Chapter 5

Application of flotation agents and their structure–property relationships

5.1. CLASSIFICATION OF FLOTATION AGENTS

In general, flotation agents are classified according to their purpose as collectors, frothers, depressants, modifiers and flocculants. Structure of those molecules consists of polar and/or non-polar portions as shown in Fig. 5.1. Non-polar portion, which may be linear, branch or ring hydrocarbon, interacts very weakly with water molecules and therefore is termed hydrophobic group. the polar portion of the molecules can be classified into two types: one which strongly interacts with water molecules and termed *hydrophilic group*; the other which interacts with the surface of polar minerals and water molecules as well and termed minerophilic group. These three basic groups can be incorporated into the molecules to make various types of flotation agents.

With non-polar minerals such as talc, mica and coal, the particle surfaces can interact with the non-polar portion of the molecules by van der Waals force. In this case, hydrocarbon portions can function as mineralophilic groups. Except in the case of depressants or some flocculants, the non-polar portions of long hydrocarbon chains in flotation agents possess only the framework formed from C–H groups with linking to polar hydrophilic and minerophilic groups [4].

It is essential to maintain a proper balance among the three basic groups (hydrophobic, hydrophilic and minerophilic) in the molecules so as to get the desired collector, frother,

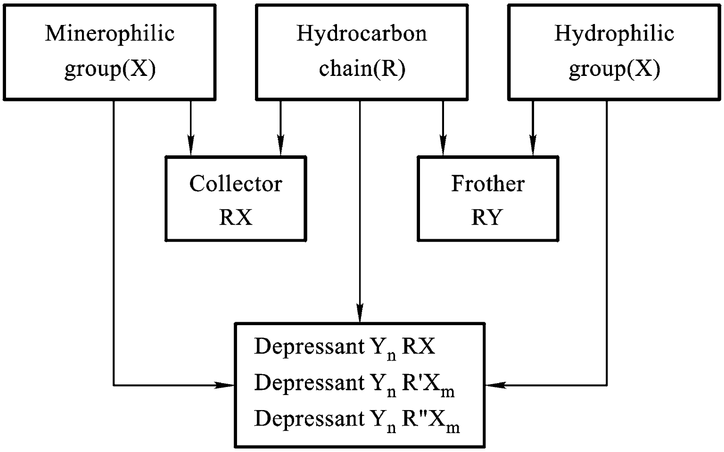


Fig. 5.1. Structure model of flotation reagents.

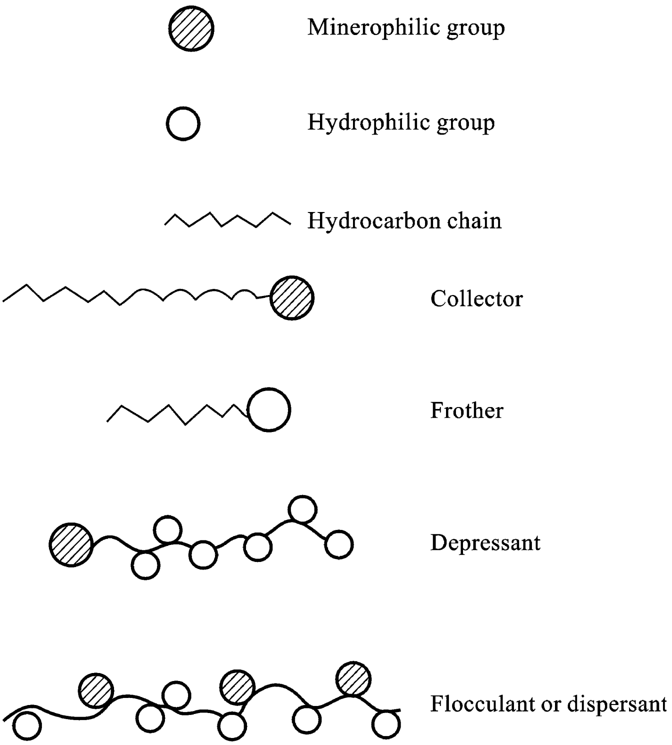


Fig. 5.2. Diagram of various flotation reagents formed from three elemental group.

depressant or flocculant properties. Various flotation agents are schematically shown in Fig. 5.2.

Each group of the molecule has an individual role in the flotation. Overall property of the molecule is a cumulative one of all the groups. A reagent molecule with various structural portions can therefore be divided into individual groups and its effect on the whole molecular property can be assessed. This facilitates evaluation of the structure–property relationships of flotation agents.

5.2. COLLECTORS—MINEROPHILIC AND NON-POLAR GROUPS

5.2.1. Structure of minerophilic groups

A collector is required to have at least two essential properties, namely adsorption on desired mineral particles and hydrophobization of their surfaces. Except for non-polar oils that are used sometimes as collectors for such naturally hydrophobic minerals like coal, the most common collector molecules possess minerophilic and hydrophobic portions in

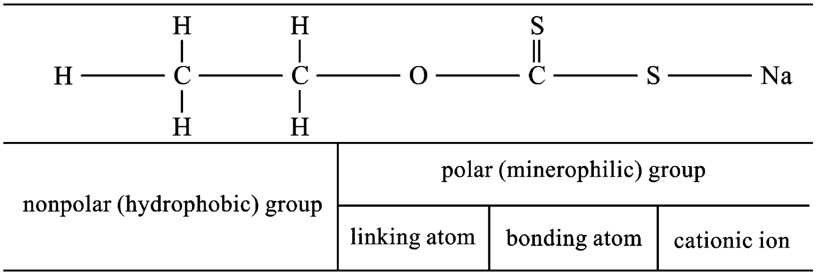


Fig. 5.3. Structure of minerophilic group of xanthate as collector for sulfides.

Table 5.1
pK_a values of various inorganic acids containing oxygen

pK_a	Acidity	Element				
		III	IV	V	VI	VII
−8	Very strong					$HClO_4$ (−8)
−3	Strong			HNO_3	H_2SO_4 (<0) H_2SeO_4 (<0)	$HClO_3$ (−3)
2	Sub-strong			HNO_2 (3.4) H_3AsO_4 (2.2)	H_2SO_3 (1.77) H_2SeO_3 (2.6)	$HClO_2$ (2.0)
7	Weak		H_2CO_3 (6.4)			$HClO$ (7.5)
12	Very weak	H_3BO_3 (9.2) $Al(OH)_3$ (12.4)	H_2SiO_3 (10)	H_3AsO_3 (9.2)		
17	Very very weak		$Sn(OH)_2$ (14.4)		$Cr(OH)_2$ (16)	$Mn(OH)_2$ (19)

order to acquire the above properties. The minerophilic portion is a chemically functional group consisting of a bonding atom and linking atoms as shown in Fig. 5.3 [4].

Minerophilic groups determine the affinity of a collector to the mineral surface by means of mechanisms involving physical adsorption, chemisorption as well as chemical reactions due to differences in dissociation, solubility and polarity of the reagents. In addition, the cross-sectional area of the polar groups is usually larger than those of the non-polar groups, the geometric size of the minerophilic groups will also determine the cross-sectional area of the entire molecule which is a parameter that affects the flotation performance of a collector.

5.2.1.1. *Relationship between the structure of the minerophilic group and its adsorption on mineral surface*

Acids and salts composed of atoms of large electronegativity values such as halogens and oxygen usually exhibit a relatively high degree of dissociation. For certain acids containing oxygen, the more the number of oxygen atoms in a molecule, the higher is the degree of dissociation [5]. it is illustrated in Table 5.1 which shows the pK_a values of inorganic acids containing oxygen.

Dissociation degree of a reagent can be predicted using the atomic bonding parameter of polar group. Pauling [20] considered that the dissociation degree of inorganic acids containing oxygen depend on the charge of the central atom (m) and the number of oxygen atoms (n) without linking to any H atoms, and could be governed by the following equation:

$$pK_a = 7.5 - 10m + 5n \tag{5.1}$$

For organic bases such as amines, due to the electron donation effect and steric effect of alkyl groups, the alkalinity is in the order: primary amine > secondary amine > tertiary amine.

5.2.1.2. *Van der Waals' interactions between collector molecules and minerals*

Van der Waals force includes the molecular effects of orientation, induction and dispersion. The dispersion effect is generally the strongest and the induction is the weakest [16].

The relationship between the molecular structure and the van der Waals interaction can be discussed as follows:

(a) van der Waals interaction is determined by the dipole moment of a molecule. For a homologous series of organic compounds with the same polar group, the values of dipole moment and ionization potential are nearly the same, but value of polarity increases markedly with molecular weight. In other words, the dispersion and induction effects for homologous molecules will increase with molecular weight so that the adsorption depending on van der Waals force will also become stronger.

(b) Since the dipole moment is a vector property, it will increase with the degree of unsymmetrical distribution of polar and non-polar groups in a molecule. In general, the dipole moment of the molecules with a straight chain and para position substitution is larger than that of a molecule with branches and ortho position substitution. Thus, the van der Waals force of the former will be stronger than that of the latter.

5.2.1.3. *The polar group and hydrogen bonding*

In a molecule, the hydrogen atom linked to an atom (X) of high electronegativity can also be bonded with another atom (Y) of high electronegativity. This type of bonding is also called hydrogen bonding:

$$\text{–X–H} \cdots \text{Y–}$$

Thus, a molecule which has atoms of O, F, Cl, N or S of high electronegativity is small in size and can attract the electron from a hydrogen atom in another molecule and form hydrogen bonding.

Hydrogen bonding can result from interactions between reagents and H^+ and OH^- ions adsorbed on mineral surfaces or O, F and Cl atoms on minerals. In many cases, hydrogen bonding is the major force for reagent adsorption on minerals. For example, nonionic polymers such as polyacrylamide and polysaccharides are absorbed on minerals by hydrogen bonding.

Table 5.2
Minerophilic groups in collectors molecules

Carboxylate	R–C(=O)–OH
Sulfonate	$R–S(=O)_2–OH$
Phosphate	$R–P(=O)(–OH)_2$
Primary amine	$R–NH_2$
Tetra ammonium salt	$R(CH_3)_3–NX$
Arsenite	$R–As(=O)(–OH)_2$
Hydroxyl	R–OH
Hydroxamate	R–C(=O)–NH–OH
Mercaptan	R–SH
Thioether	R–S–R
Dithiocarbonate	R–O–C(=S)–S–Na
Dithiophosphate	$(R–O–)_2P(=S)–S–H$
Dithiocarbamate	$R_2N–C(=S)–S–Na$
Thionocarbamate	$R–NH–C(=S)–O–R'$

The energy of hydrogen bonding is of the order of 10^{11}–10^{12} ergs/mol which is smaller than that of chemical bonding. The hydrogen bonding energy between molecules of oleic acid is 2.1×10^{11} ergs/mol, but that between double bonds in the unsaturated chain of oleic acid is 1.36×10^{12} ergs/mol.

5.2.2. Minerophilic groups and chemical bonding

5.2.2.1. *Properties of bonding atoms*

Major minerophilic groups in collector molecules are listed in Table 5.2. The common bonding atoms in minerophilic groups are O, N, P and S which can be combined with C, P, As, Cl and Br elements to form many functional groups.

Interactions between the collector and the mineral surface are usually through these bonding atoms in the minerophilic groups and surface atoms (metallic ions) of the mineral crystal lattice. This will result in chemisorption or surface reactions discussed in Chapter 4. Characteristics of these bonding atoms as summarized by Nagaraj [3] are listed in Table 5.3.

5.2.2.2. *Properties of mineral constituent elements*

Considering the chemical affinity of atoms or ions and the resultant characteristic of minerals, constituent elements of minerals are classified in geochemistry into three categories as shown in Table 5.4. Affinity of bonding atoms in minerophilic groups to metallic ions on minerals are summarized in Table 5.5 [6].

5.2.2.3. *Bonding ability and specificity*

Solubility products of collector-metallic ion compounds (see Appendix C) suggest that the sulfide mineral collectors such as xanthates, mercaptans and thiophosphates containing sulfur bonding atom in the minerophilic group can form compounds of low solubility products with ions of elements with affinity for copper(II). They can not form insoluble

Table 5.3
The characteristics of bonding atoms

Characters	O	N	P	S
Electron configuration	$[\mathrm{He}]1s^22s^22p^2$	$[\mathrm{He}]1s^22s^22p^2$	$[\mathrm{He}]1s^22s^23d^0$	$[\mathrm{He}]1s^22s^23d^2$
Electronegativity	3.5	3.0	2.1	2.5
Valence electrons	2	5	5	2
Number of orbitals	4	4	4 + d	4 + d
Lone pairs	2	1	1	1
$p\pi$–$p\pi$	Strong	Strong	None	Poor
$d\pi$–$d\pi$ (back-bonding)	None	None	Moderate	Strong
Polarizability	Nil	Good	Good	Strong
Hydrogen bonding	Strong	Strong	None	Very weak
Bonds	More ionic	Less ionic	Covalent	Covalent
Steric accessibility	Low	Low	High	High

Table 5.4
Geochemical classification of mineral elements and interaction with reagents

Elements	Electron configuration of ions	Deposite character	Bonding atoms of reagent	Bonding character	Reaction with reagent
Elements affiniting rock (1st) Li, Be, Na, Mg, K, Ca, Al, Ba, Cl, Si	Inert gas type Li^+ $(1s^2)$He Be^{2+} $(1s^2)$He Na^+ $(1s^22s^22p^6)$Ne Mg^{2+} $(1s^22s^22p^6)$Ne K^+ $[(\mathrm{Ne})3s^23p^6]$Ar Ca^{2+} $[(\mathrm{Ne})3s^23p^6]$Ar	Later period of magmatism of magmaties stability in air	O, Cl	Ionic bond	Physical adsorption, partial chemisorption (for Ca, Ba)
Elements affiniting copper (2nd) Cu, Ag, Au, Zn, Cd, Hg, As, Sb, Bi, Sn, Pb, S, Se	Filled orbits d^{10} or $d^{10}s^2$	Hot solution stage components of polysulfides instability in air	S, Se	Covalent	Chemisorption and surface reaction
Element affiniting iron (3rd) Se, Ti, V, Cr, Mn, Fe, Co, Ni	Partially filled d or f orbits	In the earth's core and early period	N, C, P	Partially ionic	Physical adsorption and partial chemisorption

products with metallic ions of elements(I). The solubility products of compounds made up of ions of elements(III) and collectors with a sulfur bonding atom of sulfur depend upon the number of d electrons in the metallic ion shell and are generally higher than those of compounds made up of elements(II).

Table 5.5
Affinities of bonding atoms to metallic ions of minerals

Element(I) affiniting rock	O > N	N >> P >> As	O >> S > Se > Te	F >> Cl > Br > I
Element(II) affiniting copper	S > O	N << P > As	O << S, Se, Te	F < Cl < Br < I
Element(III) affiniting iron	O > N	(d-electron < 5)	N > O	(d-electron > 5)

Table 5.6
Δx of three kinds bonding

1st ions	Δx			2nd ions	Δx			3rd ions	Δx		
	O	N	S		O	N	S		O	N	S
Li	2.5	2.0	1.5	Cu	1.6	1.1	0.6	Ti	2.0	1.5	1.0
Na	2.6	2.1	1.6	Zn	1.9	1.4	1.9	Mn	2.0	1.5	1.0
K	2.7	2.2	1.7	Ag	1.6	1.1	1.6	Fe	1.7	1.2	1.0
Mg	2.3	1.8	1.3	Cd	1.8	1.3	0.8	Nb	1.9	1.4	0.7
Ca	2.5	2.0	1.5	Au	1.1	0.6	0.1	Cr	1.9	1.4	0.9
Ba	2.6	2.1	1.6	Hg	1.0	1.1	0.6				

Collectors for nonsulfide minerals with an oxygen as bonding atom and with long enough hydrocarbon chain length can form less soluble compounds with all three kinds of metallic ions, except K and Na ions. In this case the values of solubility products for various ions are only slightly different from those of each other.

Solubility products are usually used as a criterion of reactivity and specificity of collectors. In general, the less the solubility, the more is collectivity, but if the solubility is small enough to result in slight differences in solubility for various metallic ions, the selectivity will decrease. For separation of two minerals, it has been suggested that the ratio of the solubility products of compounds of two mineral ions (pL_1/pL_2) or the difference ($pL_1 - pL_2$) must be maintained at a suitable value [6].

The above discussion shows that the bonding of metallic ions with O atom is of ionic character and for the bonding of metallic ions(II) with S atom is covalent. Pauling has used electronegativity difference (Δx) as a criterion of ionic character, the ionic character being equal to 50% when $\Delta x = 1.7$. The Δx values for the three kinds of bonding are given in Table 5.6.

Collectors for nonsulfide minerals containing O atom, such as fatty acids and sulfonates, react with various metallic ions by ionic bond, and they have high solubility in water. The solubility becomes low only when the hydrocarbon chains in the molecules are long. In contrast, collectors for sulfide minerals, such as xanthates possessing only a short chain, the S bonding atom reacts with metallic ions to form covalent bonds with lower polarity, so the resultant products have low solubility in water and the solubility products are quite different for each metallic ions.

