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The interaction of organic dispersant with alumina: A molecular modelling approach

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Abstract

A molecular modelling approach has been used to screen and select appropriate dispersant for a given colloidal forming process. Seven dispersants with different molecular structure based on a benzene ring substitution with (–OH) and (–COOH) functional groups have been examined on the alumina surface. Theoretically computed interaction energy between dispersant and alumina surface and its correlation with adsorption amount of dispersant on alumina surface, which was obtained experimentally in the literature was studied. The simulation results showed that when functional groups increase in organic additives, the computed interaction energy between alumina surface and organic molecules increases. The proposed methodology based on molecular modelling computations, requiring no experimental data can be used to preliminary determine the most promising dispersants from large set of possible organic additives.

Keywords: Dispersant; Molecular modelling; Alumina; Functional groups

1. Introduction

The concept of colloidal ceramic processing has been successfully applied to the ceramic industry to produce high quality, high performance and reliable ceramic parts [1,2]. The stability of suspension during the colloidal processing has a significant influence on engineering properties of ceramic products [3,4]. A stable dispersion that requires the control of the interparticle forces in suspension can eliminate structural defects and stress centers in sintered ceramics [5,6].

Colloidal stability of ceramic powders in solution, typically in water, depends on ionic strength, surface charges, types and amount of dispersants, solid loading, pH value and temperature [7,8]. When the ceramic particles are added to suspending medium, particles are charged and thus van der Waals attraction force is generated on the surface of the particles, which result in the formation of agglomerate [9]. It is necessary to overcome van der Waals attraction force to keep particles as separate. Therefore, a repulsive force needs to be introduced to the colloidal system to disperse particles in the suspension. This force can be obtained in an aqueous solution by either electrostatic, steric or electrosteric stabilization. However, it is not easy to acquire well-stabilized, homogeneous and dispersed high solid loading suspension without dispersant [3]. An efficient use of inorganic or organic surface active dispersants controls the interparticle forces (van der Waals and repulsion) affecting the rheology of systems [10]. Organic dispersants exhibit several advantages over inorganic dispersants including greater stability, greater control of flocculation state and higher consolidated green density, less impurity and reduction in sintering temperature [11]. The absorption of organic dispersant on the surface of the alumina particles increases the surface charges, which improves repulsion force.

Hidber et al. [12] described the effect of the molecular structure of low molecular weight organic dispersants upon the adsorption and dynamic electrophoretic mobility behavior of alumina suspension. In their study, the number and position of (–OH) and (–COOH) functional groups of dispersant were systematically changed and their behavior compared with each other at different pH values. They found

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that the adsorption and the dynamical electrophoretic mobility behavior of suspension depend on the nature, number and position of the benzene ring's functional groups on the properties of aqueous alumina suspensions. Likewise, this study has examined the effect of number and position of surface active groups of benzene ring's using molecular modeling approach based on theoretically calculated interaction energies between dispersant structure and alumina surface. In addition, the computed interaction energies were correlated with experimentally obtained absorption and electrophoretic mobility of dispersant on the alumina surface in the published literature.

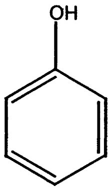
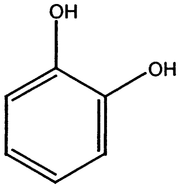
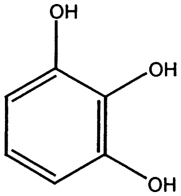
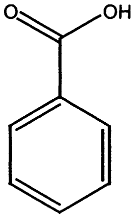
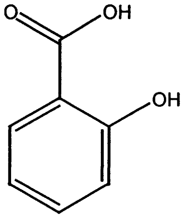
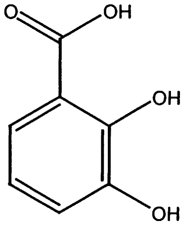
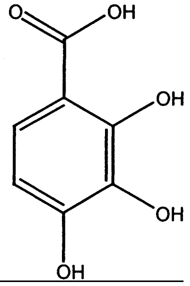
2. Molecular modelling methodology

The Cerius^2 program (Accelrys Inc., USA) at Highly Filled Materials Institute of SIT (USA) was used to model the α-Al_2O_3 surface-dispersant interactions by force field approach. The force field describes approximately the potential energy hypersurface in which the atomic nuclei move. The COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) has been chosen as a force field for all energy calculations. The COMPASS force field has broad coverage in covalent molecules including most common organics, small inorganic molecules, and polymers, which can be used to make accurate predictions of structural, conformational, vibrational, cohesive and thermophysical properties for a broad range of compounds both in isolation and in condensed phases [13]. Ewald long range summation method for electrostatic interactions (Coulombic) was selected and charges were calculated with charge equilibration (Q_{eq}) method based on electronegativity and geometry.

