

SORPTION  
AND ION-EXCHANGE PROCESSES

## Influence of Surfactants on Structuring of Molding Blends Based on ZnO

V. Yu. Prokof'ev, A. P. Il'in, and T. V. Basova

Ivanovo State Chemical-Engineering University, Ivanovo, Russia

Received October 22, 2004

**Abstract**—The correlation between the surfactant sorption and structural mechanical properties of molding blends and granulated sorbents was studied.

ZnO is widely used as a chemisorbent for removing impurities and, in particular, sulfur compounds [1], from process gases. Zinc oxide almost irreversibly sorbs hydrogen sulfide to form solid zinc sulfide, which allows almost complete removal of H<sub>2</sub>S from the gas being treated. At the same time [1, 2], granulated sorbent should have not only a strongly developed microporous structure but also large pores for penetration of reagents deep into a granule.

Uzugi and Tamia found [3] that the sorption of hydrogen sulfide on zinc oxide depends not only on its specific surface area but also, to a great extent, on the pore size distribution. Zinc oxide having, along with micropores, coarse pores with radius larger than 100 nm exhibits the highest sorption activity. As follows from the stoichiometry of the reaction of ZnO with H<sub>2</sub>S, the highest sorption capacity of zinc oxide for hydrogen sulfide is 39 wt%. The actual sorption capacity is lower than 20 wt%. Hence, the H<sub>2</sub>S sorption strongly depends on its diffusion into the sorbent matrix. Under the industrial conditions, only the external surface of zinc oxide granules is converted into the sulfide, and the internal surface does not work.

It is known that pelletized granules have a nanoporous structure, whereas extruded granules contain broad transport pores, along with narrow pores. Preparation of extruded sorbents based on ZnO was examined in our previous study [4].

Surfactants are widely used to improve the moldability of blends (including those based on ZnO) to be extruded.

### EXPERIMENTAL

We used ZnO powder with an almost 100% content of the main compound. The molding blends were

prepared by addition of polyvinyl alcohol (PVA) or carboxymethyl cellulose (CMC) solutions of different concentrations to a ZnO powder. The mixture was stirred to obtain a homogeneous suspension.

The optimal water content in the blend,  $\phi_{\text{opt}}$ , was determined on a conical Rebinder plastometer by the procedure described in [5]. The structural-mechanical constants (ultimate shear stress  $P_{k1}$  and maximum plastic viscosity  $\eta_1$ ) and parameters (plasticity  $P_s$  and relaxation time  $\Theta$ ) were calculated using the Maxwell–Shvedov and Kelvin model. For this purpose, we used the time–strain curves measured on a D.M. Tolstói's plastometer [6]. The complete rheological curves were measured on a Rheotest-2 rotary viscometer in the range of shear rates 2–4960 s<sup>−1</sup>. The data obtained were processed by the procedure described in [6, 7]. We calculated the following rheological parameters: full power consumed for flow  $N$ , power for degradation of the coagulation structure  $\Delta N$ , consistency constant  $\eta_0$ , and flow index  $n$ .

The butt crushing strength of the granules was measured on a hydraulic press [8]. The BET specific surface area was determined from low-temperature sorption of argon [9].

We studied the sorption of CMC and PVA on ZnO particles under different conditions. A maximum at a 1–2 wt % PVA concentration in the solution is observed in all the sorption curves (Fig. 1). The maxima in the sorption curves are due to structuring of more concentrated CMC and PVA solutions with the formation of aggregates. The sorption capacity of the solid phase in dispersed solutions is higher by a factor of 2 than that in the stirred solutions.

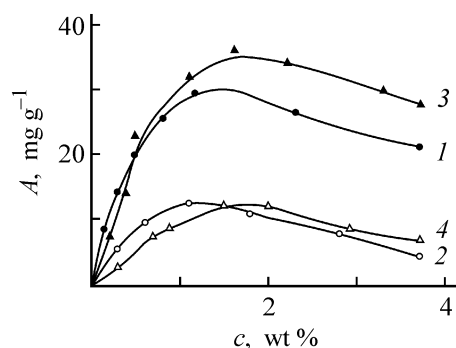
The sorption capacity depends on the hydrophilic shell on the surface and the size of oxide particles.

