THE EFFECT OF ETHYL XANTHOGENATE ON THE ELECTROKINETIC PROPERTIES AND SURFACE FREE ENERGY OF GALENA

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Received October 1, 1991
Accepted December 30, 1991

An experimental investigation is described on the zeta potential and surface free energy of the system galena/potassium ethyl xanthogenate. The behavior of the zeta potential of galena with different electrolytes and with the pH is also showed. The potential of zero charge of galena was found to be at pH 4.8. The negative zeta potential, obtained from electrophoretic measurements of the galena/ethyl xanthogenate system, increased with the increasing concentration of this compound in solution. This shows that the adsorption of the ethyl xanthogenate ion onto galena is the responsible of the above mentioned increase of the zeta potential of the system. The uptake of $-S^-$ group of ethyl xanthogenate by the oxidized products existing on the galena surface could be the cause of the increase in the negative electric charge of the interface. The surface free energy of galena and their dispersion and nondispersion components have been obtained from the contact angle measurements of both water and diiodomethane liquid drops, onto galena previously treated with different concentrations of ethyl xanthogenate in solution. While the dispersion component of the surface free energy of galena increases weakly with the concentration of ethyl xanthogenate in solution, the nondispersion component has a significant decrease with it. Therefore, the increasing hydrophobicity of the galena can be correlated with the increase in the zeta potential of this mineral, which is due to the adsorption of the collector.

The study of the adsorption of surfactants on the surface of different minerals is of a great interest for improving the technology of flotation processes of these systems[1]. The behavior of both the zeta potential and the surface free energy of the system provides a significant aid for the knowledge of the complex physicochemical processes that occur at the interface mineral/surfactant[2 – 4], closely related to the flotation process.

The interaction galena/ethyl xanthogenate has been widely studied. However, there is still controversy on the interaction mechanism of xanthates with sulfide minerals[5], and

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particularly with lead glance[6], due to both the oxidation of galena surface and the little stability of the ethyl xanthogenate in aqueous solution[7,8].

The adsorption of the collectors onto galena surface is correlated with the changes in flotation activity of the mineral. However, these results give no information on the changes of surface free energy, which surely took place during the collector adsorption[9]. On the other hand, these changes could be correlated with the behavior of the zeta potential of the system.

Considering the interest of the study of the above mentioned aspects, the purpose of the present paper is the determination of the zeta potential of galena/ethyl xanthogenate system and the correlation of this parameter with the changes of surface free energy and the hydrophobicity of this mineral, that provides their flotation activity.

Firstly, it was carried out the electrokinetic characterization of bare galena in aqueous solutions of different electrolytes, i.e. KCl, $CaCl_2$, $PbCl_2$ and $Th(NO_3)_4$, as well as the effect of pH and the pzc of the mineral. The zeta potential was determined by means of the streaming potential method. Then, the zeta potential of the system galena/ethyl xanthogenate was obtained by means of electrophoretic measurements. The polar and dispersion components of the surface free energy of galena were determined from contact angle measurements of selected liquids on galena surface. With this method, the effect of the collector on the surface free energy of galena and their relationship with the hydrophobicity of the mineral can be evaluated.

EXPERIMENTAL

Galena samples of high purity (PbS content higher than 95%), were selected by hand from Linares (Spain), and powdered in a mortar of agate. Then, they were sieved with the help of a vibrator and the fractions of particles between 200 and 500 μm and smaller than 30 μm were collected. The obtained samples were stored under inert atmosphere of N_2. The fraction between 200 and 500 μm was used for the streaming potential measurements and that below 30 μm was used for the microelectrophoretic measurements.

The electrolytes used in the experiments were KCl, $CaCl_2$, $PbCl_2$ and $Th(NO_3)_4$ of a.r. grade from Merck. The potassium ethyl xanthogenate was of a.r. grade from Fluka Chemika (Switzerland) and was used without further purification.

Water with a conductivity of ca 10^{-6} Ω^{-1} cm^{-1} was used for preparing the different solutions. Porous plugs with the same galena content and equal thickness (2.90 cm) were used in the streaming potential experiments. The streaming cell and streaming potential measurement procedure have been described elsewhere[10].

The zeta potential ζ was calculated from the Helmholtz–Smoluchowski equation

$$\zeta = \eta\, C\, \Delta\Phi_S / \varepsilon\, R\, \Delta P\,, \qquad (1)$$

where C is the streaming cell constant evaluated through streaming potential experiments conducted with 10^{-1} mol l^{-1} KCl solutions at the same temperature, at which the streaming experiments were carried out, R is the electrical resistance of the galena plug, ε and η are, respectively, the dielectric permittivity and the absolute viscosity of the permeant, $\Delta\Phi_S$ is the streaming potential generated by the applied streaming pressure ΔP.

