

Article

Application of Depletion Attraction in Mineral Flotation: II. Effects of Depletant Concentration

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Abstract: Along with the accompanying theory article, we experimentally investigate the effect of the depletion attraction force on the flotation of malachite. While varying the concentration of the depletion agent (polyethylene glycol), three different systems are studied: pure malachite, pure silica and a 1:1 mass ratio of malachite and silica binary system. We find that the recovery increases significantly as the concentration of the depletion reagents increases for all three systems. However, the recovery suddenly decreases in a certain concentration range, which corresponds to the onset of the decreased surface tension when high concentrations of the depletion agent are used. The decreased surface tension of the air/water interface suggests that the recovery rate is lowered due to the adsorption of the depletion agent to the bubble surface, acting as a polymer brush. We also perform experiments in the presence of a small amount of a collector, sodium oleate. An extremely small amount of the collector (10^{-10} – 10^{-5} M) leads to the increase in the overall recovery, which eventually reaches nearly 100 percent. Nevertheless, the grade worsens as the depletant provides the force to silica particles as well as target malachite particles.

Keywords: flotation; malachite; silica; binary mixture; depletion attraction; PEG

1. Introduction

In the field of mineral processing, froth flotation has been the most widely used technique to improve the quality of low-grade minerals [1–6]. During this process, a collector is used to impart hydrophobicity to desired mineral particles; these hydrophobic particles are then better attached onto the surface of a bubble, leaving undesired particles in the bulk solution. Among these collectors is xanthate, which is a typical collector used for sulfide minerals and for oxide minerals after the sulfidization process [7–10]. Although this collector has been exploited extensively over the last several decades, a reduction in its use is desired because it is environmentally harmful [11–13]. Accordingly, several groups have attempted to find environmentally friendly collectors [14–19]. In this regard, collector-less flotation would be the best option if shown to be feasible. In fact, attempts have been made to separate particles without a collector [10,20–23]. For example, several groups have investigated the flotation behavior of sulfide minerals without collectors (e.g., galena (PbS), pyrite (FeS₂), arsenopyrite

(FeAsS), chalcopyrite (CuFeS_2), chalcocite (Cu_2S) and sphalerite ($(\text{Zn,Fe})\text{S}$) [10,20,23–25]. These studies showed that sulfide minerals could provide better floatability in certain oxidation and reduction potential ranges by adjusting the solution pH, at which elemental sulfur forms a hydrophobic surface of sulfide minerals. However, these studies exploited only certain properties of sulfide minerals and are thus limited to them. Furthermore, these techniques still require a change of the surface properties in the same ways a collector does. Hence, considerable amounts of chemical reagents are required to achieve suitable pHs.

We suggest a route that enhances the flotation efficiency by physically changing the interaction between a bubble and a mineral particle without changing the surface chemistry. Interaction between a bubble and a particle is crucial to enhance the floatability of a particle, as it is a critical step in the flotation process. However, it remains difficult to explain the exact mechanism of such an attachment process, as it involves complicated multiphase components (liquid-air-solid) in the presence of a rapid flow. Accordingly, many researchers have focused on bubble-particle interactions rather than considering the entire complicated process [5,26–31].

Our strategy to change the bubble-particle interaction is termed “depletion attraction.” Depletion attraction is an osmotic force exerted on larger objects (e.g., colloids and droplets) by smaller objects (small molecules, polymers and surfactant micelles) [32–35]. This attractive force is employed only when the distance between two larger objects is closer than the size of the depletant, where the symmetry of the osmotic pressure is broken. Otherwise, osmotic force is isotropic and therefore does not affect the interaction between larger objects, as described in Figure 1. In terms of flotation, we can regard a mineral particle and a bubble as two large objects, with small polymer molecules added as small objects. By adding polymer molecules, also termed as a depletion agent or a depletant, we can increase the attractive interaction between a mineral particle and a bubble.