The ion-exchange sorption from 0.1 N HCl shows that the ZnO surface is almost completely coated with OH groups. In addition, the particle size of zinc oxide decreases from 250 to 20  $\mu\text{m}$  after dispersion in a high-speed homogenizer. It should also be noted that diffusion of a large polymeric molecule into a porous particle is virtually impossible. Thus, the polymer sorption depends mainly on the size and hydroxyl shell of zinc oxide particles, rather than on their specific surface area.

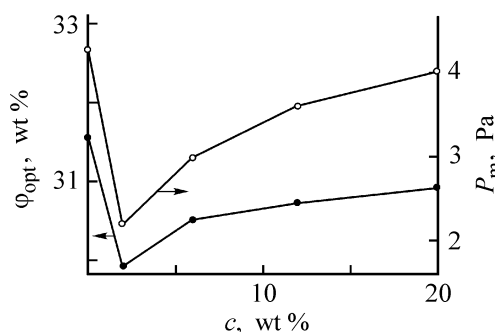
The influence of the surfactant concentration on the optimal water content in the blend,  $\varphi_{\text{opt}}$ , was studied for the example of the ZnO–CMC–water system. The  $\varphi_{\text{opt}}$  decreases from 31.6 to 29.9 wt % with the CMC concentration increasing to 2  $\text{mg g}^{-1}$  ZnO (Fig. 2). As the CMC concentration increases further, the optimal water content in the blend monotonically increases to 30.9 wt %. The dependence of the plastic strength at  $\varphi_{\text{opt}}$  is similar. At a CMC concentration of 2  $\text{mg g}^{-1}$ ,  $P_{\text{m}}|_{\varphi=\varphi_{\text{opt}}}$  decreases by a factor of 2 and then monotonically increases, virtually reaching the initial value.

Comparison of the dependences shown in Figs. 1 and 2 shows that a decrease in  $\varphi_{\text{opt}}$  and  $P_{\text{m}}|_{\varphi=\varphi_{\text{opt}}}$  corresponds to an increase in the surfactant sorption, i.e., the maximum in the  $A = f(c_{\text{surfactant}})$  curve corresponds to the minimum in the  $\varphi_{\text{opt}} = f(c_{\text{surfactant}})$  and  $P_{\text{m}}|_{\varphi=\varphi_{\text{opt}}} = f(c_{\text{surfactant}})$  curves. Hence, the intermolecular bonds of sorbed CMC macromolecules that substitute water molecules in the solvation shells make an increasing contribution to the coagulation interactions with increasing sorption. This accounts for the fact that the optimal water content in the blend decreases at a surfactant concentration of up to 2  $\text{mg g}^{-1}$ . At the same time, the strength of coagulation bonds between polymer macromolecules is lower than that of the bonds formed by the hydration shell of zinc oxide particles. As a result, the plastic strength of the molding blends decreases at the best water content in the blend. As noted above, the surfactant sorption decreases with a further increase in the CMC concentration in the system (Fig. 1). This results in the formation of additional hydration bonds between ZnO particles, and hence  $\varphi_{\text{opt}}$  and  $P_{\text{m}}|_{\varphi=\varphi_{\text{opt}}}$  increase (Fig. 2). Thus, structuring in molding blends depends not only on the total surfactant content in the system, but also, and to a greater extent, on the surfactant sorption on the surface of dispersed particles.

