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## The solvation effect in the thermal decomposition of 2,2'-azoisobutyronitrile in acrylonitrile/methyl methacrylate mixtures in diluted solutions of *N,N*-dimethylformamide

**Summary** — The thermal decomposition rate constant ( $k_d$ ) of 2,2'-azoisobutyronitrile (AIBN) was studied in acrylonitrile (AN)—methyl methacrylate (MMA) comonomer mixtures dissolved in dilute solutions of *N,N*-dimethylformamide (DMF) as a function of the comonomer mixture composition and concentration in the solvent at 60°C. The relationships  $k_d = f(x_A, C)$  ( $x_A$  — mole fraction of acrylonitrile in comonomer mixture,  $C$  — comonomer mixture concentration) produce convex curves in relation to the straight line drawn through the  $k_d$  values obtained at the boundary conditions ( $x_A = 0, x_A = 1$ ). The radius of curvature is related to concentration  $C$ , which was fixed at 0.1, 0.5, 1.0 and 3.0 mol · dm<sup>-3</sup>. The higher the dilution of the monomer mixture, the smaller the convexity of the  $k_d = f(x_A)$  curve.

All the experimental courses of  $k_d = f(x_A)$  may be interpreted in terms of solvation of the initiator by monomer A (AN), monomer B (MMA) and solvent S (DMF). The solvation forms occurring in the system AN-MMA/DMF/AIBN/60°C, their relative stability constants and relative contents, and the thermal decomposition rate constants of the solvated forms were determined (Tables 2—5).

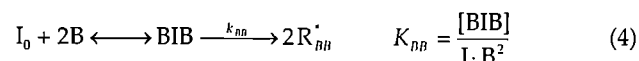
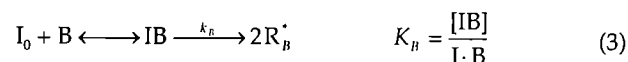
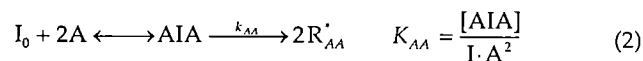
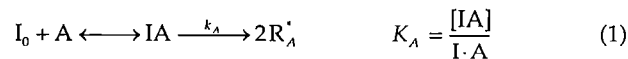
**Key words:** radical copolymerization, thermal initiation, thermal decomposition of AIBN.

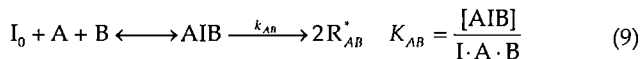
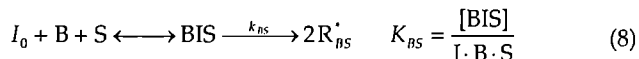
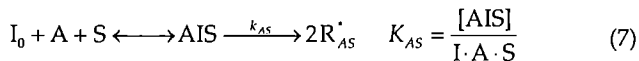
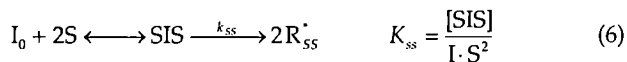
Previous work [1] has analyzed the experimental relationships of the thermal decomposition rate constant of solvated forms of AIBN in the comonomer mixture acrylonitrile—methyl methacrylate in the bulk, *viz.*, the pseudobinary AN—MMA/AIBN/60°C system involving monomer A (AN) and monomer B (MMA) as a binary solvent. The results obtained for this system could be explained by assuming AIBN to have been solvated by the monomers A and B. In work [1] the system was described to within preselected solvated forms IB or BIB and IA or AIA. The remaining solvation parameters have been unequivocally determined. The mixed solvate AIB was found to be the most stable form, characterized by the stability constant  $K_{AB} = 717$  (relative value) and the thermal decomposition rate constant  $k_{AB} = (6.5 \pm 0.03) \cdot 10^{-4} \text{ min}^{-1}$ . The investigation [1] of the three-component system AN—MMA/DMF/AIBN/60°C was found to suffice to decide the selection of the solvated forms. The objective of this work is to determine the constant  $k_d$  in the system acrylonitrile—methyl methacrylate—*N,N*-dimethylformamide in diluted solu-

tions of acrylonitrile—methyl methacrylate mixtures in *N,N*-dimethylformamide.

