

## **COMPLEXES OF ACID AMIDES WITH POLAR APROTIC SOLVENTS; III. Complexes of bis(N-phenyl)-pyromellitic acid amide with solvent mixtures**

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Solid complexes of bis(N-phenyl)-pyromellitic acid amide with equimolar binary mixtures of dimethylformamide, dimethylacetamide, dimethylsulfoxide and N-methylpyrrolidone were prepared and studied by evolved gas analysis using mass spectrometry. The activity sequence of these compounds in forming complexes with bis(N-phenyl)-pyromellitic acid amide was established.

As reported earlier [1], bis(N-phenyl)-pyromellitic acid amide (PMA) forms solid complexes with polar aprotic solvents, their composition depending on the mode of their precipitation from the solution. If precipitation is carried out in benzene, the structure of the complex corresponds to the ratio 1PMA:2solvent (the solvents applied were dimethylformamide (DMFA), dimethylacetamide (DMAA), dimethylsulfoxide (DMSO) and N-methylpyrrolidone (N-MP)).

This paper deals with the preparation, separation and study of solid complexes of PMA with solvent mixtures. PMA was synthesized in equimolar binary mixtures of DMFA and DMAA, DMFA and DMSO, DMFA and N-MP, and DMAA and N-MP, respectively, and the complexes were precipitated with benzene. Evolved gas analysis using mass spectrometry was applied to study the complexes. The relative activity of each solvent in complex formation was evaluated by determining its relative content in the corresponding solid complex.

### **Experimental**

The PMA-solvent complexes were synthesized in equimolar binary mixtures of DMFA, DMAA, DMSO and N-MP according to the method described in [1]. The PMA solutions in the mixed solvents were poured into a large excess of benzene, the mixtures were filtered, and the precipitates were washed with benzene and dried to constant mass. The complexes were white crystalline products, stable for long storage periods in air.

Evolved gas analysis by mass spectrometry was performed using the cell fitted with a flow-duct reported in [1].

### Discussion of the results

The main difference between the PMA complexes formed with mixed solvents as compared to the complexes studied earlier [1] is the lower amount of solvent complexing with PMA. When pure solvents are used, the composition of the complexes is mainly 1PMA:2solvent, whereas in the case of mixed solvents about one mol of "total" solvent is usually bound to one mol of PMA, as shown in Table 1. Another particular feature of the discussed complexes is the substantially higher degree of PMA decomposition in the cyclodehydration process. This is clearly observable in Figs 1–4, curves 4.

It is of interest to estimate the relative activity  $a$  of the studied solvents in the complexing process with PMA. The calculations were performed for mixtures with DMFA, the activity of DMFA being taken as unity. The activities of the other solvents were determined by calculating the molar ratio of the solvent in question to DMFA in the complex, utilizing the coefficient of relative sensitivity of water to the corresponding solvent. By way of example, let us consider the solid complex obtained from the equimolar mixture of DMFA (Fig. 1). The mass spectroscopic curves indicate that the evolution of 0.51 mol DMAA and 0.13 mol DMFA corresponds to one mol of water evolved in the cyclodehydration process of PMA, i.e. about 1 DMAA molecule corresponds to 1 PMA molecule, and the composition of the complex is close to 1PMA:1DMAA. It may therefore be stated that DMAA is more active than DMFA in complex formation with PMA. This activity  $a$  is quantitatively expressed by the ratio  $a = \frac{0.51}{0.13} = 3.9$ . The activity values  $a$  for the other solvents are presented in Table 1.

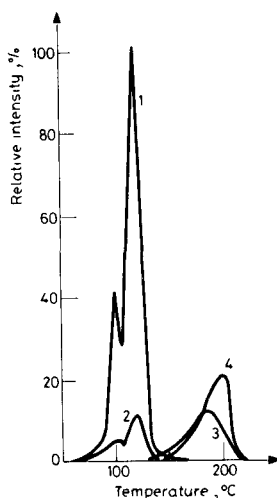
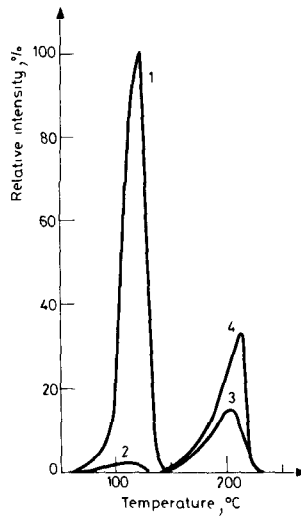


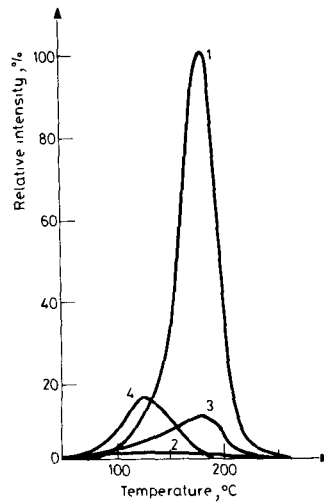
Fig. 1 Evolved gas analytical curves for the complex PMA—DMFA—DMAA  
1. m/e 87 (DMAA); 2. m/e 73 (DMFA); 3. m/e 17 (water); 4. m/e 93 (aniline)

**Table 1** Results of evolved gas analysis using mass spectrometry of mixed solid complexes of bis(N-phenyl)-pyromellitic acid amide with different solvents

