

## **ON USING EXCESS GIBBS ENERGY AS AN INDICATOR OF HYDROPHOBICITY IN THE FLOTATION PROCESS**

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**ABSTRACT.** It has been shown that the partial molar excess Gibbs energy ( $G^{\text{ex}}$ ) can be used as an indicator of hydrophobicity and hence contributes to explaining the behaviour of collectors in the recovery of minerals by flotation. This is because hydrophobicity of a mineral particle on which a collector is adsorbed is related to the fact that the alkyl chain associated with the collector behaves in the same way as any hydrocarbon would in a non-ideal mixture with water. Such mixtures are quantified thermodynamically by determining the activity coefficient of the hydrocarbon moiety of the collector and hence its  $G^{\text{ex}}$  in the mixture. The present paper is aimed at extending the above concepts in two different ways. Firstly, an investigation is made of the relationship between  $G^{\text{ex}}$  and contact angle and/or recovery for systems such as ionic liquids and aminothiophenols. Secondly, on the basis of the observation that increases in  $G^{\text{ex}}$  are indicative of increases in the hydrophobicity of the mineral particle-collector aggregate, a study was undertaken to examine, respectively, the effects of the presence of electrolytes or alcohols in the system, of pH and changing concentrations of the collector, on  $G^{\text{ex}}$  of the collector alkyl group and hence its hydrophobicity. In the first instance, the relationship between  $G^{\text{ex}}$  and contact angle and recovery is sustained. With respect to the latter, the absence of any correlation between  $G^{\text{ex}}$  and recoveries supported the proposition that the major effect of electrolytes and added alcohols is rather on particle – bubble attachment. Similarly, it is also indicated that since the change in  $G^{\text{ex}}$  is minimal when collector concentration or pulp temperature is increased these changes do not significantly affect the hydrophobicity of the collector-mineral particle and hence also the recovery in a microflotation.

**Key words:** hydrophobicity, partial molar excess Gibbs energy, reagents, flotation.

### **Introduction**

As is well known the main purpose of using a collector in the flotation of ores is to render the mineral particles which are to be recovered hydrophobically. Classical contact angle has been used to indicate hydrophobicity and there is voluminous literature on the measurement of contact angles as well as the relationship between contact angle and recovery (e.g., Fuerstenau et al., 1957; Bogdanov, 1957). However, it has been pointed out (Nagaraj and Ravishanker, 2007) that although contact angles in single mineral systems have been correlated with mineral flotation, they are poor predictors of flotation performance in real systems with complex mineralogy. There have also been attempts to use the concept of the hydrophilic-lipophilic balance (HLB) number to characterise the hydrophobicity imparted by reagents (e.g., Laskowski, 2003; Pugh, 2007; Zhang et al., 2012). The HLB number represents an empirical numerical correlation of the emulsifying and solubilising properties of different surface-active agents (Davies, 1957). However, in its original context the HLB number was an early attempt to show how the molecular structure is related to hydrophobicity. Modern thermodynamics is now far advanced in this regard through the determination of the activity coefficient or  $G^{\text{ex}}$  as the more appropriate way in which to define the behaviour of molecules in a non-ideal solution. In that regard the hydrocarbon associated with the collector adsorbed onto the mineral particle in a pulp and its water environment represents a classical non-ideal solution. Corin and O'Connor (2014) showed that using the concept of excess Gibbs free energy it was possible to predict the behaviour of frothers/surfactants in multi-component mixtures of different concentrations and is thus arguably a more robust method of characterising the hydrophilic-lipophilic behaviour of frothers than the HLB number. The excess Gibbs energy related well to the HLB number but has the added advantage of showing the effects of different concentrations of the

surfactant in water and other multi-component systems as well as, if necessary, temperature effects. Harris and O'Connor (2017) have shown how that there is generally a strong linear relationship between the excess Gibbs energy of collectors with different alkyl chain lengths and frothers with different alkyl chain lengths and bubble size, surface tension or froth behaviour. This is indicative of the key role which the non-polar group of these reagents plays in determining the changes which occur when using reagents of different alkyl chain lengths. Since the theory of the role of the alkyl chain is related to the formation of hemi-micelles those results are also proposed to provide quantitative thermodynamic confirmation of the role of hemi-micelles in the determination of the indicated flotation parameters. In a further extension of these investigations, O'Connor (2021), based on the assumption that flotation recovery in a microflotation cell is a good indicator of the hydrophobicity of a mineral particle since it simply measures the extent to which a particle is able to attach to a bubble sufficiently strongly to be able to report to the launder, showed that the behaviour of collectors with different alkyl chain lengths had a strong positive linear relationship between partial molar excess Gibbs energy of the alkyl moiety of the collector and the flotation recovery and the contact angle thus confirming that the partial molar excess Gibbs energy of the alkyl chain is indicative of the force driving the mineral particle to remove itself from the aqueous (water) to the gas (bubble) phase.