### THEORETICAL

For the system containing an additional solvent S, the assumptions that the initiator (AIBN) is solvated by monomer A and monomer B require the previous scheme [1] to be extended to the form:





where I, A, B and S designate the initiator (AIBN), monomer A (AN), monomer B (MMA), and solvent S (DMF), respectively, and they also designate their concentrations ( $\text{mol} \cdot \text{dm}^{-3}$ ),  $I_0$  is the overall initiator concentration ( $\text{mol} \cdot \text{dm}^{-3}$ );  $K_A, K_{AA}, K_B, K_{BB}, K_S, K_{SS}, K_{AS}, K_{BS}$  and  $K_{AB}$  are the stability constants of the respective solvated forms; [IA], [AIA], [IB], [BIB], [IS], [SIS], [AIS], [BIS], [AIB] designate the concentrations ( $\text{mol} \cdot \text{dm}^{-3}$ ) of the solvated forms of AIBN;  $k_A, k_{AA}, k_B, k_{BB}, k_S, k_{SS}, k_{AS}, k_{BS}, k_{AB}$  are the rate constants of the thermal decomposition reactions of the respective solvated forms;  $R'_A, R'_{AA}, R'_B, R'_{BB}, R'_S, R'_{SS}, R'_{AS}, R'_{BS}$  and  $R'_{AB}$  are symbols of the primary radicals formed on thermal decomposition of the respective solvated forms.

Solution of the equation set (1)–(9) under the condition that the total initiator concentration  $I_0$  is given by the sum of the concentrations of all the solvated forms of the initiator (as determined by their corresponding equilibrium constants) and that the global decomposition rate constant of the initiator in the solution is the sum of the decomposition rates of the various initiator solvated forms, leads to the equation:

$$k_d = \frac{K_A \cdot k_A \cdot A + K_B \cdot k_B \cdot B + K_S \cdot k_S \cdot S + K_{AA} \cdot k_{AA} \cdot A^2 + K_{BB} \cdot k_{BB} \cdot B^2}{K_A \cdot A + K_B \cdot B + K_S \cdot S + K_{AA} \cdot A^2 + K_{BB} \cdot B^2 + K_{SS} \cdot k_{SS} \cdot S^2 + K_{AS} \cdot k_{AS} \cdot A \cdot S + K_{BS} \cdot k_{BS} \cdot B \cdot S + K_{AB} \cdot k_{AB} \cdot A \cdot B} + \frac{K_{SS} \cdot S^2 + K_{AS} \cdot A \cdot S + K_{BS} \cdot B \cdot S + K_{AB} \cdot A \cdot B}{K_{SS} \cdot S^2 + K_{AS} \cdot A \cdot S + K_{BS} \cdot B \cdot S + K_{AB} \cdot A \cdot B} \quad (10)$$

Taking into account the transmission equations:

$$A = C \cdot x_A \quad (11)$$

$$B = C \cdot (1 - x_A) \quad (12)$$

$$x_A = A/(A + B) = A/C \quad (13)$$

$$S = \gamma \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]] \quad (14)$$

$$\alpha = M_A/d_A; \quad \beta = M_B/d_B; \quad \gamma = d_S/M_S \quad (15)$$

equation (10) may be transformed into:

$$k_d = k_A[IA]_r + k_B[IB]_r + k_S[IS]_r + k_{AA}[AIA]_r + k_{BB}[BIB]_r + k_{SS}[SIS]_r + k_{AS}[AIS]_r + k_{BS}[BIS]_r + k_{AB}[AIB]_r \quad (16)$$