The method followed was similar to that reported by Pradip et al [14]. A surface cell was created from {0 0 1} cleaved plane of the α-Al_2O_3 unit cell. The surface was further extended to a periodic super lattice (~20 Å × 20 Å). Energy minimization (10,000 iterations) was applied to surface cell to optimize geometry in which potential energy is minimum. The atoms at the top layer were allowed to relax and the rest of atoms were constrained during the minimizations, because only top layer atoms have interactions with dispersant molecules.

Seven dispersants based on benzene ring substitution with (–OH) and (–COOH) were used for this study (Table 1). After the dispersant molecule was sketched, amorphous cell containing ten conformations of dispersant molecule was constructed and then optimized by minimization process. Then, the dispersant molecules were docked on the alumina surface. Dynamics simulation NVT (constant-volume/constant-temperature dynamics) was conducted to dispersant-alumina surface at 300 K with 30 ps. The NVT dynamics is modified to allow the system to fully equilibrate at a controlled temperature. The single point energy of total system, the alumina surface and the dispersant, was calculated after dynamic simulation. This was called total potential energy of system. The single point energy for the dispersant was calculated in a 3D lattice but without contributions from the alumina surface that was removed

Table 1
Molecular structure of the dispersants investigated in this study

Name	Molecular formula	Structure
Phenol	C_6H_6O	
1,2-Dihydroxybenzene (catechol)	$C_6H_6O_2$	
1,2,3-Trihydroxybenzene (pyrogallol)	$C_6H_6O_3$	
Benzoic acid	$C_7H_6O_2$	
2-Hydroxybenzoic acid	$C_7H_6O_3$	
2,3-Dihydroxybenzoic acid	$C_7H_6O_4$	
2,3,4-Trihydroxybenzoic acid	$C_7H_6O_5$	

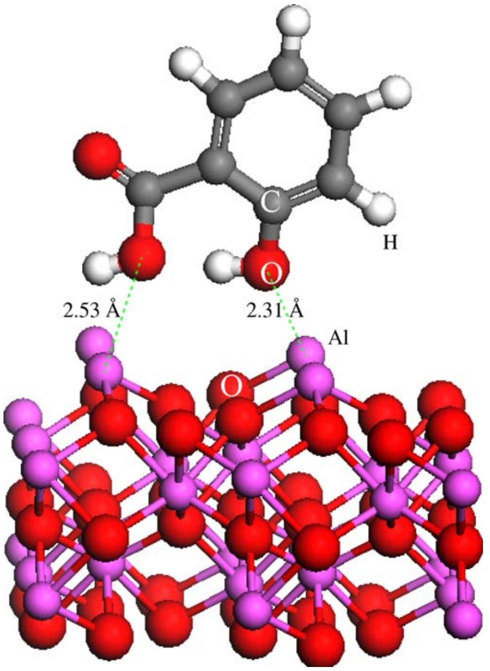


Fig. 1. Optimized complex of 2-hydroxybenzoic acid on alumina {0 0 1} surface.

during the calculation. This was recorded as energy of dispersant. The energy of surface without dispersant was determined and recorded as well. Finally, the interaction energy can be calculated by using the following equation:

$$E_{\text{Interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{dispersant}})$$

where, the E_{total} is the energy of the surface and the dispersant, E_{surface} is the energy of the surface without the dispersant and $E_{\text{dispersant}}$ is the energy of the dispersant without the surface. The concept of interaction energy calculations has been successfully applied on the mineral-reagent case by Pradip et al. [14–16].

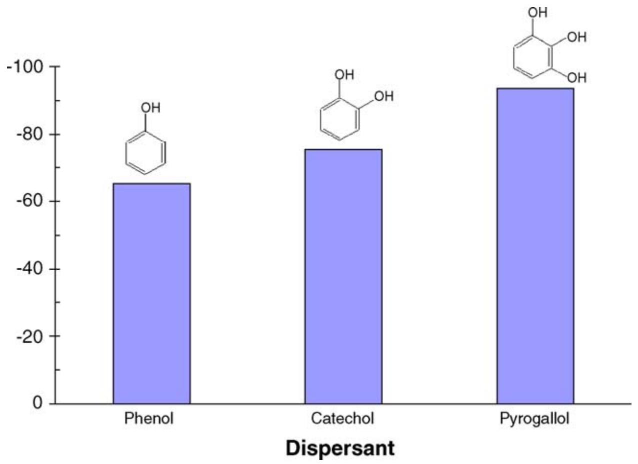


Fig. 2. Theoretically computed interaction energy of phenol, catechol and pyrogallol on alumina surface.

