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Investigations on physicochemical properties of halophosphate surfaces from liquid adsorption measurements

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Investigations of the adsorption and thermodesorption of n-octane and water from phosphor samples are presented. The dispersion and non-dispersion components of the surface free energy were calculated. Correlations between adsorption capacity and the components of surface free energy and luminous characteristic of the examined phosphors were found. The luminous quality of phosphors increased with the increasing hydrophilic nature of their surfaces.

1. Introduction

The physicochemical properties of phosphor surfaces are very important in obtaining a good quality visible luminous flux. The number and distribution of the luminescence sites (e.g. Sb^{+3} and Mn^{+2} ions) decide about the energy state, i.e. about the number of active sites on the phosphor surface. The production process consists of many operations (washing, grinding, sieving, repeated heating), which give the phosphor surface the best physicochemical properties for the optimum intensity and stability of the luminous flux [1, 2]. These surface features play the most important role in the transformation of mercury vapour radiation of wavelength 185 and 254 nm, to the visible. They are porosity, specific surface, shape of grains and content of luminescence sites formed on the surface by Sb^{+3} and Mn^{+2} ions. Various grains (porous and irregularly shaped, with impurities and OH^- groups on the surfaces) were, however, obtained during the synthesis [3]. On such grains a greater amount of activated visible radiation is dissipated in micro- and macropores and also absorbed by impurities and OH^- groups which are characterized by such properties.

One of the sources of information on the physical and energetical properties of solid surfaces is the investigation on the adsorption effect and the adsorption isotherms determined as a result of them. The physicochemical properties of the surface are related to the suitable liquid adsorption capabilities, surface free energy and also energy of interactions between active sites of the surface and molecules of adsorbing liquid, thus they can be measured and compared by means of methods and instruments applied in physical chemistry [4].

As is already known, the adsorption properties of solids are significantly affected by thermal pretreatment, which causes some changes in the chemical nature of solid surfaces (removal of adsorbed vapours and gases, increase of surface concentration of some atoms as a result of their migration from bulk solid phase, partial dehydroxylation, i.e. decrease of OH^- groups and porosity decrease).

This paper presents investigations of the adsorption properties of the surfaces of selected phosphors and other powders. The investigations were carried out by means of the derivatograph using DTA methods: a dynamic one and quasi-isothermal evaporation of non-polar liquid (n-octane) and a polar one (water) from powder surfaces and also adsorption of these liquids from the gas phase at 20 °C. The obtained results were correlated with the surface free energy values and luminous properties of the phosphors under examination.

2. Materials and instruments

In the investigations samples of phosphors: Polish-H_{11} and foreign: Sylvania-S (USA) and C (USSR) were used. Considering that halophosphate lattice is similar to apatite and phosphorite structures, the phosphorite Kuriba (Maroco) of an intermediate pore radius (8.73 nm) was used as the reference material.

The physicochemical properties of the surfaces of materials mentioned above were investigated by differential thermal analysis DTA [5, 6] using the Derivatograph Q-1500D (MOM, Hungary), with its own two programmes (dynamic and quasi-isothermal) and also the so-called "modified", a self-worked programme. A full description of applied measuring methods can be found in literature [7–13].

The specific surface area of the examined powders (Table I) was determined by the Nelsen–Eggersten method [14] using a suitable apparatus. Luminous features of the selected phosphors were measured in a self-built photometer in the following way.

The suspension of the phosphor in nitrocellulose-butyl acetate solution was placed on a microscopic