In other words, solubility products of short chain collectors for sulfides are determined mainly by the bonding character that reflects the properties of the metallic ions. With collectors of nonsulfide minerals, the lower solubility product is the result of "additive effects of long chain". In this case the bonding character is not closely related to the properties of metallic ions. Thus selectivity of collectors with S bonding atom is better than that of collectors with O bonding atom.

5.2.3. Induction effect between atoms in minerophilic groups

Polarity of unsymmetrical covalent bonds varies with the chemical structure around it. Due to differences in the electron-withdrawing power of the bonding atoms, electron clouds move toward the atom with higher electronegativity. This effect can be transmitted along the molecular chain, and this effect is called induction effect. The direction of the induction effect is determined by examining the electron-withdrawing power of an atom in relation to that of hydrogen atom. Thus if the electron-withdrawing power of an atom (X) in the molecule is larger than that of the H atom, the electron cloud moves to the X atom resulting in what is called negative induction (−I); otherwise it results in positive induction (+I) and represented as follows:

$R \rightarrow CH_2 \rightarrow X$

5.2.3.1. *Induction effect in molecules of thiocarbonates*

Among the derivatives of thiocarbonates, dithiocarbonates (xanthates) are widely used as collectors for sulfide minerals. In addition, monothiocarbonates and trithiocarbonates are also used. Bonding atoms and central atoms of all of those above thiocarbamates are the same, but the linking atoms are different:

(a) Monothiocarbonate: $R\text{–}O\text{–}(O{=})C \leftarrow S \leftarrow H(Me)$
(b) Dithiocarbonate: $R\text{–}O\text{–}(S{=})C \leftarrow S \leftarrow H(Me)$
(c) Trithiocarbonate: $R\text{–}S\text{–}(S{=})C \leftarrow S \leftarrow H(Me)$

Electronegativity of the oxygen atom is higher than that of the sulfur atom. In comparing molecule (a) with (b) above, the −I effect of =O group is larger than that of the =S group, resulting in the lower electron density and bonding ability of S bonding atom of molecule (a) than that of the S in molecule (b). Similarly, in comparing (b) with (c), the bonding ability of trithiocarbonate to sulfide minerals is stronger than that of the dithiocarbonate, xanthate. As an example, the solubility products of lead thiocarbonates are given below:

- Lead ethylmonothiocarbonate $(C_2H_5OCOS)_2Pb$ $L = 1.5 \times 10^{-8}$
- Lead ethyldithiocarbonate $(C_2H_5OCS_2)_2Pb$ $L = 1.7 \times 10^{-19}$

Table 5.7
Properties of some thiocarbamates (σ^* is Taft constant)

Reagent	pK_a	σ^*	λ_{max}
(1) C_4H_9–O–C(=S)–NH–C(=O)–C_6H_5	7.45	+2.34	266
(2) C_4H_9–O–C(=S)–NH–CH–C_6H_5	11.5	+0.6	272
(3) *i*-C_3H_7–O–C(=S)=NH=CH=C_2H_5	11.53	–	–
(4) C_4H_9–O–C(=S)–NH–CH_2–C_6H_5	12.1	+0.215	246
(5) C_4H_9–O–C(=S)–NH–C_2H_5	12.7	−0.10	243
(6) C_4H_9–O–C(=S)–NH–C_2H_4OH	12.7	−0.10	245
(7) C_4H_9–O–C(=S)–NH–S–C(=O)–C_6H_5	–	–	–

5.2.3.2. *Induction effect in molecule of thionocarbamates*

Structure of the minerophilic group of thionocarbamate is shown as follows:

–O–C(=S)–NH–

Changes in the properties of a reagent with the addition of a donor atom or group can be explained by considering the induction effect. Table 5.7 shows structures and properties of some derivatives of thionocarbamates [4].

The electron density of the thiono-group (C=S) and its bonding ability to the proton will be decreased by the addition of an acceptor group such as –COC_6H_5, –C_6H_5 with a negative induction.

The collector will transfer a proton in acidic or alkaline medium:

$$R–O–C(=S)–NH–R' \rightleftarrows R–O–C(–SH)=N–R'$$

The dissociation degree and the acidity of the –SH group are increased by the addition of an acceptor groups. In contrast, The addition of a donor group such as –C_2H_5, results in +I effect. The ability of bonding to the proton increases and the acidity decreases.

Flotation performance of the collectors can also be predicted from data in Table 5.7 [4]. For collectors (1) and (7), due to introducing an acceptor, the bonding power of sulfur atom to iron ion is decreased markedly, but the bonding power to copper ion stays strong. Therefore, the selectivity of separation of copper mineral from pyrite is improved. However, the reactivity of the collector (2) to the two minerals is increased because of introducing a donor group with poor selectivity in flotation.

5.2.3.3. *Induction effect in molecules of thiophosphates*

Derivatives of thiophosphates include monothio and dithiophosphate with the following structures:

(a) $(C_2H_5–O–)_2P(=O)–O–K$
(b) $(C_2H_5–O–)_2P(=S)–O–K$
(c) $(C_2H_5–O–)_2P(=S)–S–K$

Solubility products of potassium salts of these reagents and the contact angles on galena in solution at a concentration of 1 mmol/l are given in Table 5.8.

Table 5.8
Solubility products of lead salts of thiophosphate derivatives and contact angles on galena (at 1 mmol/l)

Reagents	L_{PbAs}	Contact angle, θ	
		Ethyl	Propyl
(a)	Easily soluble	45	53
(b)	5.9×10^{-5}	51	67
(c)	2.2×10^{-10}	59	86

Molecule (a) is compared with (b), the bonding atoms and central atom are the same, but the difference in linking atoms, =S and =O, can result in different degree of hydrophobization of mineral surfaces ($\Delta\theta = 6°$). The molecules (b) and (c) possess identical linking atom but different bonding atoms, i.e. –S– and –O–, and this results in a significant difference in hydrophobization ($\Delta\theta = 18°$). The difference in the hydrophobization property of molecules between (a) and (c) is greater ($\Delta\theta = 24°$).

5.2.3.4. *Comparison of thiocarbonates with thiophosphates and thiocarbamates*

There are three types of reagents possessing the same bonding atoms but different central or linking atoms are shown below:

(a) xanthate: R–O–C(=S)–S–H(Me)
(b) dithiophosphate: (R–O–)$_2$P(=S)–S–H(Me)
(c) dithiocarbamate: R$_2$N–C(=S)–S–H(Me)

The effect of various atoms or groups is listed as below:

	(a)	(b)	(c)
Central atom	$X_c = 2.5$ −I larger	$X_p = 2.1$ −I smaller	$X_c = 2.5$ −I larger
Linked atom	1 –O– group −I smaller	2 –O– group −I larger	=N– group −I smaller
Non-polar group	1 R-group −I smaller	2 R-group +I larger	2 R-group +I larger

In summary, the order of magnitude of solubility products of silver salts (in pL) and collective power for sulfide minerals are as follows: dithiocarbamate < xanthate < dithiophosphate as shown in Table 5.9.

5.2.3.5. *Collectors for nonsulfide minerals*

Dissociation degree and solubility products of metallic salts of common collectors are given below.

Reagent	Structure	pK_a	pL
Sulfonate	R–S(=O)$_2$–OH	~1.5	7–9
Phosphoric acid	R–P(=O)(–OH)$_2$	~2.6–2.9	
Arsenic acid	R–As(=O)(OH)$_2$	~3.7–4.7	
Carboxylic acid	R–C(=O)–OH	5	6–11

Table 5.9
Solubility products of silver alts with collectors

Non-polar group	Dithioncarbamate	Xanthate	Dithionphosphate
Ethyl	4.2×10^{-21}	4.4×10^{-21}	1.2×10^{-16}
Propyl	3.7×10^{-22}	2.1×10^{-19}	6.5×10^{-18}
Butyl	5.3×10^{-23}	4.2×10^{-20}	5.2×10^{-19}
Amyl	9.4×10^{-24}	1.8×10^{-20}	5.1×10^{-20}

5.2.4. Complexing (chelating) agents

As early as in the beginning of this century, chelating agents have been used as collectors in the flotation. For example, cupferron was used for flotation of oxidized copper minerals and 8-hydroxy quinoline for wolframite and lead–zinc minerals. Recently, chelating agents have been used as depressants by Schubert, Avotins and Nagaraj for the separation of fluorite from gangue minerals and molibdenite from copper sulfide minerals, respectively [3,13].

Complexing agents are classified as mono- and multi-dentates on the basis of the number of donors in their molecule. The multi-dentates can form ring structure with metallic ions and they are called chelating agents. The active atoms in the complexing agent are called donor or bonding atom or ligand atom and examples include mainly O, N, S and P atoms.

The common bonding atoms of chelating agents of the two-sets type includes S–S, N–N, O–O, S–N, S–O and O–N. Because most chemical groups are comprised of these atoms, many types of chelating compounds can be formed.

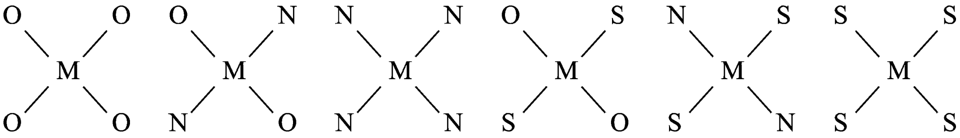
The amines commonly used in flotation processes possess one bonding atom in the molecule and hence can form only coordination compounds without a ring structure.

The stability of chelates is generally higher than that of coordination compounds, i.e. the chelating group has stronger bonding power with metallic ions. Therefore, chelating agents of lower molecular weight form less soluble chelates with metallic ions. On the other hand, complexing agents with mono-set generally produce soluble compounds and it was by increasing its molecular weight that insoluble complexes can be formed.

Structural characteristics of complexing agents are described as follows.

5.2.4.1. *Donor and acceptor atoms*

Various types of bonding of donors to Me^{2+} are described below:



Bonding characteristics depend upon the coordination number and the steric structure:

(a) Ionic bonding: donors must be negatively charged and repel each other resulting in a tetrahedral configuration of four donors or an octahedral of six donors connected to the metallic ion in the center.

(b) Covalent bonding: the structure of common metallic compounds with covalent bonds can be classified as:

Be, Si, Cu, Zn, As, Sn, Pt, Cd, Mg	tetrahedron
Al, Cr, Mn, Fe, Co, Sn, Pb, Zn, As	octahedron
Cu, Ag, Au, Ni	tetragonal plane

The selectivity of chelating agents to mineral can be estimated from information involved in the donor class of and bonding:

Bonding characteristics	Minerals
Ionic	Minerals of metallic ions (1st)
Covalent	Minerals of metallic ions (2nd)
Interim	Minerals of metallic ions (3rd)

(c) Ring structure: for steric hindering effect of chelating rings, four-, five- and six-members are generally more stable. The five-member ring formed by saturated bonds and the six-member ring formed with two or more double bonds are also stable. Thus a favorable chelating group structure is that two bonding atoms are not directly linked and separated with less than three atoms forming a four, five or six-member ring. The chelating agents commonly used as flotation collectors are listed in Table 5.10.

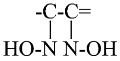
5.2.5. Non-polar groups

5.2.5.1. *Role of non-polar groups*

Non-polar groups in collector molecules play the following three roles in determining the flotation performance:

(a) Hydrophobization of the mineral surface by hydrocarbon chains of the collector molecules adsorbed on the mineral surface.

Table 5.10
Chelating agents as collectors

Bonding atom	Polar group	Metallic ions	Application
N	$-N=$	II and III metallic ions	For nonsulfide minerals
N, N	 $\mathrm{HO{-}N{=}C{-}C{=}N{-}OH}$	Ni, Pd, etc.	For nickel and copper sulfide mineral
	$-NH-C(=NH)-NH-$	Zn, etc.	For ZnS
N, O	$-N(-OH)-N=O$	Cu, Fe, etc.	For copper mineral
	$O=C=C=NO$	Co, Zr, U, etc.	For wolframite
	$O=C=C-NH-$	Cu, Zr, Cd, Ta, etc.	For Ta, Nb mineral, wolframite
	$-C(=O)-C(=NOH)-$	Fe, Cd, Co, Ni, etc.	For oxidized copper minerals
	$HOOC-(CH_2)_4-NH_2$	Great part of metallic ions	For oxidized iron minerals and wolframite
S, S	$-O-C(=S)-SH$	II, III metallic ions	For sulfides
	$(-O-)_2P(=S)-SH$	Idem.	Idem.
	$N-C(=S)-SH$	Idem.	Idem.

(b) Associative chains interactions through van der Waals force between hydrocarbon chains, hydrogen bonding and electrostatic forces between double bonds and radicals in the non-polar portion.

Desorption of collector molecules from the mineral surface can occur only by overcoming not only affinity of the minerophilic group to the surface, but also the above forces associated with the chains. Thus the affinity of the collector to the mineral surface is also dependent on the structure of the non-polar groups.

(c) Non-polar groups can affect indirectly on the adsorption of polar groups through inductive, conjugative and steric effects. These effects are illustrated in Fig. 5.4.

According to the Traube's rule, the surface activity of homologous surfactants increases by 3.2 times when one $-CH_2-$ group is added to their hydrocarbon chain:

$$\Delta\sigma = a\ln(1 + bc), \tag{5.2}$$

where $\Delta\sigma$ is the change in surface tension; a is a parameter characterizing the polar group and it is a constant for the homologous series, and b is a parameter termed the surface active coefficient characterizing the non-polar group and for two neighboring homologous $b = 0.313$.

Flotation performance of homologous collectors reported by Wark et al. [19], it was found that contact angle of minerals treated with collector solutions depends only on the structure of the non-polar groups of the reagent, and not on any other portion. In other words, for various structures of non-polar groups, contact angle on sulfide minerals in-

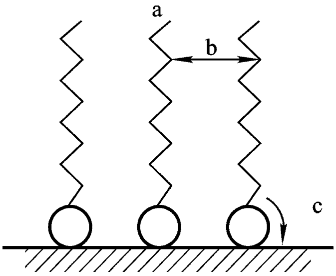


Fig. 5.4. Roles of non-polar group of collector molecule: a—hydrophobization, b—interaction between chains, c—influence of non-polar group on function of polar head (indirect influence on interaction between polar group and mineral).

Table 5.11
Contact angles of collectors for sulfide minerals

Reagents	Methyl	Ethyl	Butyl	Benzyl	Phenyl	Naphthatic
Dithiocarbamate	50	60	77	–	–	68
Mercaptan	–	60	74	71	70	68–71
Xanthate	50	60	74	72	–	71–75
Dithiophosphate	–	59	76	–	–	–

Table 5.12
Calculated values of contact angles (θ) of n-alkyl groups

Alkyl groups	Contact angle, θ^0	
	Experimental	Calculated*
C_3	68	68
C_4	74	74
C_5	80	79
C_6	90	90
C_7	94	94

*Using value of 68 for C_3.

creases only with the length of alkyl chains as shown in Table 5.11. Contact angles for various alkyl groups calculated from molecular parameters and given in Table 5.12.

Many flotation tests show that collectors possessing similar non-polar groups have different collecting properties. For example, ethyl xanthate is a good collector but acetic acid with the same ethyl group does not have any collecting property. It suggests that there is necessarily no definite parallel relationship between the above contact angle values and the flotation performance.

5.2.5.2. *Correlation of chain structure with its solubility and surface activity*

At the air/water interface adsorption is essentially an airophilic process of the hydrocarbon chains. Hence the change in free energy can be represented by the relationship for the vaporization process:

$$RT\ln(A_{n+1}/A_n) = 2950\ \text{J/mol} \tag{5.3}$$

Thus,

$$A_{n+1}/A_n = 3.29, \tag{5.4}$$

where A represents the surface activity of a chain containing one or more carbon atoms. Since the Traube's value is equal to 3.2, the corresponding relation for the solubility is given by:

$$RT\ln(S_n/S_{n+1}) = 3581\ \text{J/mol} \tag{5.5}$$

Therefore, a correlation between surface activity and solubility can be obtained as follows:

$$RT\ln(A_{n+1}/A_n) = RT(2950/3581)\ln(S_n/S_{n+1}) = RT\ln(S_n/S_{n+1})^{0.823}$$

or

$$A_n S_n^{0.823} = A_{n+1} S_{n+1}^{0.823} \tag{5.6}$$

The above equation shows that the increase in surface activity is inversely proportional to the decrease in solubility raised to the power of 0.823.

Free energies for various interactions between collectors and minerals are composed below:

Chain–chain interaction:	550–1200 cal/mol $-CH_2-$
Electrostatic interaction:	23 cal/mol per 1 mV
Hydrogen bonding:	a few kcal/mol
Chemisorption:	tens of kcal/mol

5.2.5.3. *Structure–property relationship of hydrocarbon chains*

5.2.5.3.1. *Normal saturated straight chains* Alkyl chains possess a saw-tooth planar structure with C–C–C bond angle of 109.5°. The distance between atoms linked to each other in the chain is 1.54 Å. Considering the diameter of carbon atom as 1.54 Å, the length of each $-CH_2-$ in the chain is 1.26 Å and the width is 4 Å. Since the chemical bond between two carbon atoms is formed by σ bonding of sp^3 hybridization electrons, the C–C axis can freely rotate.

