SOLVENTS, INDUSTRIAL

1. Introduction

The recorded history of solvent use spans several millennia, but only during the last few decades have been solvents subjected to scrutiny regarding their effects on human health, atmospheric changes, and soil and water pollution. Some experts predicted their complete elimination and the majority of chemists have been working on engineering the means to prevent solvent release and on the composition of solvents used in different applications aiming at reduction of their negative impacts on health and safety.

Figure 1 shows that the total use of solvents in the United States is expected to increase (1). This is consistent with a study by Fredonia (2) which predicted an increase of 2.3% per year. The total use of solvents parallels development of new products and ever increasing production output, especially now when many new markets emerge. For example, solvents are projected to grow by 4.8% in the Asia-Pacific region (2). This growth also shows that it is very unlikely that solvents will be eliminated from industrial production and commercial products, not only because they are efficacious and economically viable, but also because in many instances their use helps to preserve natural resources (for example, energy required to evaporate a solvent is substantially less than energy required to remove water used as a solvent).

Figure 1 also shows changes in the chemical composition of solvents. The use of high performance oxygenated solvents is increasing. Solvents, known to affect environment (hydrocarbons and chlorinated solvents) have been reduced.

The use of solvents requires better knowledge of properties, extensive research, and engineering controls.

2. Solvent Classification

Solvents can be classified based on a large number of parameters, including

- Chemical structure (presence of typical structural groups, reactivity, ability to dissociate, proton acceptors and donors, hydrogen bonding).
- Physical parameters (polarity, polarizability, acid/basic properties, solvatochromism, dielectric properties, hygroscopicity).
- Dissolving qualities (miscibility, solubility parameters, dissolving strength, theta temperature).
- Their influence on environment (ozone depletion, solvent partition, volatility, combustibility, biodegradability, degradation products).
- Their influence on health (toxicity, carcinogenic properties, mutagenicity, effect on reproduction, volatility, residual concentration).
- Industrial and application safety (flammability, explosion, limits, autoignition temperature).
- Cost.

A review of the selected parameters suggests that there are many important determinants of solvent quality for specific application. Some solvent parameters are conflicting, some not well quantified, and each solvent application requires a unique set of solvent performance criteria. It can be thus anticipated, prior to any analysis, that the chemical structure can be the best means of solvent classification for any application. Such a classification is also followed here. The chemical names used in this article are the common names because they are generally recognized by solvents users.

Selected means of classification are briefly analyzed below because they are used in some applications of solvents. For a classification to be useful, it must be based on a model and/or a method which permits solvent quantification.

In organic synthesis, the solvent's polarity plays an important role. Dimroth and Reichardt (3) developed a classification based on the normalized empirical parameter of solvent polarity, E_T^N, given by the following equation:

$$E_T^N = \frac{E_T(solvent) - E_T(TMS)}{E_T(water) - E_T(TMS)} = \frac{E_T(solvent) - 30.7}{32.4} \tag{1}$$

where $E_T =$ excitation energy and $TMS =$ tetramethylsilane.

The values of E_T are known for several hundred solvents based on measurements of solvent-induced shifts with betaine dye used as the solvatochromic indicator. Based on these data, solvents can be divided into 3 groups: protic (E_T^N from 0.5 to 1), dipolar nonhydrogen donating (E_T^N from 0.3 to 0.5) and apolar (E_T^N from 0 to 0.3). The values correlate with light absorption, reaction rates, and chemical equilibria. In addition, the values yield a very good correlation with the Kosower's polarity parameter, Z, for which there is also large amount of data available. Both sets of data can be converted using the following equation:

$$E_T = 0.752Z - 7.87 \tag{2}$$

Gutman (4,5) chose the reaction enthalpy of solvent with the reference acceptor (antimony pentachloride) to quantify Lewis-donor properties. The acceptor number, AN, is a dimensionless parameter obtained from negative values of reaction enthalpy. The data obtained from electrochemical and NMR studies were combined into one scale in which data are available for several hundred solvents. These data yield a linear correlation according to the following equation (6):

$$AN = -59.9 + 1.85E_T \tag{3}$$

The acceptor and donor numbers are frequently used in various fields of polymer chemistry. Another classification based on acidity/basicity of solvents allows the division of solvents into six groups containing protic-neutral; protogenic; protophilic; aprotic-protophilic; aprotic-protophobic; and aprotic-inert (6).

Snyder (7,8) developed classification of solvents for chromatography which arranges solvents according to their chromatographic strength. This classification is based on the solvent's ability to engage in hydrogen bonding or dipole interaction using the experimentally determined partition coefficients by

Rohrschneider (9). Eight groups of solvents were defined based on cluster analysis. In addition to the usefulness of this classification in chromatography, it was found recently that it is also useful in the design of coatings which do not affect undercoated paints (10).

Numerous other classification systems and sets of data are available, such as those included in various databases on solvent toxicity, their environmental fate, combustion properties, and explosive limits. (See, for example, Ref. 11).

3. Solvent Groups and their Average Properties

Solvents were divided into 14 chemical groups which include all commercial solvents used by industry (some special solvent groups (eg, supercritical liquids, ionic liquids, or terpenes) are not included in this analysis). The following chemical groups include the majority of commercial solvents: hydrocarbons (aliphatic and aromatic), halogenated hydrocarbons, nitrogen-containing compounds (nitrate and nitriles), organic sulfur compounds, monohydric alcohols, polyhydric alcohols, phenols, aldehydes, ethers, glycol ethers, ketones, acids, amines, esters.

The data for 1,145 solvents are available on CD-ROM (11) as a searchable database. Information on the properties of solvents is included in 110 fields containing chemical identification of solvent, physical chemical properties, health and safety data, and environmental fate. Here, the analysis of these data is provided in Table 1 to show the range of properties for different groups of solvents and their strengths and weaknesses. The data are analyzed to highlight the best performance of various groups of solvents in different applications.

The comparative table classifies each group from highest to lowest position in relationship to their respective values for a particular parameter. The table also shows that solvent having many good properties is not always suitable for use. For example, CFCs have many characteristics of good solvents, but they were eliminated from use because they cause ozone depletion, and they also contribute to global warming. On the other hand, esters do not appear on this table frequently, but they are very common solvents and common candidates for replacement of less suitable solvents. The difficulties in replacement of CFCs can be seen from the data of this table, considering that CFCs had some very unique characteristics.

Table 1 also shows that solvents offer very broad choice of properties, which can be selected to satisfy any practical application.

4. Solvent Characteristics

The following are the important characteristics of solvents, which influence their potential applications:

4.1. Solvent Power. An universal parameter that characterizes solvent power is very desirable. Many different methods have been proposed to characterize solvent power. The most common are (13): Kauri-butanol value; dilution ratio; and aniline point.

The Kauri-butanol value is the amount of solvent used for titrating a standard Kauri resin solution in 1-butanol required to reach the cloud point. Kauri-butanol value, KB, correlates with the solubility parameter of the tested solvent:

$$\delta = 12.9 + 0.06\,KB \tag{4}$$

Dilution ratio, DR, characterizes the tolerance of solution in the tested solvent to a diluting solvent (usually toluene). The result depends on resin concentration and temperature. DR can also be correlated with the solubility parameter, but these relationships also depend on concentration and temperature. Therefore testing requires standardized conditions.

Aniline point, AP, is a critical temperature of aniline-tested solvent system at which both liquids separate. AP can be correlated with KB (for further details see Ref. 13) and thus, also to the solubility parameter.

None of the above methods of solvent testing provides us with fundamental solution characterizing solvent power towards many solutes, and the methods do not permit solvent selection for a given pair of solvent-solute. These parameters provide some suggestions, frequently used in selected industries (eg, paints and coatings), but do not reduce necessary experimental work.

4.2. Solubility Parameters. It was long thought that thermodynamic affinity between solvent and solute should give an acceptable method of solvent selection and to help in narrowing the range of solvents suitable for particular application. After close to a century of studies, we can now differentiate between one- and multi-dimensional parameters.

One-dimensional Solubility Parameter. Hildebrand developed concept of solubility parameter based on the enthalpy of solvent-polymer interaction (14,15). The solubility parameter, δ, is given by the following equation:

$$\delta = (CED)^{1/2} = \left(\frac{\Delta E_i}{V_i}\right)^{1/2} \tag{5}$$

where $CED =$ cohesive energy density, $\Delta E_i =$ change in cohesive energy, and $V_i =$ molar volume.

The solubility parameter is an useful characteristic measure of intermolecular interactions. It varies from a magnitude of $12\,(\mathrm{MJ/m^3})^{1/2}$ for nonpolar substances up to $23\,(\mathrm{MJ/m^3})^{1/2}$ for water. Knowing solubility parameters of solvent and solute, one can estimate solvents in which a particular polymer cannot be dissolved (solvents having solubility parameter smaller or larger by 4 units or more than solubility parameter of polymer cannot usually dissolve this polymer). There are known exceptions from this rule. It is also pertinent that the magnitude of parameter does not predict which solvents can be expected to dissolve particular polymer. This is a serious limitation of this system. Numerical values of solubility parameters of solvents and polymers can be found in Refs. 11 and 12.