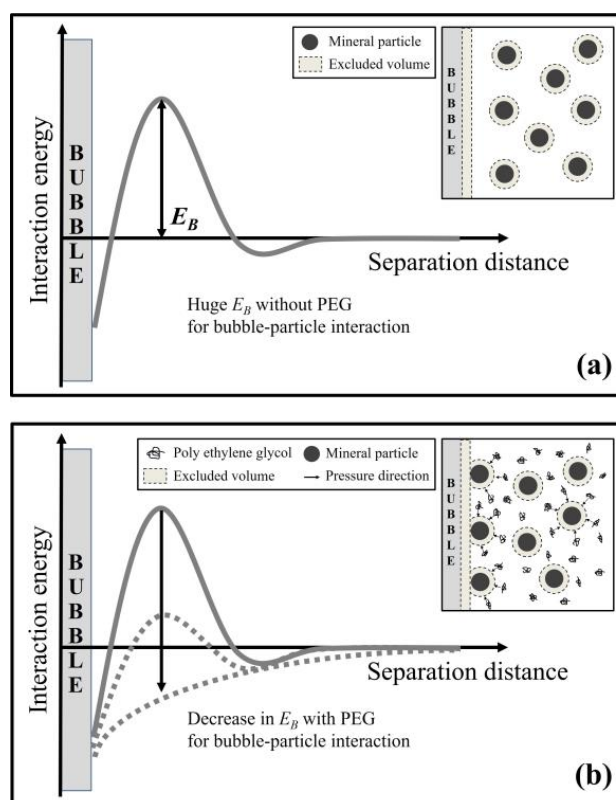


Figure 1. Schematic illustration of the depletion attraction between a bubble and minerals. The bubble-particle interaction has a huge energy barrier without a depletant, making it difficult for particles to attach the bubble surface (a). On the other hand, depletion attraction pushes the particles to the bubble surface (b).

In this study, we experimentally explore the effects of depletion agents on mineral flotation. Two hydrophilic minerals were considered for the present work: first, malachite was selected as a valuable mineral because this mineral has been actively studied in our group [5,36–38]. Second, silica is normally considered as a gangue mineral for metallic mineral flotation, thus we chose this for a gangue mineral. Using polyethylene glycol (PEG), a biocompatible polymer, as a depletion agent, pure malachite and silica particles are floated. The flotation tests were conducted at pH 7 where the bubble-particle interaction is expected to be electrostatically favorable for malachite [5,38] while electrostatically unfavorable for silica [39,40]. We hypothesized that this control would vary the attachment probability of each mineral in the presence of depletants to different degree. Malachite particle experiments show increased flotation efficiency with an increase in the concentration of PEG, whereas the floatability of silica particles increases only slightly. The flotation efficiency of malachite also increases significantly for the mixed system of malachite and silica. Furthermore, we study the effect of depletion attraction on the flotation of malachite in the presence of low concentrations of sodium oleate. The floatability becomes remarkably higher relative to that in the absence of PEG, eventually becoming close to 100 percent.

2. Materials and Methods

2.1. Samples and Reagents

In this study, malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$), considered to be a valuable mineral, was obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan). The malachite contained a minimum of 55% of Cu and 95% of CuCO_3 . Silica sand (99.5% purity, Sibelco Korea Co., Ltd., Nonsan, Korea) was used as a gangue mineral. For flotation experiments, the particle size of both malachite and silica was set using $-270 + 325$ mesh (45–53 μm , Tyler Standard). Polyethylene glycol (PEG) with an average molecular weight of 10,000 was obtained from Sigma-Aldrich (St. Louis, MO, USA) as a depletant and sodium oleate (SO) was purchased from Sigma-Aldrich as a collector for microflotation.

2.2. Characterization of the Samples

Surface Tension of PEG

In order to evaluate the change in the surface tension depending on the concentration of PEG during the flotation test, the surface tension was measured using a surface tension analyzer (DST60, SEO Co., Ltd., Suwon, Korea). In this study, we determined the surface tension through the Du Noüy ring method using a Pt ring [41]. The concentration of the PEG solution was fixed at 5×10^{-5} –30 wt %.