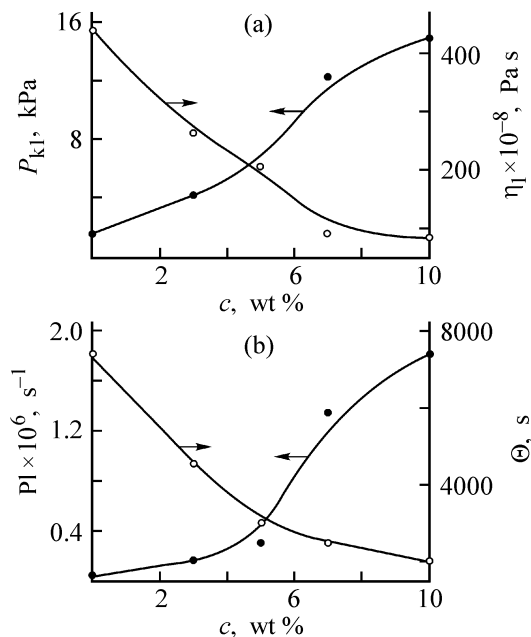
Let us consider the influence of the surfactant concentration (for the example of PVA) on the properties of molding blends based on ZnO at the optimal water content in the blend. Our experimental results (Fig. 3a) show that the dependence of ultimate shear



**Fig. 1.** Sorption  $A$  of (1, 2) CMC and (3, 4) PVA on ZnO at 25°C vs. the surfactant concentration in an aqueous solution  $c$ . Treatment conditions: (1, 3) dispersion for 15 min; and (2, 4) stirring for 2 h;  $s:1 = 1:3$ .



**Fig. 2.** Optimal water content in the blend,  $\varphi_{\text{opt}}$ , and the plastic strength  $P_{\text{m}}$  at  $\varphi = \varphi_{\text{opt}}$  vs. the CMC content  $c$  in the molding blends based on ZnO.



**Fig. 3.** (a) Ultimate shear stress  $P_{\text{kl}}$  and maximum plastic viscosity  $\eta_{\text{l}}$  and (b) plasticity  $Pl$  and relaxation time  $\Theta$  vs. the PVA content  $c$  in molding blends based on ZnO.

Rheological properties of molding blends based on zinc oxide

PVA content, wt %	$N$ , MW m <sup>-3</sup>	$\Delta N$ , MW m <sup>-3</sup>	$\eta_0$ , Pa s	$n$
0	22.7	3.1	228	0.501
3	23.6	4.7	194	0.476
5	25.6	5.2	178	0.471
7	25.8	6.2	133	0.459
10	26.1	6.3	128	0.414

stress on the PVA content is S-shaped, with the steepest portion of the curve corresponding to a PVA content of 5–7 wt %. The dependence of the maximum plastic viscosity on the surfactant concentration is initially exponential and then, at a PVA concentration higher than 7 wt %, flattens out. The dependence of the plasticity on the surfactant concentration is also S-shaped, and the dependence of the relaxation time is exponential (Fig. 3b).

These phenomena can be explained as follows. At a PVA content of up to 5–7 wt %, the polymolecular sorption layer is formed incompletely. Hence, a change in the surfactant concentration strongly affects the structuring processes in the system, namely, formation of coagulation bonds between solid particles. Structuring of the polymer solution starts to affect the structural-mechanical properties of the molding blends at PVA concentrations higher than 7 wt %, i.e., when the surfactant molecules cease to be sorbed on zinc oxide particles. Clearly, the influence of these

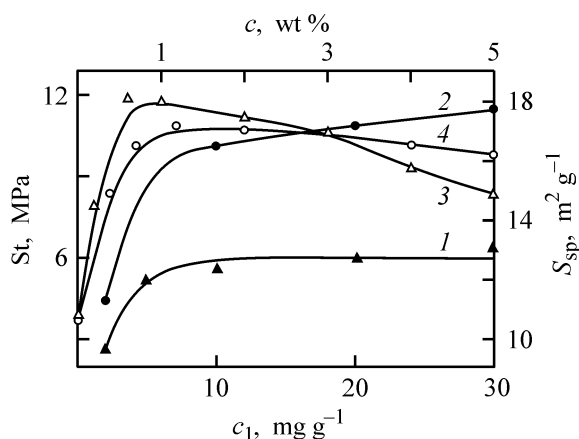
structures on  $P_{k1}$  and  $\eta_1$  and hence on  $Pl$  and  $\Theta$  is lower than that of coagulation bonds between ZnO particles.