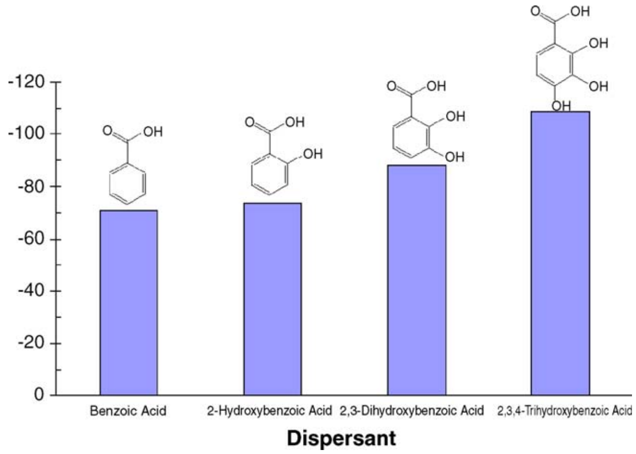


Fig. 3. Theoretically computed interaction energy benzene rings substituted with hydroxyl and carboxyl groups on alumina surface.

3. Results and discussion

Adsorption complex was created between dispersant 2-hydroxybenzoic acid and the {0 0 0 1} surface of Al_2O_3 shown in Fig. 1. The interaction between positive centers on the alumina surface and negative centers on the molecule lies over the alumina surface. The shortest distance among layers determines optimized conformation of adsorption complex [16]. The closest distance between oxygen atoms of dispersant and surface atoms of Al_2O_3 is about 2.31 Å. The interaction energy was calculated using molecular modelling tools for each dispersant, which is presented in Figs. 2 and 3. It is noticeable that the interaction energy of benzene rings substituted with hydroxyl and carboxyl groups on alumina surface were influenced by the number and positioning of these groups on the ring.

The energy results were correlated with adsorption amount of dispersant on alumina surface as obtained experimentally by Hidber et al. [12]. In Fig. 4, the adsorption

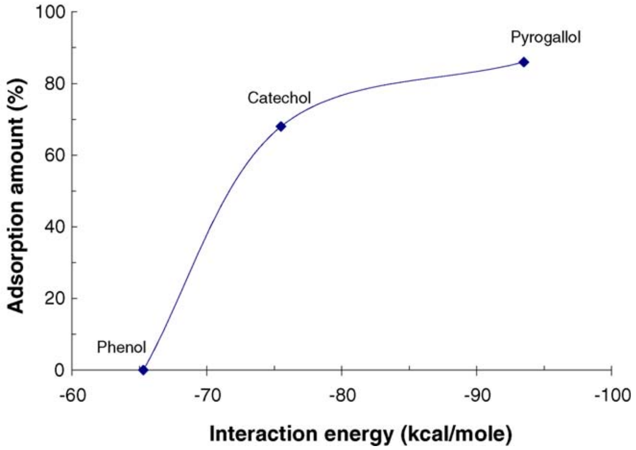


Fig. 4. Correlation of interaction energy of phenol, catechol and pyrogallol with experimental adsorption amount on alumina as reported by Hidber et al. [12].

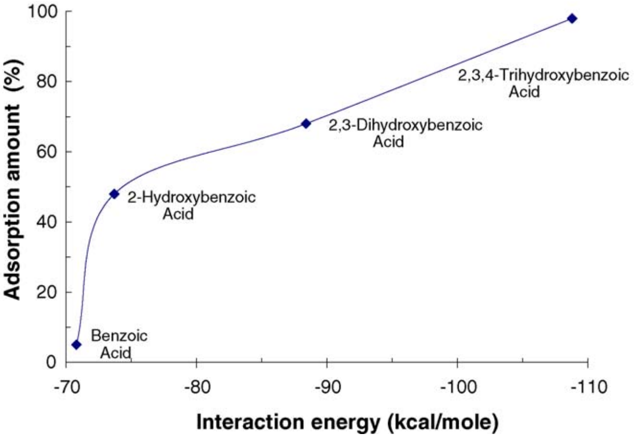


Fig. 5. Correlation of interaction energy of dispersant with experimental adsorption amount on alumina as reported by Hidber et al. [12].