where

$$[IA]_r = \frac{K_A \cdot C \cdot x_A}{A(x_A)} \quad (17)$$

$$[AIA]_r = \frac{K_{AA} \cdot C^2 \cdot x_A^2}{A(x_A)} \quad (18)$$

$$[IB]_r = \frac{K_B \cdot C \cdot (1 - x_A)}{A(x_A)} \quad (19)$$

$$[BIB]_r = \frac{K_{BB} \cdot C^2 \cdot (1 - x_A)^2}{A(x_A)} \quad (20)$$

$$[IS]_r = \frac{K_S \cdot \gamma \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]]}{A(x_A)} \quad (21)$$

$$[SIS]_r = \frac{K_{SS} \cdot \gamma^2 \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]]^2}{A(x_A)} \quad (22)$$

$$[AIS]_r = \frac{K_{AS} \cdot \gamma \cdot C \cdot x_A [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]]}{A(x_A)} \quad (23)$$

$$[BIS]_r = \frac{K_{BS} \cdot \gamma \cdot C \cdot (1 - x_A) \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]]}{A(x_A)} \quad (24)$$

$$[AIB]_r = \frac{K_{AB} \cdot C^2 \cdot x_A \cdot (1 - x_A)}{A(x_A)} \quad (25)$$

where the expression  $A(x_A)$  [eqns. (17)–(25)] is

$$A(x_A) = K_A \cdot C \cdot x_A + K_{AA} \cdot C^2 \cdot x_A^2 + K_B \cdot C \cdot (1 - x_A) + K_{BB} \cdot C^2 \cdot (1 - x_A)^2 + K_S \cdot \gamma \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]] + K_{SS} \cdot \gamma^2 \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]]^2 + K_{AS} \cdot \gamma \cdot C \cdot x_A \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]] + K_{BS} \cdot \gamma \cdot C \cdot (1 - x_A) \cdot [1 - C \cdot [\alpha \cdot x_A + \beta \cdot (1 - x_A)]] + K_{AB} \cdot C^2 \cdot x_A \cdot (1 - x_A) \quad (26)$$

In transmission equations (11)–(15),  $M_A, M_B, M_S$  are the molecular weights of monomer A (AN), monomer B (MMA) and solvent S (DMF), respectively;  $d_A, d_B, d_S$  are the densities ( $\text{g} \cdot \text{dm}^{-3}$ ) of monomers A and B, and solvent S, respectively, and  $x_A$  designates the monomer A mole fraction in the comonomer mixture;  $C = A + B$  is the symbol for the comonomer mixtures and designates their concentrations ( $\text{mol} \cdot \text{dm}^{-3}$ ).

For  $S = 0$ , equation (10) simplifies to the form given in the previous work [1]:

$$k_d = \frac{K_A \cdot k_A \cdot A + K_{AA} \cdot k_{AA} \cdot A^2 + K_B \cdot k_B \cdot B + K_{BB} \cdot k_{BB} \cdot B^2 + K_{AB} \cdot k_{AB} \cdot A \cdot B}{K_A \cdot A + K_{AA} \cdot A^2 + K_B \cdot B + K_{BB} \cdot B^2 + K_{AB} \cdot A \cdot B} \quad (27)$$

The solution of equation (27) performed on the basis of the experimental determination of  $k_d$  as a function of the comonomer mixture composition in the system AN—MMA/AIBN/60°C (in bulk [1]) demonstrates that there are four solutions which are practically similar when related to the type of solvated forms:

1. AIA, AIB, IB
2. AIA, AIB, BIB
3. IA, AIB, BIB
4. IA, AIB, IB

moreover, this results in an unequivocal solution determining the thermal decomposition rate constant of the mixed solvate:

$$k_{AB} = (6.5 \pm 0.03) \cdot 10^{-4} \text{ min}^{-1} \quad (29)$$

and unequivocal determination of the stability constants of the solvated forms:

$$K_{AB} = 747 > K_B = 377.2 > K_{AA} = 1 \text{ for position 1 in set (28)} \quad (30)$$

However, to solve eqn. (10) requires several relationships  $k_d = f(x_A, C)$ , viz., the global rate constant in the system AN—MMA/DMF/AIBN/60°C to be experimentally determined as a function of various concentrations ( $C = A + B$ ) of the mixture and as well as a function of various compositions ( $x_A = A/(A + B)$ ) of this mixture in the solvent.