2.3. Flotation

2.3.1. Depletion Effects (Single Minerals of Silica and Malachite, Respectively and a Mixture of the Two)

The flotation efficiency values of silica and malachite individually and a mixture of these two minerals were investigated depending on the concentration of PEG (5×10^{-5} –5 wt %). Flotation experiments were carried out using a well-controlled and modified Hallimond tube [42]. The samples included malachite at 1 g, silica at 1 g and a mixture (malachite 0.5 g and silica 0.5 g), separated in a Hallimond tube with 150 mL of a PEG solution. The flotation conditions were characterized by a stirring rate of 340 rpm (PC-410D, Corning Life Sciences, Tewksbury, MA, USA) with 30 mL/min of nitrogen gas of 99.99% purity for 10 min. After flotation, the concentrate—which refers to the froth and tailing as a result of flotation—was dried in a dryer (J-IB2, Jicico Co., Ltd., Seoul, Korea) at 45 °C for one day to determine the floatability, recovery and grade. The floatability was calculated by the weight ratio of the concentrate to the total mineral and the recovery was estimated according to the weight ratio of the target mineral (silica or malachite) in the concentrate to the total mineral. The grade was determined by the weight ratio of the target mineral in the concentrate to the concentrate.

2.3.2. Added Collector with PEG in a Binary System

After fixing the concentration of PEG at 5×10^{-3} wt %, the flotation efficiency of the malachite and silica mixture was investigated as a function of the concentration of sodium oleate (SO). A mixture of malachite 0.5 g and silica 0.5 g as a sample was used. The concentration of SO was fixed at 10^{-10} – 10^{-5} M. Flotation was performed using a Hallimond tube with 30 mL/min of nitrogen gas and at an agitation speed of 340 rpm (PC-410D, Corning Life Sciences, Tewksbury, MA, USA) for 10 min, identical to the conditions used earlier. After flotation, the concentrate and tailing as a result of flotation were dried in a dryer (J-IB2, Jicico Co., Ltd., Seoul, Korea) at 45 °C for one day to determine the recovery and grade. The recovery and grade were calculated in the same manner as the flotation under depletion force without a collector.

2.4. Adsorption Experiments for PEG on Minerals

In order to examine whether or not PEG was adsorbed onto the mineral surface during the microflotation process, adsorption tests were performed using a spectrophotometer (HS-3300, Humas Co., Ltd., Daejeon, Korea). The adsorption test proceeded in the same manner as the flotation assessment, with 150 mL of PEG solution per 1 g of sample stirred for 10 min at a stirring speed of 340 rpm in a Hallimond tube. The supernatant of the suspension was then taken to measure the absorbance at 194 nm. The adsorption tests were conducted at least three times per sample.

2.5. Viscosity Measurement of PEG Solution

Rheological property of PEG solution was further examined by measuring solution viscosity with different PEG concentrations. Shear stress of PEG solution was measured as a function of shear rate using a Brookfield viscometer (DV2TCP, Brookfield AMETEK, Middleboro, MA, USA). The measurements were carried out at constant room temperature (~25 °C).

3. Results and Discussion

3.1. Flotation Results

3.1.1. Single Minerals of Silica and Malachite

The floatability measurements of each pure mineral, that is, malachite and silica particles, were taken first. Figure 2 shows the floatability as a function of the PEG concentration. In general, malachite shows higher floatability than silica over all concentrations of PEG; this results from the differences in an electrostatic force of malachite and silica to the bubble because identical depletion force is expected to be present for both minerals at the same PEG concentration [1]. For malachite particles, the natural floatability is roughly 20% and adding a small amount of PEG, 5×10^{-5} wt %, does not change this value. However, as the concentration of PEG was increased, the floatability increased sharply to approximately 80% at 5×10^{-3} wt %, appearing to remain constant at 5×10^{-2} wt %. The floatability of malachite suddenly dropped to 35%, which is still higher than the natural floatability. However, this represents a twofold decrease compared to lower concentrations. At an even higher concentration of 5 wt %, floatability increased to nearly 90%. Solutions with more than 5 wt % of PEG became too viscous; therefore, we conducted experiments only up to 5 wt %. On the other hand, the silica floatability remains very low for the entire concentration range of PEG, except at 5 wt %. It showed a similar trend, although it was not as clear as that of malachite due to the low floatability.