The microelectrophoretic measurements have been carried out by means of a Malvern Zetasizer/2c. The samples of particles of galena smaller than 30 μm were conditioned, before the electrokinetic experiments, with different solutions of potassium ethyl xanthogenate for 24 h, this time being sufficient to attain equilibrium. Only the supernatant, with particles of galena with size between 0.15 and 1 μm, was used. The zeta potential was then calculated from Eq. (2)

$$\zeta = 4 \pi \eta \mu / \varepsilon \, , \qquad (2)$$

where μ is the electrophoretic mobility.

For contact angle measurements, galena plates were obtained from selected pieces after cleavage by the exfoliation planes. The surface free energy of galena was determined from contact angle measurements with diiodomethane and water drops onto the uncovered galena plates and afterwards with galena plates contacted previously with ethyl xanthogenate in solution. The contact angle measurements were carried out with a Ramé-Hart, Inc. goniometer, model 100-00, the device having a thermosttated recepient which allows us to use saturated liquid vapor during the experiments. The temperature was maintained constant at 20 ± 1 °C. The contant angles measured with this method are within ±2 degrees.

RESULTS AND DISCUSSION

Electrokinetic Characterization of Galena

The streaming potential experiments were conducted with plugs of galena with a definite conformation. No significant differences were detected between the values of streaming potential $(\Delta\Phi_S)_{I=0}$ obtained for each direction of flow. Thus, the systems can be considered isotropic. Figure 1 shows the streaming potential measured as a function of the applied pressure difference for KCl, $CaCl_2$, $PbCl_2$ and $Th(NO_3)_4$ electrolytes in solution at different concentrations and at constant temperature. The linearity of the $(\Delta\Phi_S)_{I=0} - \Delta P$ plots indicates that the flow of solution through the plug is laminar and there is no turbulence in the range of applied pressured employed.

The zeta potential values of galena in aqueous solutions of KCl, $CaCl_2$, $PbCl_2$ and $Th(NO_3)_4$, respectively, are plotted in Fig. 2 as a function of the electrolyte concentration at constant temperature. It can be seen that, while the electrolytes of single and bivalent cations, KCl, and $CaCl_2$, are not surface activators, the $PbCl_2$ and $Th(NO_3)_4$, which display specific adsorption, reverse the sign of ζ for 10^{-4} mol l^{-1} in the case of $PbCl_2$ and in the case of $Th(NO_3)_4$ the sign is positive in the whole range of concentration. These results agree with the Shulze–Hardy rule. The slight increase of ζ in the case of KCl and $CaCl_2$ in the higher range of concentration can be attributed to a specific adsorption of coions (Cl^-) in these conditions. The increase of positive zeta potential in the case of solutions of lead and thorium ions, is mainly due to the adsorption in the Stern plane of the double layer of these ions. Hence, the presence of lead and thorium ions into the flotation bath should have a strong influence on the adsorption of ethyl xanthogenate onto the surface of galena. This activator effect in the case of lead salts on the mechanism of adsorption of collector on the surface of the mineral has been described by other authors[11].

Figure 3 shows the dependence of the electrokinetic potential on the pH of deionized water used as permeant. The potential of zero charge (pzc) obtained for galena is at pH 4.8. Yarar and Kitchener[12] obtained a pzc between pH 2 and 3. This shows that the physicochemical characteristics of galena and the grade of purity of mineral have a significant influence of pzc. At both alkaline and low pH, ζ is governed by the preferential adsorption of OH^- and H^+ ions, respectively, in the electrical double layer, while at pH in the range 5 – 8 it appears an extended plateau with a constant zeta potential value of –3 mV.

Zeta Potential of Galena/Ethyl Xanthogenate System

The zeta potential values of galena/ethyl xanthogenate ion system, obtained from electrophoretic mobility measurements, are plotted in Fig. 4 as a function of concentration of this compound at constant temperature. All values of zeta potential are negative and a marked increase in $|\zeta|$ with the increase in concentration of ethyl xanthogenate in solution can be observed. These results reveal that the uptake by galena of ethyl xanthogenate ion, charged negatively, could be the cause of the strong increase in ζ with the concentration of potassium ethyl xanthogenate in solution. This sorption of ethyl xanthogenate could be carried out on the oxidized products originated on the galena surface, being the ionized $-S^-$ group of ethyl xanthogenate uptaked by the galena, probably, the responsible of the strong increase of the charge onto the surface of mineral[5].