The present paper further interrogates the hypothesis that it is the non-ideality of the hydrocarbon-water system, as indicated by the  $G^{\text{ex}}$  of the hydrocarbon moiety of the collector, which provides the driving force to transfer the mineral-collector particle aggregate from the water to the bubble and that the greater the value of the  $G^{\text{ex}}$  the greater is that driving force. Given that the hydrophobicity of the particle, especially in a microflotation cell, is reflected in its recovery there should be a robust relationship between  $G^{\text{ex}}$  and recovery. In

particular, ionic liquids and aminothiophenols were investigated. This paper has also investigated the extent to which factors such as pH, presence of other species such as electrolytes or alcohols in the water, changes in concentration and pulp temperature, affect the  $G^{\text{ex}}$  and hence whether these changes can be used to interpret previously reported results, where available, on the influence these factors have on flotation recoveries.

## Methods to estimate activity coefficients and partial molar excess Gibbs energy

As indicated above the hydrocarbon associated with a collector molecule adsorbed onto a mineral particle when located in an aqueous environment represents a classical thermodynamically non-ideal solution. Such non-ideal solutions are quantified by determining the activity coefficient, and subsequently the  $G^{\text{ex}}$  of the hydrocarbon at a given molar concentration. The collector molecule is adsorbed onto the mineral particle via a chelating ligand such as typically represented by a thiol end group in the case of xanthates or an  $\text{NH}_2$  /  $\text{HS}$  group in the case of aminothiophenols. The hydrocarbon is associated with the collector in these instances via an oxygen atom and thus using the alcohol of the relevant alkyl group is an appropriate proxy for the behaviour of the hydrocarbon group of the collector.

There are many methods described in the literature to estimate activity coefficients. Of the more modern methods the UNIFAC (Uniquac Functional-group Activity Coefficient) method (e.g., Fredenslund et al., 1977; Sandler, 2006) has been widely used. More recently the COSMO-SAC model (Xiong et al., 2014) has been used. There are numerous papers in the literature comparing these approaches and some suggest that COSMO-SAC may be slightly superior for aqueous systems (e.g., Gerber and Soares, 2010). In any event the activity coefficient is an indicator of the combined effects of properties such as total molecular surface area, molecular volume, molar volume and molecular weight of the constituent functional groups for each of the compounds. In determining activity coefficients using COSMO-SAC the temperature was set at 298.15 K, total pressure at 101.325 kPa and, unless otherwise stated, the mole fraction of the collector at 0.0001 which equates fairly well to typical concentrations used in industrial flotation plants. The activity coefficient in turn is used to determine the  $G^{\text{ex}}$ , the excess value being the difference between the values for a real as opposed to an ideal mixture. The most useful excess thermodynamic property is the  $G^{\text{ex}}$  since this term incorporates the enthalpic and entropic contributions. The  $G^{\text{ex}}$  is calculated using its relationship to the activity coefficient,  $\gamma_i$ , viz

$$\bar{G}_i^{\text{ex}} = RT \ln \gamma_i(T, P, \underline{x}) \quad (1)$$

where  $R$  is the universal gas constant and  $T$  is the absolute temperature. It is important to note that the  $G^{\text{ex}}$  is not the same as the surface free energy (e.g., van Oss and Good, 1988) or the free energy of collector adsorption as expressed by, for example, the Stern-Grahame equation (e.g., Fuerstenau et al., 1970). As mentioned in the introduction the various experimental values of recovery and/or contact angles used in this investigation were obtained from the published literature. The source of the data is indicated in the references in the relevant sections. Unless otherwise stated the flotation recovery data were obtained in microflotation cells.