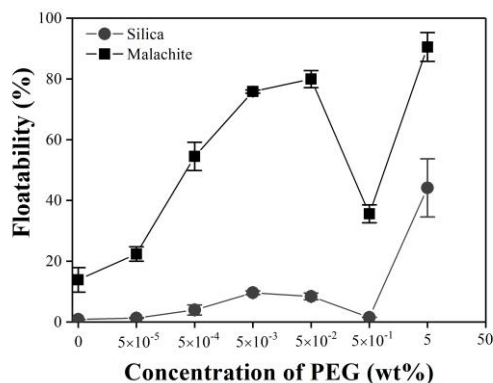


Figure 2. Microflotation measurements of malachite and silica for 10 min at pH 7 using a Hallimond tube. An increase in the concentration of PEG results in an increase in the overall floatability for both particles, although the floatability of malachite is far higher than that of silica. The floatability at the PEG concentration of 0 wt % means natural floatability.

To explain this interesting flotation behavior of both particles, we first performed the adsorption test of PEG onto the minerals, as it may act as a collector by being adsorbed on the mineral surface. In particular, we focused on higher concentrations of PEG because we could not measure the absorbance reliably at lower concentrations. The absorbance values of PEG suspension before and after adsorption tests are presented in Table 1. The trends obtained suggest that PEG adsorption onto malachite or silica surfaces is almost negligible. To further support the adsorption test results, we conducted a flotation test using the suspension with PEG-adsorbed malachite yet without non-adsorbed PEG in solution by filtering the mixture of malachite and PEG using a membrane filter with a pore size of 0.45 μm . The test was carried out at 5 wt % PEG concentration where greatest PEG adsorption is expected if any. The floatability of the filtered malachite (i.e., adsorbed PEG on the malachite) was determined to be about 20%; this value was similar to the natural floatability of malachite, clearly supporting the observations obtained from the adsorption tests. Moreover, contact angle values measured by a bubble captive method [38,43] show negligible changes with different PEG concentrations: 27.4°, 30.7° and 27.1° for no PEG, 5×10^{-5} wt % PEG and 5 wt % PEG. Accordingly, all of these test results are in agreement with the characteristics of PEG, which is a neutral polymer and known as a weakly-adsorbing polymer on the solid surface [44,45].

Table 1. UV-vis absorbance value of PEG suspension at 194 nm before and after adsorption tests onto the mineral surface.

Concentration of PEG (wt %)	Before Adsorption	After Adsorption onto Silica	After Adsorption onto Malachite
5×10^{-2}	0.093 ± 0.006	0.100 ± 0.012	0.101 ± 0.002
5×10^{-1}	0.743 ± 0.011	0.759 ± 0.003	0.773 ± 0.010
5	1.417 ± 0.068	1.432 ± 0.028	1.558 ± 0.125

Therefore, we turned our attention to the surface of a bubble and tested whether PEG could be adsorbed onto to the bubble surface. Although we used water-soluble polymers, their surface activities at the air/water interface were known and measured beforehand. Because the surface activity depends on many factors, such as the molecular weight and concentration [44,46], we measured our own 10⁴ Da PEG as a function of the concentration, as shown in Figure 3. For all concentrations of PEG, the surface activity was found to be very weak compared to a typical surfactant. The surface tension immediately decreased to 65 mN/m after an addition of 5×10^{-4} wt % of PEG, remaining constant at a concentration range of nearly three orders of magnitude, from 5×10^{-4} wt % to 5×10^{-1} wt %. Subsequently, it started to decrease slightly again from 5×10^{-1} wt %.