It was found by Stambodliadis [12] that solubility product (pL) of salts of copper, iron and nickel with dialkyl dithiophosphates of various chain lengths is linearly related to the

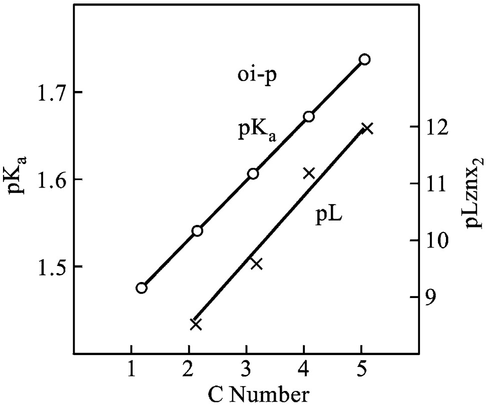


Fig. 5.5. pK_a and pL values as a function of the n values.

number of CH_2 groups (n):

Cu salt: $pL = 10.77 + 12.58 \log n$

Fe salt: $pL = -10.07 + 39.6 \log n$

Ni salt: $pL = -20.54 + 40.96 \log n$ (5.7)

The solubility products (pL) and the dissociation constants (pK_a) of zinc-xanthates as a function of chain length (n) are illustrated in Fig. 5.5. The recovery of galena flotation using xanthates and fatty acids with various chain lengths is shown in Fig. 5.6 [1].

In the case of quartz flotation using primary amines and quaternary ammonium salts, as collectors, Somasundaran [24] found that the concentration ($\log C$) of collectors at the critical flotation condition is linearly related to n values as shown in Fig. 5.7. In addition, the concentration ($\log C$) at which the zeta-potential of quartz in alkylamine solutions is equal to zero was found to have similar linear relationship with n values (Fig. 5.8).

5.2.5.3.2. *Iso-alkyl chains* Flotation performance of collectors with an iso-structure chain is different from that of collectors with a linear structure. This is summarized below:

(a) Branched chains hinder proximately between the chains and these weaken the van der Waals force and results in low melt point, high solubility and CMC.

(b) Branched chain near to a polar group may possess steric hindrance between the polar group and the mineral surface.

(c) The effect of methyl group in an iso-structure close to the polar end and with inductive effect donating electrons from the methyl group can increase electron density of the bonding atom resulting in a strong bonding and have more collective power. For example, in the case of normal propyl xanthates and iso-propyl xanthate with the following structure:

normal: $CH_3–CH_2–CH_2–OCSSH$

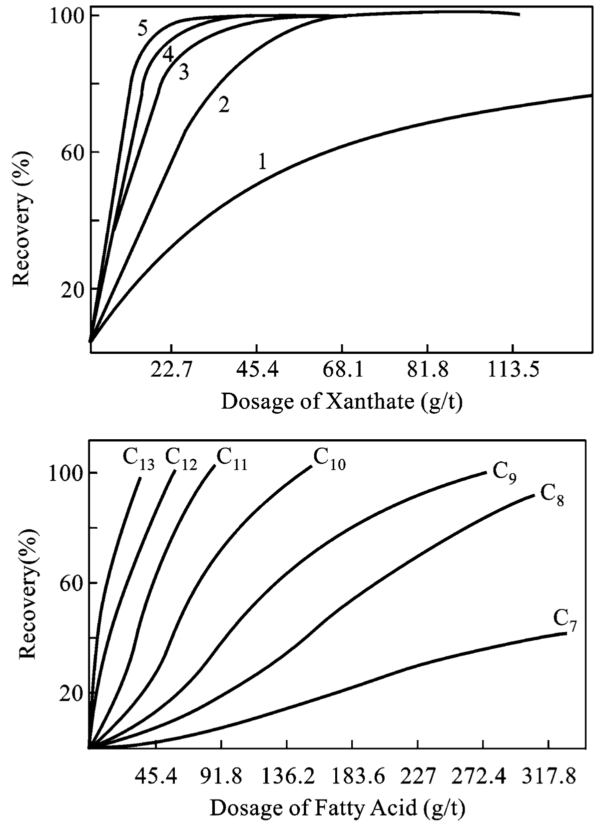


Fig. 5.6. The performance of xanthate and fatty acids with various chains for galena flotation: 1—methyl; 2—ethyl; 3—propyl; 4—butyl; 5—amyl.

iso-: $(CH_3-)_2CH-OCSSH$

Iso xanthates have two methyl groups linked to the carbon atom of the –CH in iso-propyl xanthate, hence the performance of iso-propyl xanthate is better than that of normal one.

(d) Chains with iso-structure possess larger cross-sectional area and thus yield a larger hydrophobic area when adsorbed on the mineral surface. This results in weak selectivity and strong frothing.

In summary, for reagents with short chains among the above factors, (c) is a major one and thus reagents with iso-structure are better collectors than the normal ones. However, for long chains, (a) and (b) factors are also important. The solubility of iso-structure can be increased as desired by decreasing the hydrophobic chains.

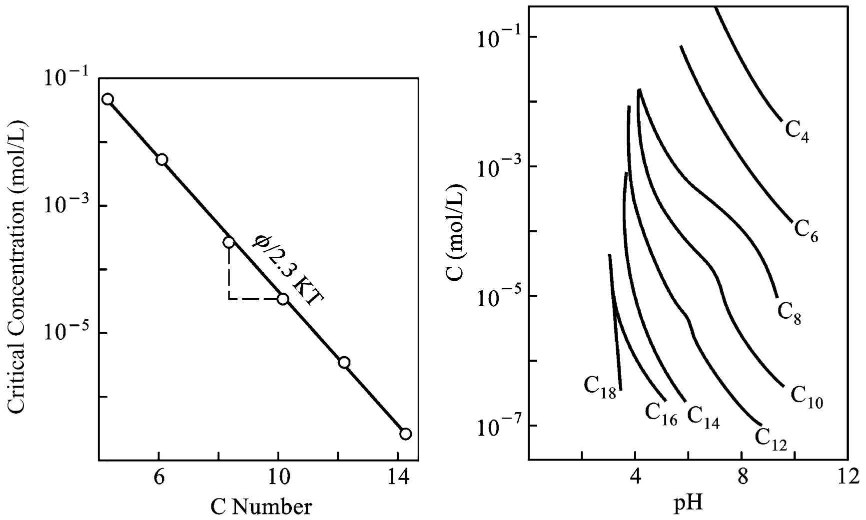


Fig. 5.7. Critical concentration of amines in quartz flotation (by P. Somasundaran, D.W. Fuerstenau).

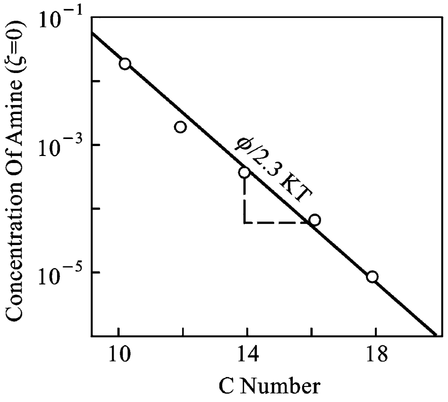


Fig. 5.8. Concentration of amines as a function of n values for quartz flotation (by P. Somasundaran).

5.2.5.4. *Unsaturated chains*

In comparison with saturated chains containing the same number of carbon atoms, organic compounds possessing unsaturated chains exhibit a lower melting point, higher solubility, CMC, chemical activity, and larger chain cross-sectional area. This is shown in Table 5.13. Four factors that affect the solubility products of reagents with unsaturated chains are:

(a) The number of double bonds.
(b) Position of double bonds in the chain.
(c) Steric structure in trans and cis forms of the chains.

Table 5.13
Properties of unsaturated fatty acids

Acid	Formula	CMC of K or Na salt	K_3P CaA_2 (20°C)	Melt point (°C)	Cross-sectional area of chain (λ_2)
Stearic acid	$CH_3(CH_2)_{15}COOH$	0.0045*	17.4	65	24.4
Oleic acid	$CH_3(CH_2)_7CHCH(CH_2)_7COOH$	0.0012*	12.4	16.3	56.6
Linoleic acid	$CH_3(CH_2)_4CHCHCH_2CHCH(CH_2)_2COOH$	0.15*	12.4	–	59.9
Linolenic acid	$CH_3(CH_2CHCH)_3CH_2(CH_2)_6COOH$	0.20**	12.2	12.5	68.2

*For K salt.
**For Na salt.

(d) Conjugated and separated double bonds.

5.2.5.5. *Aromatic groups*

A typical non-polar group with aromatic structure present in collector molecules is benzene in which six carbon atoms and six hydrogen atoms are formed into a closed conjugation system. Although the benzene ring contains six carbon atoms, its bonding and steric characteristics are quite different from those of molecules with straight alkyl chains containing the same number of carbon atoms. A benzene ring has a length of 2.84 Å and a width of 1.85 Å, which is analogous to ethyl group with higher hydrophilicity resulting from its conjugative structure.

It has been reported that the effect of adding phenyl group in non-polar portion on CMC value is analogous to the addition of 3.5 $-CH_2-$ groups. Solubilities of zinc-xanthate salts with phenyl group are given below along with those of corresponding alkyl xanthates:

Zn benzyl xanthate $(C_6H_5CH_2OCSS)_2Zn$	$S = 1.5 \times 10^{-4}$
Zn *n*-butyl xanthate $(C_4H_9OCSS)_2Zn$	$S = 2.1 \times 10^{-4}$
Zn *n*-amyl xanthate $(C_5H_{11}OCSS)_2Zn$	$S = 0.73 \times 10^{-4}$

Floatability obtained when benzyl xanthate is used as collector is analogous to that of butyl xanthate, However, the conjugated system is larger in $C_6H_4{-}CH{=}CH{-}CH_2OCSSNa$ than in C_6H_5. Comparison of thiophenols with various structures is listed in Table 5.14.

5.2.5.6. *Other non-polar groups*

Other non-polar groups in collectors include naphthalene and alkaryl groups. The naphthenic group exists in naphthenic acids and some xanthates. The length of a six member

Table 5.14
Properties of various thiophenols

Reagents	Structure	pK_a	Order of floatability
Butyl mercaptan	C_4H_9–SH	10.7	↓ Decreasing
Ethyl mercaptan	C_2H_5–SH	9.4	↓
Methyl thiophenol	$C_6H_5C_2$–SH	6.82	↓
Thiophenol	C_6H_5–SH	6.5	↓

naphthenic ring is 2.8 Å, which is analogous to ethyl or benzyl group. Their floatabilities are also similar.

Alkoxyl group exists in the non-polar position of some xanthates and dithiophosphates, which have properties similar to those of alkyl group and produce more froth. For example, etheralkyl carboxylate (ECA), R_{n_1}–$(OC_2H_4)_{n_2}$–OCH_2COOH, has been reported as a collector where n_1 is C_{8-18} chain and n_2 is the number of alkoxyl groups (0–16). Since its Ca or Mg salts with $n_1 = 10, 12, 14, 17$ and $n_2 = 10, 20$ 30 are soluble in water, ECA is suitable under hard water and low pH (<6) conditions for the flotation of calcium or magnesium minerals, chalcopyrite and beryl with better selectivity. Floatability of Ca minerals is found to linearly decrease with n_1 values and increase with n_2 values.

5.3. FROTHERS AND MODIFIERS

5.3.1. Criteria of frother performance and interactions between frothers and other flotation agents

5.3.1.1. *Criteria for frother performance*

Frother performance can be evaluated by considering the following factors:

(a) Flotation (recovery and quality of the concentrate).
(b) Foam volume and life.
(c) Aeration rate of pulp and energy consumption.
(d) Size distribution of bubbles.
(e) Moving characteristics of bubbles (rising rate).
(f) Rate of coalescence of bubbles.
(g) Mechanical property of foam (tenacity, viscosity).
(h) Electrostatic properties of bubbles (zeta-potential).
(i) Interaction of frother with the mineral surface (coadsorption with collector).

It has been reported that in the case of flotation of galena, flotation performance depends on the micro-bubbles contained in the pulp as follows [17] (Table 5.14a).

Listed in Tables 5.15 and 5.16 are various properties of bubbles with frothers [7]. Dudenkov [2] classified frothers as two types with given fractions of 0.2 mm and −0.2 mm bubbles (Table 5.14b).

Table 5.14a

Particle size	Without micro-bubbles	With micro-bubbles
$-0.15+0.044$	21	31
$-0.044+0.063$	14	24

Table 5.14b

Type of frothers	Surface area (%)	
	−0.2 mm bubbles	+0.2 mm bubbles
Strong	70–90	20–50
Weak	15–50	80–90

Table 5.15
Size distribution of bubbles with various frothers (at 10^{-4} mol/l)

Frother	Size distribution (m.m. %)					
	+0.6	−0.6 +0.42	−0.42 +0.35	−0.35 +0.28	−0.28 +0.20	−0.20
Distilled water	22	26	25	16	9	2
Phenol	21	25	25	14	11	4
Methyl phenol	19	23	19	18	13	80
Dimethyl phenol	20	25	19	18	13	5
Aliphatic alcohol C_3	15	25	25	14	8	13
C_4	14	24	25	11	8	18
C_5	12	23	25	11	6	23
C_6	10	20	20	10	6	34
C_7	6	18	19	10	8	39
C_8	5	16	19	11	9	40
C_9	4	15	18	13	10	40
C_{10}	4	13	16	15	11	40
Cyclohexanol	13	25	20	17	9	18
Methyl cyclohexanol	12	22	13	12	6	35
Ethyl cyclohexanol	6	21	10	9	88	46
Propyl cyclohexanol	5	19	9	9	10	48
Polyglycol $-(O-C_4H_8)_n-$	–	3	3	5	12	77
$-(O-C_3H_6)_4-$	2	8	9	11	20	50
Alkoxyl triethoxybutane	–	5	5	7	15	70
$(CH_3)_2C_6H_2(COOH)_2$	10	21	10	18	12	23

In flotation, foam life and size distribution of the bubbles are mainly determined by the adsorption characteristics of the frother at the air/water interface including hydrophobic association between the chains, surface migration behavior of the molecule adsorbed in

Table 5.16
Dispersion state of bubbles with various frother (at 10^{-4} mol/l) (after Dudenkov [2])

Frother	Volume fraction of 0.2 mm bubbles	Surface area fraction 0.2 mm bubbles
Polyglycol $R–(O–C_4H_8)_2–OH$	0.23	0.830
Triethoxybutane	0.30	0.836
Polyglycol $R–(O–CH_2)_n–OH$	0.48	0.713
$R–(O–C_2H_5)_4–OH$	0.50	0.703
Aliphatic alcohol C_2	0.61	0.687
C_8	0.60	0.687
$C_4–C_8$	0.62	0.686
C_7	0.66	0.680
C_5	0.77	0.554
Dimethyl benzene dicarboxylic acid $(CH_3)_2C_6H_2(COOH)_2$	0.77	0.498
Cyclohexanol		0.457
Pine oil	0.83	0.478
Resol	0.92	0.250
Phenol	0.92	0.150
Distilled water	0.98	0.081

the liquid film and the zeta-potential of the bubble surface. These properties are closely dependent on surface viscosity of dilute solution and the adsorption density of frother.

5.3.1.2. *Effect of frothers on other flotation agents*

Possible interactions of frothers on the collector and other dissolved species include:

- Coadsorption of frother with collector on the mineral surface.
- Change in the surface tension of the flotation pulp.
- Enhancement of the collector role in frothing.
- Influence of inorganic ions on frothing.

The effect of surface tension change on flotation is shown in Fig. 5.9a and the effects of collectors and inorganic salts on frothing properties are illustrated in Figs. 5.9b and 5.9c.

5.3.2. Polar groups of frothers

The polar groups depending on its structure can be expected to influence the physical properties of frothers such as solubility, degree of dissociation and viscosity, and chemical properties such as bonding with minerals and reactions with the ions in the pulp. Characteristics of common polar groups of frothers are listed in Table 5.17.