of phenol, catechol and pyrogallol having hydroxyl groups was shown in the percent of the added amount dispersants versus interaction energy between dispersant molecules and alumina surface. The phenol containing only one hydroxyl groups has been illustrated almost zero adsorption with lowest interaction energy. The presence of a second hydroxyl in the *ortho* position (catechol) altered adsorption behavior with higher energy. When three hydroxyl groups were present, the interaction energy was 93.5 kcal/mol.

Isoelectric point (IEP) indicating electrophoretic mobility of suspension decreased upon increasing hydroxyl number with interaction energy (Fig. 5). The surface charge on Al_2O_3 particles in water is a function of pH and it is neutral at the IEP of alumina that indicates no electrical repulsive force resulting in agglomeration. The surface charge of Al_2O_3 becomes positive when the pH is below the IEP (9.2 for alumina [12]) and negative when the pH is above the IEP [17]. Phenol does not change apparently the electrophoretic mobility of particles, because no absorption was observed for this molecule on the surface of alumina [12]. The addition of catechol leaded to a shift of IEP of over 1.5 pH unit with −75.5 kcal/mol interaction energy. The IEP of pyrogallol reduced considerably to pH 6.2, which decreased positive surface charge. The influence of the number of functional groups in a benzoic acid molecule on its adsorption behavior was illustrated by comparing interaction energy of benzoic, 2-hydroxy-, 2,3-dihyroxy- and 2,3,4-trihydroxybenzoic acids which contain combination of hydroxyl and carboxyl groups (Fig. 6). The more hydroxyl groups that were present in a molecule, the higher was the interaction energy with higher adsorption density. 2,3,4-Trihydroxybenzoic acid with three hydroxyl groups has showed almost complete adsorption. The IEPs of them were also shown as a function of calculated interaction energy (Fig. 7). At pH less than the IEP of alumina, the density of positive charges on the surface of the alumina particles exhibits electrostatic interactions with COO^- and OH groups. Therefore, the IEP of 2,3,4-trihydroxybenzoic acid was shifted from pH 9.2 down to 5.5, which revealed highest interaction energy (−108.8 kcal/mol) among the seven dispersants. The difference in the adsorption ability and the number of dissociate groups were influenced of the molecules on the IEP and on the electrophoretic mobility curves of alumina [12].

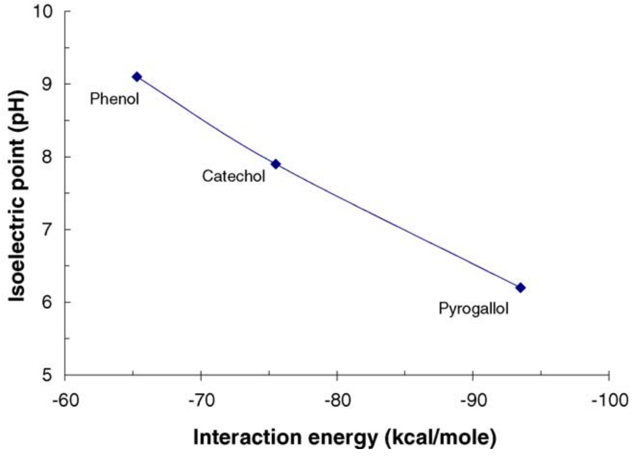


Fig. 6. Correlation of IEP for phenol, catechol and pyrogallol as a function of interaction energy with alumina surface.

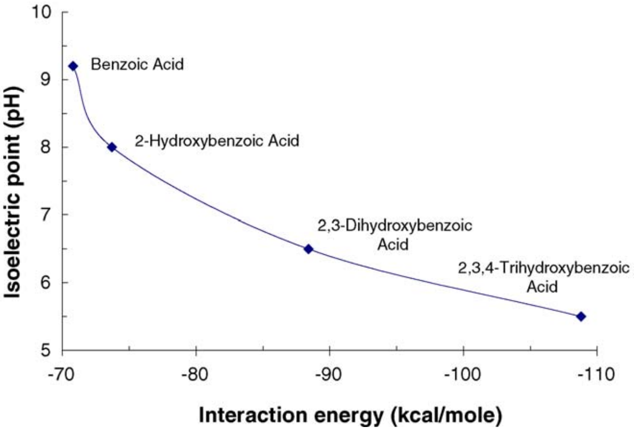


Fig. 7. Correlation of IEP for benzene rings substituted with hydroxyl and carboxyl groups as a function of interaction energy with alumina surface.