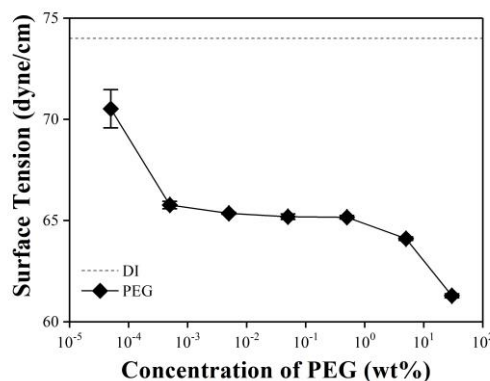


Figure 3. Measurements of the surface tension for various PEG concentrations at room temperature (~25 °C). These were averaged from at least three individual measurements.

This surface tension behavior of PEG was previously investigated. PEG is a nonionic polymer that is however soluble in water. Active materials on a soluble surface typically form a Gibbs monolayer. Generally, this monotonically reduces the surface tension, after which it becomes constant, which is the typical indication of micelle formation. However, previous studies showed that PEG does not form micelles [47]. One previous study showed that the constant surface tension of PEG at intermediate concentrations is likely to be a sublayer which is formed from excess molecules [46]. It was proven that a semi-dilute monolayer forms at the interface at these concentrations. Although the bubble interface accepts more PEG molecules with an increase in the concentration, the surface tension can remain constant due to the formation of a layer underneath the semi-dilute monolayer, hindering the adsorption of more PEG to bubble surface. This also explains why the increased floatability begins to slow down in this regime. The decreased surface tension after the constant regime was previously explained in terms of the solubility of PEG; this additional decrease in the surface tension depends on its solubility in water. This second decrease in the surface tension at higher PEG concentration indicates that PEG occupies a greater free interfacial area on bubbles, thus reducing the probability of successful particle attachment to a bubble surface. This onset of a decrease in the surface tension is in good agreement with the floatability measurements; the floatability decreases sharply at the point where the surface tension decreases again.

3.1.2. Mixture of Malachite and Silica

We successfully demonstrated that depletion attraction could result in high floatability of each mineral individually. We then tested a mixed system of both particles. Figure 4a shows the overall floatability at a 1 to 1 mass ratio of malachite and silica. It is immediately noticeable that the overall trend is nearly identical to those of the individual results. This is important because it proves that many factors, such as particle-particle interactions and flow effects, are negligible. Figure 4b shows the grade of the concentrate. The grade worsens as the concentration of PEG increases. In fact, the overall trend is precisely opposite to that noted with the floatability. The grade decreases slightly and then increases suddenly at the point the floatability becomes severely decreased. Eventually, it reaches its worst point at the highest concentration, because the depletion force at that point is large enough and allows both particles to be attached onto the bubble surface. This is likely to stem from the fact that stronger depletion attraction leads to a reduction of the energy barrier and thus to an increase in the attachment probability of silica particles.