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TABLE I

	Phosphorite	Phosphors				
	K	S	H_{11}	F-3	ZWLE	C
n-octane						
a (mmol g^{-1})	0.595	2.38×10^{-3}	1.5×10^{-3}	2.57×10^{-3}	3.84×10^{-3}	2.96×10^{-3}
n	7.4	2.2	0.86	2.85	0.6	4.44
γ_s^d (mJ m^{-2})	57.77	63.94	80.0	83.54	79.1	96.5
Water						
a (mmol g^{-1})	0.45	4.32×10^{-2}	3.89×10^{-2}	1.1×10^{-2}	2.42×10^{-2}	2.38×10^{-2}
n	0.87	6.65	3.68	2.0	0.64	5.97
γ_s^p (mJ m^{-2})	133.29	120.64	117.0	88.3	84.3	68.0
$\gamma_s = \gamma_s^d + \gamma_s^p$ (mJ m^{-2})	191.06	184.58	197.0	171.84	163.4	164.5
E_a (kJ mol^{-1})	143.1	125.7	90.9	65.1	86.9	23.4
ΔH (kJ mol^{-1})	160.3	142.5	107.9	82.7	86.7	41.4
ΔS (J mol^{-1} K^{-1})	140.8	109.1	41.5	− 22.3	36.5	− 104.6
E (%)	–	100	92.8	81.8	78.7	75.6
S (m^2 g^{-1})	22.0	0.277	0.448	0.227	1.619	0.166

cover glass. After drying, the glass was placed in a photometer chamber and the total emission of luminous flux was measured (E %).

3. Results and discussion

Investigations on liquid thermal desorption from solid surfaces provide a great deal of valuable information about an energy state, type of investigated surface, nature of liquid–solid interactions and also about the mechanism of liquid evaporation. The results of thermal desorption of n-octane and water from completely wetted samples of Sylvania and H_{11} phosphors, obtained by the dynamic and quasi-isothermal methods, are shown in Figs 1 to 4. It results from Fig. 1 (where the obtained DTA curves are shown) that dynamic thermodesorption of n-octane and water from the Sylvania sample (curve 1) and the H_{11} one (curve 2) shows low-temperature peaks or inflections. From the data presented in Fig. 1 it can be seen that the complete desorption of n-octane from the investigation samples takes place at temperatures up to 127 °C.

A different course of thermal desorption process was observed in the case of water desorption from the samples of phosphors (Fig. 2; curve 1-Sylvania, curve 2-H_{11}). As it can be seen in Fig. 2, the thermal desorption of water from the investigated samples shows only one endotherm with strongly marked inflections on the curves (point A on DTA curves). These inflections are probably connected with the final stage of desorption of bulk water added in excess and the beginning of desorption of water bonded to the surface, which has different properties from those of the bulk water [20]. The temperatures, at which