Multidimensional Representation of Solubility. Hansen concluded that the cohesive energy can be divided into contributions of dispersion, polar, and hydrogen bonding interactions, which can be written as follows (13,16):

$$E = E_D + E_P + E_H \tag{6}$$

where $E =$ total cohesive energy, $E_D =$ dispersion cohesion energy, $E_P =$ polar cohesion energy, and $E_H =$ hydrogen bonding cohesion energy.

If both sides of equation 6 are divided by molar volume, V,

$$\frac{E}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V} \tag{7}$$

then

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{8}$$

where $\delta =$ Hildebrand (total) solubility parameter, $\delta_D =$ dispersion cohesion (solubility) parameter, $\delta_P =$ polar cohesion (solubility) parameter, $\delta_H =$ hydrogen bondbonding cohesion (solubility) parameter.

This is very meaningful transformation. On one hand, it permits the use of accumulated data on Hildebrand parameters, and on the other hand, underlines the importance of potential interactions between solvents and solutes, which depend on the characters of solvent and solute. Hansen and Skaarup (17) developed this concept further by adapting the following equation:

$$(Ra)^2 = 4(\delta_{D_2} - \delta_{D_1})^2 + (\delta_{P_2} - \delta_{P_1})^2 + (\delta_{H_2} - \delta_{H_1})^2 \tag{9}$$

where $Ra =$ solubility parameter distance and 1, 2 = subscript of solute and solvent, respectively.

Unlike with the one-dimensional solubility parameter, one can determine here whether a particular solvent can dissolve a given solute. Large sets of data are available (11,12,16), which permit effective use of this concept for solubility prediction of numerous materials, such as polymers, plasticizers, biological materials, and drugs, as well as for characterization of pigments, fillers, fibers, coatings, and surfaces. This method still requires substantial work to evaluate consistency of the existing data and to produce more results.

4.3. Activity Coefficient. Molecules interact in solution therefore their solutions deviate from ideal behavior. The idea of "effective concentration"or "activity" was introduced by Lewis. Activity can be thought of as a correction factor to the concentration. Activity is related to concentration by the activity coefficient, given by the following equation:

$$a_i = \gamma x \tag{10}$$

where $a_i =$ activity of substance, $\gamma =$ activity coefficient, and $x =$ concentration.

The activity coefficient equals one in an ideal solution, and it approaches one in very dilute solutions. The activity coefficient of a solute is constant in any given solution, but its value may change if the properties of the solution are changed (eg, by changing the ionic strength or temperature). There are many applications of activity coefficients; reactivity is the most common. Reaction rate in solution depends on concentration and concentration is corrected by the activity coefficient to account for solvent-solute interactions and solute-solute interactions which affect "effective" concentrations of reactive species.

Many methods are used to determine activity coefficients of solutes in solvents. These include scattering methods in dilute solutions, osmometry, vapor pressure techniques, cryoscopy, ebulliometry, inverse gas chromatrography, and others. The selection of method depends on solute concentration (17). Vapor–liquid equilibrium measurements are the most common in the case of polymer solutions. A large number of data can be found elsewhere (17).

4.4. Solvent–Solute Interactions.

In a mixture of a solute and a solvent, their molecules attract one another. This interaction can only be electrical in its nature, because other known interactions are much more intense. These intermolecular forces are known as van der Waals forces. The intermolecular forces cause interactions between solutes and solvents and determine the properties of gases, liquids and solids (18).

The intermolecular interaction theory predicts effect of electrostatic forces; polarization; dispersion; and repulsion.

Specific interactions (eg, hydrogen bonding), hydrophobic interactions, and acid/base interactions also influence the nature of solvent–solute interactions.

Electrostatic Forces. The electrostatic contribution arises from the interaction of the unpolarized charge distribution of the molecules. If both the solute and the solvent form neutral polar molecules (with a permanent dipolar moment different from zero), due to an asymmetric distribution of their charges, the electric interaction of the dipole-dipole type is usually the most important term in the electrostatic interaction. The intensity of this interaction depends on the relative orientation of the dipoles, and it is given by the following equation (18):

$$\langle E_{d-d} \rangle = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{(4\pi\varepsilon)^2 kTr^6} \tag{11}$$

where μ_i, μ_j = dipole moments, k = Boltzmann constant, ε = dielectric constant, T = absolute temperature, and r = intermolecular distance.

The antiparallel orientation is the most stable with exception of very voluminous molecules. Two dipoles, because of their rapid thermal movement, are sometimes attracted and, at other times, they are repelled. On the average, the net energy turns out to be attractive. The thermal energy of the molecules is a serious obstacle for the dipoles to be oriented in an optimum manner. The average potential energy of the dipole-dipole interaction, or of orientation, is, therefore, very dependent on the temperature (18) (See Fig. 2).

If one of the species involved is not neutral (for example an anionic or cationic solute), the electrostatic interaction is of the ion-dipole type, given by the expression:

$$\langle E_{i-d} \rangle = -\frac{q_i^2\mu_j^2}{6(4\pi\varepsilon)kTr^4} \tag{12}$$

Polarization. If a polar substance is dissolved in a nonpolar solvent, the molecular dipoles of the solute are capable of distorting the electronic clouds of the solvent molecules inducing the appearance of new dipoles. The dipoles of solute and those induced will line up and will be attracted. The energy of this interaction (also called interaction of polarization or induction) is (18):

$$\langle E_{d-id} \rangle = -\frac{\alpha_j \mu_i^2}{(4\pi\varepsilon)^2 r^6} \tag{13}$$

where $\mu_i =$ dipole moment, $\alpha_j =$ polarizability, and $r =$ intermolecular distance.

In a similar way, the dissolution of an ionic substance in a nonpolar solvent also occurs with the induction of the dipoles in the molecules of the solvent by the solute ions.

Dispersion. If the solvent and solute are nonpolar molecules, there is still an interaction between them (18). The forces of interaction are known as London's forces, but also as dispersion forces, charge-fluctuations forces, or electrodynamic forces. Their origin is as follows: when is stated a substance is nonpolar, it is indicated that the distribution of the charges of its molecules is symmetrical throughout a wide average time span. But, without doubt, in an interval of time sufficiently restricted, the molecular movements generate displacements of their charges which break that symmetry giving birth to instantaneous dipoles. Because the orientation of the dipolar moment vector is varying constantly because of the molecular movement, the average dipolar moment is zero, which does not prevent the existence of these interactions between momentary dipoles. Starting with two instantaneous dipoles, these will be oriented to reach an arrangement which will favor them energetically. The energy of this dispersion interaction can be given, as a first approximation, by (18):

$$E_{disp} = -\frac{3I_i I_j}{2(4\pi\varepsilon)(I_i + I_j)} \frac{\alpha_i \alpha_j}{r^6} \tag{14}$$

where I_i, I_j = ionization potentials, α_i, $\alpha_j =$ polarizabilities, and $r =$ intermolecular distance.

Equation 14 shows that dispersion increases with volume of the interacting molecules increasing. The dispersion forces are often more intense than the electrostatic forces and they are universal for all the atoms and molecules, considering that they do not need to contain permanent dipoles. These forces are responsible for the aggregation of the substances which do not possess free charges nor permanent dipoles, and are also the protagonists of phenomena such as surface tension, adhesion, flocculation, and physical adsorption. Although the origin of the dispersion forces may be understood intuitively, it is of a quantum mechanical nature (18).

Repulsion. Repulsive forces also exist between two molecules subjected to dispersion forces (18). They determine a distance to which the molecules (or the atoms) approach one another. These repulsive forces are a consequence of the overlapping of the electronic molecular clouds when these are nearing one another. These are also known as steric repulsion, hard core repulsion, or exchange repulsion. They are short range forces that grow rapidly when the interacting molecules approach one another. Throughout the years, different empirical potentials have been obtained with which the effect of these forces can be reproduced. In the model of hard-sphere potential, the molecules are assumed to be rigid spheres such that the repulsive force becomes suddenly infinite after a certain distance during the approach. Mathematically this potential is (18):

$$E_{rep} = \left(\frac{\sigma}{r}\right)^{\infty} \tag{15}$$

where $r =$ intermolecular distance and $\sigma =$ hard-sphere diameter.

Other repulsion potentials are the power-law potential:

$$E_{rep} = \left(\frac{\sigma}{r}\right)^{n} \tag{16}$$

where $r =$ intermolecular distance, $n =$ integer, usually between 9 and 16, and $\sigma =$ sphere diameter, and the exponential potential is given by:

$$E_{rep} = C \exp\left(-\frac{r}{\sigma_0}\right) \tag{17}$$

where $r =$ intermolecular distance, $C =$ adjustable constant, $\sigma_0 =$ adjustable constant.