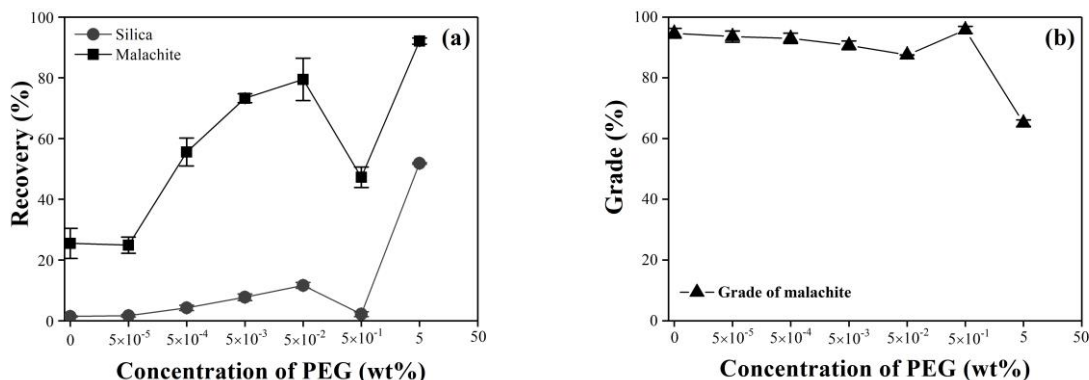


Figure 4. (a) Overall recovery of malachite (square) and silica (circle) from a mixture with a 1:1 mass ratio using a Hallimond tube for 10 min at pH 7 while increasing the PEG concentration and (b) grade of malachite (triangle).

3.2. Flotation with a Small Amount of Collector with PEG in a Binary System

In some cases, a considerable grade with very high recovery is required. For example, precious metal minerals must be fully recovered even with a slight grade improvement. To achieve this, we measured the floatability of malachite in a silica mixture in the presence of 10^{-10} – 10^{-5} M SO as a collector. It should be noted that this concentration range used can be considered extremely low because previous studies used at least 10^{-5} M SO for oxide mineral flotation [38,48–50]. Figure 5a shows the floatability of the silica and malachite mixture while varying the concentration of the anionic surfactant SO with a fixed concentration of 5×10^{-3} wt % of PEG. As expected, the recovery of malachite becomes significantly higher compared to the entire SO concentration in all cases. At a SO concentration of 10^{-5} M, malachite is almost completely recovered. For comparison, the same malachite/silica system is tested without PEG and is presented in Figure 5a. It should be noted that for concentrations of $<10^{-5}$ M, malachite showed natural floatability without PEG, indicating that lower concentrations of SO does not serve as a collector until it reaches to 10^{-5} M. Figure 5b shows the computed grade of this system. It decreases slightly as SO is added but remains at a constant (~80%) for the entire range of our SO concentrations.

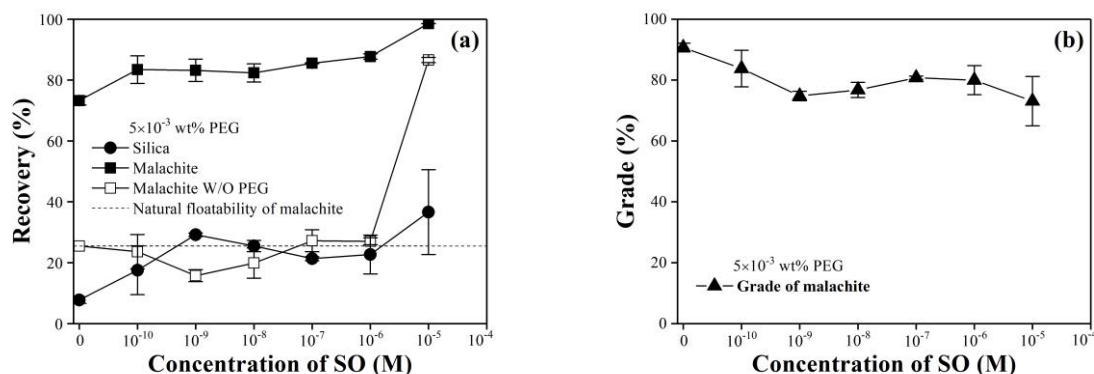


Figure 5. (a) Recovery measurements of malachite (square) and silica (circle) from a mixture with a 1:1 mass ratio at a fixed PEG concentration of 5×10^{-3} wt % while varying the concentration of SO and recovery of malachite (opened square) in the absence of PEG and (b) the grade of malachite (triangle).