## Results and discussion

### Further evidence that partial molar excess Gibbs energy ( $G^{\text{ex}}$ ) is indicative of hydrophobicity as indicated by flotation recovery in the case of ionic liquids and aminothiophenols

As previously reported (O'Connor, 2021) flotation recovery in a microflotation cell is an excellent indicator of the extent to which a mineral particle has been rendered hydrophobic since it allows for all the variables resulting from a complex mineralogy of the particle and simply indicates the propensity of the collector-particle aggregate to attach to a bubble and ultimately to report to the concentrate. Sahoo et al (2016) reported on the flotation of quartz using ionic liquids with different functional groups and varying alkyl chain lengths. They concluded that the flotation results imply that the alkyl chain length plays a major role in determining the floatability of the quartz compared to the interaction pattern of the ionic liquid with the quartz. This can be confirmed by applying the concept of  $G^{\text{ex}}$  to the flotation results. Table 1 shows the values of the  $G^{\text{ex}}$  for the respective alkyl groups for each ionic liquid (as determined for the alcohol of that alkyl group) and the recoveries of quartz (Figure 1). Clearly there is a good relationship between recovery and  $G^{\text{ex}}$  ( $R^2=0.93$ ).

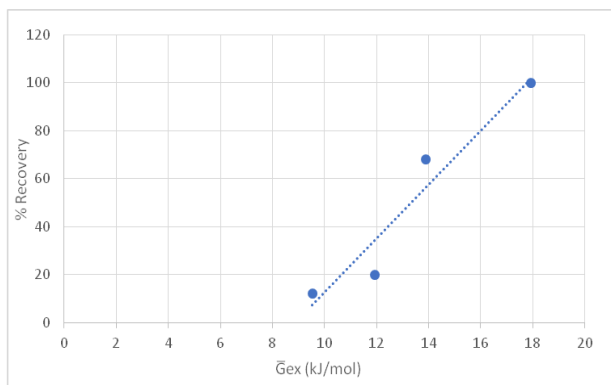
Table 1. Correlating quartz recovery and  $G^{\text{ex}}$  for various ionic liquids

Reagent	Activity coeff.	$G^{\text{ex}}$ (kJ/mol)	Quartz recovery*
1-methyl-3-octyl imidazolium chloride	123	11.92	20
1-n-decyl-3-methyl imidazolium tetrafluoroborate	273	13.89	68
1 n hexyl 3 methyl imidazolium chloride	47	9.54	12
cetyl pyridinium bromide	1393	17.93	100

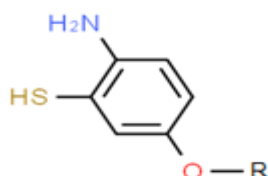
\*Est. from Figure 3

In a similar context it is of interest to use results reported by Marabini et al. (2007) studying the effect of changing structures of various collectors, on the recoveries of Zn (mainly smithsonite) and Pb (mainly cerussite). In one set of studies the effect of changing the alkyl group on aminothiophenol reagents for which the core structure is shown in Figure 2 and the variations in the alkyl group,  $R$ , bonded to the oxygen atom. Reagents in which the alkyl group  $R$  ranged from methoxy ( $\text{CH}_3\text{O}$ ) to hexyloxy ( $\text{C}_6\text{H}_{13}\text{O}$ ) were used in the flotation tests.

The flotation tests were carried out in a standard laboratory batch flotation cell which, for the present purposes, is less ideal than using a microflotation cell. The results of Zn recoveries as a function of  $G^{\text{ex}}$  are shown in Figure 3 which shows that there is a clear trend in the relationship between the recovery of Zn and the  $G^{\text{ex}}$  of the various alkoxy chain lengths.

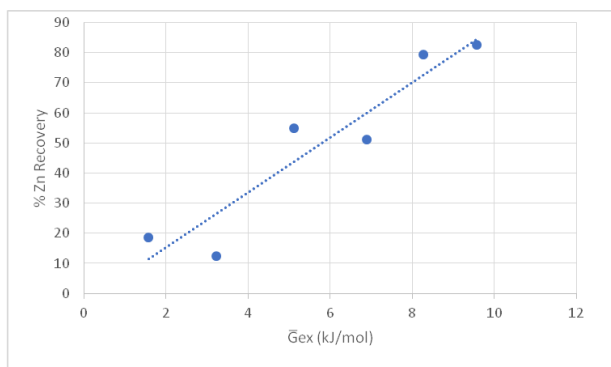


**Fig. 1. Quartz recovery (%) vs  $G^{\text{ex}}$  (kJ/mol) for various ionic liquids used in flotation ( $R^2=0.93$ ) (Sahoo et al., 2016)**



**Fig. 2. Basic structure of aminothiophenol ion (Marabini et al, 2007)**

It must be emphasised that the chelating action of the backbone structure (Figure 2) of the aminophenol on the Zn mineral is a constant in all cases.