These last two potentials allow a certain compressibility of the molecules, more in consonance with reality, and for this reason they are also known as soft repulsions.

If the repulsion energy is represented by a term proportional to r^{-12}, and the energy of attraction between molecules decreases in proportion to r^{-6} at distances larger than the molecular diameter, the total potential of interaction is

$$E = -Ar^{-6} + Br^{-12} \tag{18}$$

where $r =$ intermolecular distance, $A =$ constant, and $B =$ constant, which received the name of potential "6-12" or potential of the Lennard-Jones (19), widely used for its mathematical simplicity (Fig. 3).

Hydrogen Bonding. Hydrogen bonds appear in substances where there is hydrogen covalently bound to very electronegative elements (eg, F, Cl, O, and N). Water is the most common example of such liquid (18). The hydrogen bond can be either intermolecular (eg, H_2O) or intramolecular. The protagonism of hydrogen is due to its small size and its tendency to become positively polarized. In this way, hydrogen is capable, such as in the case of water, of being doubly bonded. On the one hand it is covalently bound to an atom of oxygen belonging to its molecule and, on the other, it is electrostatically attracted by atom of oxygen belonging to another molecule, so strengthening the attractions between molecules. In this way, each atom of oxygen of a molecule of water can take part in four links with four more molecules of water, two of these links are covalently bound to it and the other two links through hydrogen bonds thanks to the two pairs of solitary electrons which it possesses (18).

The energy of hydrogen bond (10−40 KJ/mol) is between that corresponding to the van der Waals forces (∼1 KJ/mol) and that corresponding to the simple covalent bond (200−400 KJ/mol). An energetic analysis of the hydrogen bond interaction shows that the leading term is the electrostatic one which explains that strong hydrogen bonds are found between hydrogen atoms with a partial positive charge and a basic site. The second term in the energy decomposition of the hydrogen bond interaction is the charge transfer (18,20).

Hydrogen bonds are crucial in explaining the form of the large biological molecules, such as the proteins and the nucleic acids, as well as how to begin to understand more particular chemical phenomena (18,21).

Those solutes which are capable of forming hydrogen bonds have a well known affinity to the solvents with similar characteristics, which is the case of water. The formation of hydrogen bonds between solute molecules and those of the solvent explains, for example, the good solubility of ammonia in water and of the short chain organic acids. It also affects solutes activity (see Section 4.3).

Hydrophobic Interactions. Nonpolar solutes which are not capable of forming hydrogen bonds (eg, hydrocarbons) interact in a particular way (18).

Imagine a molecule of solute that is incapable of forming hydrogen bonds. The molecules of water which come close to the solute molecules will lose some or all of the hydrogen bonds which they were sharing with the other water molecules. This forces the water molecules, which surround molecules of the solute to arrange themselves in space so that there is a loss of the least number of hydrogen bonds with other molecules of water. Solvation or hydration of the water molecules around the nonpolar molecule depends on the form and size of nonpolar molecule. All this amounts to the relatively low solubility of nonpolar substances in water, which is known as the hydrophobic effect. Now imagine not one, but two nonpolar molecules in the midst of the water, it emerges that the interaction between these two molecules is greater when they are interacting in a free space. This phenomenon, also related to the rearrangement of the molecules of water around those of the solute, receives the name of hydrophobic interaction (18).

The hydrophobic interaction term is used to describe the tendency of nonpolar groups or molecules to aggregate in water solution (18,22). Hydrophobic interactions are believed to play a very important role in a variety of processes, specially in the behavior of proteins in aqueous media. The origin of this solvent-induced interactions is still unclear. In 1945, Frank and Evans (18,23) proposed the so-called iceberg model where emphasis is made on the enhanced local structure of water around the non-polar solute. However, computational studies and experimental advances have yielded increasing evidence against this interpretation (18,24), and other alternative explanations, such as the reduced freedom of water molecules in the solvation shell (18,25), have emerged.

To understand the hydrophobic interaction at the microscopic level, molecular simulations of nonpolar compounds in water have been carried out (18,26). The potential of mean force between two non-polar molecules shows a contact minimum with an energy barrier. Computer simulations usually predict the existence of a second solvent-separated minimum. Although molecular simulations provide valuable microscopic information on hydrophobic interactions, they are computationally very expensive, specially for large systems, and normally make use of oversimplified potentials. The hydrophobic interaction can also be alternatively studied by means of continuum models (18,27). Using this approach, a different, but a complementary view of the problem has been obtained.

Acid/Base Interactions. Acid/base interactions have found numerous applications in research dealing with the adsorption of molecules of liquids on the surfaces of solids. The main focus of this research is to estimate the thermodynamic work of adhesion, determine the mechanism of interactions, analyze the morphology of interfaces and various surface coatings, develop surface modifiers, study the aggregation of macromolecular materials, explain the kinetics of swelling and drying, understand the absorption of low molecular weight compounds in polymeric matrices, and determine the properties of solid surfaces. In addition to these, acid/base interactions affect activity coefficient of solutes in interacting solvents.

Several techniques are used to determine and interpret acid-base interactions. These include: contact angle, inverse gas chromatography, igc, Fourier transform infrared, ftir, and X-ray photoelectron spectroscopy, xps. Application of these methods to solvents is discussed elsewhere (12).

5. Solvent Behavior

5.1. Electronic and Electrical Effects.

The electronic-vibrational spectra of molecules can be influenced by the surrounding condensed medium. The resultant effects arise from a variety of intermolecular interactions between the chromophoric solute and the solvent molecules in such media. Experimentally, these effects can be observed as the shifts of the spectral maxima (solvatochromic shifts); change in the intensity of the spectral line or band and change of the shape and width of the spectral band.

Each of those, so-called solvent effects, can be described theoretically using different model approaches (28).

The solvatochromic spectral shifts are expected to arise from the difference in the solvation of the ground and the excited states of the molecule. As a result of the spectroscopic excitation, the charge distribution of the molecule changes and thus the interaction will be different in the ground state and in the excited state of the molecule. The direction and the size of the respective spectral shift depends directly on the difference in the solvation energy of the molecule in these two states. The larger solvation energy of the ground state (S_0), when compared to that of the excited state (S_1), results in the negative solvatochromic shift (blue shift) of the spectral maximum. Alternatively, the stronger solvation of the excited state, when compared to the solvation of the ground state, leads to the decrease of the excitation energy and is reflected by the positive solvatochromic shift (red shift) in the spectrum of the compound (28).

The solvent-induced broadening of the spectral lines and bands arises primarily from the variation of the local environment of the chromophoric solute molecule in the condensed medium caused by the thermal motion of the surrounding solvent molecules. At any given moment in time, there is a distribution of differently solvated solute molecules, each of which has characteristic transition energy to the excited state. The respective distribution of the transition energies leads to the broadening of the spectral band. The broadening of spectral lines and bands can also originate from adjoining the rotational and vibrational energy levels in the polyatomic molecule or from the Doppler and natural broadening of spectral lines. These are more significant in the case of atoms and small molecules. The theoretical assessment of the solvent-induced spectral broadening has to rely on a proper statistical treatment of the solvent distribution around the chromophoric solute molecule, both in the ground and in the excited state of the latter (28). The surrounding solvent can also influence the intensity of the spectral transition (absorption or emission). Extensive review of the above influences can be found elsewhere (28).

5.2. Swelling and Plasticization. Polymers differ from other solids because they may absorb large amounts of solvents without dissolving (12). Polymers also undergo large deformations when relatively small forces are involved (29). Swelling occurs in a heterogeneous two-phase system with a solvent surrounding a swollen body, also called gel. Both phases are separated by the phase boundary that is permeable to solvent (30).

The swelling process (or solvent diffusion into to the solid) occurs as long as the chemical potential of solvent is large. Swelling stops when the potentials are the same and this point is called the swelling equilibrium. Swelling equilibrium was first recognized by Frenkel (31) and the general theory of swelling was developed by Flory and Rehner (32,33).

The general theory of swelling assumes that the free energy of mixing and the elastic free energy in a swollen network are additive. The chemical potential difference between gel and solvent is given by the equation:

$$(\mu_1 - \mu_1^0) = (\mu_1 - \mu_1^0)_{mix} + (\mu_1 - \mu_1^0)_{el} \tag{19}$$

where $\mu_1 =$ chemical potential of gel and $\mu_1^0 =$ chemical potential of solvent.