Moreover, some unknown parameters in eqn. (10), viz.,  $k_A$ ,  $k_B$ ,  $k_S$ , were determined directly in pure media A, B, and S [2, 3]. Equation (10) was solved without the use of data (29) and (30) from work [1], nevertheless the result is reported for comparison purposes.

### EXPERIMENTAL

Acrylonitrile, methyl methacrylate and *N,N*-dimethylformamide were purified by standard methods [2–4]. The initiator (AIBN) was crystallized twice from methanol. The thermal decomposition rate constant was measured by two methods, volumetric and manometric. The two methods gave consistent results. The average error of measurement of  $k_d$  amounted to 5–6%.

### RESULTS AND DISCUSSION

Released nitrogen volumes and/or nitrogen pressures measured at various concentrations of the comonomer mixture in the solvent as well as at various compositions of the comonomer mixtures, allow to conclude that the thermal decomposition of the nitrogen bond AIBN follows a first-order reaction course. The calculated values are collected in Table 1. As can be seen, the  $k_d$  values vary with the composition of the acrylonitrile—methyl methacrylate mixture expressed by the acrylonitrile mole fraction ( $x_A = A/(A + B)$ ), and they are also related to concentration ( $C = A + B$ ) of the mixture in DMF, therefore, they form a series of functions  $k_d = f(x_A, C)$  of the two variables.

The character of these relationships is shown in Figs. 1a–d. Each Figure represents the relationship  $k_d = f(x_A)$

at a fixed concentration  $C$ , viz., 3 (Fig. 1a), 1 (Fig. 1b), 0.5 (Fig. 1c) and 0.1 mol · dm<sup>-3</sup> (Fig. 1d). The experimental points allow to draw smooth (solid) curves. The radius of curvature of these relationships ( $k_d = f(x_A)$ ) varies with concentration  $C$ ; this dependence is not linear even at the smallest value of  $C$ .

The results (Figs. 1a–d) were interpreted in terms of solvation of AIBN by the components of the mixture (A, B, S). By this assumption, the experimental points in Figs. 1a–d should determine the curves in accordance with eqn. (10), namely, for each series of measurements, equation (10) should yield  $k_d$  or be solved for unknown parameters according to the algorithm [5]. It turned out that equation (10) could describe all the relationships in Figs. 1a–d. Thus, the curves (Figs. 1a–d) comprise such courses of eqn. (10) which enable the fractions of individual (occurring) solvated forms in the constant  $k_d$  to be determined according to eqn. (16).

The relationship  $k_d = f(x_A)$  presented in Fig. 1a is seen to reveal the largest curvature in relation to the straight line drawn through the points  $k_d(x_A = 0)$  and  $k_d(x_A = 1)$  (the smallest radius of curvature). Such a course of the curve results from the fractions of the solvated forms formed on thermal decompositions according to the decreasing magnitudes of AIB, BIS, IB, SIS and AIS. The presence of the AIA solvate is also shown in Fig. 1a; however, its fraction ( $k_{AA}[AIA]_r$ ) is negligible. It follows from these results that monomer B (methyl methacrylate) is the readily solvating component, also in the mixed solvate AIB, followed by solvent S (DMF), whereas monomer A (acrylonitrile) participates in the formation of solvates AIS, AIA to a small degree only.

The situation resulting when the AN—MMA mixture is diluted with solvent S (DMF) is illustrated in Fig. 1b. The curvature of the curve is seen to diminish, the curve becomes concave, and the fractions of the solvated forms in the constant  $k_d$  become arranged in the decreasing order: SIS, BIS, IB, AIB, AIS. The double solvate involving the solvent molecules assumes the highest value, then follows monomer B with solvent S in the mixed solvate, and subsequently monomer B. The solvate AIB is considerably less significant (as compared with Fig. 1a), whereas the solvate AIA is practically negligible.