It should be noted that the total power  $N$  consumed for flow of the blends remains unchanged, and the power for degradation of the coagulation structure  $\Delta N$  increases by a factor of 2 (see table) with increasing PVA content. At the same time, the constant  $\eta_0$  decreases by a factor of 2, and the flow index  $n$  only slightly varies in the range 0.4–0.5. It should be noted that the rheological parameters also noticeably change at the PVA concentrations lower than 7 wt %. This is also due to the processes occurring in sorption of PVA molecules on ZnO particles. These processes have the strongest effect on the structure of the system, i.e., on  $\Delta N$  and  $\eta_0$ .

The mechanical strength and specific surface area of extruded articles strongly depend on the concentration and type of a surfactant. In our case, the strength of ZnO granules grows as the polymer concentration increases to 15–20 mg g<sup>-1</sup> (Fig. 4). The strength is the highest at the surfactant concentration of about 5 wt %. Our calculations show that the sorbent prepared under these conditions contains about 1.5–2.0 wt % surfactant. As can be seen from Fig. 1, this surfactant content is close to the maximum sorption. Hence, the mechanical strength of the extrudate will be the highest when the surface of solid particles is completely covered with a polymer layer. It should be noted that the mechanical strength of the granules increases at high concentration of the polymeric adsorbate (PVA) in the extrudate.

The specific surface area of molded zinc oxide prepared from 0.5–0.2 wt % solutions of CMC or PVA increases from 12 to 18 m<sup>2</sup> g<sup>-1</sup> (Fig. 4). At surfactant concentrations higher than 2 wt %, the specific surface area does not exceed 13–14 m<sup>2</sup> g<sup>-1</sup> due to three-dimensional structuring of the polymer in the solution, which prevents dispersion and stirring of the system.

It is known that the properties of a ready extrudate depend not only on the physicochemical properties of the initial composition, but also on the extrusion conditions. We have shown previously [10] that the mechanical strength of extruded granules depends on the molding rate. These dependences may pass both through maxima and through minima. One of parameters depending both on the properties of the molding blend and on the extrusion conditions is the Weissenberg criterion [11].



**Fig. 4.** (1, 2) Mechanical strength  $St$  and (3, 4) specific surface area  $S_{sp}$  of granulated sulfur adsorbent based on ZnO vs. the polymer content  $c$  and  $c_1$ . Surfactant: (1, 3) CMC and (2, 4) PVA.

The dependences of the mechanical strength and pore volume of ZnO sorbent on the Weissenberg criterion  $We$  are shown in Fig. 5. The dependence of the mechanical strength passes through a maximum, and the dependence of the pore volume, through a minimum. All the extrema appear at Weissenberg criteria of 200–300. The opposite course of these dependences is due to the fact that the strength of granules decreases with an increase in their porosity, all other conditions being the same.

Let us consider the factors responsible for appearance of the extrema. The relaxation time  $\Theta$  entering into the equation for calculation of  $We$  characterizes the development of the plastic strain [6, 11]. When the extrusion is slow and, hence,  $We$  is low (up to 200), the plastic strain develops to a high extent and the sample is not ruptured. To increase the extrusion rate, the molding stress should be increased, which results in densification of the sample and, hence, in shortening of the interparticle distance. As result, the mechanical strength of the granules increases and their pore volume decreases.

At a higher extrusion rate, the strain of the molding charge at the extruder outlet is incomplete and fluctuations appear. The sorbent prepared under these conditions has a defective structure; its mechanical strength decreases and pore volume increases.

One more feature of the dependence of the pore volume on  $We$  is a strong influence of the extrusion rate on the volume of open pores (Fig. 5).

The total porosity strongly depends on the volume of open pores. This is probably due to the fact that, in accordance with Poiseuille's law, the flow rate of the molding charge at the center of a channel is substantially higher than that in the near-wall layer [7]. Hence, the defectiveness of the structure at the center of granules, where the flow rate is the highest, will be more pronounced than that at the periphery. The porosity of peripheral layers largely determines the volume of open pores.