The chemical potential is the sum of the terms of free energy of mixing and the elastic free energy. At swelling equilibrium, $\mu_1 = \mu_1^0$, and thus the left hand term of the equation becomes zero. The equation 19 takes the following form:

$$(\mu_1 - \mu_1^0)_{mix} = -(\mu_1 - \mu_1^0)_{el} = RT[\ln(1 - v_2) - v_2 + \chi v_2^2] \tag{20}$$

where $v_2 = n_2V_2/(n_1V_1 + n_2V_2)$ volume fraction of polymer, n_1, n_2 = moles of solvent and polymer, respectively, V_1, V_2 = molar volumes of solvent and polymer, respectively, $R =$ gas constant, $T =$ absolute temperature, and $\chi =$ Flory-Huggins, polymer-solvent interaction parameter.

The interaction between the solvent and solid matrix depends on the strength of intermolecular bonds such as polymer-polymer, solvent-solvent, and polymer-solvent. If the interaction between these bonds is similar, the solvent will easily interact with polymer, and a relatively small amount of energy will be needed to form a gel (29). The Hildebrand and Scatchard hypothesis assumes that interaction occurs between solvent and a segment of the chain which has a molar volume similar to that of solvent (29). Following this line of reasoning, the solvent and the polymer differ only in potential energy and this is responsible for their interaction and for the solubility of polymer in the solvent. If the potential energies of solvents and polymeric segments are similar they are readily miscible. In crosslinked polymers, it is assumed that the distance between crosslinks is proportional to the molecular volume of the polymer segments. This assumption is the basis for determining molecular mass between crosslinks from the results of swelling studies.

For practical purposes, simple equations are used to study swelling kinetics. The degree of swelling, α, is calculated from the following equation (34):

$$\alpha = \frac{V_1 - V_0}{V_0} \tag{21}$$

where V_1 = volume of swollen solid at time $t = t$ and V_0 = volume of unswollen solid at time $t = 0$.

The swelling constant, K, is defined by:

$$K = \frac{k_1}{k_2} = \frac{\alpha}{1 - \alpha} \tag{22}$$

where k_1 = rate constant of the swelling process and k_2 = rate constant of the deswelling process. This assumes that the swelling process is reversible and in a dynamic equilibrium.

The distance of diffusion is time-dependent:

$$\text{distance} \propto (\text{time})^n \tag{23}$$

The coefficient n is between 0.5 for Fickian diffusion and 1.0 for relaxation-controlled diffusion (diffusion of solvent is much faster than polymer segmental relaxation) (35). This relationship is frequently taken literally (36) to calculate the diffusion distance from a measurement of the change of the linear dimensions of swollen material.

Figure 4 shows swelling kinetic curves for two solvents. Toluene has a solubility parameter of 18.2 and that of *i*-octane is 15.6. The degree to which a polymer swells is determined by many factors, including the chemical structures of polymer and solvent, the molecular mass and chain flexibility of the polymer, packing density, the presence and density of crosslinks, temperature, and pressure. In the example presented in Figure 4, the solubility parameter has a strong influence on swelling kinetics (34).

Much less is known about solvent plasticizing effect. Such effect is frequently used in polymer and asphalt processing but was not subjected to systematic studies.

5.3. Rheological Properties of Solvent-containing Systems. The modification of rheological properties is one of the main reasons for adding solvents to various formulations. Rheology is also a separate complex subject which requires an in-depth understanding that can only be accomplished by consulting specialized sources such as monographic books on rheology fundamentals (37,38). Rheology is such a vast subject that the following discussion will only outline some of the most important effects of solvents.

When considering the viscosity of solvent mixtures, solvents can be divided into two groups: interacting and noninteracting solvents. The viscosity of a mixture of noninteracting solvents can be approximated using a simple rule of additivity:

$$\log\eta = \sum_{i=1}^{i=n} \phi_i \log\eta_i \tag{24}$$

where η = viscosity of solvent mixture, $i =$ iteration subscript for mixture components ($i = 1, 2, 3, \ldots, n$), $\phi =$ fraction of component i, and $\eta_i =$ viscosity of component i.

Interacting solvents are either strong polar solvents or solvents which have the ability to form hydrogen bonds or influence each other on the basis of acid–base interaction. Solvent mixtures are complex because of the changes in interaction that occurs with changes in the concentration of the components. Some general relationships describe viscosity of such mixtures but none is sufficiently universal to replace actual measurements.

The addition of solute(s) further complicates rheology because in such mixtures, solvents may not only interact among themselves but also with the solute(s). There are also interactions between solutes and the effect of ionized species with and without solvent participation. Only very dilute solutions of low molecular weight substances exhibit Newtonian viscosity. In these solutions, viscosity is a constant proportionality factor of shear rate and shear stress. The viscosity of these solutions is usually well described by the classical, Einstein's equation:

$$\eta = \eta_s(1 + 2.5\phi) \tag{25}$$

where $\eta_s =$ solvent viscosity and $\phi =$ volume fraction of spheres (eg, suspended filler) or polymer fraction.

If ϕ is expressed as solute mass concentration, the following relationship is used:

$$\phi = \frac{NVC}{M} \tag{26}$$

where $N =$ Avogadro's number, $V =$ molecular volume of solute ($(4/3)\pi R^3$) with $R =$ radius, c = solute mass concentration, and M = molecular weight.

Combining equations 24 and 25 yields:

$$\frac{\eta - \eta_s}{\eta_s c} = \frac{2.5NV}{M} \tag{27}$$

Existing theories are far from being universal and in agreement with experimental data. A more complex treatment of measurement data is needed to obtain characteristics of these "rheological" liquids.

Figure 5 gives one example of complex behavior of a polymer in solution. The viscosity of PMMA dissolved in different solvents depends on its concentration but there is no one consistent relationship (Fig. 5). Instead, three separate relationships exist each for basic, neutral, and acid solvents, respectively. This shows that solvent acid-base properties have a strong influence on viscosity.

Two polymers in combination have different reactions when dissolved in different solvents (Fig. 6). In MEK, intrinsic viscosity increases as polymer concentration increases. In toluene, intrinsic viscosity decreases as polymer concentration increases. The polymer-solvent interaction term for MEK is small (0.13) indicating a stable compatible system. The interaction term for toluene is much larger (0.58) which indicates a decreased compatibility of polymers in toluene and reduces the viscosity of the mixture.

The above data illustrate that the real behavior of solutions is much more complex than it is intuitively predicted based on simple models and relationships. The selection of a solvent can be used to tailor properties of formulation to the processing and application needs. Solution viscosity can be either increased or decreased to meet process requirements or to give the desired material properties.

5.4. Transport Phenomena (Diffusion and Drying).

The free-volume theory of diffusion was developed by Vrentas and Duda (41). This theory is based on the assumption that the movement of a small molecule (eg, solvent) is accompanied by a movement within the solid matrix to fill the free volume (hole) left by a displaced solvent molecule. Several important conditions must be described to model the process. These include the time scales of solvent movement and the movement of solid matrix (eg, polymer segments, called jumping units), the size of holes which may fit both solvent molecules and jumping units, and the energy required for the diffusion to occur.

The time scale of the diffusion process is determined by the use of the diffusion Deborah number, *De*, given by the following equation:

$$De = \frac{\tau_M}{\tau_D} \tag{28}$$

where $\tau_M =$ the molecular relaxation time and $\tau_D =$ the characteristic diffusion time.

If the diffusion Deborah number is small (small molecular relaxation time or large diffusion time) molecular relaxation is much faster than diffusive transport (in fact, it is almost instantaneous) (42). In such case, the diffusion process is similar to simple liquids (for example, diluted solutions and polymer solutions that are above glass transition temperature fall into this category).

If the Deborah number is large (large molecular relaxation time or small diffusion time), the diffusion process is described by Fickian kinetics, and it is denoted by an elastic diffusion process (41). The polymeric structure in this process is essentially unaffected and coefficients of mutual and self-diffusion become identical. Elastic diffusion is observed at low solvent concentrations below the glass-transition temperature (42).

The relationships below give the energy required for the diffusion process and compare the sizes of holes required for the solvent and polymer jumping unit to move within the system. The free-volume coefficient of self-diffusion is given by the equation (42):

$$D_1 = D_0 \exp\left[-\frac{E}{RT}\right] \times \exp\left[-\frac{\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}}\right] \tag{29}$$

where D_1 = self-diffusion coefficient, D_0 = pre-exponential factor, E = energy per molecule required by the molecule to overcome attractive forces, R = gas constant, T = temperature, γ = overlap factor introduced to address the fact that the same free volume is available for more than one molecule, ω = mass fraction (index 1 for solvent, index 2 for polymer), $\hat{V}^*$ = specific free hole volume (indices the same as above), ξ = the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit (see equation 30), and $\hat{V}_{FH}$ = average hole free volume per gram of mixture.

$$\xi = \hat{V}_1^*/\hat{V}_2^* = \hat{V}_1^* M_1/\hat{V}_2^* M_2 \tag{30}$$

where M = molecular weight (1 - solvent, 2 - polymer jumping unit).