5.3.2.1. *Polar groups and solubility*

Since the surface activity of highly soluble frothers is not very high, they require more dosages for sufficient frothing or multi-stage addition for keeping the foam alive. Frothers with low solubility need strong agitation for proper dispersion in the pulp. For longer life of

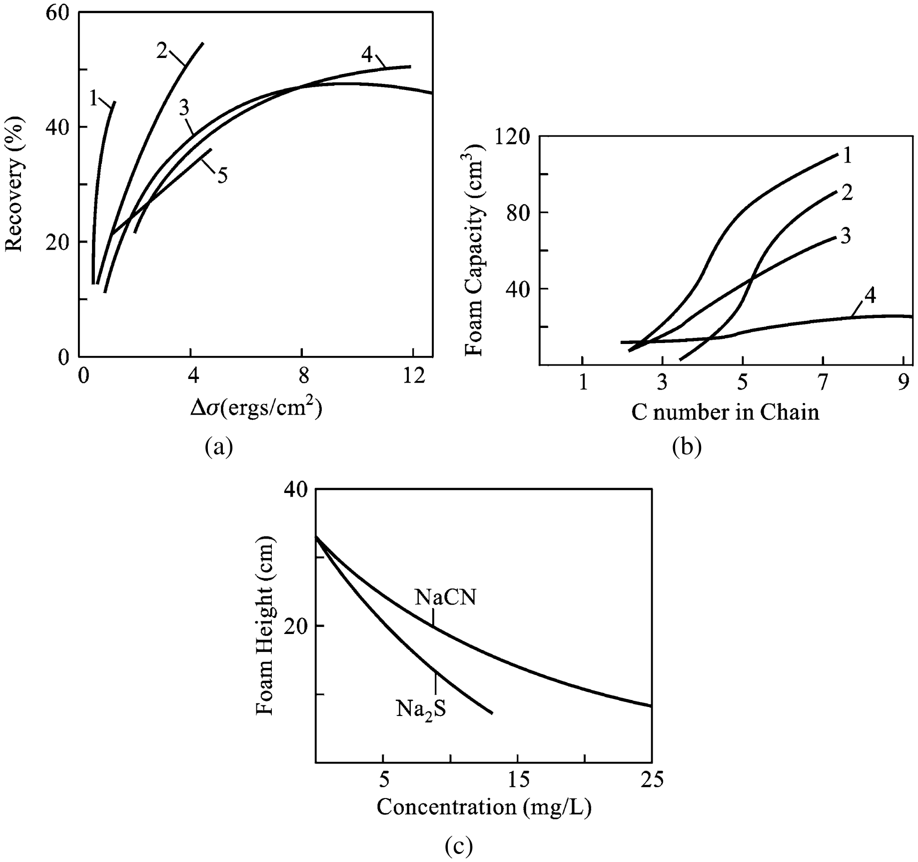


Fig. 5.9. (a) Influence of surface tension change on flotation of sphalerite and pyrite: 1—ZnS, FeS_2, quinoline; 2—ZnS, methyl quinoline; 3—ZnS, terpenol, cresol; 4—FeS_2, terpenol, cresol; 5—FeS_2, methyl quinoline. (b) Influence of xanthates on frothing of alcohols: 1—0.001 mol/l amyl xanthate + alcohols; 2—0.001 mol/l ethyl xanthate + alcohols; 3—only alcohols; 4—only xanthate. (c) Influence of inorganic salts on frothing of pine oil. Pine oil: 11.3 mg/l; $CuSO_4 \cdot 5H_2O$: 20 mg/l.

the foam, the chain length of less soluble frothers is limited to a narrow range. In addition, the required chain length of molecules of highly soluble frothers is longer, but the foam life may be short as shown in Fig. 5.10.

Poorly soluble frothers with long chains may have thicker adsorbed films and strong interactions between chains. Therefore, the stability and tenacity of foam can be expected to be high, however too long a chain can produce unstable films.

In flotation practice, less soluble frothers may also produce low frothing rate, finer bubbles and higher viscosity, and this can lead to higher flotation recovery. In contrast, soluble frothers exhibit fast frothing, coarser bubbles and brittle foam, and yield higher concentrate grade.

Table 5.17
Characteristics of polar groups of frothers

Polar groups	Interactions with		Foam stability & solubility
	Water molecules	Similar molecules	
$–CH_2I$, $–CH_2Br$, $–CH_2Cl$	Strong	Strong	No froth
$–CH_2OCH_3$, $–C_6H_5OCH_3$, $–COOCH_3$, $–OC_2H_3$	Strong	Weak	Not stable Low solubility
$–CH_2OH$, $–COOH$, $–CN$, $–CONH_2$, $–CHNOH$, $–C_6H_4OH$, $–CH_2COOH$, $–NHCONH_2$, $–NHCOCH_3$	Very strong	Intermediate	Stable & intermediate solubility
$–C_6H_4SO_3H$, $–SO_3H$, $–SO_4H$	Very strong	Intermediate	Stable & high solubility

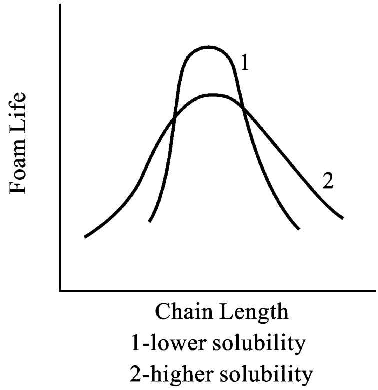


Fig. 5.10. The solubility of frother and their performance.

Solubilities of commonly used frothers are listed in Table 5.18. Solubility of frothers used commercially is about 0.0013%. Table 5.19 lists solubilities of frothers with given polar groups and various non-polar groups. It is shown that frothers with hydroxyl groups possess higher solubility.

5.3.2.2. *Degree of dissociation and frothing performance*

The pH value of medium controls the degree of dissociation of the ionic frothers and their dissolution. As a result, the frothing ability of ionic frothers is influenced markedly by the pH value of the media. Dissolution and the degree of dissociation of acidic frothers are high in alkaline media resulting in a decrease in the surface activity and the frothing ability. On the other hand, frothing ability of alkaline frothers increases in the alkaline media. This effect is illustrated in Figs. 5.11 and 5.12.

Table 5.18
Solubility of frothers (g/l)

Frother	Solubility	Frother	Solubility
n-amyl alcohol	21.9	*n*-TEB	0.586
i-amyl alcohol	26.9	*i*-TEB	1.28
λ-hexyl alcohol	6.24	Pine oil	2.50
MIBC	17.0	α-terpenol	1.88
MIBC	1.81	Camphor oil	0.74
i-MIBC	4.00	Cresol	1.66
TEB	~8	Polyglycol M.W. 400–450	Easily soluble

Table 5.19
Solubility of frothers with various polar and non-polar groups (mg/l)

Non-polar group	Polar group			
	–OH	$-NH_2$	–COOH	$-NO_2$
$-C_4H_9$	1055	–	333	–
$-C_6H_5$	874	383	24	15
$-C_6H_4CH_3$	202	–	7	5
$-C_6H_4CH_3$	227	158	9	–

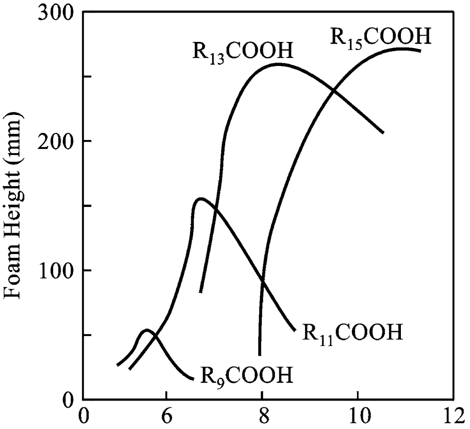


Fig. 5.11. Frothing power of fatty acid as a function of pH (concentration 0.1%).

As listed in Table 5.20, the electrostatic charge on bubbles is controlled by charge of the frother ions and the concentration of electrolyte in solution. In addition, the hydration of the frother molecule is important for the stability of foam bubbles. Interaction between polar groups of the frothers and water molecules can increase the strength of the film between bubbles.

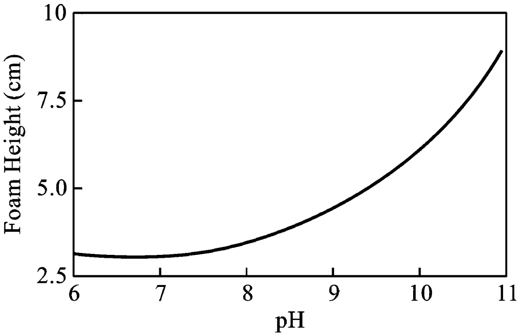


Fig. 5.12. Frothing power of pine oil as a function of pH values. Concentration: 11 mg/l (by Mitrofanov).

Table 5.20
Surface charge of bubbles in various electrolyte solutions

Electrolyte	Concn. (N)	Charge (V)	Electrolyte	Concn. (N)	Charge
KNO_3	0.01	−0.474	KI	0.001	−0.316
	0.0102	0.0		0.0075	0.0
	1.00	+0.068		1.00	+0.078
KCl	0.01	−0.294	$Al(NO_3)_3$	0.001	−0.024
	0.012	0.0		0.0203	0.0
	1.00	+0.079		1.022	+0.064
KBr	0.001	−0.344	$Mg(NO_3)_2$	0.0012	−0.562
	0.014	0.0		0.0025	0.0
	1.00	+0.080		1.2448	+0.058

5.3.3. Non-polar groups of frothers

5.3.3.1. *Normal alkyl group*

As stated above, the surface activity of a surfactant with normal alkyl chain in its molecule increases 3.2 times because of the addition of every –CH= group in the molecule. Table 5.15 shows that with the increase in the chain length especially in the range of carbon number of C_3–C_8, fraction of the fine bubbles increases.

5.3.3.2. *Iso-alkyl and unsaturated chain*

Frothers with highly branched chains possess high frothing ability. Such frothers which are widely used in flotation are methyl isobutyl carbinol and triethoxybutane:

MIBC: $H_3C–CH(CH_3)–CH_3–CH(OH)–CH_3$

TEB: $CH_3–CH(OC_2H_5)–CH_2–CH(OC_2H_5)_2$

The floatability of terpinol and resinolic acid are improved with the introduction of double bonds in molecules. Conversely, if the existing double bonds are eliminated, the result would be a decrease in frothing ability. Natural frothers with double bonds, branched chain or unsymmetrical structures such as terpinols, resinolic acids usually possess good frothing ability.

5.3.3.3. *Aromatic and alkyl-aromatic groups*

Commonly used aromatic frothers are phenols, cresols, pyridines. These are mixtures of various methylphenols, naphthols, quinolines, anilines, naphthalene, amines, etc. extracted from coal tars. These frothers have been widely used in the flotation of coal. Apart from the frothability, these reagents have certain ability as collector especially with the increase in their molecular size.

Commonly used alkyl-aromatic frothers are alkyl-benzene sulfonates (sodium salt) which possess not only frothability but can also be used as collectors especially for sulfide minerals. The effect of an alkyl chain linked with benzene ring on frothing performance is an increase in the frothability with increase in the length of alkyl chains of C_5–C_{12} over which the frothability will usually decrease.

5.3.3.4. *Alkoxyl group*

General formula is as follows:

$R\text{–}(OC_nH_{2n})_m\text{–}$

By introducing $-CH_2-$ groups among with an –O– group, the following characteristics are obtained.

In the presence of an –O– group, the polarity, hydrophilicity and solubility in water is higher than those of the same $-CH_2-$ number of alkyl groups. The surface activity of the reagents increases with the increase of n in a certain range.

Hydrophilization of –O– group in the non-polar portion of the molecule is brought about by the interaction with water molecules through hydrogen bonding and van der Waals force. Such hydrophilization decreases with increase in temperature. In aqueous solution, the configuration of the chain is tortuous with the hydrophilic oxygen atoms outside and the $-CH_2-$ groups inside, resulting in hydration of the chains. As the temperature is raised, the water molecules attached to the chains are removed and the frother molecules become less soluble in water. In addition, interaction of –O– group with other reagents becomes stronger leading to higher coadsorption.

5.4. DEPRESSANTS

5.4.1. Classification

Depressants are usually divided into three types:

(a) Inorganic depressants: acids, bases and salts.
(b) Low molecular weight organic depressants: containing –OH, –COOH, –SH or =S, $-NH_2$ and $-SO_3H$ groups.
(c) High molecular weight organic depressants: reagents such as tannin, starch, cellulose, lignin, gum and polyacrylic acids.

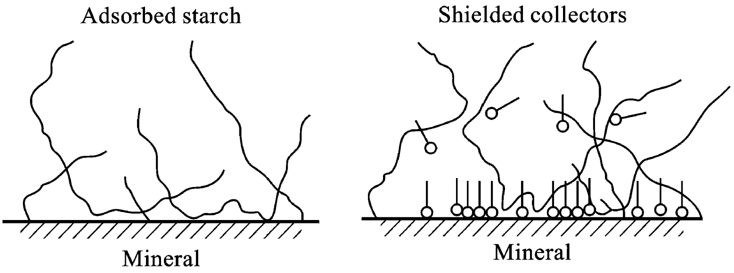


Fig. 5.13. Depression of polymer (by Somasundaran).

5.4.2. Depression mechanisms

Use of various reagents for the depression of mineral flotation is often needed for the following purposes:

(a) pH and E_h control in flotation pulp [26]: pH value in the pulp directly determines the hydration, oxidation–reduction and the double layer structure of mineral surface, thereby regulating the hydrophilic properties of mineral surfaces and their interaction with collectors or other reagents. Another important role of pulp pH is to control chemical state of the species in aqueous solution resulting from mineral dissolution and dissociation, hydrophobic association with polymers or micelles and oxidation–reduction reactions. Recent studies have shown that E_h control by oxidizing or reducing agents are very important, especially for the flotation of sulfide minerals and for collectorless flotation.

(b) Regulation of ionic components in the pulp: dissolved mineral species such as Cu^{2+}, Fe^{2+}, Pb^{2+}, Ca^{2+} and Mg^{2+} can change flotation behavior of minerals, through activation, depression or by precipitation of the collectors, all of which can result in poor separation.

(c) Hydrophilization of mineral surfaces by direct adsorption of depressants: inorganics such as sodium sulfide, sodium silicate and sodium cyanide and organics such as hydroxyl acids and thioglycols are often used as depressants.

Polymeric depressants adsorbed on mineral surfaces can directly cause the hydrophilization since their long chains can mask the adsorbed collectors. Somasundaran et al. [14] have investigated depression of calcite by starch. Their work has revealed that the starch does not decrease the adsorption of oleic acid on the mineral, flotation is prevented by hydrophilization by starch being more than hydrophobization by oleic acid as shown in Fig. 5.13.

(d) Desorption of collector from the mineral surface or collector coadsorption: competitive adsorption of similarly charged ions is an important mechanism of depression. It has been reported that depression of feldspar by sodium salicylate is due to the retardation of the adsorption of oleic acid on the mineral surface [4]. In the flotation system of hematite–oleic acid–tannin, it is observed that while oleic acid or tannin reacts individually with hematite with significant flotation effects, their adsorption is reduced

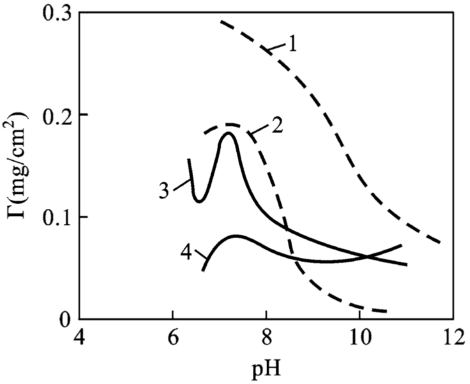


Fig. 5.14. Adsorption of oleic acid and tannin on hematite: 1—tannin S 40 mg/l; 2—tannin 40 mg/l (oleate 5×10^{-5} mol/l); 3—oleate 5×10^{-5} mol/l; 4—tannin S 40 mg/l (oleate 5×10^{-5} mol/l).

when both the reagents are present. This indicates clearly the role of the competitive adsorption between the collector and the depressant (see Fig. 5.14).

Various interactions of mineralophilic groups of depressants on the minerals can be summarized as follows:

(a) Adsorption in the double layer on the mineral surface: one of the examples in this category is modified ionic starches which are able to adsorb on negatively charged quartz and cationic starches to adsorb on positively charged hematite.

(b) Adsorption through hydrogen bonding and van der Waals forces: many hydroxyl, carboxyl and sulfonate organic depressants are known to adsorb on the mineral surfaces as a result of hydrogen bonding. For example, starch derivatives, especially natural starch and unmodified dextrin products have been considered to adsorb through hydrogen bonds between hydrogen atoms in the hydroxyl groups of the starch molecules and the oxygen atoms of minerals as in the case of minerals such as quartz. The magnitude of free energy of adsorption of starch on minerals, about 5 kcal/mole, is a characteristic of hydrogen bonding and van der Waals force.