Thus, PVA is a more effective surfactant, since it strengthens the interparticle interactions, whereas CMC promotes structuring of the dispersion medium. This is confirmed by the change in all the rheological properties of the suspensions. The influence of PVA on the rheological behavior of the ZnO suspension is stronger than that exerted by CMC.

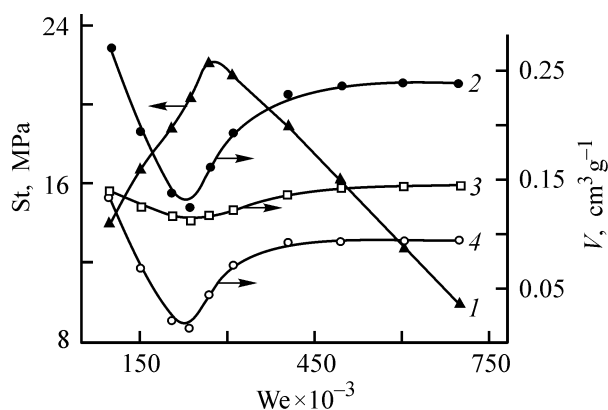


Fig. 5. (1) Mechanical strength  $St$  and (2) total pore volume, (3) volume of closed pores, and (4) volume of open pores,  $V$ , of ZnO sorbent vs. the Weissenberg criterion  $We$ .

## CONCLUSIONS

(1) The curves of sorption of the surfactants from aqueous solutions on zinc oxide have maxima at a surfactant concentration of 1–2 wt %. This is due to structuring of the surfactants in the solution.

(2) The correlations between the surfactant sorption on ZnO particles and the structural-mechanical and rheological parameters of the molding formulation were revealed, as well as the correlation between the mechanical strength and the specific surface area of granules. All these phenomena are caused, on the one hand, by formation of sorption layer on the particle surface and, on the other, by structuring of the polymer solutions.

(3) The mechanical strength and pore structure of the granules are determined both by the properties of the molding blends and by the extrusion conditions. These parameters are related by the Weissenberg criterion. Hence, if the properties of a molding blend are known, the granules with required strength and porosity can be prepared by varying the extrusion rate and the die size.

## REFERENCES

1. Ganz, S.N., *Ochistka promyshlennykh gazov* (Treatment of Industrial Gases), Dnepropetrovsk: Promin', 1977.
2. *Physical and Chemical Aspects of Adsorbents and Catalysts*, Linsen, B.G., Ed., London: Academic, 1970.
3. Uzugi, K. and Tamia, H., *J. Chem. Soc. Japan*, 1965, vol. 86, no. 7, pp. 699–704.
4. Shirokov, Yu.G., Ul'in, A.P., Kirillov, I.P., *et al.*, *Zh. Prikl. Khim.*, 1979, vol. 52, no. 6, pp. 1228–1233.

5. Il'in, A.P., Shirokov, Yu.G., and Titel'man, L.I., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1984, vol. 27, issue 1, pp. 78–80.
6. Kruglitskii, N.N., *Osnovy fizikokhimicheskoi mekhaniki* (Foundations of Physicochemical Mechanics), Kiev: Vishcha Skola, 1975, part 1.
7. Prokof'ev, V.Yu., Il'in, A.P., Shirokov, Yu.G., and Yurchenko, E.N., *Zh. Prikl. Khim.*, 1995, vol. 68, no. 4, pp. 613–618.
8. Shchukin, E.D., Bessonov, A.I., and Paranskii, S.A., *Mekhanicheskie ispytaniya katalizatorov i sorbentov* (Mechanical Tests of Catalysts and Sorbents), Moscow: Nauka, 1971.
9. Buyanova, N.E., *Opredelenie udel'noi poverkhnosti katalizatorov* (Determination of the Specific Surface Area of Catalysts), Moscow: Khimiya, 1973.
10. Prokof'ev, V.Yu., Il'in, A.P., Shirokov, Yu.G., *et al.*, *Zh. Prikl. Khim.*, 1996, vol. 69, no. 10, pp. 1685–1690.
11. Il'in, A.P. and Prokof'ev, V.Yu., *Katal. Prom.*, 2002, no. 6, pp. 45–51.