The first exponent in equation 29 is the energy term and the second exponent is the free-volume term. There are three regions of temperature dependence of free-volume: I - above glass-transition temperature, II - close to transition temperature, and III - below the transition temperature. In the region I, the second term of the equation 29 is negligible and thus diffusion is energy-driven. In the region II, both terms are significant. In the region III, the diffusion is free volume-driven (43).

The mutual diffusion coefficient is given by the following equation:

$$D = \frac{D_1 \omega_1 \omega_2}{RT} \left(\frac{\partial \mu_1}{\partial \omega_1}\right)_{T,p} = D_1 Q \tag{31}$$

where D = mutual diffusion coefficient, μ_1 = chemical potential of a solvent per mole, and Q = thermodynamic factor.

These equations form the core of diffusion theory and are commonly used to predict various types of solvent behavior in polymeric and other systems. One important reason for their wide application is that all essential parameters of the equations can be quantified and then used for calculations and modeling. The examples of data given below illustrate the effect of important parameters on the diffusion processes.

Figure 7 shows the effect of temperature on the diffusivity of four solvents. The relationship between diffusivity and temperature is essentially linear. Only solvents having the smallest molecules (methanol and acetone) depart slightly from a linear relationship because of the contribution of the energy term. The diffusivity of the solvent decreases as temperature decreases. Several other solvents show a similar relationship (43).

Figure 8 shows the relationship between the solvent's molar volume and its activation energy. The activation energy increases as the solvent's molar volume increases then it levels off. The data show that the molar volume of a solvent is not the only parameter which affects activation energy. Flexibility and the geometry of solvent molecule also affect activation energy (43). Branched aliphatic solvents (eg, 2-methyl-pentane, 2,3-dimethyl-butane) and substituted aromatic solvents (eg, toluene, ethylbenzene, and xylene) show large departures from the free volume theory predictions.

Many experimental methods such as fluorescence, reflection Fourier transform infrared, nmr, quartz resonators, and acoustic wave admittance analysis, are used to study diffusion of solvents (45–52). Additional experimental data and discussion of the subject can be found elsewhere (12).

Solvent removal can be accomplished by one of three means: deswelling, drying or changes in the material's solubility. The deswelling process involves the crystallization of solvent in the surrounding gel. Material solubility and swelling were previously discussed. Here attention is focused on the drying process.

Figure 9 shows three regions during drying process:

- Region 1 which has a low concentration of solid in which solvent evaporation is controlled by the energy supplied to the system.
- Region 2 in which both the energy supplied to the system and the ability of polymer to take up the free volume vacated by solvent are important.
- Region 3 where the process is free-volume controlled.

Regions 2 and 3 are divided by the glass-transition temperature. Drying processes in region 3 and to some extent in region 2 determine the physical properties of dried material and the amount of residual solvent remaining in the product. A sharp transition between region 2 and 3 (at glass-transition temperature) might indicate that drying process is homogeneous, but it is not and this oversimplifies the real conditions at the end of drying process. The most realistic course of events occurring close to the dryness point is presented by these four stages (53,54):

(1) Elimination of the volatile molecules not immobilized by adsorption onto the polymer.
(2) Elimination of adsorbed molecules from the polymer in its rubbery state.
(3) Evaporation-induced self-association of the polymer with progressive entrapment of adsorbed volatile molecules in the glassy microdomains (during transition from a rubbery to a glassy state).
(4) Elimination of residual molecules entrapped in the polymer.

The last two stages are discussed elsewhere (12). This discussion concentrates on the effect of components on the drying process and the effect of the drying process on the properties of the product.

The change in thickness of the material during drying is given by:

$$v_1 \frac{dL}{dt} = \left(D \frac{\partial v_1}{\partial x} \right)_{x=L} \tag{32}$$

where $v_1 =$ volume fraction of solvent, L = thickness of slab, t = time, D = diffusion coefficient, and $x =$ coordinate of thickness.

The rate of change of the crystalline volume fraction is given by:

$$\frac{\partial v_{2c}}{\partial t} = k_1 v_1 \tag{33}$$

where $v_{2c} =$ volume fraction of crystalline phase and $k_1 =$ rate change of crystalline phase proportional to folding rate.

The rate of change of the amorphous volume fraction is given by:

$$\frac{\partial v_{2a}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial v_1}{\partial x}\right) - k_1 v_1 \tag{34}$$

where $v_{2a} =$ volume fraction of amorphous phase.

The rate of drying process is determined by the diffusion coefficient:

$$D = D_0\ [\exp(\alpha_D v_1)](1 - v_{2c})/\tau \tag{35}$$

where $D_0 =$ initial diffusion coefficient dependent on temperature, $\alpha_D =$ constant which can be determined experimentally from spin echo nmr studies (55), and $\tau =$ constant equal to 1 for almost all amorphous polymers ($v_{2c} \leq 0.05$) and 3 for semicrystalline polymers.

According to this equation, the coefficient of diffusion decreases as crystallinity increases.

Figure 10 shows that the fraction of solvent (water) decreases gradually as drying proceeds. Once the material reaches a glassy state, the rate of drying rapidly decreases. This is the reason for two different regimes of drying. Increasing temperature increases the rate of drying (56).

The initial rate of evaporation of solvent depends on both relative humidity and cosolvent presence (Fig. 11). As relative humidity increases the initial evaporation rate decreases. The addition of cosolvent doubles the initial evaporation rate.

In convection drying, the rate of solvent evaporation depends on airflow, solvent partial pressure, and temperature. By increasing airflow or temperature, higher process rates can be achieved, but the risk of skin and bubble formation is increased. As discussed above, the Vrentas-Duda free-volume theory is the basis for predicting solvent diffusion, using a small number of experimental data to select process conditions. The design of a process and a dryer which uses a combination of convection heat and radiant energy is a more complex process. Absorption of radiant energy is estimated from the Beer's Law, which, other than for the layers close to the substrate, predicts (58).

$$Q_r(\xi) = I_0 \alpha \exp[-\alpha(\beta h - \xi)] \tag{36}$$

where $Q_r =$ radiant energy absorption, $\xi =$ distance from substrate, $I_0 =$ intensity of incident radiation, $\alpha =$ volumetric absorption coefficient, $\beta =$ fractional thickness of the absorbing layer next to the substrate, and $h =$ thickness.

The radiant energy delivered to the material depends on the material's ability to absorb energy which may change as the solvent evaporates. Radiant energy compensates for energy lost resulting from the evaporative cooling, this is most beneficial during the early stages of the process; improves performance of the dryer when changes to either airflow rate or energy supplied are too costly to make.

Radiant energy can be used to improve process control. For example, in a multilayer coating (especially wet on wet), radiant energy can be used to regulate heat flow to each layer using the differences in their radiant energy absorption and coefficients of thermal conductivity and convective heat transfer. Experimental work by Cairncross and co-workers (58) shows how a combination dryer can be designed and regulated to increase the drying rate and to eliminate bubble formation. Shepard (59) shows how drying and curing rates in multilayer coating can be measured by dielectric analysis. Koenders and co-workers (60) give information on the prediction and practice of evaporation of solvent mixtures.

Papers by Vrentas and Vrentas provide relevant modeling studies (61,62). These studies were initiated to explain the earlier observations by Crank (63) which indicated that maintaining a slightly increased concentration of solvent in the air flowing over a drying material may actually increase the evaporation rate. Modeling of the process shows that although the diffusion of solvent cannot be increased by an increased concentration of solvent on the material's surface, an increased concentration of solvent in the flowing air may be beneficial for the evaporation process because it prevents the formation of skin which slows down solvent diffusion.

Additional information on drying application and theories can be found elsewhere (12).

5.5. Chemical Reactivity.

Solvents may influence chemical reactivity by affecting:

- Reaction rate.
- Position of chemical equilibria.
- Selectivity.
- Yield.
- Catalysis.
- Transfer of heat (exothermic and endothermic reactions).
- Crystallization and recrystallization of reaction product.
- Product precipitation.
- and many other physical properties.

These influences are a subject of numerous studies initiated more than a century ago. Many monographic sources contain details of these studies and their findings (12,64–66).

The dielectric constant is a simple characteristic of solvent that can be used for solvent selection. Occasionally dielectric constant correlates with the rate constants of some reactions but there are too many exceptions and thus dielectric constant is rarely used in practical applications. Several experimental scales were developed based on solvatochromic and nmr shifts, donor-acceptor concept, and enthalpy data. Some of these scales can be presented as follows (67):

Cation (or positive dipole's end) solvation	
Gutmann	DN
Kamlet and Taft	β
Koppel and Palm	B (B^*)
Anion (and negative dipole's end) solvation	
Gutmann	AN
Dimroth and Reichardt	$E_T(30)$
Kosower	Z
Kamlet and Taft	α,π^*

These two sets of scales agree in their general trend, but are often at variance when values for any two particular solvents are taken. Some intercorrelations have been presented for E_T, AN, Z and α, π^*. These scales and many others (eg, Y, G, P_y, SPP, SA, and SB) are compared and values of parameters are given elsewhere (68).