(c) Chemisorption and other surface reactions: certain organic depressants possess chemically active groups such as thiol, carboxyl and amino groups, which are capable of reacting with elements on the mineral. Hence, chemisorption or such chemical reactions on the surface can be major mechanisms for adsorption of these reagents. Investigation by Schubert on adsorption of collectors and depressants on fluorite has shown that adsorption of various reagents is in the order [13]:

$$C_{12}H_{25}NH_3^+ < C_{12}H_{25}OSO_3^- < C_{11}H_{23}(COO^-)_2 < C_{10}H_{21}CH(COO^-)_2$$
$$< \text{alizarin} < \text{citric acid} < \text{Congo Red}$$

Chemisorption of dicarboxylic acid as a collector is considered to be strong, but these results show that the above depressants can be even more strongly adsorbed on the minerals. The above mechanisms are considered to be part of the adsorption of many other

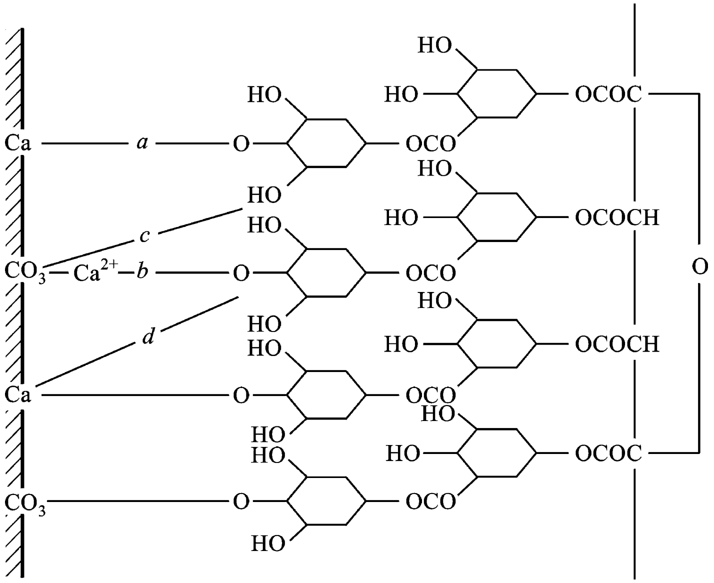


Fig. 5.15. Adsorption of tannin as a depressant on calcite. (*a*) Interaction between –OH group of tannin and Ca ions on mineral. (*b*) Adsorption of the depressant on the Ca ions on the mineral depressant. (*c*) Hydrogen bonding. (*d*) Reaction due to electrostatic forces.

reagents. Somasundaran et al. [25] proposed the adsorption of tannin as a depressant on calcite to be due to (Fig. 5.15).

5.4.3. Inorganic depressants

Inorganic depressants are usually used in combination with other flotation agents. Inorganic reagents used as depressants are listed in Table 5.21 and commonly used ones are classified below according to their application:

(a) For depression of copper minerals: P–S compounds, for example, called "Notes Depressants", sulfides, oxidizing agents such as air, $KMnO_4$ and H_2O_2 have been used for primary copper minerals, and cyanides like $K_4Fe(CN)_6$ and $Zn(CN)_2NH_3$ for secondary copper minerals.

(b) For depression of PbS: reducing agents especially S–O salts such as H_2SO_3, SO_2, $Na_2S_2O_3$, $K_2Cr_2O_3$, sulfides, iron salts and phosphates.

(c) For depression of ZnS: compounds such as H_2SO_3, SO_2, Na_2SO_3, $ZnSO_4$, CaO, sulfides and cyanides.

5.4.4. Structure of organic depressant

The structural characteristics of organic depressants may be summarized as follows: the molecule must have as a small hydrocarbon framework as possible with several (over two) polar groups; the polar groups located anywhere at the two ends; a fraction of the

Table 5.21
Inorganic reagents commonly used as depressants

Type		Depressants	Application
Anionic	Cyanide	NaCN	For depression ZnS, FeS_2
		$Ca(CN)_2$	Idem.
	Ferricyanide	$K_4Fe(CN)_6$	Idem.
		$K_3Fe(CN)_6$	Idem.
	Zinc cyanide	$K_2Zn(CN)_4$	Idem.
		$Zn(CN)_2(NH_3)_2$	Idem.
	Sulfide	Na_2S	For depression ZnS, FeS_2
		NaHS	Idem.
		Na_2S_x	Idem.
		CaS_x	Idem.
	Acid containing S	H_2SO_3	ZnS
		Na_2SO_3	Idem.
		SO_2	Idem.
		$Na_2S_2O_3$	Idem.
		HOC_2SNa	Idem.
		$(HO)_2PS_2Na$	Sulfide minerals
	Chromate	K_2CrO_7	Idem.
	Silicate	Na_2SiO_3	Silicate minerals
		Na_2SiF_6	Idem.
	Fluoride	HF	Silicate minerals
		NaF	Idem.
	Phosphate	Na_3PO_4	Gangue minerals
		Na_2HPO_4	Idem.
		$(NaPO_3)_n$	Idem.
Cationic	Zinc salt	$ZnSO_4$	ZnS
	Calcium compound	CaO	FeS_2
		$CaCl_2$	Idem.
		$CaOCl_2$	CuS and iron minerals
	Iron salt	$FeSO_4$	Idem.
		$Fe_2(SO_4)_3$	Idem.
	Aluminium salt	$Al_2(SO_4)_3$	Idem.

polar groups being minerophilic and other groups projecting outward so as to bring about hydrophilization of the mineral. The bonding of the minerophilic group must be stronger than that of the collector and the hydrophilic groups must have high hydration power.

The minerophilic groups of various collectors may also be used as depressants as in, for example:

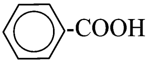
- thiocarbonates: HOCSSH, HSCSSH;
- thiophosphates: $(HO)_2PSSH$, $(HO)_2POSH$;
- thiocarbamates: NH_2CSSH, $(NH)_2PSSH$;
- thio groups: –SH, $(NH_2)_2CS$, $NH_2C(SH)_2$
- carboxylates: –COOH, –CH(OH)COOH, $–CH(NH_2)COOH$
- sulfonates, sulfates, phosphates, etc.

The hydrophilic groups commonly used are –COOH, –OH, –O– and $-SO_3H$.

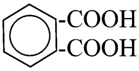
The structure–property relationship of the depressants used in some flotation systems are discussed below.

5.4.4.1. *Structure of organic depressants for Cu^{2+}-activated quartz* [27]

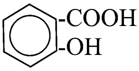
(I) Benzoic acid



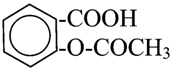
(II) Phthalic acid



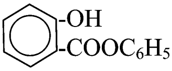
(III) Salicylic acid



(IV) Methyl salicylate



(V) Phenyl salicylate



The order of the ability of the above reagents to depress (depressability) is:

(II) > (III) > (I) > (IV) > (V).

Reagent (V) does not seem to have any role in causing depression and reagent (IV) depresses the flotation only at high dosages. It must be noted that the depressability of the reagents increases with increase in the number and activity of the polar groups. Hydration and adsorption capacity of these groups have been discussed in Sections 5.1 and 5.2. The order of the depression obtained with the above three groups is –COOH > –OH > $-COOCH_3$. Reagent (II) with two –COOH radicals is the most powerful agent while reagent (III) with one –COOH and –OH groups is the next. Reagents (IV) and (V) have only a –OH group yielding low depression.

The order of depression of these reagents when used on Ca^{2+}-activated quartz is as follows: (XI) > (X) > (VII) > (VIII) > (IX) > (VI).

Citric acid with three –COOH and one –OH groups and tartaric acid with two –COOH and two –OH groups are excellent depressants, oxalic and amberic acid possessing two COOH groups also exhibit good depression, but the two $-CH_2-$ groups on the latter molecule reduces its hydrophilicity; acetic acid and lactic acid which have only one –COOH group are very weak depressants.

Comparison between aromatic and aliphatic acids: dosages (mol/t) of the above depressants required for depression of 96–99% quartz are used as the criterion for evaluating the reagent power. The order for the above reagents are as follows (the data in brackets are dosages):

$$\text{(XI)}_{(2.5)} > \text{(X)}_{(4.0)} > \text{(II)}_{(4.5)} > \text{(III)}_{(9.0)} > \text{(VII)}_{(11.0)} > \text{(I)}_{(12.3)} > \text{(VIII)}_{(12.75)}$$
$$> \text{(IX)}_{(17.6)} > \text{(VI)}_{(33.2)}$$

This order shows that the depressability of the reagents with aromatic framework is higher than that of the reagents with aliphatic framework having the same polar groups.

5.4.4.2. *Organic depressants for fluorite flotation [18]*

(I) Citric acid
(II) EDTA-Na
(III) Tartaric acid
(IV) Maleic acid
(V) Butyl dicarboxylic acid
(VI) Lactic acid
(VII) Benzene dicarboxylic acid
(VIII) Congo Red
(IX) Alizarin Red
(X) Gallic acid

When a mixture of sulfonate and sulfate is used as the collector, the order of depressability of the above reagents is: (I) $>$ (II) $>$ (IV) $>$ (III) $>$ (X) $>$ (VII) $>$ (VI) $>$ (V). This order shows that higher depression ability is possessed by those molecules which have more polar groups, higher activities of such groups and less non-polar portion.

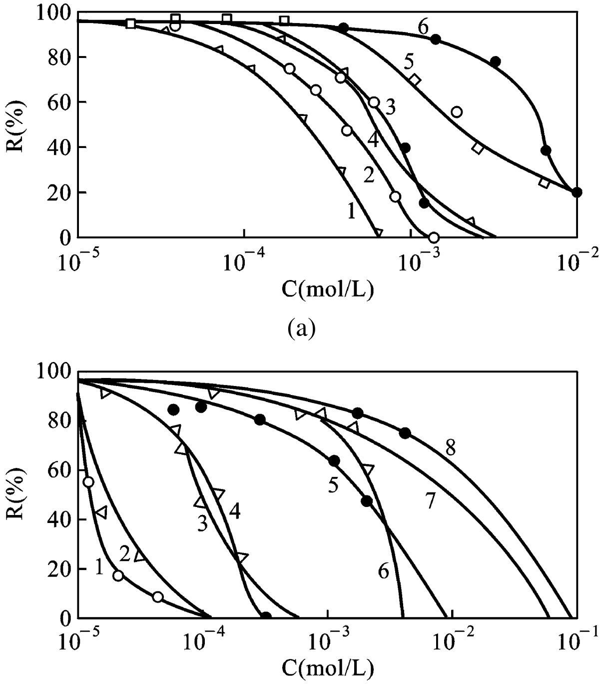
Adsorbability of various reagents and collectors on fluorite is as follows: (III) $<$ (VI) $<$ (V) $<$ (VII) $<$ (IX) $<$ (I) $<$ (VIII).

Depressants can impede adsorption of collectors on the mineral surfaces in the following order: citric acid $>$ Alizarin Red S $>$ EDTA-Na. But adsorption of these depressants themselves on the minerals is in the order of: (VIII) $>$ (I) $>$ (VII) $>$ (III) $>$ (VI). These order show that adsorbability of effective depressants is higher than that of carboxylate collectors which chemisorb on mineral surfaces.

5.4.4.3. *Organic depressants for Fe^{3+}-activated wolframite and quartz*

Depression of wolframite–quartz flotation with various flotation agents is shown in Figs. 5.16a and 5.16b. Experimental results for the concentration of the reagents for good depression of the above two minerals are listed in Table 5.22. The structural characteristics of the depressant molecules can be summarized as follows:

(a) The depressability of organic depressants is determined by the number of polar groups in their molecules. Reagents with only one polar group do not possess any ability to depress. Those that exhibit depression property will have two or more polar groups some of which are minerophilic and others are hydrophilic.
(b) Depressability also depends on the reactivity of the polar groups towards water or minerals.
(c) furthermore depressability is influenced by the extent to which the polar groups in a molecule project outwards or inwards. This is exemplified by the fact that amine groups in EDTA molecules do not play any role in depression.



(a)

(b)

Fig. 5.16. (a) Depression of various reagents on wolframate flotation: 1—citric acid, 2—tartaric acid, 3—oxalic acid, 4—EDTA, 5—succinic acid, 6—lactic acid. (b) Depression of various reagents on flotation of Fe^{3+} activated quartz: 1—tartaric acid, 2—citric acid, 3—EDTA, 4—oxalic acid, 5—succinic acid, 6—butyl dicarboxylic acid, 7—lactic acid, 8—acetic acid.

Table 5.22
Concentration of reagents for depression of minerals, mole/l

Reagents	For quartz	For wolframite
Citric acid	4.0×10^{-5}	4.6×10^{-4}
Tartaric acid	3.0×10^{-5}	2.0×10^{-4}
EDTA	1.3×10^{-4}	1.2×10^{-4}
Oxalic acid	2.2×10^{-4}	1.0×10^{-3}
Butyl dicarboxylic acid	4.0×10^{-3}	–
Succinic acid	4.0×10^{-3}	3.0×10^{-2}
Lactic acid	6.0×10^{-3}	3.0×10^{-2}
Acetic acid	1.5×10^{-1}	–

(d) Depression by the reagents with aromatic framework is always higher than those with aliphatic ones. In addition to the above, there is another class of organic depressants which are used as oxidizing or reducing agents to control E_h potential of the pulp or the redox reaction of the collector on the surface of sulfide minerals.

The hydrophilicity of the polar groups of the above reagents is not very high and the depression is caused mainly through the chemical activity or nature of the reagents.

5.4.5. Structure of polymeric depressants

5.4.5.1. *Structural characteristics of polymeric depressants*

Their characteristics listed in Table 5.23 include those of various types of polar groups and C–H frameworks. Two special mechanisms of depression of polymeric depressants are described below:

(a) As polymeric depressants possess long and branched chains, they can get adsorbed on mineral surfaces not only maintaining their hydrophilicity but also masking collectors that are adsorbed on such surfaces and thus restoring their hydrophilicity. They can also indeed prevent adsorption of the collectors.
(b) Polymeric depressants have both depression and flocculation properties with the result that the particles are aggregated and the flotation behavior of the minerals is changed.

5.4.5.2. *Structure–property relationship of natural starch [17]*

Various starches have been used in industry for depressing talc, mica, natural sulfur, carbon gangue and sulfide minerals, and especially for depressing oxidized iron minerals in the reverse flotation of iron ore and the separation of Cu–Mo in the copper–molybdenite sulfide flotation.

Starches made from stem tubers of plants have various chemical components and structures. According to the different configurations of chains in their molecules, starch can be divided into amylose (with straight chain) and amylopectin polymer (branched or gelatinized). The characteristics of these two kinds of starch are as follows (Table 5.23a).

Common natural starch contains less of amylose than the amylopectin one, and 3–25% of the former is wrapped within a framework of the latter. Composition of starches from different plants with respect to the above two classes are shown in Table 5.23b.

5.4.5.3. *Modified starch*

A common example of the modified starch is dextrin made by the hydrolysis of natural starch with dilute acids. Its molecular weight is lower than that of the natural starch. In the literature, the dextrin is also called British gum which has a molecular weight of about 800–79 000. Application of dextrin is similar to that of starch as a depressant for molybdenite and hematite used alone or in combination with other reagents such as aniline employed for depression of gangue slime and carbon gangue. It has been reported that adsorption of dextrin on molybdenite conform to the Langmuir equation with the free energy of adsorption as 5.4 kcal/mol-dextrin unit. Since dextrin is nonionic, its adsorption on the minerals has no direct influence on the double layer of the mineral surface. While the relative value of the zeta-potential does change with the addition of dextrin, there is no change

Table 5.23
Structural characteristics of commonly used polymeric depressants

Reagent	Structural characteristics		
	Polar group		Framework
Starch			
Natural	–O–, –OH	α-glucose	Corn, cassava for hematite & MoS_2
Cationic	$-N(CH_3)_2$, –O–	…	Silicate
Anionic	–COOH, –O–	…	Hematite & gangues
Dextrin	–O–, –OH	…	…
Cellulose			
Carboxyl methyl	–COOH(Na), –O–	β-glucose	Ca–Mg minerals & slimes
Hydroxyl ethyl	–OH, –O–	…	…
Sulfonate	$-SO_3HNa$, –O–	…	…
Xanthate	–OCSSHNa, –O–	…	Sulfides
Polyglucose			
Natural gums	–O–, –OH	Glucose	Ca–Mg minerals & slimes
Modified	–O–	…	…
Lignin			
Natural	–OH	$-C_2H_4-$, $-C_3H_6-$	RE minerals & gangues
Sulfonate	–SOH(Na,Ca), –OH	…	…
Chloride	–Cl, –OH	…	…
Tannin			
Natural	–COOH, –OH	$-C_6H_4-$, etc.	…
Oxide	…	…	…
Sulfide	… & –SH, =S	…	…
Synthetic	$-SO_3H$, –Cl	…	…
Acrylic polymers			
Polyacrylic acid	–COOH	$-CH_2-$	Flocculant for gangues
Polyacrylamide			

Table 5.23a

	Amylose	Amylopectin
Linking position	1,4 chain	1,6 or 1,3 chain
Polymerization degree	200–980	600–6000
Molecular weight	32 000–160 000	10^5–10^6
Solubility in water	Soluble	Limited

Table 5.23b

Plants	Amylose	Amylopectin
Corn	15	85
Potato	3	97
Rice	12	88
Wheat	23.5	76.5

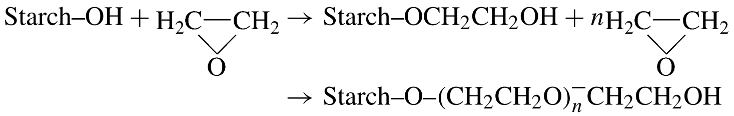
with the solution pH itself. It has been suggested that adsorption of dextrin on the minerals is mainly due to hydrogen bonding and van der Waals forces.

Modification of starch molecules is carried out by the addition of various chemical radicals through oxidation, etherification, esterification, and introduction of anionic or cationic groups, generally at 2 and 6 sites. Major chemical reactions involved in the preparation of modified starches are given below.