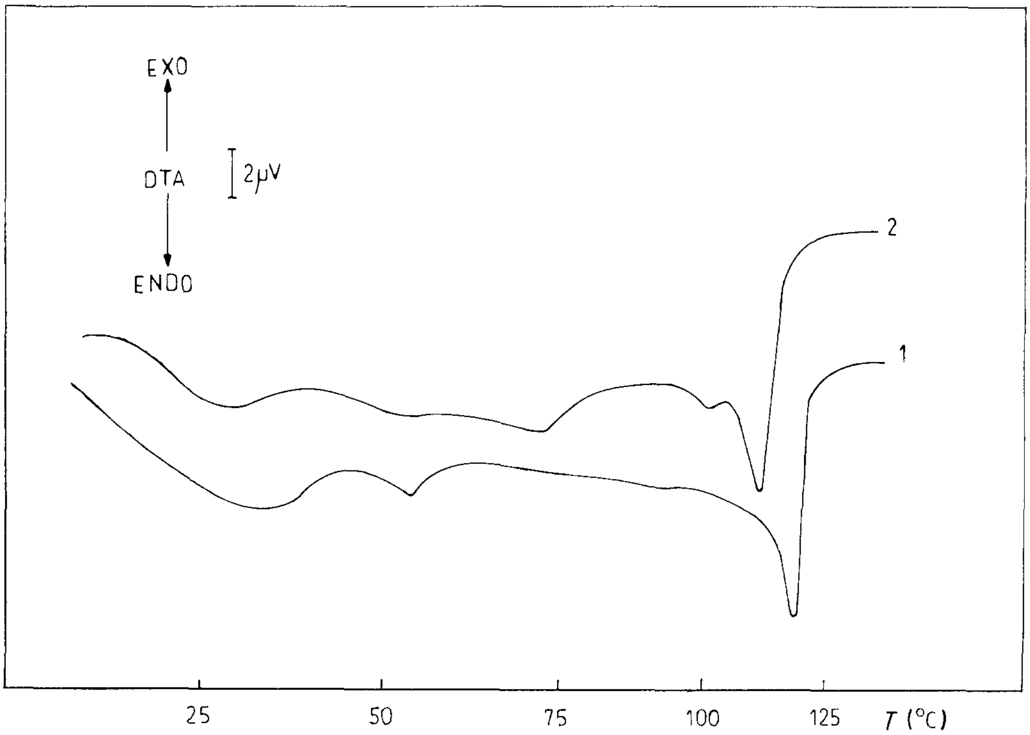

Figure 1 DTA curves of n-octane thermodesorption from phosphor Sylvania sample (curve 1) and H_{11} one (curve 2).

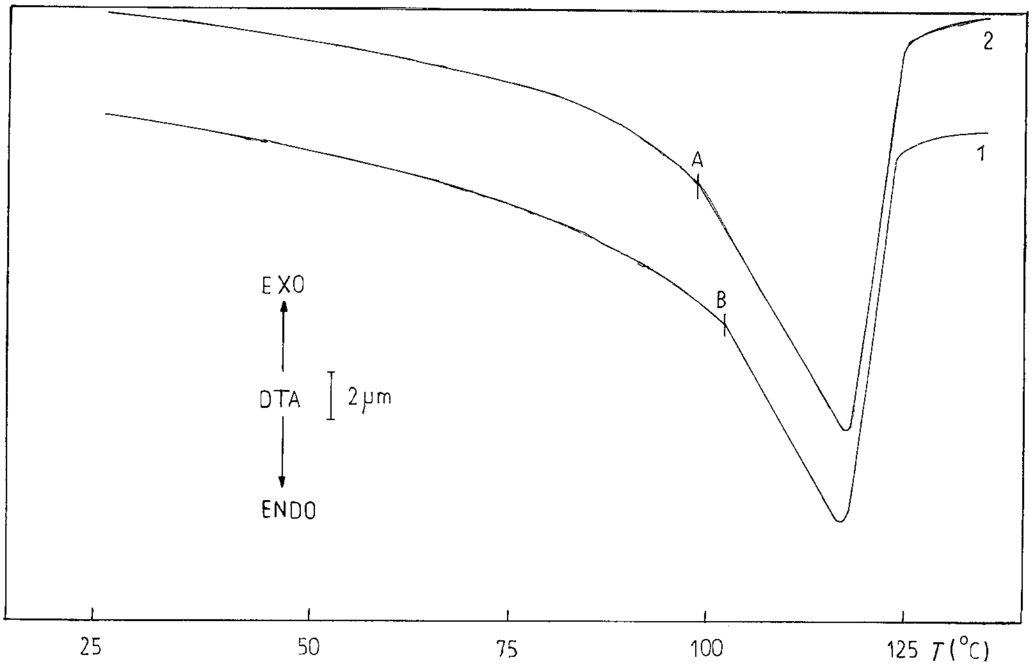

Figure 2 DTA curves of water thermodesorption from phosphor Sylvania sample (curve 1) and H_{11} one (curve 2).

water desorption is completed, are also higher: depending on the sample type they are in the range from 111 °C (phosphor S) to 127 °C (phosphorite K) which is the effect of the difference in bonding energy between water and the sample surface.

To make more detailed interpretations of the above results, the thermal desorption of water and n-octane from solid surface under quasi-isothermal conditions was carried out. Figs 3 and 4 show the selected TG curves obtained during the quasi-isothermal desorption of n-octane from the samples of phosphors: Sylvania (curve 1) and H_{11} (curve 2). Comparing the data presented in Figs 3 and 4, it may be stated that curves courses of n-octane thermodesorption are different from those obtained during the water thermodesorption. First of all, they differ in the number of inflections and in higher temperatures, which correspond to individual inflections and to the end of the desorption process. This is undoubtedly connected with the higher boiling point of n-octane (125 °C).