Common solvents can be divided into six classes using these concepts (67):

(1) Nonpolar aliphatic solvents.
(2) Protic or protogenic solvents (at least one hydrogen atom is bonded to oxygen).
(3) Aromatic solvents.
(4) (Poly)halogenated solvents.
(5) Amines.
(6) Select solvents defined as non-protonic, non-chlorinated, aliphatic solvents with a single dominant bond dipole.

This is consistent with the general classification of solvents, but of little use in selection of solvents for chemical reaction. The selection of solvents for chemical reaction is usually based on expectations regarding the reaction product and reaction yield, and solvent scales discussed above prove to be very useful in the selection.

In addition to affecting chemical reactions as discussed in this section, reactive solvents are used in some applications. Reactive solvents help to comply with VOC requirements, because part or all solvent is reacted or polymerized and it becomes nonvolatile.

5.6. Behavior in Mixtures. In addition to the effect of solvents on chemical reactivity, the selection of solvent for a reaction depends on some physical constraints such as viscosity, density, solubility, and permittivity. The realization of a process in individual solvent often complicates such controls, and in some cases makes synthesis completely impossible. At the same time, it is possible to tailor properties that determine the process characteristics by selection of mixed solvents. Studies on this subject have been in progress for more than a century, and there is a body of scientific literature which helps in their selection (69).

The solvation of a solute, whether ionic or neutral, in a mixture of solvents is even more complex than that in a pure solvent, because a solvent mixture involves interactions not only between the solute and solvent, but also among different molecules present in the mixture; the latter type of contribution also plays a central role in the solvation process. Among others, it results in significant deviations of the vapor pressure of a mixture with respect to the ideal behavior described by Raoult's law (68).

Solvation studies of solutes in mixed solvents have led to the conclusion that the above-mentioned deviations may arise from the fact that the proportion of solvent components may be significantly different around the solute and in the bulk solution. This would be the case if the solute was preferentially surrounded by one of the mixture components, which would lead to a more negative Gibbs energy of solvation. Consequently, the solvent shell around the solute would have a composition other than the macroscopic ratio. This phenomenon is known as "preferential solvation"; a term that indicates that the solute induces a change with respect to the bulk solvent in its environment. However, such a change takes place via either nonspecific solute–solvent interactions called "dielectric enrichment" or specific solute-solvent association (eg, hydrogen bonding) (68).

These aspects of research and practice in the use of mixed solvents in many industries is broadly discussed elsewhere (12).

6. Environmental Impact

Organic solvents are released into the environment by air emissions, industrial and waste-treatment effluents, accidental spillages, leaking tanks, and the land disposal of solvent-containing wastes (69). As an example of the magnitude of these releases, it is estimated that about 82 million kg of acetone was released into the atmosphere from manufacturing and processing facilities in the United States in 1990, and about 582,000 kg was discharged to the water bodies (69).

There are numerous physical and chemical mechanisms that control solvent movement in the environment. As solvents are released into the environment, they may partition into air, water, and soil phases. While in these phases, solvents may be chemically transformed into other compounds that are less problematic (or more toxic) to the environment. Understanding how organic solvents partition and behave in the environment is one of important requirements for environmental protection.

6.1. Solvents in Water. The fate of solvents in water is determined by their solubility, volatilization, degradation, and adsorption (69).

Solvent solubility affects its extent of leaching into groundwater. The movement of water-soluble solvent in rivers and water reservoirs, and groundwater is much easier and thus danger of pollution is increased. Solvent water-solubility also diminishes the efficiency of efforts of its removal through dissolution and precipitation (69).

Solvent initially released into water may be removed by natural volatilization (although it will then increase air pollution). If the Henry Law constant of solvent is smaller than 10^{-4} atm-mol/m^3 volatilization is probably not significant (69).

Chemical reactions, photodegradation, or abiotic and biotic processes may transform solvents to chemically different compounds. Depending on the properties of these compounds, water contamination may become less or more severe after these transformations. This subject is a matter of extensive studies (69).

Solvents may also be removed from water by their adsorption on sediment or soil. In most cases, water-soluble solvent have lesser tendency to be adsorbed (69).

6.2. Solvents in Soil. Solvents can be removed from soil because of volatilization, desorption, and degradation (69).

Volatilization is an important mechanism of solvent removal from soil. The efficiency and the rate of solvent removal depends on solvent properties, such as vapor pressure, its solubility in water, solvent-soil interaction, and many physical parameters such as temperature, air flow rate, diffusion characteristics of soil, and water content in soil (69).

Solvent movement in soil depends on adsorption and desorption rates. An adsorption isotherm is usually used to describe solvent partitioning between liquid phase and soil. Organic carbon-water partitioning coefficient is a well-known measure of solvent partitioning between water and soil (69).

Similar to water, solvents can be degraded in soil by similar mechanisms. The probability of biodegradation increases with the extent of water solubility of the compound. Biodegradation can depend on the concentration of the solvent itself, competing processes that can make the solvent less available to microorganisms (such as adsorption), the population and diversity of microorganisms, and numerous soil properties such as water content, temperature, and reduction-oxidation potential. Based on results of testing, the half-life of solvent is calculated which is a good measure of its persistence in soil (69).

There are several indicators of solvent biodegradation. Most solvents have a biodegradation half-life of days to weeks and some biodegrade even faster.

The amount of oxygen required for its biodegradation is a measure of a solvent's impact on natural resources. Several factors are used to estimate this, such as biological oxygen demand, BOD, after 5-day and 20-day aerobic tests, chemical oxygen demand, COD, and theoretical oxygen demand, TOD. All results are given in grams of oxygen per gram of solvent. COD is the amount of oxygen removed during oxidation in the presence of permanganate or dichromate. TOD is the theoretically calculated amount of oxygen required to oxidize solvent to CO_2 and H_2O. Most alcohols and aromatic hydrocarbons have the highest BOD5. They consume twice their own weight in oxygen.

6.3. Solvents in Air. Degradation is one means of solvent removal from air (also dissolution of contaminants in rain) (69). Some solvent molecules are capable of absorbing uv radiation and form radicals, but in the majority of the cases, the radicals are formed from solvent reaction with molecular oxygen or other radical-generating species. Once radicals are formed, solvent molecules may undergo internal conversions without chemical changes or degrade forming products of degradation which may continue to degrade, ultimately producing simple compounds such as water or carbon dioxide.

Atmospheric residence times or half-lives of solvents are usual measures of their persistence in atmosphere. More on the subject of photolytic degradation can be found elsewhere (70).

Some solvents have been found to affect the ozone layer that filters solar radiation and protects the Earth from extensive uv radiation. The ozone depletion potential is measured relative to CFC-11, and it represents the amount of ozone destroyed by the emission of a vapor over its entire atmospheric lifetime relative to that caused by the emission of the same mass of CFC-11.

On the other hand, some solvents are precursors of ozone formation close to the Earth surface. This ozone is dangerous to human health. Urban ozone formation potential is expressed relative to ethene. It represents the potential of an organic solvent vapor to form ozone relative to that of ethene [(g O_3/g solvent)/(g O_3/g ethene)]. Several groups of solvents, including alcohols, aldehydes, amines, aliphatic and aromatic hydrocarbons, esters, ethers, and ketones are active in ozone formation. Aldehydes, xylenes, some unsaturated compounds, and some terpenes are the most active among these.

6.4. Indoor Pollution.

Solvents are usually the most significant emission products coming from building materials and interior furnishing. All painted products are potential sources of emission. Similarly sealants, glues, and many other building materials are potential sources of solvent emissions (71).

Most emissions occur immediately following material application. This emission process is initially rapid. It is then followed by a long-term emission of residual quantities. Emission processes of solvents (and other volatile materials) are determined by surrounding conditions: eg, parameters of the ambient air, indoor air parameters, eg, ventilation (ventilation rates), air distribution, air movements, composition of ambient air, concentrations of air compounds, humidity, temperature, volume of the indoor air, and extreme conditions (71).

Many recent studies indicate that indoor pollution causes that indoor air to carries up to several times higher concentrations of industrial pollutants than the external air.

6.5. Contamination Cleanup.

Chlorinated solvents and their natural degradation or progeny products have become some of the most prevalent organic contaminants found in the shallow groundwater (72). Many of these solvents have long half-lives (eg, dichloroethane, 990 days; dichloroethene, 173 days; trichloethene, 151 days). Some chlorinated solvents have shorter half-lives (eg, vinyl chloride and carbon tetrachloride, 14 days) (72).

