	T_0	S	T^+	$Q/2$	K_{12}	$\overline{K}_{12}$
Adipic	0·371	404·79	0·114	405·74	0·0659	1·38	
			0·227	406·99	0·1155	1·55	1·60 ± 0·22
			0·418	409·55	0·1746	1·84	
Pimelic	0·390	404·39	0·100	405·14	0·0605	1·57	
			0·201	406·24	0·1059	1·68	1·78 ± 0·28
			0·403	408·80	0·1735	2·11	
Suberic	0·381	404·58	0·093	405·14	0·0596	1·75	
			0·188	406·44	0·0969	1·44	1·55 ± 0·18
			0·377	409·30	0·1514	1·45	
Azelaic	0·376	404·69	0·086	405·34	0·0520	1·40	
			0·172	406·34	0·0907	1·47	1·43 ± 0·05
			0·345	408·89	0·1441	1·41	
Sebacic	0·381	404·58	0·081	405·19	0·0494	1·42	
			0·161	406·09	0·0863	1·43	1·44 ± 0·03
			0·322	408·39	0·1390	1·46	

are valid within the temperature interval of the boiling points of reaction mixtures ($138-143°C$) and their values are listed in Table II.

The ebulliometric method can also be used for determinig the equilibrium constant for the reaction (A) provided that the temperature difference between the boiling point of the mixture acetanhydride–acetic acid before addition of the dicarboxylic acid and that of the reaction mixture after the reaction, is caused by the presence of non-volatile components and by the change of the acetanhydride–acetic acid ratio. The results are summarized in Table III.

The equilibrium constant for the reaction of polymethylenedicarboxylic acids with acetanhydride determined by the ebulliometric method ($\overline{K}_{12} = 1·56 \pm 0·2$) is by 18% higher than the value obtained by measuring the liquid–vapour equilibrium $\overline{K}_{12} = 1·27 \pm 0·28$; the mean value of the equilibrium constant for the reaction A at temperature $138-143°C$ is thus $1·35 \pm 0·29$.

The results indicate that there is no substantial difference between the two experimental methods. Moreover, reactivities of homological acids are approximately equal. This is in agreement with the hypothesis about independent and equal reactivity of carboxylic groups belonging to acids whose acidities do not differ markedly. The experimental data show certain tendency towards increasing values of K_{12} with increasing initial concentration of carboxyls. Changing this concentration from $1·83$ to $7·93$ mol/kg causes unavoidable change of the boiling point of the reaction mixture, within 138 to 143°C (the mixture containing a maximum concentration of dicarboxylic acid used in our experiments boiled as high as at 150°C). The increasing tendency of K_{12} is not statistically important. It corresponds to the temperature change caused by heat evolution from the reaction (A) having $\Delta H \leqq 15$ kcal/mol. On the other hand the fluctuation of the K_{12} value could also be explained by inaccuracies arising as a consequence of neglecting the reaction (B). Mironov and Žarkov[6] used Raman spectroscopy to study the reaction of propionic and butyric acid respectively with acetanhydride. They reported following values for equilibrium constants:

Acid	K_{12}	K_{34}
Propionic	3·8	0·22
Butyric	2·4	0·50

It can be seen that the published data are in a good order of magnitude agreement with the results presented in this paper. Both tested methods can be used to study equilibria of reaction mixtures that are difficult to analyse.

REFERENCES

1. Mark H., Whitby G. S.: *Collected Papers of Wallace Hume Carothers on High Polymeric Substances.* Interscience, New York 1946.
2. Flory P. J.: *Principles of Polymer Chemistry.* Cornell University Press, Ithaca 1953.
3. Zvonař V., Klaban J., Krejcar E.: Chem. průmysl *18*, 407 (1968).
4. Gault H., El-Kik E.: Compt. Rend. *232*, 2225 (1951).
5. El-Kik E., Gault H.: Compt. Rend. *238*, 2428 (1954).
6. Mironov D. P., Žarkov V. V.: Ž. Org. Chim. *1*, 1731, 1965.
7. Stevens W., van Es A.: Rec. Trav. Chim. *83*, 863 (1964).
8. Schijf R., Scheeren J. W., van Es A., Stevens W.: Rec. Trav. Chim. *84*, 594 (1965).
9. Zvonař V.: Czechoslov. Pat. 124 968 (1966).
10. Hoftyzer P. J., van Krevelen D. W.: *International Symposium on Macromolecular Chemistry*, Preprint 1/28, Budapest 1969.
11. Dufka O.: Private communication.
12. Ewell R. H., Harrison I. M., Berg L.: Ind. Eng. Chem. *36*, 871 (1944).
13. Jones H. E.: J. Chem. Eng. Data *7*, 13 (1962).
14. Marek J.: Chem. listy *49*, 1756 (1955).
15. Othmer D. F.: Ind. Eng. Chem., Anal. Ed. *4*, 232 (1932).
16. Povarin C., Markov V.: Ž. Rus. Fiz. Chim. Obšč. *55*, 375 (1924); Chem. Zentr. *96*, 706 (1925).

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