3.3. Viscosity Effect of a High PEG Concentration and Polyelectrolytes as a Depletant

Our experimental findings may be well explained by the theoretical calculation from the accompanying article [1]. The bubble surface adsorption of depletion agents hinders mineral attachment and this occurs in a certain some PEG concentration range. One must be careful when PEG is used, as various molecular weights and different end groups can lead to distinctly different surface

activities [51]. However, we found that an increase of the PEG concentration to 5 wt % can overcome the energy barrier created by polymer brushes, implying that other mechanisms are involved in this process. Hence, we measured viscosity of PEG suspension as a function of PEG concentration and the results are presented in Figure 6. The result suggests that the abnormal increase in floatability at 5 wt % PEG is due to the sudden increase of solution viscosity, which in turn would provide longer residence time of bubbles and particles and eventually increase the probability of bubble-particle interaction. However, too high a concentration of PEG increases the viscosity of solution significantly, resulting in an unsuccessful process. This indicates that there exists an optimum concentration for this process.

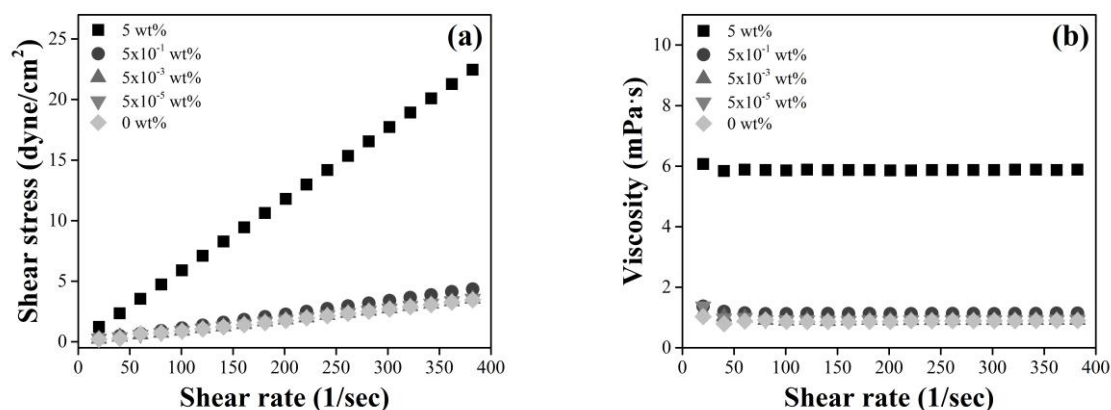


Figure 6. (a) Shear stress and (b) solution viscosity as a function of shear rate with different PEG concentrations at constant room temperature ($\sim 25^{\circ}\text{C}$). 5×10^{-5} wt % (inverted triangle), 5×10^{-3} wt % (triangle), 5×10^{-1} wt % (circle) and 5 wt % (square) PEG were used.

In principle, polymers that are not adsorbed onto a bubble surface and which are soluble in water simultaneously are available, such as polyelectrolytes. In addition, they may provide better results at high concentrations. Moreover, polyelectrolytes have a larger radius of gyration for the same molecular weight and their charges increase their effective size. This larger size would result in higher depletion force. However, polyelectrolytes can also stick to oppositely charged patches or particle surfaces. This would worsen the floatability, as it such action also acts as a polymer brush.

4. Conclusions

In conclusion, we experimentally investigated how depletion interaction affects mineral floatability. Malachite, silica and a mixture of these two minerals were each tested while varying the concentration of PEG as a depletion agent. We found that the floatability generally increases as PEG is added while the grade remains nearly identical, except at very high concentrations. However, our experiments revealed two important features: (1) because PEG itself is a surface-active material, it can be adsorbed onto a bubble surface, acting as a polymer brush. This polymer brush hampers the attachment of mineral particles, reducing the floatability. (2) If too much PEG is added, it aggravates the grade because the depletion interaction begins to facilitate the attachment of silica particles as well as malachite particles. Furthermore, we found that adding an extremely low amount of collector increases the floatability even more, allowing it ultimately to reach nearly 100 percent despite the fact that the grade decreases slightly. Flotation using depletion attraction with minimal use of a collector could be eco-friendly and it would be particularly useful in systems that require a high recovery rate with a considerable grade.

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