Subsurface contamination of soils and aquifers by chlorinated hydrocarbons (CHC) and nonchlorinated hydrocarbons (HC) is likely the largest environmental issue in industrialized nations worldwide. Decades without controlled disposal practices, inadequate storage and distribution systems, and accidental releases have resulted in a large number of contaminated drinking water and aquifer systems. In addition, an untold number of ecosystems are subject to future contamination by impinging hydrocarbon plumes. The extent of potential contributors ranges from local facilities, such as laundries or gasoline stations, to major fuel refineries, industrial operations and chemical manufacturing facilities (73).

Many impacted areas, however, do not represent a significant risk to human health or the environment. In other areas, natural attenuation processes are effective in controlling the migration of the dissolved-phase plume (72).

Although the majority of the CHC is used in a safe and conscientious manner, some materials result in environmental contamination. This is often a result of accidental releases, although improper disposal is also a common problem. Unfortunately, as a group, CHCs represent the most problematic of the environmental contaminants because of their toxicity and environmental persistence. Thus, effective means of remediating soil and water potentially impacted by CHCs is often necessary (73).

When the degree of impact or nature of contamination exceeds safe conditions then environmental remediation is needed. If the contamination is confined and physically accessible, impacted soils can be excavated and disposed in a safe manner (73). In other cases, more complex remediation techniques are used. These can be divided into (73):

- *in situ* biotreatment (microbial-enhanced natural attenuation and phytoremediation).
- *in situ* treatment technologies (vertical groundwater circulation wells, surfactant-enhanced product recovery, foam-enhanced product recovery, thermal desorption, steam-enhanced extraction, and permeable reactive barriers).

Many other technologies were developed for managing hydrocarbon remediation (eg, pump and treat or air sparging) and other emerging technologies do exist. The basic themes of preventing migration passively, and the removal of contaminant via degradation (biotic and abiotic) are present in all the technologies. The proper use of particular technology and strategy is very dependent on the extent and type of contamination, the site characteristics (hydrology, lithology, etc.), the cleanup goals, and applicable regulations to name a few. Unfortunately, there are no hard and fast rules for the use of a particular technology; past experience suggests that the more that is known about site characteristics, the greater the success of technology applied (73). More information on contamination, results of self-attenuation and remediation can be found elsewhere (72,73).

7. Health and Safety Factors

7.1. Toxicity Indicators. Lethal dose, LD50, and lethal concentration, LC50, are commonly used indicators of substance toxicity. LD50 is reported in milligrams of substance per kilogram of body weight causing death in 50% of tested animals (exception is LC50 which is given in ppm usually over the period of 4 hours to produce the same effect). It is customary to use three values: LD50-oral, LD50-dermal, and LC50-inhalation which determine the effect of a chemical substance on ingestion, contact with the skin, and inhalation, respectively. The preferred test animal for LD50-oral and LC50-inhalation is the rat. The rabbit is commonly used for LD50-dermal determination, but other test animals are also used.

There is no official guideline on how to use these data but the Hodge-Sterner table is frequently referred to in order to assign a particular substance to a group which falls within certain limits of toxicity. According to this scheme, dangerously toxic substances are those which have LD50$<$ 1 mg/kg, seriously toxic; 1–50, highly toxic; 50–500, moderately toxic; 500–5,000, slightly toxic; 5,000–15,000; and extremely low toxic, $>$ 15,000 mg/kg. Using this classification system, one may assess the degree of toxicity of solvents based on a lethal-dose scale. No solvent has been classified as a dangerously toxic material. Ethylenediaminetetraacetic acid and furfural are seriously toxic materials. Butoxyethanol, ethylene oxide, formaldehyde, metasulfonic acid, 3-methyl-2-butanone, N-nitrosodimethylamine, and triethylamine are classified as highly toxic materials. The remaining solvents fall into the moderately, slightly, and extremely low-toxic material classes.

The LD50-oral is usually assigned a lower value than LD50-dermal, but there are many cases where the opposite applies. Toxicity information is usually expanded by adding more details regarding test animals and target organs.

In addition to LD50 values the NOAEL values are becoming very popular. NOAEL stands for “no observable adverse effect levels”, which are the greatest concentrations or amounts of a substance, found by experiment or observation, which cause no detectable adverse alteration of morphology, functional capacity, growth, development, or life span of the target organism under defined conditions of exposure.

In addition to estimates of toxicity for individual solvents, there are lists which designate individual solvents as carcinogenic, mutagenic, and reproductively toxic. These lists contain the name of solvent with yes or no remark (or similar). If a solvent is not present on the list, that does not imply that it is benign. Only materials that have been tested are included on the lists. To further elaborate, materials are usually divided into three categories: substances known to effect humans, substances which have caused responses in animal testing and given reasons to believe that similar reactions can be expected with human exposures, and substances which are suspected to cause responses based on experimental evidence.

In the United States, four agencies generate lists of carcinogens. These are: the Environmental Protection Agency (EPA), the International Agency for Research on Cancer (IRAC), the National Toxicology Program (NTP), and the Occupational Safety and Health Administration (OSHA). Although, there is a good agreement between all four lists, each assessment differs in some cases. The following solvents made at least one of the lists no distinction is given here as to the category assignment but any known or suspected carcinogen found on any list is given; acetone, acrolein, benzene, carbon tetrachloride, dichloromethane, 1,4-dioxane, ethylene oxide, formaldehyde, furfural, *d*-limonene, *N*-nitrosodimethyl amine, propylene oxide, tetrachloroethylene, 2,4-toluenediisocyanate, 1,1,2-trichloroethylene, and trichloromethane. More details can be found in Refs. 11 and 12.

Mutagenic substances have the ability to induce genetic changes in DNA. The mutagenicity list maintained in the U.S. includes the following solvents: all solvents listed above for their carcinogenic properties with exception of dichloromethane, *d*-limonene, and tetrachloroethylene. In addition, the following solvents were found to have mutagenic properties: 1-butanol, 2-butanol,γ-butyrolactone, 2-(2-*n*-butoxyethoxy)ethanol, chlororodifluoromethane, chloromethane, diacetone alcohol, dichloromethane, diethyl ether, dimethyl amine, dimethylene glycol dimethyl ether, dimethyl sulfoxide, ethanol, 2- ethoxyethanol, 2-ethoxyethanol acetate, ethyl acetate, ethyl propionate, ethylbenzene, ethylene glycol diethyl ether, ethylene glycol methyl ether acetate, ethylene glycol monophenyl ether, ethylenediaminetetraacetic acid, formic acid, furfuryl alcohol, heptane, hexane, methyl acetate, 3-methyl-2-butanol, methyl ester of butyric acid, methyl propionate, *N*-methylpyrrolidone, monomethylamine, 1-octanol, 1-pentanol, 1-propanol, propyl acetate, sulfolane, 1,1,1-trichloroethane, triethylene glycol, triethylene glycol dimethyl ether, trifluoromethane, trimethylene glycol, and xylene (mixture only). It is apparent that this much longer list includes commonly used solvents from the groups of alcohols, halogenated solvents, hydrocarbons, glycols, and esters.

The following solvents are reported to impair fertility: chloroform, ethylene glycol and its acetate, 2-methoxypropanol, 2-methoxypropyl acetate, dichloromethane, methylene glycol and its acetate, and *N*,*N*-dimethylformamide.

7.2. Occupational Exposure Indicators. The measurement of solvent concentration in the workplace place is required by national regulations. These regulations specify, for individual solvents, at least three different concentrations points: the maximum allowable concentration for an 8 hour exposure, the maximum concentration for short exposure (either 15 or 30 min), and concentration which must not be exceeded at any time. These are listed in the regulations for solvents. The listing is frequently reviewed and updated by the relevant authorities based on the most currently available information. In the USA, the threshold limit value, time-weighted average concentration, TLV-TWA, is specified by several bodies, including the American Conference of Governmental Industrial Hygienists (ACGIH), the National Institute of Safety and Health (NIOSH), and the Occupational Safety and Health Administration (OSHA). Usually the NIOSH TLV-TWA are lower than on the other two lists. Similar specifications are available in other countries (for example, OES in UK, or MAK in Germany). The values for individual solvents are selected based on the presumption that the maximum allowable concentration should not cause injury to a person working under these conditions for 8 hours a day.

The maximum concentrations for short exposure is the most frequently specified for an exposure of 15 min with a maximum of 4 such occurrences per day each occurring at least 60 min apart from each other. These concentrations are 1–4 times larger than TLVs. They are selected based on the risks associated with an individual solvent.

Solvent concentrations which should not be exceeded at any time are seldom specified in regulations but, if they are, the values stated as limits are similar to those on the three lists. In addition to maintaining concentrations less than limiting values, adequate protection should be used to prevent the inhalation of vapors and contact with the skin.

7.3. Flammability Limits. Two limits of solvent flammability exist. The lower flammability limit is the minimum concentration of solvent vapor in oxidizing gas (air) that is capable of propagating a flame through a homogeneous mixture of the oxidizer and the solvent vapor. Below the lower flammability limit the mixture is too lean to burn or explode. The upper flammability limit is the maximum concentration of solvent vapor in an oxidizing gas (air) above which propagation of flame does not occur. Mixtures with solvent vapor concentrations above the upper flammability limit are too rich in solvent or too lean in oxidizer to burn or explode.