Further dilution of the comonomer mixture by solvents is illustrated in Figs. 1c and 1d. The shape of

**Table 1.** The thermal decomposition rate constant ( $k_d$ ) · 10<sup>4</sup> min<sup>-1</sup> of AIBN in the three-component system: monomer (A), viz., acrylonitrile (AN), monomer (B), viz., methyl methacrylate (MMA), solvent (S), viz., *N,N*-dimethylformamide (DMF) (AN—MMA/DMF/AIBN/60°C)

C = A + B mol · dm <sup>-3</sup>	$x_A^{*)}$													
	0.0	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	1.0	
3	5.21	5.29	5.36	5.48	5.57	5.64	5.70	5.75	5.78	5.80	5.81	5.80	5.76	
1.0	5.45	5.48	5.51	5.56	5.62	5.68	5.74	5.81	5.88	5.96	6.06	6.12	6.20	
0.5	5.75	5.75	5.77	5.82	5.86	5.91	5.96	6.02	6.08	6.15	6.23	6.27	6.32	
0.1	6.23	6.25	6.25	6.27	6.28	6.30	6.32	6.34	6.36	6.38	6.40	6.41	6.42	

<sup>\*)</sup>  $x_A = A/(A + B)$ . The average error of the determination of  $k_d = \pm 3\%$ .

