Solubility

A general guideline for solubility is *like dissolves like*. "Substances with similar molecular structures are likely to exhibit similar intermolecular forces of attraction and to be soluble in one another."[1] While dispersion forces are usually more significant than dipole forces when comparing substances of widely different molecular masses, we often focus on whether substances are nonpolar or polar or ionic.

A *nonpolar* substance has an *even* distribution of electron density. Some simple examples are homonuclear diatomics such as H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. Polyatomic molecules such as H-C≡C-H, O=C=O, BF_3, CH_4, PF_5, and SF_6 are nonpolar by symmetry.

A *polar* substance has an *uneven* distribution of electron density. Polarity often arises from differences in electronegativity which are not cancelled out by symmetry, and examples include H_2O and CH_3F and CH_3OH. But O_3 is polar despite all atoms having the same electronegativity. O_3 is a bent molecule with the central atom having a +1 formal charge in both resonance structures. According to https://www.chemguide.co.uk/atoms/bonding/electroneg.html , a polar molecule must be "lop-sided" in some way.

Even though a polar substance has an uneven distribution of electron density, bonding electrons are still shared between atoms. But if the difference in electronegativity between bonded atoms is great, the substance can act as if ions are formed with one of more electrons completely transferred from one atom to another; NaCl and MgO are examples. An ionic compound also forms if polyatomic ions are involved in forming a compound; $(NH_4)_2SO_4$ is an example.

There is a continuum from a symmetrical distribution of electron density in perfectly nonpolar substances to an asymmetric distribution in polar substances to practically complete transfer of electrons in a very ionic substance such as LiF. C-H bonds have an electronegativity difference of $2.5 - 2.1 = 0.4$ which is small but not zero. While a C-H bond is slightly polar, symmetry of CH_4 and CH_3CH_3 make these molecules exactly nonpolar. One can draw structures for $CH_3CH_2CH_3$ and higher molecular mass linear hydrocarbons where the bond polarities approximately cancel, giving molecules which act nonpolar.

The difference between polar and ionic is also somewhat subjective, and https://www.chemguide.co.uk/atoms/bonding/electroneg.html describes LiI as "ionic with some covalent character." Figure 10-7 in our textbook[1] shows a graph of % ionic character as a function of electronegativity difference, emphasizing a continuum instead of sharp divisions between nonpolar and polar and ionic.

"Like dissolve like" implies that polar substances dissolve polar substances, nonpolar substances dissolve nonpolar substances, and nonpolar substances are immiscible with polar substances. Both CH_3CH_2OH and sucrose ($C_{12}H_{22}O_{11}$) are polar molecules, and they dissolve well in polar water but only slightly in nonpolar hexane, C_6H_{14}. Nonpolar I_2 dissolves well in nonpolar hexane, but I_2 dissolves only slightly in polar water. We say that CH_3CH_2OH and sucrose are soluble in water and insoluble in hexane. And we say that I_2 dissolves in hexane but not in

water. These statements about solubility ignore the huge range of solubilities and the effect of temperature. CH_3CH_2OH is miscible with water in all proportions, while sucrose is soluble to the extent of 180 g/100 g water at 0°C, and its solubility increases to 287 g/100 g water at 60°C. These polar molecular compounds are much more soluble in water than ionic compounds. For example, the solubility for $NaNO_3$ is 73 g/100 g water at 0°C and 188 g/100 g water at 60°C.[2]

Ionic substances are more similar to polar substances than to nonpolar substances, so some ionic substances dissolve in polar water, but we expect ionic substances to be very insoluble in nonpolar solvents. The ease with which an ionic solute dissolves partly depends on the magnitude of the forces holding the ionic compound together. A simplistic approach uses Coulomb's law. The force of attraction between unlike charges is proportional to $\frac{q_1 q_2}{r^2}$ where q_1 and q_2 are the magnitudes of charges on the cation and anion of the ionic compound, and r is the distance between the centers of the ions. (We also use Coulomb's law to estimate relative melting points of ionic compounds.) Unfortunately, solubility of ionic compounds in water is more complicated, but this simplistic approach suffices to give the first two guidelines below.

Our textbook says: "For practical purposes, we consider a compound to be insoluble if the maximum amount that can dissolve is less than about 0.01 mol/L."[1] Another textbook says: "Soluble means that 1 g or more of the compound dissolves in 100 mL of water. Insoluble means that less than 0.1 g of the compound dissolves in 100 mL of water. Slightly soluble means that the solubility of the compound is between 0.1 g and 1 g per 100 mL of water."[3]

Solubility Guidelines for Common Inorganic Ionic Compounds in Water

1. Compounds of NO_3^-, ClO_4^-, and CH_3COO^- are soluble.

2. Compounds of alkali metal cations and NH_4^+ are soluble. Some compounds involving lithium are insoluble, perhaps because the lithium cation is so small. In CHEM 130 you precipitated $KAl(SO_4)_2 \cdot 12H_2O$ from water, even though K^+ is an alkali metal cation and you would predict solubility.

3. Compounds of Ag^+, Pb^{2+}, and Hg_2^{2+} are insoluble. $AgNO_3$ is soluble because guideline 1 takes precedence.

4. Compounds of Cl^-, Br^-, and I^- are soluble. AgCl is insoluble because guideline 3 takes precedence. $PbCl_2$ is also insoluble from guideline 3, but $PbCl_2$ dissolves in hot water or in more dilute solutions.

5. $Ca(OH)_2$ and $Sr(OH)_2$ and $Ba(OH)_2$ are slightly soluble. Sulfides of all Group 2 cations are slightly soluble.

6. Compounds of CO_3^{2-}, OH^-, O^{2-}, PO_4^{3-}, and S^{2-} are insoluble. Na_2CO_3 and NaOH are soluble because guideline 2 takes precedence.

7. $CaSO_4$ and $SrSO_4$ and $BaSO_4$ are insoluble. Note same cations as in guideline 5.

8. Compounds of SO_4^{2-} are soluble. Guideline 3 says $PbSO_4$ and Ag_2SO_4 are insoluble. Experimental data shows solubility of 0.004 g $PbSO_4$ per 100 mL water and 0.6 g Ag_2SO_4 per 100 mL water.[4] Ag_2SO_4 is slightly soluble and you might not see a precipitate when expected.

These guidelines ignore possible formation of complex ions. For example, adding a little hydroxide to Al^{3+}(aq) first precipitates $Al(OH)_3$(s) but continued addition of hydroxide gives the soluble complex ion $Al(OH)_4^-$(aq). Zn^{2+}(aq) and Pb^{2+}(aq) behave similarily.

References

1. Petrucci, Ralph H.; Herring, F. Geoffrey; Madura, Jeffry D.; Bissonnette, Carey; General Chemistry: Principles and Modern Applications, 10th ed.; Toronto: Pearson Canada, ©2011, pages 158, 406, 506, 565.

2. Zumdahl, Steven S; Chemical Principles, 4th ed.; Boston: Houghton Mifflin, ©2002, page 820.

3. Umland, Jean B; Bellama, Jon M; General Chemistry,2nd ed.; St. Paul: West Publishing, ©1996, page 115.

4. CRC Handbook of Chemistry and Physics, 56th ed., ©1975.