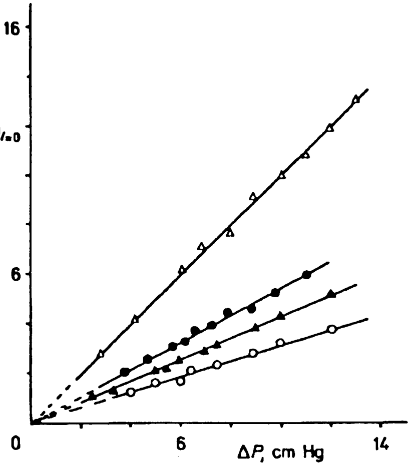

FIG. 1

Streaming potential $(\Delta\Phi_S)_{l=0}$ dependence on the applied pressure difference ΔP: ● 5 . 10^{-6} M KCl; ○ 10^{-6} M $CaCl_2$; ▲ 5 . 10^{-4} M $PbCl_2$; Λ 10^{-5} M $Th(NO_3)_4$

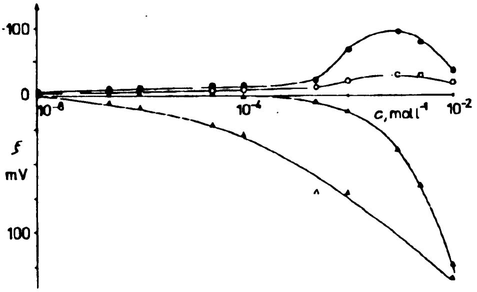

FIG. 2

Dependence of zeta potential of galena on the electrolyte concentration: ● KCl; ○ $CaCl_2$; ▲ $PbCl_2$; Λ $Th(NO_3)_4$

Surface Free Energy of Galena/Ethyl Xanthogenate System

The work of adhesion W_a of a liquid onto a solid can be expressed by the equation

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} , \tag{3}$$

where γ_S is the surface free energy of the solid, γ_L the surface tension of liquid and γ_{SL} the free energy at the interface liquid–solid. The energy γ_S can be obtained by indirect methods. Most frequently, contact angle measurements are used for this purpose, being the Young's equation which gives the adequate relationship:

$$\gamma_L \cos \Theta = \gamma_S - \gamma_{SL} - \pi_e , \tag{4}$$

where π_e is the film pressure, i.e., the decrease in the surface free energy of the solid due to the vapor phase adsorbed on the solid surface.

If $\gamma_S < \gamma_L$, then π_e is practically negligible. Therefore,

$$W_a = \gamma_L (1 + \cos \Theta). \tag{5}$$

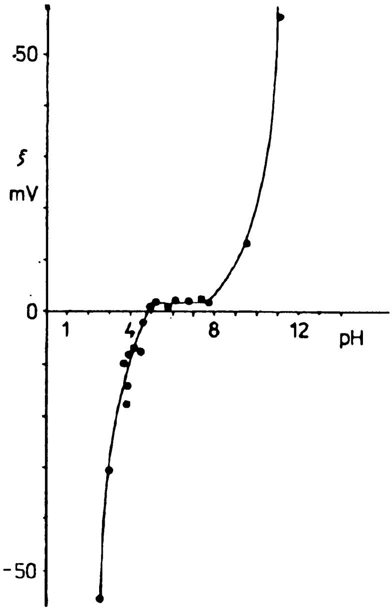

FIG. 3
Dependence of zeta potential of galena on pH

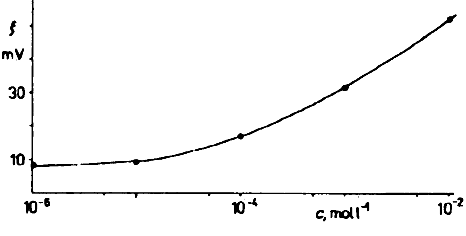

FIG. 4
Dependence of zeta potential of galena on the concentration of ethyl xanthogenate ion in solution

According to Fowkes[13], the surface free energy of a solid or a liquid can be expressed by the following form:

$$\gamma = \gamma^{d} + \gamma^{n} , \tag{6}$$

where γ^d and γ^n are, respectively, the dispersion and nondispersion (sometimes called "polar") components of the surface free energy.

Expressing γ_{SL} as a function of these two components (geometric–geometric mean criterium, see refs [13 – 16]), Eq. (*4*) may be written in the form:

$$\gamma_L \cos \Theta = -\gamma_L + 2\,(\gamma_S^d\,\gamma_L^d)^{1/2} + 2\,(\gamma_S^n\,\gamma_L^n)^{1/2} , \tag{7}$$

where it has been assumed that $\pi_e = 0$.

If Θ_1 and Θ_2 meant the contact angles measured with liquids L1 and L2 onto the surface, it can be obtained from Eq. (*7*) for both liquids[9]:

$$(\gamma_S^d)^{1/2} = \frac{\gamma_{L1}\,(\cos \Theta_1 + 1) - 2\,\gamma_{L2}\,(\gamma_{L1}^n/\gamma_{L2}^n)^{1/2}\,(\cos \Theta_2 + 1)}{2\,[(\gamma_{L1}^d)^{1/2} - (\gamma_{L1}^n/\gamma_{L2}^n)^{1/2}]} , \tag{8}$$

where the subscripts L1 and L2 refer to water and diiodomethane, respectively.