Phosphate starch (anionic):

$$\text{Starch–OH} + \text{Na}_5\text{P}_3\text{O}_{10} \rightarrow \text{Starch–OPO}_3\text{Na} + \text{Na}_3\text{HP}_2\text{O}_7 \tag{5.8}$$

Alkoxyl starch (nonionic):



$$\text{Starch–OH} + \underset{\text{O}}{\text{H}_2\text{C—CH}_2} \rightarrow \text{Starch–OCH}_2\text{CH}_2\text{OH} + n\underset{\text{O}}{\text{H}_2\text{C—CH}_2} \rightarrow \text{Starch–O–(CH}_2\text{CH}_2\text{O)}_n^{-}\text{CH}_2\text{CH}_2\text{OH} \tag{5.9}$$

Tertiary amine starch (cationic):

$$\text{Starch–OH} + \text{ClCH}_2\text{CH}_2\text{N(CH}_3)_2 + \text{NaOH} \rightarrow \text{Starch–OCH}_2\text{CH}_2\text{N(CH}_3)_2 + \text{NaCl} + \text{H}_2\text{O} \tag{5.10}$$

Depression mechanisms of various modified starches are different from that of each other. In aqueous solution, starch molecules are associated with each other by means of hydrogen bonding. While the unmodified starch is negatively charged in the pH range of 3 to 11, the charge of modified starch molecules depends on the substituted groups in them.

As expected, cationic starches adsorb on negatively charged mineral such as quartz while anionic starches adsorb more on positively charged minerals such as hematite in the low pH range. Since mineral surface will become more negatively charged with increase in pH, the adsorption of anionic starches decreases with rising pH and that of cationic starches increases. Natural starches are slightly negatively charged and hence adsorb more on hematite than on quartz in the low pH range and more in the lower pH range than in the higher pH range. On the contrary, adsorption of the cationic starch on hematite is lower than that on quartz and increases with increase in pH.

In summary, adsorption of starches on minerals takes place through hydrogen bonding, the van der Waals force and electrostatic force while chemisorption also plays a role in the area of adsorption of modified starches.

5.4.5.4. *Tannin*

Tannin, which is available as dry powder or as concentrated aqueous solution, is extracted from plants commonly called quebracho. Often the portions of the plant containing large amounts of tannin are broken up directly to make tannin powders. While the composition of the various quebrachos can vary greatly depending on their source and processing, basic structural units are all phenol groups linked to the molecule that have a molecular weight of 2000 or more.

Tannins are usually divided into two kinds depending on the components and properties: soluble gallic acid and cationic acid. They are obtained through heating and hydrolysis in dilute inorganic acid, and are called hydrolyzed tannin and agglomerated tannin, respectively.

Tannin is soluble in water and alcohol. It can form colored complexes or precipitates with calcium, iron and lead ions. The tannin that is commonly used as a depressant is called quebracho, which is extracted from apocynaceae, a plant species in South America. It contains agglomerated tannin.

Tannins are mainly used as depressants for dolomite, calcite and silicate minerals in the flotation of scheelite, apatite, fluorite and copper sulfide. Like starch, tannins after modification by oxidation, sulfidization and aminization (tannin O, S and A, respectively) have been used as a depressant for hematite in the reverse flotation of quartz with oleic acid or dodecylamine as collectors [22]. Flotation results show quartz to be depressed by tannins in the order of tannin A $>$ S at low concentrations of dodecylamine. When an anionic collector is used for the reverse flotation of Ca^{2+}-activated quartz with tannins as depressant for hematite, the order of depression is tannin A $>$ O $>$ S.

5.4.5.5. *Lignin*

Lignin is one of the complex organic substances occurring as a major constituent in the stems, roots and leaves of trees and plants, with about 60–70% of wood being lignin. Essentially, lignin is a natural polymer containing a variety of isomers with –OH and $–OCH_3$ groups. This polymer possesses a lower degree of polymerization than cellulose along with which lignin invariably occurs in nature and has a molecular weight of about 800 to 1000.

Materials used for obtaining lignin depressants are usually wastes and by-products of various industrial processes which use wood and seeds as raw materials. Compounds such as soluble lignin sulfonic acid, chloride and alkaline lignin can be made by treating lignin with various chemicals. The polar groups in lignin may be added on to the branched chains of the propane or the phenyl ring.

Selective flotation of fluorite and barite is usually very difficult using water glass and tannic acid. However, good separation of these minerals has been achieved with the use of lignosulfonate [18]. Lignosulfonate can also selectively depress molybdenite and some rare earth metal minerals. In the reverse flotation of hematite and quartz, lignosulfonate has been used as a depressant of hematite.

5.4.5.6. *Gums*

Gums are macromolecular substances containing polysaccharides extracted from natural plants. Gums can be used as depressants directly or after chemical modification. Guar gum which is a depressant for silicate minerals is a product obtained from the processing of the guar seeds common to the Arabic countries and India.

Gum arabic is a mixture of Ca, Mg and K salts of Arabic saccharinic acid which consists of 1-D-hexanic acid, 3-D-galactose, 2-L-arabic saccharide and 1-L-rhamnose. The saccharosan is contained in seeds, bud stems, roots, leaves and skins of many plants. In general, all the gums, including starches and cellulose, are natural polymers of the saccharide units although their structures are quite different from one another. Starch has a simpler struc-

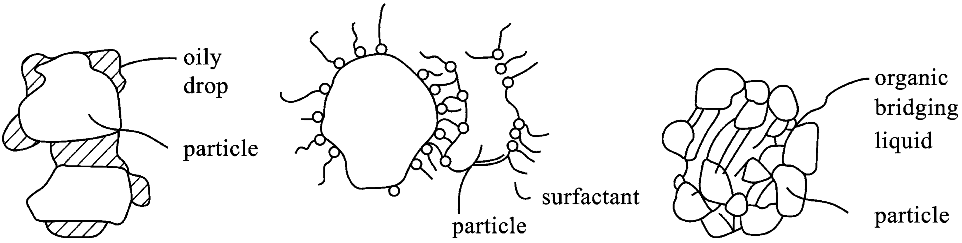


Fig. 5.17. Hydrophobic agglomeration process.

ture with less number of branches in the molecules while cellulose has a more twisted structure and gums have more complex and branched structure. They all are capable of conversion to macromolecules containing –COOH and –OH groups by appropriate chemical processes. Such modified gums find application in the flotation of various minerals. For example, etherized gum is mainly used as a depressant for silicate minerals such as talc, mica, serpentine and chlorite and also in the flotation of potash, Ni sulfide and other nonferrous metal sulfides.

5.5. FLOCCULANTS

5.5.1. Types of flocculants and flocculation

In general, flocculants are used in solid–liquid separation processes such as thickening and filtration. Inorganic salts are also used sometimes to aggregate fine particles. Flocculation technique has been developed further for special applications of selective flocculation, selective dispersion and agglomeration flotation.

Aggregation of fine particles can be classified mainly into four types:

(a) Coagulation by electrolytes: settling of fines can be achieved by the addition of electrolytes which can decrease the zeta-potential of the particles and the electrostatic repulsion between them and resultant aggregation of the particles in the medium. Inorganic compounds and polymeric electrolytes usually belong to this category.

(b) Hydrophobic agglomeration: mineral particles possessing hydrophobicity on the surface are agglomerated in this case owing to association of hydrocarbon chains of adsorbed surfactants and non-polar oil (in Fig. 5.17). If sufficient oil is added, hydrophobic particles are wetted by the oil which form an organic bridge between them. These agglomerates are not only large but also possess high hydrophobicity and floatability.

(c) Bridging by polymers: polymer molecules possess long chains which contain number of minerophilic groups so that they can get absorbed on the particles and lead to bridging them by polymer chains and consequently to flocculation.

(d) Aggregation of particles by magnetic force or other forces: in a magnetic field, fine particles of magnetic minerals such as magnetite are aggregated by the force produced

Table 5.24
Types of flocculants

Reagents	Mechanism	Structure	Examples
Soluble inorganic compound	Coagulation	Inorganic salts, acids, bases	$Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $FeSO_4$ $NaAlO_2$, $FeCl_3$, $ZnCl_2$, $TiCl_4$, H_2SO_4, HCl, CO_2, NaOH, CaO, Na_2CO_3
Inorganic colloid particles	Neutral charge of particles and coprecipitation	Hydrolysis products of metallic ions, solid powder, inorganic polymer	$Al(OH)_3$, $Fe(OH)_3$
Organic surfactants	Hydrophobic agglomeration	Heteropolar molecule	Sodium oleate, sulfonate, xanthate
Hydrocarbon oil	Oil bridging	Non-polar molecule	Kerosene, fuel oil
Organic low M.W. polymer	Bridging and coagulation	Anionic	Alginate-Na, carboxyl-methyl cellulose-Na, sodium humate
(M.W. thousand to tens of thousands)		Cationic	Soluble aniline resin, polythiourea, polyvinyl ethylamine
		(P225)	Poly-2-methacryloyloxy ethylene Trimethyl ammonium chlorate
		Amphoteric	Animal gelatins
		Nonionic	Starches, gums
Organic high M.W. polymer	Bridging and coagulation	Anionic	Polyacrylic acid (-Na) Hydrolyzed polyacrylamide
		Cationic	Polyethylene pyridine chloride
		Nonionic	Polyacrylamide, polyhydroxyethylene

by a magnetic equipment or magnetic particles present in the pulp. Commonly used flocculants are listed in Table 5.24.

Coagulation by inorganic electrolytes is caused by adsorption in the double layer of the mineral particles and resultant reduction in the magnitude of the zeta-potential into the range for instability, i.e. usually from 0 to 15 mV in magnitude. The coagulation power of these reagents depends on the properties of relevant counterions of the electrolyte as well as the mineral surface. Types of inorganic ions that can act as coagulants are discussed below.

5.5.2. Inorganic electrolytes as coagulants

(a) Potential-determining electrolytes: an electrolyte containing the potential-determining ions for the mineral particles can adsorb on the surface deep within the Stern plane of the double layer or as a part of the mineral crystal lattice and influence the magnitude of the zeta-potential drastically. Therefore, the potential-determining ions which are the

Table 5.25
Potential determining ions, point of zero charge (PZC) and solubility products, pK_{sp} of minerals

Minerals	Potential determining ions		Point of zero charge		pK_{sp}
$BaSO_4$	Ba^{2+},	SO_4^{2-}	pBa	6.7	1.5×10^{-9}
CaF	Ca^{2+},	F^-	pCa	3	1.7×10^{-10}
$CaWO_4$	Ca^{2+},	WO_4^{2-}	pCa	4.8	8×10^{-3}
AgCl	Ag^+,	Cl^-	pAg	4	1.56×10^{-10}
AgI	Ag^+,	I^-	pAg	5.6	1.5×10^{-16}
Ag_2S	Ag^+,	S^{2-}	pAg	10.2	1.6×10^{-49}

mineral lattice constituent or isomorphous substituents may be used as an effective coagulant. Listed in Table 5.25 are certain potential-determining ions and concentrations at the point of zero charge (PZC) of the minerals.

(b) Inorganic acids and bases: hydrogen and hydroxyl ions are potential-determining ions for certain minerals such as oxides, silicates and salts of oxygen-containing acids. Therefore, pH of the medium has a major influence on the surface charge density of the mineral particles, and can cause their coagulation at certain value.

(c) Indifferent electrolytes: ions adsorbed to maintain the electroneutrality of the mineral surface are called counterions and most inorganic ions charged oppositely to the mineral surface can function as counterions. Based on the Gouy–Chapman treatment of the double layer, the relationship between the concentration of the counterions, zeta-potential value and diffuse layer charge density is given as follows:

$$\sigma_d^+ = \sqrt{2\varepsilon nkT/\pi}\,\sinh(ze\zeta/2kT), \tag{5.11}$$

where σ_d^+ is charge density of the diffuse layer of a negatively charged mineral particle; n the number of ions per cm^3 in solution; z the valency of the ion; e the electronic charge and ε the dielectric constant.

It can be seen that the effect of indifferent electrolytes on the zeta-potential of the mineral particle depends not only on its concentration but also on the valency of the counterions involved. The Schultz–Hardy rule expresses the dependence of the ability of a coagulant on the valency of the ions as follows:

$$C = 1/z^n, \tag{5.12}$$

where C is the critical concentration of the ions required for coagulation.

The ratio of the critical coagulation concentration value for mono, di- and tri-valent ions has been reported to be 500 : 10 : 1 as well as 100 : 20 : 1 [4]. Coagulation concentrations of various electrolytes for colloidal suspension of arsenic sulfide are listed in Table 5.26.

Schultz–Hardy rule can also be applied to organic ions. For example, the coagulation concentration of amine ions depends on the number of alkyl groups linked to the nitrogen atoms of the amine group. In other words, the coagulation concentrations depend in this

Table 5.26
Coagulation concentrations of certain electrolytes for As_2S_3 colloid (mM)

Reagents	Values	Reagents	Values
NaCl	51.0	Oxalate	0.36
KCl	49.5	Ferric cyanide	0.10
KNO_3	50.0	Ferrous cyanide	0.08
$1/2K_2SO_4$	65.5	$MgCl_2$	0.72
NH_4Cl	42.0	$MgSO_4$	0.91
HCl	31.0	$CaCl_2$	0.65
Aniline-HCl	2.5	$BaCl_2$	0.69
Morphia-HCl	0.42	$AlCl_3$	0.093
Magenta-HCl	0.11	$1/2Al_2(SO_4)_3$	0.096
Salicylate	3	$Al(NO_3)_3$	0.095
Picrate	4	$Ce(NO_3)_3$	0.08

case indirectly on the chain length (number of carbon atoms, C_n) of the alkyl groups. This effect can be considered to be similar to that suggested by the Traube's rule, which states the ratio of concentration for equal surface tension reduction by homogeneous surfactants to depend on the ratio of C_n/C_{n+1}. Critical coagulation values of aliphatic amines and their chlorides for As_2O_3 colloids are listed below:

$$\alpha = C_n/C_{n+1} = (C_n/C_{n+a})^{1/2},$$

where α is flocculation valence.

Electrolytes	*C* (mmol/l)	$(= C_n/C_{n+1})$
NH_3	2.66	–
$C_2H_5NH_2$	0.23	3.4
$(C_2H_5)_2NH$	0.0206	3.34
$(C_2H_5)_3N$	0.00223	3.04
NH_4Cl	42	–
$C_2H_5NH_3Cl$	15.2	1.66
$(C_2H_5)_2NH_2Cl$	10	1.23
$(C_2H_5)_3NHCl$	2.8	1.88
$(C_2H_5)_4NCl$	0.89	1.77

For C_n/C_{n+a}, $\delta = (C_n/C_{n+a})^{1/a}$. Experiments have shown the coagulation power of cationic counterions for negatively charged surfaces of minerals to be in the order:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < NH_4^+ < Mg^{2+} < Ca^{2+} < Ra^{2+} < Al^{3+} < Fe^{3+}$$

The coagulation power of ions of the same valency increases with its ionic weight.

For positively charged minerals, the order of coagulation power of anionic counterions is:

$$1/2SO_4^{2-} < F^- < NO_3^- < Cl^- < Br^- < I^- < CNS^- < OH^-$$

Coagulation by inorganic electrolytes has been found to be effective only for fine colloids and not for suspensions of coarse particles, for example, of size over 0.074 mm.

5.5.3. Structure of minerophilic groups in organic flocculants

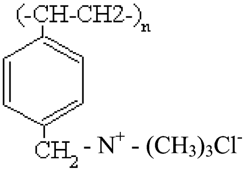
Minerophilic groups of organic flocculants can be classified into the following four categories based on the interaction forces of minerophilic groups with particle surface.

5.5.3.1. *Adsorption by electrostatic force*

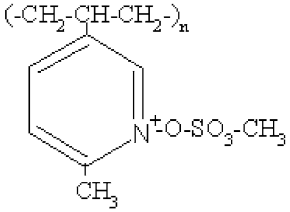
Ionic flocculants whose charge is opposite to that of the mineral surface adsorb easily on minerals by bridging and affecting the sign of the interface charge to cause the flocculation of the particles. For example, cationic flocculant, polyethyldiamine, is effective for negatively charged quartz, but the anionic carboxy-ethyl-cellulose and hydrolyzed polyacrylamide do not coagulate quartz particles.

The effect on the zeta-potential of mineral particles in a medium due to the adsorption of ionic flocculants on the mineral surface is illustrated using the changes produced by the following reagents [15]:

(i) Poly-4-ethylene-*n*-benzene-trimethyl ammonium chloride



(ii) Copolymer of 2-methyl-5-ethylene-pyridine and dimethyl sulfate



The change in the zeta-potential values of the minerals are listed in Table 5.27.

The adsorption of cationic flocculants on the minerals makes the negative zeta potential of quartz and scheelite move to positive. Charge reversal occurs at high concentrations.

The flocculation power of polymers depends on the number of ionic groups attached to the long chains of the polymers. Multi-valent flocculants possessing a number of ionic groups in their molecules will adsorb more on oppositely charged mineral surfaces, suggesting the validity of the Schultz–Hardy rule as shown in Table 5.28.