**Fig. 3. Relationship between Zn recoveries using C1 to C6 alkoxy aminothiophenols and the  $G^{\text{ex}}$  of the respective alkoxy groups ( $R^2 = 0.88$ ) (Marabini et al, 2007)**

### Effect of electrolytes on partial molar excess Gibbs energy ( $G^{\text{ex}}$ )

As shown above, as well as in studies previously referred to, it now appears to be reasonable to hypothesise that  $G^{\text{ex}}$  is a good indicator of the hydrophobicity of a mineral-collector aggregate both in terms of recovery, especially in a microflotation cell, and of contact angle. On that basis it was decided to investigate whether the presence of electrolytes had any significant positive effect on  $G^{\text{ex}}$ . If such an effect was observed, it could be deduced that changes in flotation recovery in the presence of such electrolytes could be due to their effect on the non-ideal behaviour of the alkyl group of the collector in the aqueous environment. To investigate this hypothesis, data generated by October et al. (2020) on the effect of the presence of electrolytes on flotation recoveries as well as on bubble-particle attachment was used. In this study

they had reported that the presence of nitrate and sulphate ions resulted in a significant increase in recovery of both galena and chalcopyrite. The microflotation tests were carried out in water with an ionic strength of 0.0241 mol/L and 0.241 mol/L respectively as well as in deionised water and using SIBX as the collector. In the case of galena the recoveries were 58% and 87% for the two increasing ionic strengths and for chalcopyrite were 84% and 88%, respectively. Not surprisingly, given how easily chalcopyrite floats even in the absence of a collector, the effect of the ionic strength was minimal. The effect of the presence of electrolytes on  $G^{\text{ex}}$  was then investigated by using  $\text{H}_2\text{SO}_4$  (sulphate ions) at constant mole fraction of 0.05 and of the alkyl group of 0.05. The calculations were carried out for a range of xanthates from ethyl to pentyl. The effect of the presence of sulphate ions on  $G^{\text{ex}}$  of the alkyl group compared to the values in the absence of the acid is shown in Table 2.

**Table 2. Effect of presence of  $\text{H}_2\text{SO}_4$  on  $G^{\text{ex}}$  of various alkyl groups represented by their respective alcohols**

Alkyl group of xanthate	$G^{\text{ex}}$ (kJ/mol) in presence of $\text{H}_2\text{SO}_4$	$G^{\text{ex}}$ (kJ/mol) in absence of acid
Ethyl	1.95	3.24
Propyl	3.77	5.13
1 butyl	5.33	6.74
2-butyl	6.52	7.84
isobutyl	6.78	8.01
1-pentyl	6.83	8.28

As expected, the values of  $G^{\text{ex}}$  in the absence of acid increased as the alkyl chain length increased as had been previously reported. However, it is clear that the presence of  $\text{SO}_4^{2-}$  ions in fact reduced the values of  $G^{\text{ex}}$  indicating that the presence of ions had not increased the hydrophobicity of the mineral – collector aggregate as per the underlying hypothesis. Similar observations were made for the effect of the presence of nitrate ions ( $\text{HNO}_3$ ). These results are therefore consistent with the proposition by those authors that the main effect of the presence of the electrolytes was on the extent of bubble-particle attachment.