The value of γ_S can be obtained from Eqs (*6*) and (*8*), using literature values of surface tension of the two liquids (Table I).

The free energy of galena and their dispersion and nondispersion components have been obtained from the Eqs (*6*) – (*8*) by means of the contact angle measurements of both water and diiodomethane liquids, separately, onto the mineral surface. The mean values of γ_S, γ_S^n and γ_S^d for the galena are also shown in Table II, together with the standard deviation in each case.

From Table II it can be observed that the surface free energy of galena is less than surface tension of both water and diiodomethane. Therefore, the hypothesis that $\pi_e \cong 0$ is reasonably well supported.

To investigate the effect of the ethyl xanthogenate ion onto the surface free energy of galena, the mineral was covered with different amounts of this collector.

TABLE I
Values of dispersion (γ_L^d) and nondispersion (γ_L^n) components of liquids surface tension (γ_L) taken from literature

Compound	γ^n mJ m^{-2}	γ^d mJ m^{-2}	γ mJ m^{-2}	Ref.
Water	51.0	21.8	72.8	17
Diiodomethane	0.38	50.42	50.8	17

Figure 5 shows the contact angle values obtained for water and diiodomethane, respectively, onto galena treated with ethyl xanthogenate ion, as a function of the concentration of this compounds in solution. It can be deduced from Figs 4 and 5 that while the zeta potential of the system galena/ethyl xanthogenate increases notably with the concentration of ethyl xanthogenate in solution, the contact angle of water increases weakly, this being in correspondence (Fig. 5) with the strong decrease in Θ by the diiodomethane with the increasing concentration of ethyl xanthogenate in solution. This suggests a correlation between the behavior of the zeta potential of the system and the increase in the hydrophobicity of the mineral, which is due to the adsorption of ethyl xanthogenate ion onto the galena surface.

In Table II, the surface free energy of galena as well as its components is given as a function of the initial concentration of ethyl xanthogenate in solution. It can be seen in this Table that while the dispersion component of surface free energy increases slightly

TABLE II
Values of surface free energy of galena as well as its components as a function of the initial concentration of ethyl xanthogenate in solution

Concentration mol l^{-1}	γ_S^d mJ m^{-2}	γ_S^n mJ m^{-2}	γ_S mJ m^{-2}
0	29.0 ± 0.5	7.9 ± 0.5	36.9 ± 1
10^{-6}	41.0 ± 0.5	10.5 ± 0.5	51.5 ± 1
10^{-5}	45.0 ± 0.5	7.0 ± 0.5	52.0 ± 1
10^{-4}	46.0 ± 0.5	4.0 ± 0.5	50.0 ± 1
10^{-3}	48.0 ± 0.5	2.5 ± 0.5	50.5 ± 1
10^{-2}	48.0 ± 0.5	1.0 ± 0.5	49.0 ± 1

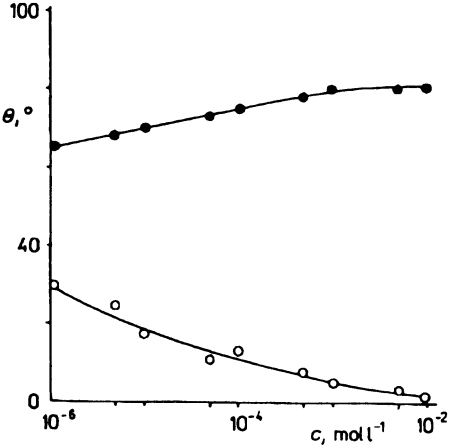

FIG. 5
Dependence of the contact angle Θ for galena treated with ethyl xanthogenate ion as a function on the concentration of this compound in solution: ● water; ○ diiodomethane

with concentration, the nondispersion component decreases significantly with the increase of concentration of ethyl xanthogenate in solution. This is in agreement with the increasing hydrophobicity of the galena due to the adsorption of the collector onto the mineral surface.

On the other hand, the surface free energy of galena treated with ethyl xanthogenate has a nearly constant value of ca 50.6 mJ m^{-2}, being therefore not depending on the concentration of the collector in solution. The above mentioned value of γ is higher than the value of γ of ca 36.9 mJ m^{-2}, obtained for the untreated galena. This shows that the physicochemical properties of the mineral surface suffer a strong modification with the ethyl xanthogenate adsorbed onto the galena surface.

The notable decrease in the polar component of the surface free energy of galena with the increasing concentration of ethyl xanthogenate shown in Table II corresponds with the increase in the hydrophobicity of the mineral. In this conditions, the flotation recovery of the galena should be the optimum.

This work is part of a research program on electrokinetic and surface free energy properties of galena supported by the Excma. Diputación Provincial of Jaén (Spain). This support is hereby gratefully acknowledged.

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