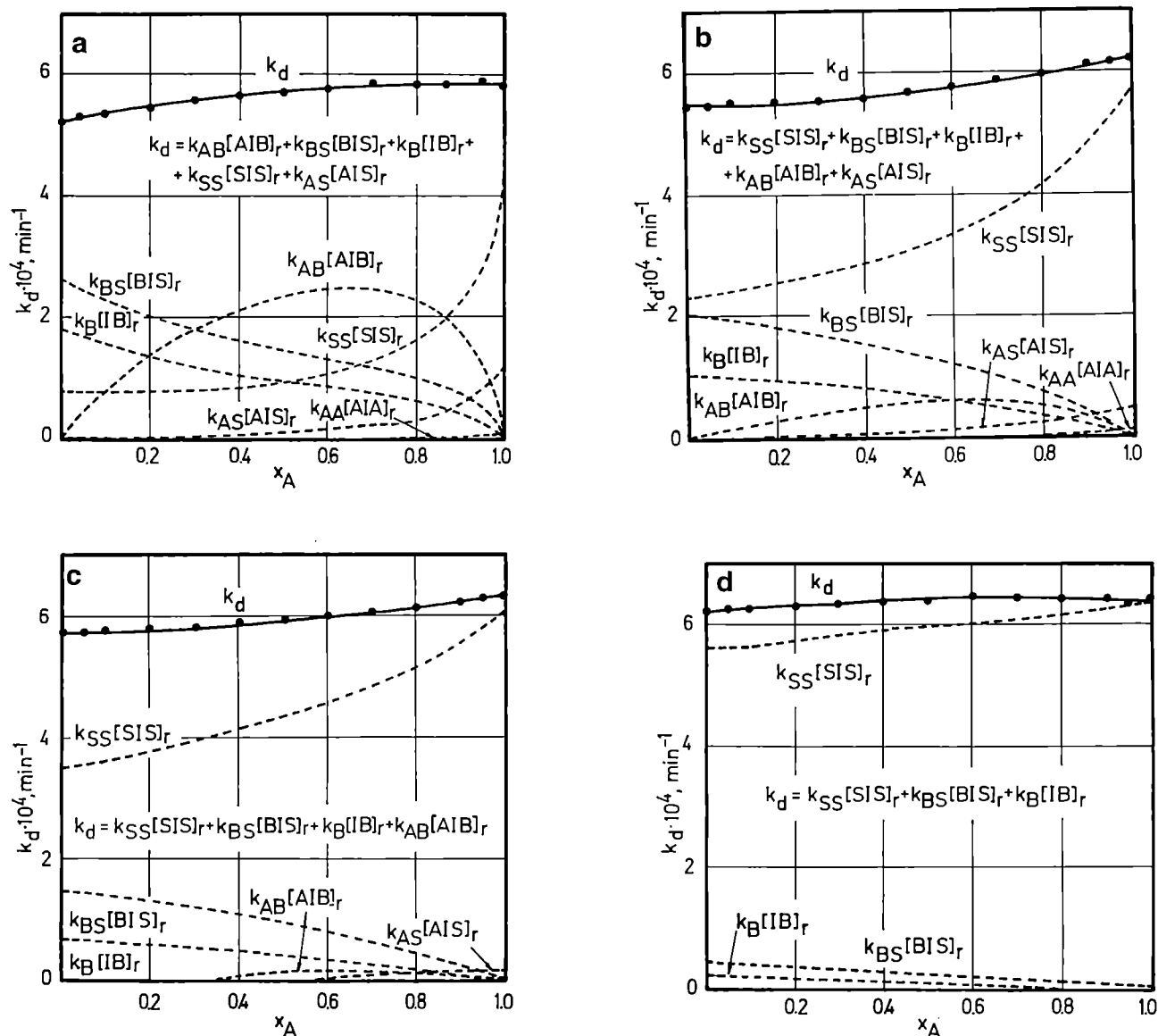


Fig. 1. The AN—MMA/DMF/AIBN/60°C system. The global decomposition rate constant ( $k_d$ ) according to eqn. (10) (solid line) and the fraction of the decomposition rate constants of initiator solvated forms according to eqns. (16) and (17)—(25) (dashed lines), as a function of acrylonitrile mole fraction ( $x_A$ ) in mixture of monomers acrylonitrile (A) — methyl methacrylate (B). Concentration of comonomer mixture  $C = A + B$  is equal: a — 3, b — 1, c — 0.5, d — 0.1 mol · dm<sup>-3</sup>

the curve  $k_d = f(x_A)$  in Fig. 1c is seen to be affected mostly by the solvate SIS, then by BIS and IB, whereas the mixed solvate AIB is becoming less and less significant, and the contribution of the solvates AIS and AIA negligibly small.

A more enhanced fraction of the solvate SIS is seen to occur in Fig. 1d, and the fractions of BIS and IB are decreasing. The remaining solvates may be omitted.

Since the fractions of solvates, especially AIS and AIB, decrease dramatically, the accuracy of Fig. 1d is too low to present them; however, they do not disappear completely, and their numerical values are given in Table 2.

The compilation of the types of solvated forms, determined by matching eqn. (10) successively to the results of the determination of the dependence  $k_d = f(x_A)$  at va-

rious concentrations  $C$  (Figs. 1a—d) by the nonlinear least-squares method [5] is given in Table 3.

The influence of the concentration  $C$  is better visible in this Table than in Figs. 1a—d. The solvated form AIA occurs only at  $C = 3 \text{ mol} \cdot \text{dm}^{-3}$ ; at lower concentrations, this form practically does not occur (Tables 3 and 4) and, at  $C = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ , completely disappears (Tables 3 and 4).

The results in Table 3 also show that the forms IB, SIS and BIS occur independently of the concentration used. The forms AIS exist at concentrations of  $C = 1$  and  $3 \text{ mol} \cdot \text{dm}^{-3}$ ; at lower concentrations they are not formed. Similarly, the form AIB disappears at  $C = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ .

Another important conclusion results from Table 3. If the concentration of the monomer mixture ( $A + B$ ) is increased up to  $S = 0$ , then the system

**Table 2.** Relative fractions of the solvated forms containing acrylonitrile (A), (AIS, AIB, AIA), in relation to the concentration and composition of the acrylonitrile—methyl methacrylate mixture in *N,N*-dimethylformamide