Equimolar solvent mixture	Peak area, conv. units			Rel. sensitivity of solvent	Molar ratio solvent to water	Rel. activity of solvent	Composition of complex
	more active solv.	less active solv.	water				
DMFA+DMAA	DMAA	DMFA		$\frac{17}{73} = 0.24$	DMAA: 0.51	$a_{DMFA} = 1$	1PMA:1DMMA
	552	88	156 (4%)	$\frac{17}{87} = 0.15$	DMFA: 0.13	$a_{DMAA} = 3.9$	
DMFA+DMSO	DMSO	DMFA		$\frac{17}{78} = 0.17$	DMSO: 0.52	$a_{DMSO} = 34.6$	1PMA:1DMSO
	499	10	153 (5.5%)		DMFA: 0.015		
DMFA+N-MP	N-MP	DMFA		$\frac{17}{99} = 0.14$	N-MP: 0.14	$a_{N-MP} = 3.7$	1PMA:1[DMAA+N-MP]
	258	42	213 (27.4%)		DMFA: 0.038		
DMAA+N-MP	N-MP	DMAA			N-MP: 0.31		1PMA:1[DMAA+N-MP]
	333	220	137 (10.5%)		DMAA: 0.22		



**Fig. 2** Evolved gas analytical curves for the complex DMA-DMFA-DMSO  
1. m/e 78 (DMSO); 2. m/e 73 (DMFA); 3. m/e 17 (water); 4. m/e 93 (aniline)



**Fig. 3** Evolved gas analytical curves for the complex PMA-DMFA-N-MP  
1. m/e 93 (aniline); 2. m/e 73 (DMFA); 3. m/e 17 (water); 4. m/e 99 (N-MP)

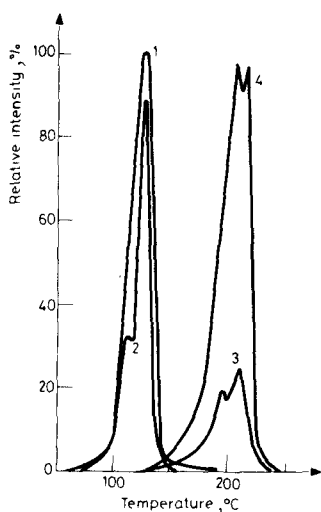


Fig. 4 Evolved gas analytical curves for the complex PMDA-DMAA-N-MP  
 1. m/e 99 (N-MP); 2. m/e 87 (DMAA); 3. m/e 17 (water); 4. m/e 93 (aniline)

A comparison of the activities in complex formation for these solvents with their basicities indicates, in general, a parallel trend, i.e. the higher the basicity of the solvent, the higher its activity in complex formation. The  $pK_a$  values reported in the literature [2] for DMAA, N-MP and DMSO are  $-0.19$ ,  $-0.17$  and  $0$  respectively, and the enthalpy values of complex formation of DMFA, DMAA and DMSO with  $SbCl_3$  reported in [3] are  $111.5$ ,  $116.9$  and  $125.5$  kJ/mol, respectively. As regards N-MP, contradictory data are to be found in the literature. In [4] for example a  $pK_a$  value of  $-0.92$  is reported. On the basis of our findings, the basicity of N-MP should be close to that of DMAA, so that the value  $pK_a = -0.17$  appears more probable.

The activity of N-MP (3.7) was found to be slightly lower than that of DMAA (3.9) in the relative activity sequence (DMFA = 1). However, a comparison of the amounts of N-MP and DMAA in the complex obtained directly from the mixture of these solvents indicates a somewhat higher activity of N-MP.

Finally, it should be noted that solid complexes of acid amides cannot always be separated from binary solvent mixtures. For instance, no solid complex of PMA was obtained with the solvent pair N-MP-DMSO.

To summarize the results of this study, it may be concluded that the activities of DMFA, DMAA, DMSO and N-MP in mixed complex formation with PMA show the same trend as their basicities.

## References

- 1 S.A. Dauengauer, L.A. Shibaev, N.G. Stepanov and Yu.N. Sazanov, Theses of the papers read at the Conference: *Dissolution and Solvents in the Technology of Polymers* (in Russian), Leningrad, 1981, p.27.
- 2 B.A. Zhubanov, I.A. Arkhipova and O.Ya. Almabekov, *Novye termostoykie geterociklicheskie polimery* (New heat-resistant heterocyclic polymers), Alma-Ata, 1979, p.30.
- 3 V. Gutmann, *Coordination Chemistry in Non-Aqueous Solutions*, Springer, Vienna, 1968 (Russian edition: Mir, Moscow, 1971).
- 4 I.E. Kardash, A.Ya. Ardashnikov, F.S. Yakushin and A.N. Pravednikov, *Vysokomolekul. Soedin.*, A17 (1975) 598.

**Zusammenfassung** — Feste Komplexe von Bis(N-phenyl)-pyromellithsäureamid mit äquimolaren Mischungen von Dimethylformamid, Dimethylacetamid, Dimethylsulfoxid und N-Methylpyrrolidon wurden hergestellt und die daraus bei thermischer Analyse entwickelten Gase massenspektrometrisch untersucht. Die Aktivitätsreihenfolge für die Bildung von Komplexen mit Bis-(N-phenyl)-pyromellithsäureamid wurde ermittelt.

**Резюме** — Синтезированы и исследованы методом масс-спектрометрического термического анализа твердые комплексы бис-(N-фенил)-пиромеллитамидокислоты с парами апротонных растворителей типа ДМФА, ДМАА, ДМСО, N-МП. По результатам анализа комплексов был построен ряд относительной активности указанных растворителей к комплексообразованию, который, как оказалось, совпадает с рядом основностей этих растворителей.