The above results of thermal desorption of n-octane and water under dynamic and quasi-isothermal conditions may be interpreted as follows. At the beginning, the desorption of the liquid added to the sample in excess, which has the properties of a common liquid (a bulk liquid) is observed. In Figs 1 to 4 this process can be seen as peaks–inflections denoted by II or A. Further, the intergranular liquid and that filling pores and capillaries are desorbed. In this case, the physicochemical properties of the selected liquid (n-octane and water) are changed as a result of capillary forces as confirmed by the higher desorption temperature. In the presented figures this process corresponds to the region between peaks–inflections I–II or I–A. In the final stage of desorption, at temperatures higher than those suitable for peaks–inflections I, the desorption of liquid bonded most strongly to the surface is observed. Under the influence of surface forces, n-octane and especially water show completely different physicochemical properties (first of all the structure) and the removal of these liquids from the sample surface requires a lot of energy (under the measurement conditions considered – heating at a high temperature). From the data presented in Fig. 4, it can be seen that the complete removal of n-octane from the Sylvania sample under quasi-isothermal conditions requires it being heated to 130 °C, and for the evaporation of water to 115 °C. It is remarkable that the

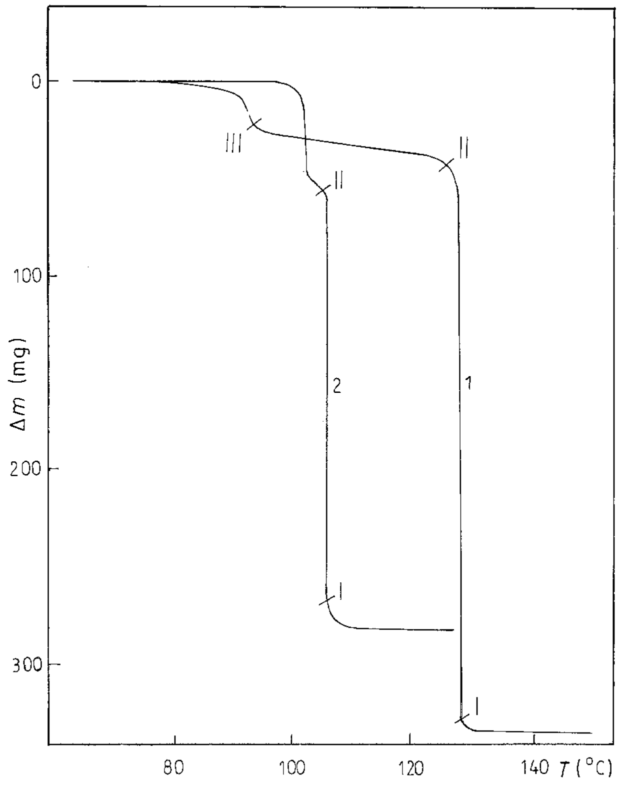

Figure 3 Curves of quasi-isothermal desorption of n-octane (curve 1) and water (curve 2) from phosphor Sylvania sample.