4. Conclusions

The molecular modelling methodology used in this study offers a convenient and efficient screening of dispersant from a set of organic additives for colloidal processing of ceramics. The conventional trial and error methods with time consuming experiments for selection of dispersant can be eliminated by molecular modelling tools.

Theoretically computed interaction energy between dispersant and the alumina surface was calculated by molecular modelling. The interaction energy of dispersants based on benzene rings that have been substituted with hydroxyl and carboxyl group were influenced by the number and the position of the groups in the ring. The interaction energy increased in terms of the number and position of functional groups. A correlation of calculated interaction energy with experimentally obtained adsorption amount of dispersant on the alumina surface in the literature has been attempted in this work. It was observed that theoretical predictions are consistent with the experimental findings, thus molecular modelling approach is a promising auxiliary screening step from a set of large number of possible candidates to select of an appropriate dispersant for a colloidal system.

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References

[1] F.F. Lange, Powder processing science and technology for increased reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.
[2] R.H.R. Castro, B.B.S. Murad, D. Gouvea, Influence of the acid–basic character of oxide surfaces in dispersants effectiveness, Ceram. Int. 30 (2004) 2215–2221.
[3] T. Fengqiu, H. Xiaoxian, Z. Yufeng, G. Jingkun, Effect of dispersants on the surface chemical properties of nano-zirconia suspension, Ceram. Int. 26 (2000) 93–97.
[4] Y. Liu, L. Gao, Dispersion of aqueous alumina suspension using copolymers with synergistic functional groups, Mater. Chem. Phys. 82 (2003) 362–369.
[5] W.M. Sigmund, N.S. Bell, L. Bergstrom, Novel powder-processing methods for advanced ceramics, J. Am. Ceram. Soc. 83 (2000) 1557–1574.
[6] S. Zurcher, T. Graule, Influence of dispersant structure on the rheological properties of highly concentrated zirconia dispersion, J. Eur. Ceram. Soc. 25 (2005) 863–873.
[7] G. Tari, S.M. Olhero, J.M.F. Ferreira, Influence of temperature on the colloidal processing of electrostatically stabilized alumina suspension, J. Mater. Process. Technol. 137 (2003) 102–109.
[8] J.A. Lewis, Colloidal processing of ceramics, J. Am. Ceram. Soc. 83 (2000) 2341–2359.
[9] L. Bergstrom, Colloidal processing of ceramics, in: K. Holmberg (Ed.), Handbook of Applied Surface and Colloid Chemistry, John Wiley & Sons Ltd., 2001, pp. 201–218.
[10] B.J. Briscoe, A.U. Khan, P.F. Luckham, optimizing the dispersion on an alumina suspension using commercial polyvalent electrolyte dispersants, J. Eur. Ceram. Soc. 18 (1998) 2141–2147.
[11] K. Vishista, F.D. Gnanam, Role of defloculants on the rheological properties of boehmite sol, Mater. Lett. 58 (2004) 1576–1581.
[12] P.C. Hidber, T.J. Graule, L.J. Gauckler, Influence of the dispersant structure on the properties of electrostatically stabilized aqueous alumina suspension, J. Eur. Ceram. Soc. 17 (1997) 1387–1392.
[13] Cerius^2 Molecular Modelling Program Manual, Molecular Simulations Inc., USA.
[14] B.R. Pradip, T.K. Rao, S. Krishnamurty, R. Vetrivel, J. Mielczarski, J.M. Cases, Molecular modelling of interactions of alkyl hydroxamates with calcium minerals, J. Colloid Interface Sci. 256 (2002) 106–113.
[15] B.R. Pradip, Design of tailor made surfactants for industrial applications using a molecular modelling approach, Colloids Surf. A 205 (2002) 139–148.
[16] B.S. Pradip, Molecular modelling and rational design of flotation reagents, Int. J. Miner. Process 72 (2003) 95–110.
[17] S. Sumita, W.E. Rhine, H.K. Bowen, Effects of organic dispersant on the dispersion, packing and sintering of alumina, J. Am. Ceram. Soc. 74 (1991) 2189–2196.