Table 5.27
Effect of ionic flocculants on zeta-potential of minerals

	Reagents (g/l)	Zeta-potentials, mV		
		Quartz	Scheelite	Fluorite
(i)	2–4	0	0	–
	75	16–18		
	25			24–26
(ii)	4–6	0	0	
	75	20–25	5	6–18

Table 5.28
Flocculation power of polyacrylamides with different amounts of ionic groups on various minerals

Minerals	Anionic		Nonionic	Cationic	
	High	Low		High	Low
Quartz (fresh surface)	0	0	+	+	+
Quartz (old surface)	0		0	(+)	+
Hematite	+	+	+		+
Alumina	+		+	(+)	0
Fluorite	+		+		+
Calcite	+	+	+	+	+
Galena	+		+		+
Kaoline	+		+		+
Mica	+		+	+	+
Talc (fresh surface)	+		+	+	+
Talc (old surface)	(+)		+	+	+

+, effective; 0, none.

5.5.3.2. *Adsorption by hydrogen bonding and van der Waals force*

Hydrogen bonding is always a major force in interactions between nonionic flocculants and minerals. For example, nonionic polyacrylamide, PAM, adsorbs on quartz, calcite and galena mainly through the hydrogen bonding and van der Waals forces.

Adsorption through the formation of hydrogen bonds depends also on the ability of the mineral surface itself to form the bonding. Thus, fresh quartz surface that is just formed by breakage along its cleavage exhibits strong tendency to form hydrogen bonds, but the "oxidized surface" can not easily form such bonds.

Formation of intra-molecular hydrogen bonds also affects the function of the flocculants. Anionic hydrolyzed polyacrylamide molecules possessing carboxyl and amide groups can form intramolecular hydrogen bonding as shown below:

$$\begin{array}{ccccccc} -\mathrm{C} & =\mathrm{O}\cdots\mathrm{H}- & \mathrm{N}- & \qquad & \mathrm{O}=\mathrm{C}- & \qquad & -\mathrm{N}-\mathrm{H} \\ | & & | & & | & & | \\ -\mathrm{N} & -\mathrm{H}\cdots\mathrm{O}= & \mathrm{C}- & & \mathrm{N}-\mathrm{H}\cdots & & \mathrm{O}=\mathrm{C} \end{array}$$

Formation of such intra-molecular hydrogen bonds can cause the polymer chains to crimp and as a result cause a decrease in the flocculation efficiency.

5.5.3.3. *Adsorption by chemical bonding*

This includes reactions of the polymer groups with metallic sites on the particle surface that may result in the formation of stable or insoluble compounds through covalent, ionic or coordination bonding. Carboxyl flocculants such as polyacrylic acid and carboxyl-methyl cellulose can chemisorb on the surface of calcite and sphalerite which have calcium or zinc sites on them. Certain flocculants, such as cellulose and starch with xanthate and polyacrylamide with dithiocarbamate with high chemically active groups, have been found to exhibit selective reaction with sulfide minerals. Such complexing polymers have been investigated for their use in selective flocculation processes.

5.5.4. Activation processes by flocculants

5.5.4.1. *Activation of metallic ions in flocculation process*

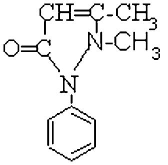
Activation of flocculation by metallic ions is similar to that of mineral flotation using collectors discussed earlier. Metallic ions can activate minerals that do not normally have chemical reaction activity with the functional groups of flocculants, which enhance the flocculation effect. For example, for Cu^{2+} $–SiO_2–$ polymer system, the reaction can be illustrated as below:

$$–SiOH^+ + –COOH + Cu^{2+} \rightarrow –SiO^- \cdot Cu^{2+} \cdot COO^- + 2H^+ \qquad (5.13)$$

Listed in Table 5.29 are examples of the activation phenomena of the above type in various systems.

5.5.4.2. *Activation between organic flocculants and collectors or depressants*

Organic collectors and depressants adsorbed on mineral surfaces can activate reactions between the surface and flocculants in contrast to the flocculants used to activate reaction of collectors or depressants. For example, tannin has been reported [8] to form coordination bonds with Ti^{4+} at the surface of rutile through –OH or –CO groups. With the addition of antipyridine which has =O and =N– group, they form further hydrogen bridging with –OH groups of the tannin molecules. The hydrophobization of the mineral surface can be illustrated for Ti–TA–AP system, where Ti represents the metallic sites on rutile, TA the tannin molecule and AP the anti-pyridine which has following structure:



Another example is the ethyldiamine used for the activation of flotation of oxidized copper mineral by xanthate. It is believed that the ethyldiamine salt gets adsorbed on copper

Table 5.29
Metallic ions as activators in flocculation

Minerals	Flocculants	Conc. (%)	pH	Activators	Conc. (M)	Results
SiO_2 (fresh)	AP-30*	5×10^{-3}	5.0	$CuSO_4$	1	pH = 9, weak flocculation
...	...	1×10^{-3}	2.5	$Al_2(SO_4)_3$	0.1	pH = 7, none
...	...	5×10^{-4}	11.0	$CaCl_2$	1	...
...	...	5×10^{-4}	6.0	$CoCl_2$	1	...
SiO_2 (old)	P-250*	5×10^{-4}	2.0	$Al_2(SO_4)_3$	1	None
$CaCO_3$	Sedomax-F*	5×10^{-4}	7.0	$Pb(NO_3)_2$	0.1	Flocculation
PbS	AP-30	5×10^{-4}	6.4	...	1	Slight improvement
...	...	...	8.0	...	1	pH = 8, none
SnO_2	Sedomax-F*	5×10^{-4}	5.0	$CuSO_4$	1	pH = 5, none
Fe_2O_3	...	...	8.0	$Ca(NO_3)_2$	10	None
CaF_2	A-150*	...	0.5	...	1	
PbS	AP-30*	5	6.4	Na_2S	1	Anti-activation

*Ap-30 is hydrolyzed polyacrylamide with –COOH and –$CONH_2$ groups (30% concentration); P-250 is anionic polyacrylamide; Sedomax-F is anionic polyacrylic acid; A-150 is cationic polyacrylamide.

Table 5.30
Flocculation values (F.V.) of copoly-aniline-aldehyde with different molecular weights used for coal suspension (mM)

Molecular weight	Flocculation values (F.V.)
Increasing ↓	200
↓	75
↓	10
↓	4
↓	2

minerals making the mineral surface positively charged and improving the adsorption of the xanthate.

5.5.5. Effect of the molecular weight and the chain structure of flocculants on their performance

5.5.5.1. *Molecular weight*

In general, larger the molecule and longer the polymer chain, higher is the flocculation power of the reagent in the molecular weight range of 10^5–10^7. The rate of adsorption and the reduction of the zeta-potential increase with the molecular weight of the polymer, since the increase in the length of polymer chain will increase the van der Waals force and the number of functional groups. Listed in Table 5.30 are the flocculation values, i.e. concentration for flocculation, of flocculants of different molecular weights for the case of coal suspensions.

Organic polymers of low molecular weight, for example 10^3–10^4 or less, can adsorb on mineral surfaces without causing any flocculation because of shorter chain lengths. On the contrary, hydrophilic or charged groups adsorbed on mineral surface can produce repulsive forces between particles leading to dispersion. In certain ranges, less the molecular weight of polymer, more is the dispersion power. It has been reported that polyacrylic acid can be used as a dispersant in the flotation separation of limestone and dolomite, oxidized copper and zinc minerals. The effectiveness of the reagents of low molecular weight has been found to be good. This is illustrated by the following data:

Polymers	A	B	C	D	E
M.W.	5.4×10^3	10^4	2×10^4	3×10^5	$>10^6$
Dosage (g/t)	150–200	250	300–350	Weak	

5.5.5.2. *Tortuosity and steric configuration of chains*

The tortuosity of polymer chains is also a major factor that can affect the performance of a flocculant. Tortuous aliphatic chains can be crimped by hydrogen bonding between functional groups on the chains resulting in lower flocculation efficiency. On the contrary, the rigid chains such as in cellulose and starch can not be crimped. It is known that the flocculation efficiency of an anionic polymer such as polyacrylic acid possessing –COOH groups always decreases in acidic medium because the hydrogen bonding between the unassociated carboxylic acid groups is stronger than the bonds in alkaline medium.

The effect of steric configuration of the chain is exemplified with the following types of polymers [6]: galactomannan (guar), dihydroxypropyl cellulose and starch all of which possess neighboring hydroxyl groups but in different steric configuration as shown in Fig. 5.18.

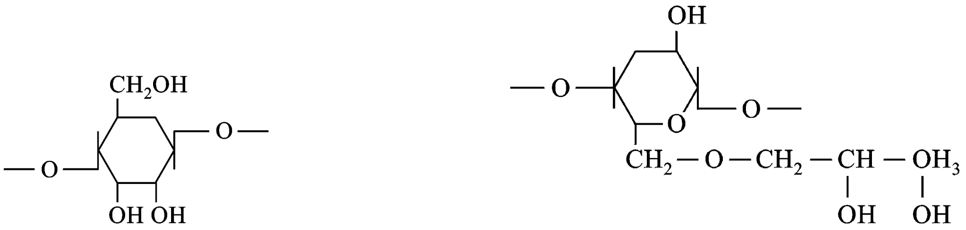
Galactomannan has been found to adsorb more effectively on kaolinite than starch. Presumably this is due to the ability of the cis-hydroxyl groups in galactomannan to simultaneously associate with the neighboring sites on the surface of the mineral particles; the trans-hydroxyl groups of starch do not have the same capability as illustrated in Fig. 5.19.

5.5.6. Selection criteria for various types of flocculants

The factors that influence the selection of flocculants include particle size, reaction rate, and conditioning.

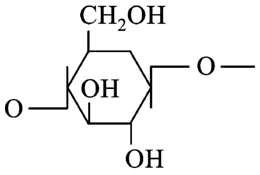
5.5.6.1. *Particle size vs. chain length and dissociation property of the polymer*

For flocculation of coarse particles, bridging by organic polymers is very effective, especially that by the nonionic polymer. Inorganic electrolyte and surfactants do not have high flocculation efficiency.



Galactomannan
(cis)

Dihydroxypropyl cellulose
(cis, trans)



Starch
(cis)

Fig. 5.18. Steric configuration of hydroxyl groups in polymers.

Cis-OH

Trans-OH

Fig. 5.19. Adsorption of starch on mineral surface.

In the case of fine colloidal particles, coagulation by electrolytes exhibits a strong effect so that inorganic electrolytes and ionic polymers perform well. Also, surfactants and oils are found to be effective for agglomeration of fine particles.

Data for the settling of suspension of diatomite with different particle size has been reported, where the flocculants used were:

Cationic polymer:

(i) Copolymer of aniline and aldehyde
(ii) Polyhexamethylene thiourea

Nonionic polymer:

(iii) Copolymer of urea and aldehyde
(iv) Polyacrylamide: M.W. 1.78×10^4, 4.27×10^4 and 3.9×10^4.

Table 5.31
The effect of different flocculants particle size on flocculation properties

Particle size	Low M.W.			High M.W.			
	Inorganic counter-ions	Surfactants		Low M.W. polymer		High M.W. polymer	
		Counter-ions	Nonionic or same ions	Counter-ions	Nonionic or same ions	Counter-ions	Nonionic or same ions
Coarse (-1 mm $+74$ μm)	×	×	×	△	△	○	○
Fine (-74 μm)	×, △	△	△	○	○	○	○
Colloid size	○	○	×	○	×		×, △

○, effective; ×, none; △, partially effective.

Surfactant:

(v) Aniline · HCl

Inorganic electrolyte:

(vi) $BaCl_2$.

The effects of molecular weights and charge characteristics of flocculants on the flocculation behavior of particles of different sizes are summarized in Table 5.31.

The results of these studies show that:

(a) For coarse particles (74–297 μm): surfactant and inorganic electrolyte are not effective but nonionic polyacrylamide reacts remarkably with increase in molecular weight of the polymer.
(b) For particles of intermediate sizes (7.2–74 μm): $BaCl_2$ and aniline surfactant have only slight reaction but nonionic polyacrylamide and copolymer of urea and aldehyde have the highest flocculation efficiency.
(c) For colloidal particles (less than 7.2 μm): nonionic polymers have poor effectiveness, but ionic polymers and are effective. In addition, surfactants and inorganic electrolytes all have high flocculation efficiencies.

5.5.6.2. *Reaction rate and conditioning for various flocculants*

5.5.6.2.1. *Coagulation by electrolytes* These are reactions taking place in the double layer of the mineral surface, and can be classified into two categories.

The zeta-potential of the mineral particle shifts into the "unstable range" (in general about 10 to 20 mV), and this flocculation stage is slow, since the surface can retain some charge with resultant repulsive force. Every collision is effective and the flocculation rate is thus affected markedly by the type and the concentration of electrolytes.

When the zeta-potential equals zero, “fast flocculation stage” prevails and the probability of collision–adhesion of particles increases. In addition, the effect of electrolytes is also small.

As far as conditioning is concerned, in the case of slow flocculation, controlled conditioning is necessary. If the conditioning is weak, the flocculation rate will be slow, but on the other hand intense conditioning can result in fast relative motion of particles which is also unfavorable for their attachment to each other.

5.5.6.2.2. *Bridging by organic polymers* At suitable conditioning speeds, large flocks can form whereas at too high a speed only smaller floccs may form.

5.5.6.2.3. *Hydrophobic agglomeration by surfactants* In the presence of surfactants, the agglomerate size can increase with increase in the intensity of conditioning, with the efficiency being maximum under conditions of shear flocculation. The above is illustrated in Fig. 5.15.

Conditions for use of various types of flocculants are summarized below:

Reagents	Conditioning	Other conditions
Electrolyte	Low speed	
Polymer	Moderate	Activator
Surfactant	Strong	Electrolyte

5.5.6.3. *Effect of flocculant dosage*

The flocculant dosage is an important factor in the flocculation process. The optimum polymer dosage (OPD) depends on the available surface area of the particles and the molecular weight and adsorption density of the flocculant. In general, OPD has a direct relationship with the surface area of particles and the addition of polymers above the OPD will result in dispersion. The OPD can be experimentally determined and this is illustrated in Fig. 5.20.

The effect of the concentration of the potential-determining ions and the counterions on the interface potential of the particles has been discussed earlier in this section. Also, it was stated that the critical flocculation concentrations (CFC) of inorganic electrolytes of different valencies are related to each other in the following manner:

Effect of valency of electrolytes on the CFC

z	1	2	3
CFC (M)	10^{-1}	2×10^{-3}	2×10^{-4}

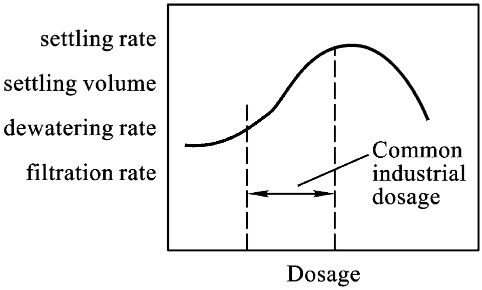


Fig. 5.20. Optimum dosage of flocculant.

5.6. MOLECULAR DESIGN OF FLOTATION AGENTS

In this section, the structure–performance relationship of flotation reagents and its molecular design are briefly introduced.

The effectiveness of flotation agents is one of critical factors that determine the efficiency of flotation processes. It is well known that the use of synthetic and water soluble reagents such as thio-type, carboxylic acids, cyanides, silicates and phosphates make it possible to apply flotation technology on a large industrial scale. The exploration of new types of flotation reagents was, however, done mainly by empirical means. The need for more efficient reagents has become acute due to the increase of finely disseminated and low quality ores that have to be processed now worldwide. During the past decades, researchers around the world have done a great amount of work on the development of new types of reagents with higher efficiencies based on the principles of surface chemistry, coordination chemistry and quantum chemistry. Especially, the development of theories of molecular design of flotation reagents have made it possible to predict and design the molecular structure of the flotation reagent required for a given mineral system [9–11,23].

5.6.1. Structural factors and quantitative criteria

The structure–property relationship of flotation agents is determined by three factors related to structure: bonding, hydrophilic–hydrophobic property and steric interactions. A number of quantitative criteria such as molecular orbital (MO) index, group electronegativity and hydrophilic-hydrophobic balance (HHB) has been used.

5.6.1.1. *Bonding factor*

The bonding characteristics determine the properties of the minerophilic and hydrophilic groups. The selectivity of the mineral–reagent interactions can be estimated using a bonding criterion.