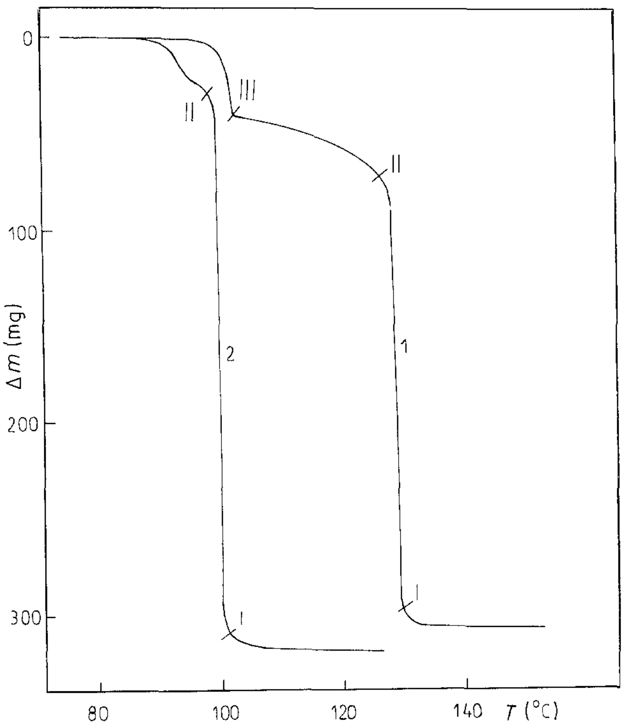

Figure 4 Curves of quasi-isothermal desorption of n-octane (curve 1) and water (curve 2) from phosphor H_{11} sample.

temperatures corresponding to the final stage of thermal desorption of n-octane and water from the samples under dynamic and quasi-isothermal conditions (Figs 1 to 4) reflect (in a way) the magnitude of interaction energy between liquid molecules and the solid surface and are also correlated with the surface free energy of the examined solids.

Considering those relations, the measurements of adsorption and desorption of n-octane and water from the gaseous phase were carried out and the results were used to estimate this parameter. Based on these data the adsorption isotherms at 20 °C were determined, from which it results that the highest water adsorption capacity occurs for phosphorite K (0.45 mmol g^{-1}), and the lowest for phosphor C (2.38×10^{-2} mmol g^{-1}). The n-octane adsorption capacity for these phosphors is lower (about 1.5 to 2.96×10^{-3} mmol g^{-1}). The number of statistical monolayers of water adsorbed on the surface was calculated from the determined specific surfaces (i.e. the factor corresponding to the sample porosity). The highest specific surface area is shown by phosphorite K (22 $m^2 g^{-1}$) and H_{11} of the phosphors applied in the experiments (0.448 $m^2 g^{-1}$). Considering the specific surface of Sylvania (0.277 $m^2 g^{-1}$), i.e. the best reference phosphor, it can be presumed that the optimum specific surface of a high quality phosphor should be about 0.3 $m^2 g^{-1}$. Both the higher value (e.g. H_{11} – more porous phosphor) and the lower one (e.g. C – with the melted surface, which can be seen on the SEM photos) are disadvantageous for their luminous features.

It was assumed in the calculations that one water molecule occupied an area of 0.0706 nm^2. The calculated number of statistical monolayers of water adsorbed from a gaseous phase at 20 °C is equal 6.65 for Sylvania and 0.87 for phosphorite K. For n-octane, assuming the horizontal orientation and the area of 0.42 nm^2 occupied by one molecule, the number of statistical monolayers is equal to 4.44 for phosphor C and 7.4 for phosphorite K. These data, necessary for further calculations of the surface free energy, reflect the energetical state of the surface, especially for the phosphors, because the liquid adsorption is dependent on the active sites energy (i.e. on the luminescence sites number, which are Sb^{3+} and Mn^{2+} ions).

The dispersion component γ_s^d and the polar one γ_s^p of surface free energy were calculated using n-octane and water adsorption data from Bangham–Razouk equation [15]. The full description of the calculation method is given by Staszczuk in [16, 17]. Fig. 5 shows the relation between water adsorption capacity (maximum adsorption at 20 °C) of the investigated phosphors and the dispersion component value (curve a) or the non-dispersion one (curve b) of the surface free energy. As can be seen in the figure, those relations are directly or inversely proportional. The increasing dispersion component value causes the decrease of water adsorption capability of phosphors. The increasing non-dispersion component value causes, however, an increase in water adsorption capacity. It also results from Fig. 5 that the high quality phosphors (e.g. Sylvania type) show the low values of dispersion γ_s^d and the high values of the polar one γ_s^p. The measurements of luminous features (the emission intensity, E) carried out with the photometer showed, that for H_{11} phosphor $E = 90\%$ of the Sylvania emission value, while for the phosphor C-E = 75.6%.