	C, mol · dm <sup>-3</sup>	$x_A$										
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$k_{AS} \cdot [AIS]_r^{(1)}$	3	0.000	0.023	0.046	0.070	0.097	0.131	0.177	0.242	0.349	0.561	1.203
$k_{AB} \cdot [AIB]_r^{(2)}$		0.000	0.774	1.340	1.761	2.072	2.292	2.423	2.450	2.316	1.831	0.000
$k_{AA} \cdot [AIA]_r^{(3)}$		0.000	0.000	0.000	0.001	0.002	0.003	0.005	0.008	0.013	0.024	0.056
$k_{AS} \cdot [AIS]_r$	1	0.000	0.019	0.040	0.063	0.089	0.119	0.155	0.199	0.255	0.330	0.436
$k_{AB} \cdot [AIB]_r$		0.000	0.164	0.302	0.415	0.500	0.555	0.575	0.551	0.469	0.302	0.000
$k_{AA} \cdot [AIA]_r$		0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.003	0.004	0.006
$k_{AS} \cdot [AIS]_r$	0.5	0.000	0.014	0.028	0.044	0.062	0.081	0.102	0.126	0.154	0.185	0.223
$k_{AB} \cdot [AIB]_r$		0.000	0.000	0.055	0.101	0.138	0.164	0.179	0.181	0.167	0.135	0.081
$k_{AA} \cdot [AIA]_r$		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001
$k_{AS} \cdot [AIS]_r$	0.1	0.000	0.014	0.028	0.044	0.062	0.081	0.102	0.126	0.154	0.185	0.223
$k_{AB} \cdot [AIB]_r$		0.000	0.055	0.101	0.138	0.164	0.179	0.181	0.167	0.135	0.081	0.000
$k_{AA} \cdot [AIA]_r$		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

<sup>1)</sup>  $k_{AS} = 4.09 \cdot 10^{-4} \text{ min}^{-1}$ ; <sup>2)</sup>  $k_{AB} = 6.5 \cdot 10^{-4} \text{ min}^{-1}$ ; <sup>3)</sup>  $k_{AA} = 7.2 \cdot 10^{-4} \text{ min}^{-1}$ .

**Table 3.** Determination and comparison of the types of solvated forms in the three-component system AN—MMA/DMF/AIBN/60°C at low concentrations of the comonomer mixtures

Concentration <sup>*)</sup> C mol · dm <sup>-3</sup>	Type of solvation forms								
	IA	AIA	IB	BIB	IS	SIS	AIS	BIS	AIB
3	—	AIA	IB	—	—	SIS	AIS	BIS	AIB
1	—	—	IB	—	—	SIS	AIS	BIS	AIB
0.5	—	—	IB	—	—	SIS	—	BIS	AIB
0.1	—	—	IB	—	—	SIS	—	BIS	—

<sup>\*)</sup> C = A + B.

**Table 4.** Determination and comparison of the stability constants of the solvated forms in the three-component system AN—MMA/DMF/AIBN/60°C at low concentrations of the comonomer mixtures

Concentration <sup>*)</sup> C, mol · dm <sup>-3</sup>	Stability constants of solvated forms									Figure
	$K_A$	$K_{AA}$	$K_B$	$K_{BB}$	$K_S$	$K_{SS}$	$K_{AS}$	$K_{BS}$	$K_{AB}$	
3	0	1	421.2	0	0	8.73	11.80	129.3	750.0	1a
1	0	1 <sup>**)</sup>	412.3	0	0	8.75	11.81	128.6	756.6	1b
0.5	0	1 <sup>**)</sup>	408.7	0	0	8.70	11.79	128.8	755.8	1c
0.1	0	0	406.4	0	0	8.69	11.78	128.2	756.3	1d
0.1—3.0	0	1	408.6	0	0	8.70	11.78	128.0	766.0	

<sup>\*)</sup> C = A + B; <sup>\*\*)</sup> the value  $K_{AA} = 1$  was assumed for the conservation of the AIA solvated form under the conditions  $x_A = 1$  (Table 2).

AN—MMA/AIBN/60°C includes the following solvated forms: AIA, IB, AIB, *viz.*, the same forms that were obtained in the set (28), position 1. Positions 2, 3 and 4 do not correlate with the data in Table 3. Hence, the results in Table 3 comprise a criterion for deciding the solutions of the set (28), to select those correlating well with the experimental results of the AN—MMA/AIBN/60°C system [1].

