

Characterization of frothers and their behavior using partial molar Excess Gibbs energy

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ABSTRACT

Frothers, which are widely used as key reagents in the flotation of ores, are generally alcohols of varying structures. There is abundant experimental data which illustrates that frothers cause changes in froth behavior, bubble size/coalescence and surface tension and that these changes are closely associated with changes in the molecular structure of the frothers. Partial molar Excess Gibbs energy is a thermodynamic property which quantifies the difference between the partial molar value of the Gibbs energy of a species in a real mixture and that for the same species in an ideal mixture and this difference in mixture properties is due to differences in the molecular structures of the constituent species. It is thus reasonable to hypothesize that partial molar Excess Gibbs energy may be a useful parameter to quantify the changes which occur when using frothers of different molecular structures. In this paper it is shown that there is a generally strong relationship between measured characteristics such as froth volume/height, surface tension, hemi-micelle formation and the partial molar Excess Gibbs energy of alcohol frothers and these correlations provide robust evidence that many of the characteristics of frothers are strongly related to their molecular structure which in turn is related to the total surface area, molecular volume, and molar volume of the molecule, the molecular weight of the constituent functional groups and the interaction energies between the species present.

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1. Introduction

Frothers are used in the flotation process and are often characterized as anionic, cationic, non-ionic or zwitterionic. Typical examples of non-ionic frothers are alcohols. These non-ionic frothers contribute significantly to the formation of a stable population of bubbles (typically ~1–2 mm dia.) in the pulp phase as a result of the role they play in lowering surface tension and inhibiting bubble coalescence. Alcohols form non-ideal mixtures with water and their behavior has often been characterized using the so-called HLB (hydrophobic–lipophilic balance) number. Comley et al. (2002) have also used properties such as dynamic surface tension to explain the role of frothers with a view to providing a quantifiable link between measurable frother properties and flotation system responses so as to interpret their behavior. Both the HLB number and dynamic surface tension approaches are dependent on the chemical structure of the frother. Davies (1957) studied the relationship between HLB numbers and the solubility of emulsifying agents in the oil or water phases. He proposed that HLB values of surface active agents could be

calculated from the chemical formulae using group numbers. One drawback of the use of the HLB concept however is that it is not easily amenable to the characterization of mixtures at various concentrations and moreover the advances in determining the behavior of such molecules in an aqueous environment have advanced significantly in recent years due to major advances in thermodynamic modelling (Gmehling et al., 2002). Recently it was shown that the use of activity coefficients (γ_i) or partial molar Excess Gibbs energy (\bar{G}_i^{ex}) which is calculated for species i in an aqueous mixture using Eq. (1) is a more rigorous way than HLB number to describe the behavior of these frother molecules in non-ideal mixtures with water (Corin and O'Connor, 2014).

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

where \bar{G}_i^{ex} = partial molar Excess Gibbs energy of component i in the aqueous mixture, and γ_i is the activity coefficient of species i , and R , T and P have their usual meanings and \underline{x} represents the set of liquid phase mole fractions.

It is proposed in the present paper that partial molar Excess Gibbs energy is a more appropriate and rigorous way in which to link the behavior of frothers to their chemical structure. Structure-activity relationships of molecules such as frothers in mixtures are based on the premise that several molecular properties control their activity such as

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total surface area, molecular volume, the molar volume, molecular weight of the functional groups in the molecule and interaction energies. Thermodynamic analysis of such systems separates the molecular interactions controlling aqueous solubility into the interactions between solute and water molecules and between solute and solute molecules. In flotation systems the water phase is in great Excess and thus the focus of attention in terms of the non-ideality of the solution is the behavior of the frother. The introduction of a frother into water is thus associated with an unfavourable free-energy change due to the interaction between frother and water molecules. It is well known that there are many models available to estimate the activity coefficients of polar species such as alcohols in water. It is recommended that for the systems discussed in this paper (water-alcohols) the most appropriate model to use is the UNIFAC (Uniquac Functional-group Activity Coefficient) method (Dortmund Data Bank, 2016; Fredenslund et al. 1977; Fredenslund et al. 1975; Sandler, 2006). The basis of the UNIFAC method is the UNIQUAC (Universal quasi-chemical) approach proposed by Abrams and Prausnitz (1975). The UNIQUAC model contains, first, a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions between molecules in the mixture. Second, functional group sizes and interaction surface areas are introduced from independently obtained pure-component, molecular structure data. The pure component parameters in UNIQUAC, r_i and q_i , are, respectively, measures of molecular van der Waals volumes and molecular surface areas (Fredenslund et al., 1975). Apart from influencing surface tension and bubble coalescence it has been shown that the frothers retard the drainage of liquid from the bubble lamella in the froth phase (Laskowski et al., 1998) and it is proposed that by investigating the relationship between froth behavior and the partial molar Excess Gibbs energy of the frother it may be possible to gain a further insight into the role which the molecular structure of frothers play in influencing factors such as the film drainage phenomenon. Finally hemi-micelles form as a result of the attraction of the hydrophobic tails of the polar hydrocarbons dispersed in the water and this interaction will most likely be influenced by the molecular structure of the hydrocarbon and hence the relationship between partial molar Excess Gibbs energy and hemi-micelle formation should provide further evidence of the ability of Excess Gibbs energy to predict such behavior.