### Effect of pH on partial molar excess Gibbs energy ( $G^{\text{ex}}$ )

In a manner similar to the behaviour of the electrolytes the role that pH has on hydrophobicity and hence recovery can be investigated using  $G^{\text{ex}}$ . In a study of the effect of pH on the contact angle and recovery in a quartz / dodecylamine (DDA) system it was shown that as pH increased from 2 to 10 the contact angle increased from about  $20^\circ$  to  $> 80^\circ$  (Fuerstenau, 1957). In order to investigate whether this effect was also observed in the values of  $G^{\text{ex}}$ ,  $G^{\text{ex}}$  values for DDA were determined at decreasing mole fractions of  $\text{H}_2\text{SO}_4$  of 0.15, 0.1, 0.05 and 0.005 while maintaining a constant mole fraction of DDA at 0.05. These reduced acid concentrations equate to an increase in pH. At these acid concentrations the values of  $G^{\text{ex}}$  are 9.69, 12.93, 13.56 and 15.07 kJ/mol respectively. The increase in the values of  $G^{\text{ex}}$  as pH increased are consistent with increasing hydrophobicity (microflotation recovery) and contact angles reported in the reference above. Although this result does not explain fundamentally the effect of changing pH, viz.  $\text{H}^+/\text{OH}^-$  ratio, on the behaviour of the alkyl group it

does infer that, in terms of the underlying hypothesis, changes in pH do seem to have a direct impact on the hydrophobicity of the mineral-collector aggregate.

### Effect of alcohol species on partial molar excess Gibbs energy ( $G^{\text{ex}}$ )

It has been previously shown that many of the functions of a frother such as their effect on froth height, surface tension and critical coalescence concentration respectively are strongly related to the  $G^{\text{ex}}$  of the alkyl groups associated with the reagent. It was demonstrated that it was possible to reasonably predict the performance of frothers based on the value of their  $G^{\text{ex}}$  (Harris and O'Connor, 2017). Frothers are usually alcohols and there are numerous reports on the role which the addition of frothers may have on flotation behaviour. Hence, it is of interest to investigate whether the presence of an alcohol may influence the  $G^{\text{ex}}$  of the collector being used given that the hypothesis proposed in the present paper is that the absence of such an effect would point to the role of the alcohol being other than influencing the hydrophobicity of the collector-particle aggregate. In the present instance data generated by Pienaar et al. (2019) on the effect of adding hexanol to SEX on the recovery of galena in a batch flotation cell showed that the effect of adding hexanol was to increase the first order flotation rate constant from 0.091 min.<sup>-1</sup> to 0.190 min.<sup>-1</sup> with the recovery after 6 min increasing from ~40% to 69%. This addition of hexanol, not surprisingly, resulted in a decrease in  $G^{\text{ex}}$  of the ethyl group from 3.23 kJ/mol to 1.23 kJ/mol since hexanol as the 3<sup>rd</sup> phase in this non-ideal solution is more amenable to the presence of the ethyl group associated with the SEX. It can therefore be deduced that this reduction in  $G^{\text{ex}}$  on the addition of hexanol suggests that the hydrophobicity is, if anything, reduced and that hence the increase in recovery when hexanol was present is arguably related to its effect on particle-bubble attachment phenomena at the air-water interface as was indeed proposed by these authors.

### Effect of increases in concentration of the reagents on partial molar excess Gibbs energy ( $G^{\text{ex}}$ )

In the flotation of sulphide minerals xanthates of varying alkyl chain lengths are widely used. The underlying hypothesis of this paper is that the alkyl groups increase the hydrophobicity of the mineral (sulphide)-collector (xanthate) aggregate by increasing the non-ideality of the solution in which these aggregates occur. The dosage of these collectors is an area of much research since it is often proposed that it is not necessary to add more than a pseudo-monolayer of collector to impart adequate hydrophobicity onto the mineral particle to which the collector is attached. To explore this further the effect of concentration on  $G^{\text{ex}}$ , viz. the hydrophobicity of the mineral-collector aggregate, was investigated. Table 3 shows how the partial molar excess Gibbs energy changed as the concentration of a range of alkyl groups increased. The groups investigated are ethyl, propyl, 1-butyl, 2-butyl, 2-methyl-1-propyl and 1-pentyl. In each case the alcohol of the particular alkyl group was used.