The solution of equation (10) by the algorithm [5], applied consecutively to achieve the results presented in Figs. 1a—d, in addition to establishing the types of

actual solvated forms (Table 3) allows to determine their stability constants and the thermal decomposition rate constants of the solvated forms. These values are collected in Tables 4 and 5.

In parallel with the determination of eqn. (10) for the dependence  $k_d = f(x_A)$  separately for each concentration C, calculations were performed in order to select eqn. (10) for the global dependence, a function of two variables  $k_d = f(x_A, C)$ . The method of nonlinear least-squares using the Marquardt algorithm [5] was jointly applied to achieve all the results presented in Table 1.

**Table 5.** Determination and comparison of the thermal decomposition rate constants of the solvated forms in the three-component system AN—MMA/DMF/AIBN/60°C at low concentrations of the comonomer mixtures

Concentration <sup>*)</sup> C, mol · dm <sup>-3</sup>	Thermal decomposition rate constants of solvated forms <sup>**) (· 10<sup>4</sup> min<sup>-1</sup>)</sup>									Figure
	$k_A$	$k_{AA}$	$k_B$	$k_{BB}$	$k_S$	$k_{SS}$	$k_{AS}$	$k_{BS}$ <sup>****)</sup>	$k_{AB}$	
3	—	7.2	7.2	—	—	6.45	4.09	4.2	6.5	1a
1	—	7.2	7.2	—	—	6.45	4.09	4.2	6.5	1b
0.5	—	7.2	7.2	—	—	6.45	4.09	4.2	6.5	1c
0.1	—	7.2 <sup>***)</sup>	7.2	—	—	6.45	—	4.2	—	1d
0.1—3.0	—	7.2	7.2	—	—	6.45	4.09	4.2	6.5	

<sup>\*)</sup> C = A + B; <sup>\*\*) for  $k_A = 7.2 \cdot 10^{-4} \text{ min}^{-1}$ ;  $k_B = 7.2 \cdot 10^{-4} \text{ min}^{-1}$  and  $k_S = 6.45 \cdot 10^{-4} \text{ min}^{-1}$  for pure acrylonitrile (AN), methyl methacrylate (MMA) and N,N-dimethylformamide (DMF); <sup>\*\*\*)</sup> hypothetical value, since  $K_{AA} = 0$  for C = 0.1 (Tables 2 and 4); <sup>\*\*\*\*)</sup> for assumed  $K_{AA} = 1$ .</sup>

The results of computation for the entire system investigated are collected in Table 4 (stability constants), and in Table 5 (thermal decomposition rate constants of solvated forms).

Extrapolation of the results from Table 4 to S = 0 leads to the sequence:

$$K_{AB} = 766 > K_B = 408.6 > K_{AA} = 1 \quad (31)$$

and

$$k_{AB} = 6.5 \cdot 10^{-4} \text{ min}^{-1} \quad (32)$$

The value of  $k_{AB}$  (32) obtained in this work is seen to be identical with that,  $k_{AB}$  (29), obtained in previous work [1]. The stability constants (31) and (30), also demonstrate a very good consistency. The differences in the determinations of  $K_{AB}$  and  $K_B$  amount to +2.54% and +8.33%, respectively.

#### CONCLUSIONS

The study of the AN—MMA/DMF/AIBN/60°C system, *i.e.* a three-component monomer A (AN) — monomer B (MMA) — solvent S (DMF) mixture, is necessary for an unequivocal determination of the solvated forms occurring both in this system and in the system

AN—MMA/AIBN/60°C [1], *i.e.*, a two-component system which comprises monomer A (AN) and monomer B (MMA), in the system AN/DMF/AIBN/60°C [3] comprising monomer A (AN) and solvent S (DMF), and also the system MMA/DMF/AIBN/60°C [2] with monomer B (MMA) and solvent S (DMF).

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