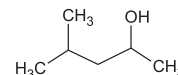
The aim of the present paper is to investigate the relationships between the partial molar Excess Gibbs energy of various frothers in flotation systems and their impact on factors such as froth behavior (such as indicated by froth height or volume), hemi-micelle formation and surface tension. The experimental data used in the paper have been extracted from a variety of sources which are referenced in the appropriate sections.

2. Experimental methods

The values of \bar{G}_i^{ex} , the partial molar Excess Gibbs energy of component i in the system, were determined using Eq. (1) where the values of the activity coefficients, γ_i , were obtained using the UNIFAC method. The temperature was set at 298 K and the default concentration of the frother was set at a mole fraction of 0.0001. It can be shown that at such low concentrations the calculated value of the partial molar Excess Gibbs energy of the frother in the mixture with water did not vary significantly from values at concentrations an order of magnitude greater or lesser. Moreover such concentrations are typical of those used in practice on flotation operations. Frothers are generally alcohols of either a simple linear structure or branched isomers of such alcohols. In the present study, apart from n -alcohols, other alcohols with the following molecular formulae were used in the various data sets presented:

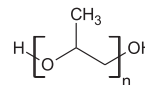
Methyl isobutyl carbinol (MIBC)

Methyl isobutyl carbinol (MIBC)



Polypropylene Glycol (PPG)

Polypropylene Glycol (PPG)



In the case of the PPGs the values of n used in the calculations are as shown in Table 1. As is well known commercial frothers are often not totally pure but the values of n shown, and hence the molecular weights and number of various functional groups used in this paper, demonstrate to an extent the robustness of the approach of using Excess Gibbs energy. The goodness of fit for the various cases presented illustrate this well.

3. Results and discussion

3.1. Relationship between foam/froth stability and partial molar Excess Gibbs energy

The Bikerman test has been widely used as a simple and effective method to quantify the effect of frothers on the stability of foams (Bikerman, 1973). Gas is sparged at a constant flow rate through a defined volume of fluid, generating a characteristic volume of foam. After an initial increase, the foam column reaches a maximum height, which is typically linearly proportional to the flow-rate of the gas. The height of the foam generated in the Bikerman test is determined by the lifetime of the films at the foam surface. The time taken to reach maximum height is about 3 min. Capillary pressure draws fluid from the films into the channels, or Plateau borders of the bubbles, thinning the films to the point where they rupture. The surface tension of the films provides a disjoining pressure that defines the extent to which this process is retarded. In the absence of any retarding force, the average film lifetime is only of the order of milliseconds (Narsimhan & Ruckenstein, 1996). Hence an adsorbed frother is a prerequisite for the existence of a froth or foam.

A number of studies have been undertaken on the effect of different frother types on the Bikerman foam height. For the present purposes, a two phase air-liquid system will be referred to as “foam”, while “froth” will designate the presence of a solid phase comprised of mineral particles typically in the 1 to 100 μm range. Fig. 1 gives an example of the relationship between froth height and the partial molar Excess Gibbs energy of the frother species in a 3-phase air-liquid-solid system. The frothers used were straight chain C2–C8 alcohols and the procedure used was similar to that used for a Bikerman test (Leja & Schulman, 1954). The experimental procedure is described in their paper. The data used in this figure were obtained from Fig. 7 of that paper for the case of alcohols alone. Homogeneous solid particles of various sulphides including galena and sphalerite were used in these experiments. In all the figures the solid line shown simply represents a fit to the data. There is clearly a close linear relationship ($R^2 = 0.98$) between the partial molar Excess Gibbs energy and the froth height which indicates that there is a strong relationship between froth height and the molecular

Table 1
Value of n for various polypropylene glycols (PPGs) studied.

PPG frother (approx. mol. wt.)	n
1000	17
725	12
425	7
192	3

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