These results highlight a number of issues related to the use of reagents with these alkyl group moieties. In fact they are typical of the range of xanthates which are widely used in industry such as sodium ethyl xanthate (SEX) or sodium iso-

Table 3. Effect of increasing concentration (mole fraction) on  $G^{\text{ex}}$

Alcohol	Mole fraction			
	0.95	0.90	0.85	0.80
	Excess Gibbs energy (kJ/mol)			
Ethanol	1.56	1.54	1.53	1.51
Propanol	1.99	1.96	1.92	1.88
1-butanol	2.34	2.31	2.27	2.22
2-butanol	3.62	3.40	3.20	3.02
2-methyl-1-propanol	3.97	3.71	3.46	3.23
1-pentanol	2.77	2.71	2.65	2.59

butyl xanthate (SIBX), i.e. 2-methyl-1-propyl xanthate. From this table it can be deduced that the alkyl group with the strongest ability to render the mineral particle hydrophobic is the isobutyl or 2-methyl-1-propyl group. This is consistent with the fact that SIBX is so widely used in industry. On the other hand, the ethyl group (e.g. SEX) is the weakest in that regard even though it is also widely used in industry. However, it is also interesting to observe that if increasing  $G^{\text{ex}}$  values are indicative of increasing hydrophobicity, which has been amply demonstrated to be the case in the present and previous publications, then increasing the concentration of the reagent in the flotation process is fundamentally not necessarily conducive to increasing the hydrophobicity of the mineral-particle aggregate. This observation is also consistent with the widely held view that in many concentrators the operators may be overdosing with collectors. There are obviously many other factors to consider when selecting a collector since flotation is a highly complex process involving many interactions between collectors and, for example, frothers, activators, etc.

### Effect of increases in temperature of the pulp on partial molar excess Gibbs energy ( $G^{\text{ex}}$ )

It was mentioned in the Introduction that another advantage of using  $G^{\text{ex}}$  instead of, for example, HLB as an indicator of hydrophobicity, is that it can also predict the effect of pulp temperature. Table 4 shows the effect of an increase in temperature from 298.15K to 308K for the range of alkyl groups covered in Table 3.

In each case an increase in temperature results in a very slight decrease in the value of  $G^{\text{ex}}$  except for, interestingly, a slight increase in the value for the ethyl group. However, clearly in terms of the underlying hypothesis changes in temperature do not appear to significantly affect the hydrophobicity of the mineral-collector aggregate. It is much more likely that such changes will affect the rheology of the pulp which could have a significant effect on the flotation performance.

## Conclusions

Previous publications by the authors and colleagues have indicated that a mineral particle, on which a collector containing a hydrocarbon moiety is adsorbed, when present in an aqueous system such as a flotation pulp, represents thermodynamically a classical non-ideal mixture.

Table 4. Effect of increases in temperature of the pulp on  $G^{\text{ex}}$

Alkyl Group	$G^{\text{ex}}$ at 298.15 K (kJ/mol)	$G^{\text{ex}}$ at 308 K (kJ/mol)
Ethyl	3.69	3.73
Propyl	7.92	7.89
1-butyl	15.18	14.96
2-butyl	23.60	22.89
Iso-butyl	25.35	24.53
1-pentanol	28.24	27.55

Such systems are characterised by activity coefficients and hence  $G^{\text{ex}}$ . This has led to the hypothesis that there could be a relationship between the  $G^{\text{ex}}$  of the hydrocarbon moiety associated with the adsorbed collector and its hydrophobicity as indicated by, for example, recovery in a microflotation cell or contact angle. The present paper provides further evidence that continues to sustain this hypothesis when considering collectors such as ionic liquids or aminothiophenols in a quartz or sphalerite system respectively. It is shown that the effect of pH on hydrophobicity as indicated by  $G^{\text{ex}}$  is consistent with previously reported contact angle and recovery results in a quartz / DDA system. In a further development of this hypothesis, it has been shown that when factors such as the presence of electrolytes or alcohols in the flotation pulp are investigated there was no indication that there was any increase in the hydrophobicity of the mineral-collector aggregate as indicated by  $G^{\text{ex}}$  and recovery and that hence it may be reasonably deduced that the changes observed in flotation recovery in such cases are related to other phenomena such as particularly bubble-particle attachment. Similarly, it is also indicated that since the change in  $G^{\text{ex}}$  is minimal when collector concentration or pulp temperature is increased these changes do not significantly affect the hydrophobicity of the collector-mineral particle and hence the recovery in a microflotation recovery. Clearly, in a large turbulent tank cell, for example, there are many other factors which affect recovery but the entire recovery process is initially dependent on the attachment of the mineral particle to the bubble which is driven by the hydrophobicity of the mineral-particle aggregate which in turn appears to be a strong function of the partial molar excess Gibbs energy of the alkyl group associated with the collector.

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