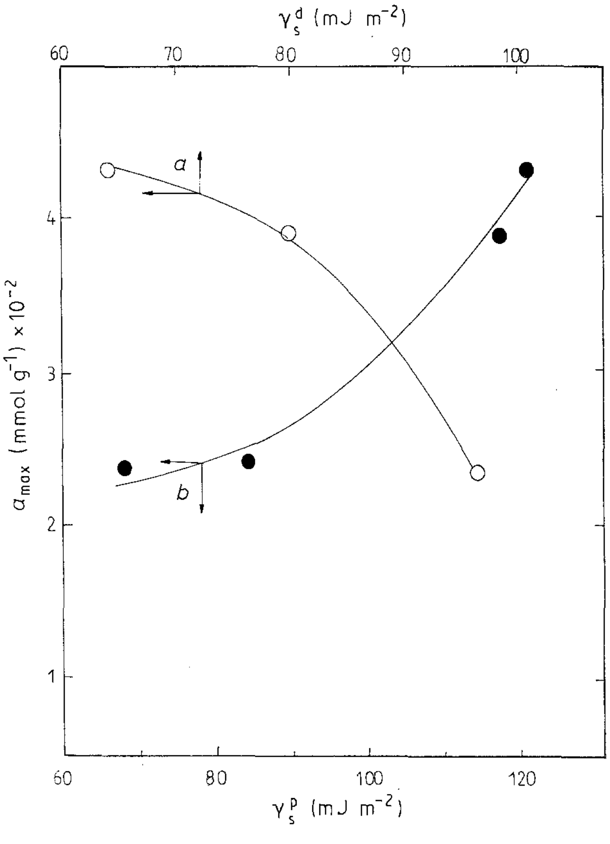

Figure 5 Correlation between water adsorption capacity (a_{max}) and dispersion component value (curve a) and non-dispersion one (curve b) of surface free energy for Sylvania phosphor.

The relations presented above indicate that the luminous quality of the phosphors increases with increasing hydrophilic properties of their surfaces (γ_s^d decreases and γ_s^p increases). It is a result of the increase in luminescence sites number, i.e. Sb^{3+} and Mn^{2+} ions which are simultaneously very strong adsorption sites for water on the surface.

4. Conclusions

From the results presented above it may be concluded that the liquid adsorption capability of phosphors especially for water, reflect their luminous properties. The phosphors of good quality are characterized by the high value of water adsorption capacity and the non-dispersion component of the surface free energy. It is caused by the presence of the luminescence sites (ions) on the surface, which are the high-energy adsorption sites.

References

1. H. DURALSKA, *Zeszyty Naukowe Politechniki Rzeszowskiej* **21** (1984) 39.
2. I. GORZKOWSKA and R. RUDNICKI, *Prace Naukowe AE Wrocław, Chemia* **338** (1986) 231.
3. "Investigations on Physicochemical Properties of Powders Useful in Technology, Including Phosphors", Report, UMCS, Lublin (1988).
4. J. OŚCIK, "Adsorption" (PWN, Warsaw, 1979).
5. D. SCHULTZE, "Termiczna analiza różnicowa" (PWN, Warsaw, 1974).
6. P. STASZCZUK, *J. Thermal Anal.* **29** (1984) 217.
7. P. STASZCZUK and J. ZIELSKA, *Przem. Chem.* **69** (1990).
8. P. STASZCZUK and B. BILIŃSKI, *Thermochimica Acta* **122** (1987) 363.
9. *Idem.*, *J. Thermal. Anal.* **32** (1987) 1457.
10. P. STASZCZUK, *ibid.* **30** (1985) 1115.
11. *Idem.*, *ibid.* **30** (1986) 911.
12. *Idem.*, *ibid.* **31** (1986) 1055.
13. *Idem.*, Patent PRL, 249 986 (1988).
14. F. M. NELSEN and F. T. EGGERTSEN, *Anal. Chem.* **30** (1958) 1387.
15. A. C. ZETTLEMOYER, in "Hydrophobic Surface" (Academic, New York, 1969) p. 1.
16. P. STASZCZUK, *Chromatographia* **20** (1985) 724.
17. *Idem.*, *J. Mater. Sci.* **22** (1987) 4011.

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