5.6.1.1.1. *Molecular orbital (MO) index* Molecular orbital indices are calculated in the light of quantum chemistry and used to characterize the bonding atoms and the ability as a

Table 5.32
HMO indices of bonding atoms of some collectors for sulfide minerals

Reagents	Q_B	S_r^N
(1) dithiocarbonate		
$-O_1-C_2(=S_3)-S_4-(H)$	−0.6493	0.25
(2) dithionocarbamate		
$=N_1-C_2(=S_3)-S_4-(H)$	−0.7078	0.18
(3) thionocarbamate		
$-N_1H-C_2(=S_3)-O_4-$	−0.5333	0.42
(4) xanthate ester		
$-O_1-C_2(=S_3)-S_4-(R)$	−0.4733	0.52
(5) thiourea		
$(R)-N_1H-C_2(=S_3)-N_4H-(R)$	−0.5850	0.35

flotation reagent. Major indices for the flotation agents involve:

(a) Electron density (q_r) and net charge (Q_r): the bonding atoms can be identified by comparing the values of q_r and Q_r of atoms in the polar groups of the molecule. The bonding atoms have relatively larger positive q_r value and negative Q_r value. In addition, the reagent whose bonding atoms have larger q_r value exhibits higher floatability.

(b) Frontier electron density (f_r^E, f_r^N) and superlocazability (S_r^E, S_r^N): the values of f_r^E and S_r^N represent the ability of atoms to form bonds and normal coordination bonds through the donation of electrons from bonding atoms of the reagent to the mineral MOs. The floatability can, therefore, be determined by f_r^E and S_r^E. The values of f_r^N and S_r^N show the ability for forming feedback coordination bonds through the acceptance of electrons of MOs of bonding atoms from d orbital of the mineral surface species. The selectivity of a reagent for a given mineral system can be estimated from f_r^N and S_r^N values.

The MO indices calculated for some collectors for sulfide minerals are given in Table 5.32. It can be seen that the bonding atom usually has a relatively high negative Q_B value.

Flotation agents such as dithiocarbonate (1), dithiocarbamate (2) and xanthate ester (4) belong to the S.S. type bonding whereas thionocarbamate (3) and dialkylamino thiourea (5) belong to the S.N. type bonding. The electron density (q_B) of the bonding atoms indicates the floatability of the reagents which follows the order: (1) > (2) > (5) > (3) > (4). On the other hand, the f_r^N and S_r^N values suggest the selectivity of the reagents which follows the order: (4) > (3) > (5) > (2) > (1).

In addition, the selectivity is also related to the electron number of the d-orbital of the mineral surface species. More the number of d electrons, greater is the ability to form feedback bond. Therefore, these reagents appear to have better selectivity for minerals such as copper sulfide containing metals with d^{10}.

5.6.1.1.2. *Group electronegativity*

(a) Formula for calculations. Group electronegativity is the electronegativity of bonding atoms in the polar groups of the organic molecule taking the effects of other atoms into consideration. Group electronegativity, usually expressed as X_g, is used to evaluate the reactivity of polar groups of the reagent. The X_g value can be calculated using the following equation [11]:

$$X_g = 0.31(n^* + 1)/r + 0.5$$

$$n^* = (N - P) + \sum \alpha m_0 \varepsilon_0 + \sum s_0 \delta_0 + \sum \frac{\alpha m_i + s_i}{\alpha_i} \delta_i \tag{5.14}$$

where n^* is the effective number of valency electrons of the coordination atom in a reagent molecule; N the number of its valency electrons; P the combined electron number of the coordination atom and the connect atom; m_i the number of the ith order bond in the molecule; s_i the uncombined electron number of the ith order connect atom ($i = 0, 1, 2, \ldots$); ε_0 and δ_i are constants related to the electronegativity of the connect atoms; α is a constant (2.7); and r the covalent radius of the coordination atom.

(b) Classification of collectors using X_g values. Group electronegativity values of some collectors calculated using Eq. (5.14) are given in Table 5.33. It can be seen that the group electronegativities of collectors are 2.5–3.3 for sulfides, 3.7–3.9 for transitional metal oxides and 4.0–4.6 for other oxides or salt-type minerals, respectively. In other words, the reagents with larger X_g values may be suitable for the flotation of non-sulfide minerals and the collectors with smaller X_g values for sulfides.

(c) Evaluation of collector–metal bonds by X_g values. The percentage ionic character (polarity) of the collector–metal bond can be estimated using the following equation:

$$\Phi\% = 16(\Delta X_H) + 3.5(\Delta X_M)^2, \tag{5.15}$$

where X_H and X_M are the electronegativity of hydrogen and metal elements.

The X_g and Φ values of various collectors and minerals are given in Table 5.33. It is noted that larger the X_g value of a collector, greater is its polarity and ionic character in the collector–metal bonds, suggesting stronger covalent bonding character and better selectivity. Collectors with smaller X_g value need shorter hydrocarbon chains than those with larger X_g.

5.6.1.2. *Hydrophilic–hydrophobic factor and criteria*

Hydrophilic characteristics of a reagent molecule include hydration tendency of the polar head itself and hydrophilicity of the reagent–metal bond at the mineral surface. The characteristics of the non-polar group of a reagent determine its use. The criteria of hydrophilic–hydrophobic factors affecting the structure property relationship of the reagent include characteristic index i and hydrophilic–hydrophobic balance (HHB).

Table 5.33
X_g and Φ values of some collectors for various mineral systems

Mineral systems	Sulfide minerals	Transitional metal oxide minerals	Oxide or salt-type minerals
X_g	2.5–3.2	3.7–3.9	4.0–4.6
$X_g - X_H$	0.4–1.2	1.6–1.8	1.9–2.5
$\Phi\%$	7–24	20–40	40–62
X_M	1.8 (Fe)–2.4 (Au)	1.5 (Ti)–1.8 (Fe)	0.9 (Ba)–1.5 (Mn)
$X_g - X_M$	0.1–1.5	1.9–2.4	2.5–3.7
$\Phi\%$	2–30	37–46	50–100

5.6.1.2.1. *Characteristic index i of flotation agents*

(a) Formulae for calculation of i. The characteristic index i of the reagents can be calculated using the following two formula:

$$i = \frac{\sum(X_g - X_H)}{\sum n\Phi}, \quad \text{or} \quad i = \sum(\Delta X)^2 - \sum n\Phi + k \tag{5.16}$$

where $X = X_g - X_H$ represents the hydrophilicity of the reagent; $n\Phi$ is the hydrophobicity of non-polar group; n the carbon number in the hydrocarbon chain; Φ the hydrophobic association energy of $–CH_2–$ group and k the constant. It is evident that larger the i value of a reagent, greater is the hydrophilicity of the reagent molecule. The reagent with a large i value may be used as a depressant while the one with small i value may be used as a collector.

(b) Classification of flotation agents by i values. The i_1 values of some flotation agents calculated using Eq. (5.16) are listed in Table 5.34. It can be seen that the i_1 values may be used to classify the reagents. The i_1 values are about 0.2–0.4 for collectors, 0.4–1.2 for frothers and >3 for depressants.

(c) Estimation of ability of depressants. Larger the i_1 values of the depressants, greater is the hydrophilicity of the depressant molecules and their depressing ability. Fig. 5.21 shows a linear relation between i_2 value and concentration required for depressing Cu^{2+}-activated quartz.

5.6.1.2.2. *Hydrophilic–hydrophobic balance (HHB) of collector molecule* It is required that the hydrophobicity of the non-polar group of the collector must overcome the hydrophilicity of the mineral surface and the collector–metal bond. Let $(\Delta X_R)^2 = (X_g - X_M)^2$ represent the hydrophilicity of the bond, and $(\Delta X_M)^2 = (X_A - X_B)^2$ the hydrophilicity of the mineral, where X_A and X_B are the electronegativity of different mineral elements. HHB value of a collector is given by the following equation:

$$k\Phi n = \Delta X_R^2 + \Delta X_M^2 \tag{5.17}$$

The carbon number required in the hydrocarbon chains of a collector for a given collector–mineral system can be estimated using Eq. (5.17) (in Table 5.35). It is evident

Table 5.34
Classification of flotation agents on the basis i values

Reagents	i_1	i_2
Collectors		
Ethyl xanthate, C_2H_5OCSSH	0.18	18.4
Ethyl dithiophosphate, $(C_2H_5)_2OPSSH$	0.20	16.8
Decyl acid, $C_9H_{19}COOH$	0.14	14
Frothers		
$C_7H_{15}OH$	0.49	16.2
MIBC, $C_6H_{13}OH$	0.54	17.2
Terpinol, $C_{10}H_{17}OH$	0.32–0.46	13.2
Cresol, C_7H_8OH	0.54–1.08	7.2
Depressants		
$(COOH)_2$	8.0	28.0
$CH_3CH_2OHCOOH$	3.62	25.2
Starch, $C_6H_{10}O_5$	2.7	30.0
Gallic acid	2.3–4.6	27.6

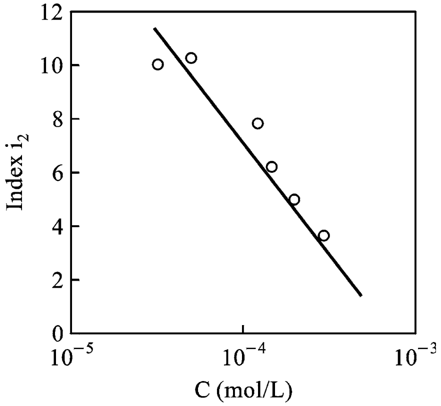


Fig. 5.21. The characteristic index (i_2) as a function of the concentration required for depression of quartz by Cu^{2+}.

that the calculated carbon number is close to those of reagents used in practice. Eq. (5.17) provides a method to design the non-polar group of a collector for any given mineral.

5.6.1.3. *Steric factors*

The selectivity of a collector can also be influenced by steric factors which include mainly group diameter (d_g) and the van der Waals' volume of the collector.

(1) Calculation of group diameter, d_g: the cross-sectional width (group diameter) of a polar group of a collector can be calculated using the data for bond angle, covalent radius and the van der Walls' radius of the compound.

Table 5.35
Estimation of chain length of non-polar group of collectors required for given minerals

Collectors (X_g)	Metal (X_M)	ΔX_R	Mineral	ΔX_R	Theoretical *n* value
Xanthate (2.7)	Pb (1.8)	0.81	PbS	0.49	2.0
			PbO	2.89	4.0
Dithiophosphate (3.0)	Pb	1.44	PbS	0.49	2.0
			PbO	2.89	5.0
Dithiocarbamate (2.6)	Pb	0.64	PbS	0.49	1–2
Carboxylic acid (4.1)	Ca (1.0)	9.61	CaO	6.25	16
	Fe (1.8)	5.29	FeO	2.89	9
Sulphonic acid (4.3)	Ca	10.89	CaO	6.25	17
	Fe	6.25	FeO	2.89	9
Phosphonic acid (4.3)	Fe	6.25	FeO	2.89	9
Hydroxamic acid (3.8)	Fe	4.0	FeO	2.89	7.0
	Ti (1.5)	5.29	TiO	4.0	10
Primary amine (3.7)	Na (0.9)	7.84	NaO	6.76	15

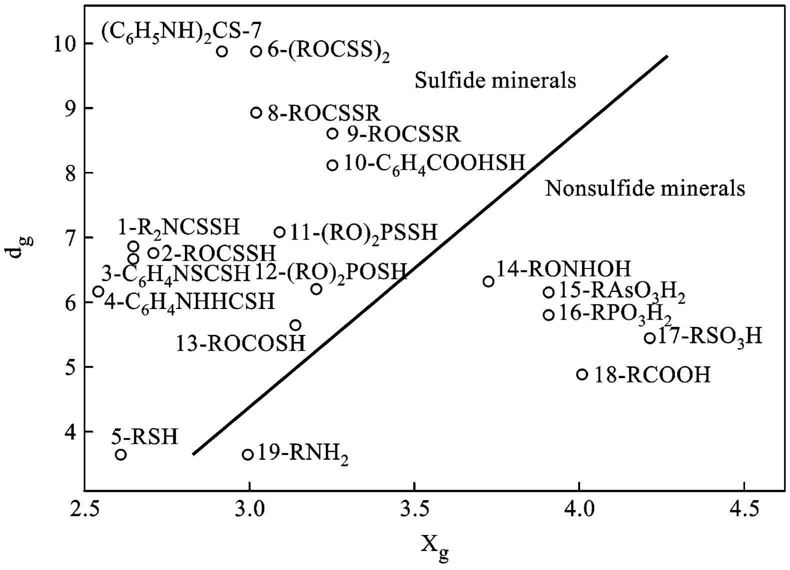


Fig. 5.22. Classification of collectors by group electronegativity X_g vs. diameter d_g.

(2) Group diameter and selectivity of the collector: flotation studies show that the selectivity of a collector is closely related to its group diameter.

(3) Group electronegativity vs. diameter (X_g vs. d_g) of collectors: the relationship between X_g and d_g of collectors is plotted in Fig. 5.22. It shows a straight line that divides the collector–mineral systems into two classes. Sulfide minerals and their collectors are located above the line and oxide minerals and their collectors below the line. The collectors located in the upper left part in Fig. 5.22 exhibit higher floatability and better

Table 5.36
The quantitative criteria of structure–property factors and their user for estimation of properties of flotation reagents

Factors	Criteria	Uses
Bonding factors	MO indices net charge Q_r electron density q_r frontier electron density f_r^E, f_r^N superlocazability S_r^E, S_r^N	To identify bonding atoms q_r, f_r^E, S_r^E implying ability to form normal chemical bond f_r^N, S_r^N indicating the ability to form feedback π coordination bond and selectivity
	Group electronegativity X_g	$X_g = 2.5$–3.3 collector for sulfide $X_g = 3.3$–3.9 collector for transitional metal oxide $X_g = 4.0$–4.6 collector for oxide
Hydrophilic–hydrophobic factors	Characteristic index $I = \sum(\Delta X)^2 / \sum n\Phi$	Collector $i < 0.4$ Frother $i = 0.4$–1.2 Depressant $i > 3$
	HHB value $K\Phi n = \Delta X_r^2 + \Delta X_m^2$	To determine the chain length of non-polar group of a collector
Steric factors	Group diameter d_g	To determine the selectivity of a reagent

selectivity for sulfide minerals, while the collectors in the lower left region have higher floatability and relatively poorer selectivity for sulfides. The collectors in the upper right region have higher floatability and relatively better selectivity for oxide minerals, while those in the lower right region have relatively poorer selectivity for oxides.

5.6.2. Molecular design of new collectors

As above, the criteria for structure factors affecting the properties of flotation reagent can be used to determine the bonding atoms, evaluate the reactivity and selectivity of reagent–metal, estimate the length of hydrocarbon chain required for a collector and classify flotation reagents. Table 5.36 summarizes various quantitative criteria of structure factors and the application in prediction of properties of flotation reagents. The design of molecular structure of flotation reagent required for flotation of given mineral systems can be conducted in the light of various quantitative criteria.

The molecular structures of several new collectors have been designed as shown in Table 5.37 [21]. The carbon numbers of non-polar group required for given collector–mineral systems are also calculated and given in Table 5.37. The results in Table 5.38 show that the collector synthesized according to the calculated carbon numbers of non-polar group is the best one for given collector–mineral systems. These new collectors can be used as selective collectors for flotation separation of chalcopyrite from sphalerite, cassiterite or wolframite from calcite, malachite from smithsonite and calcite.

Table 5.37
Molecular designs of some new collectors for flotation of sulfide and oxide minerals

Collectors	Structure formulae	X_g	n value required for given minerals
(A) Dialkyl thiophosphinic acid	A_1, R = C_5H_{11} A_2, R = C_6H_{11}	Thione type 4.14 Thiol type 2.90	Cassiterite 8.37 Malachite 7.58 Smithsonite 10.06 Calcite 16.11 Chalcopyrite 5.83 Sphalerite 7.26
(B) Dialkyl thiophosphonate ammonium	B_1, R = C_2H_5 B_2, R = C_4H_9 B_3, R = C_6H_{13}	Thione type 4.59 Thiol type 3.19	Cassiterite 10.67 Malachite 9.8 Smithsonite 12.55 Calcite 19.14 Chalcopyrite 7.6 Galena 8.27 Sphalerite 9.75
(C) Alkyl phenylphosphonate	C_1, R = C_2H_5 C_2, R = C_4H_9 C_3, R = C_6H_{13} C_4, R = C_8H_{17}	4.57	Cassiterite 10.56 Wolframite 10.56 Malachite 9.69 Smithsonite 12.43 Calcite 18.99

Table 5.38
Collecting properties of new synthesized collectors

Collectors	Orders of collecting ability for minerals
A_1***	Chalcopyrite > sphalerite Malachite–cassiterite > smithsonite > calcite
A_2*	Chalcopyrite > sphalerite
B_1*	Chalcopyrite > sphalerite
B_2**	Chalcopyrite > galena > sphalerite Malachite > cassiterite > smithsonite > calcite
B_3***	Malachite–cassiterite > smithsonite > calcite
C_1*	Malachite
C_2**	Malachite > cassiterite–wolframite > smithsonite ≫ calcite
C_3***	Malachite–cassiterite–wolframite > smithsonite ≫ calcite
C_4***	Malachite–cassiterite–wolframite > smithsonite ≫ calcite

Collecting ability:
***strong,
**middle,
*weak.

In conclusion, it is clear that molecular design of flotation reagents open a new avenue producing novel classes of reagents in an efficient manner.

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