The flammability limits depend on oxygen concentration, concentration of gases other than oxygen, the inert gas type and concentration, the size of the equipment, the direction of flame propagation, and the pressure, temperature, turbulence and composition of the mixture. The addition of inert gases to the atmosphere containing solvent is frequently used to reduce the probability of an explosion. It is generally assumed that if the concentration of oxygen is less than 3%, no ignition will occur. The type of inert gas is also important. Carbon dioxide is more efficient inert gas than nitrogen. The size of equipment matters because of the uniformity of vapor concentration. A larger head space tends to increase the risk of heterogeneity. The cooling effect of the equipment walls influences the evaporation rate and the vapor temperature and should be used in risk assessment.

The flash point is not the temperature at which the vapor pressure in air equals the lower flammable limit. Although both parameters have some correspondence there are large differences between groups of solvents. There is a general tendency for solvents with a lower flammability limit to have a lower flash point. The flash point determination uses a downward and horizontal propagation of flame. Flame propagation in these directions generally requires a greater vapor concentration than it is required for the upward flame propagation used to determine flammability limits. The flame in a flash point determination is at some distance from the surface where the vapor concentration is greatest (because vapors have higher density than air) than exists on the liquid surface thus flash point analysis underestimates concentration of vapor.

An increased vapor pressure typically increases the upper limit of flammability, and reduces the lower limit of flammability. Pressures below atmospheric have little influence on flammability limits. An increase in temperature increases the evaporation rate, and thus decreases the lower limit of flammability.

There are a few general rules which help in the estimation of flammability limits. In the case of hydrocarbons, the lower limit can be estimated from simple formula: 6/number of carbon atoms in molecule; for benzene and its derivatives the formula changes to: 8/number of carbon atoms. To calculate the upper limits, the number of hydrogen and carbon atoms is used in calculation.

The lower flammability limit of a mixture can be estimated from Le Chatelier's Law:

$$LFL_{mix} = \frac{100}{\frac{\phi_1}{LFL_1} + \frac{\phi_2}{LFL_2} + \cdots + \frac{\phi_n}{LFL_n}} \tag{37}$$

where:

ϕ_i fraction of components 1, 2,..., n

LFL_i lower flammability limit of component 1, 2,..., n

7.4. Flash Point. The flash point is the lowest temperature, corrected to the normal atmospheric pressure (101.3 kPa), at which the application of an ignition source causes the vapors of a specimen to ignite under the specific conditions of the test. Flash point determination methods are designed to be applied to a pure liquid but, in practice, mixtures are also evaluated. It is important to understand limitations of such data.

The flash point of a solvent mixture can be changed by adding various quantities of other solvents. For example, the addition of water or halogenated hydrocarbons will generally increase the flash point temperature of mixture. The flash point can also be changed by forming an azeotropic mixture of solvents or by increasing the interaction between solvents. At the same time, the flash point of single component within the mixture will not change. If conditions during production, application, or in a spill allow the separation or removal of a material added to increase the flash point, then the flash point will revert to that of the lowest boiling flammable component.

An approximate flash point can be estimated from the boiling point of a solvent using the following equation:

$$\text{Flash point} = 0.74\,T_b \tag{38}$$

The correlation coefficient for different groups of solvents varied between 0.89 to 0.96.

Flash point can also be estimated from vapor pressure using the following equation:

$$\text{Flash point} = a \log p + b \tag{39}$$

The constants a and b are specific to each group of solvents.

7.5. Source of Ignition and Autoignition. Sources of ignition can be divided into mechanical sources (impact, abrasive friction, bearings, misaligned machine parts, choking or jamming of material, and drilling and other maintenance operations), electrical (broken light, cable break, electric motor, switch gear, liquid velocity, surface or personal charge, rubbing of different materials, liquid spraying or jetting, lightning, stray currents, radio frequency), thermal (hot surface, smoking, hot transfer lines, electric lamps, metal welding, oxidation and chemical reactions, pilot light, arson, and change of pressure), and chemical (peroxides, polymerization, catalysts, lack of inhibitor, heat of crystallization, thermite reaction, unstable substances, decomposition reactions). This long list shows that when making efforts to eliminate ignition sources, it is also essential to operate at safe concentrations of volatile, flammable materials because of the numerous and highly varied potential sources of ignition.

The energy required for ignition is determined by the chemical structure of the solvent, the composition of the flammable mixture, and temperature. The energy of ignition of hydrocarbons decreases in the order alkanes > alkenes > alkynes (the presence of double or triple bond decreases the energy required for ignition). The energy requirement increases with an increase in molecular mass and an increase in branching. Conjugated structure generally requires less ignition energy. Substituents increase the required ignition energy in the following order: mercaptan < hydroxyl < chloride < amine. Ethers and ketones require a greater ignition energy, but an aromatic group has little influence. Peroxides require extremely little energy to ignite.

Figure 12 shows the effect of changing the ratio of air to methyl ethyl ketone on the minimum spark ignition energy. The ignition energy decreases within the studied range as the amount of air increases (less flammable content). Temperature has also effect on the minimum ignition energy of selected solvents. There are differences between solvents resulting from their chemical structure, as discussed above, but the trend is consistent decrease of required energy as temperature increases.

The autoignition temperature is the minimum temperature required to initiate combustion in the absence of a spark or flame. The autoignition temperature depends on the chemical structure of solvent, the composition of the vapor/air mixture, the oxygen concentration, the shape and size of the combustion chamber, the rate and duration of heating, and on catalytic effects. Figure 13 shows the effect of chemical structure on autoignition temperature. The general trend for all groups of solvents is that the autoignition temperature decreases as molecular weight increases. Esters and ketones behave almost identically in this respect and aromatic hydrocarbons are very similar. The presence of a hydroxyl group substantially reduces autoignition temperature.

The effect of the air to solvent ratio on autoignition temperature is similar to that on ignition energy (see Fig. 12). As the oxygen concentration increases within the range of the flammability limits, the autoignition temperature increases. The autoignition temperature increases when the size of combustion chamber decreases. Rapid heating reduces the autoignition temperature and catalytic substance may drastically reduce it.

7.6. Toxic Effects of Solvent Exposure. Exposure to solvents may cause many chronic reactions, such as (75): hepatotoxicity (76,77); nephrotoxicity (78); reproductive toxicity (79); hemopoietic toxicity (80); neurotoxicity (81); ocular toxicity; brain, lung, and heart effects (82); and allergic reactions (immunological effects).

Solvents which are inhaled, or introduced to organism in any other way, are processed by the liver, therefore it is no surprising that they may cause liver damage. The circumstances of exposure to hepatotoxic agents are divided to (76):

> Occupational: either through a routine daily inhalation or skin absorption of solvents which have been shown to be toxic to the liver (accidental exposure).
>
> Domestic during either accidental or intentional suicidal exposure, ingestion in foods or as a toxic contaminant of food, exposure to toxic agents such as in the form of glue sniffing.
>
> Environmental, most common exposure through contaminated water with solvents (drinking water contamination) or through atmospheric pollution such as a release to the environment from plants utilizing solvents.

The following solvents are considered potential hepatotoxic agents: bromobenzene, bromotrichloromethane, CCl_4, chlorobenzenes, chloroform, dichloropropane, dinitrobenzene, dinitrotoluene, ethylene dichloride, methylene chloride, and naphthalene (76).

There is a number of pathologic manifestations of solvent induced hepatotoxicity, including inflammation, fat accumulation in the liver (steatosis), hepatocellular necrosis and carcinogenesis. Functional disturbances in liver physiology have also been associated with solvent exposure (77).

The metabolites of the organic solvents are eliminated via the kidneys through urine excretion and to some extent, by exhalation of the unchanged original solvent. Commonly, the parent solvent is eliminated by the kidneys and this amounts to less than 1%. The metabolites are the main source of excretion of the metabolized parent solvent (78).

Nephrotoxicity is believed to be caused by hydrocarbon solvents, such as gasoline-based, turpentine, and Stoddard solvent. The most common pathological process described in association with solvent exposure and chronic glomerular nephritis has been that of IgA nephropathy, Good Pasture's syndrome, and proliferative glomerulonephritis (78).

Occupational exposure to organic solvents during pregnancy is associated with an increased risk of major fetal malformations. This risk appears to be increased among women who report symptoms associated with organic solvent exposure (79).

Many organic solvents are teratogenic and embryotoxic in laboratory animals depending on the specific solvent, dose, route of administration and particular animal species. The various malformations described include hydrocephaly, exencephaly, skeletal defects, cardiovascular abnormalities and blood changes. Also, some studies suggest poor fetal development and neurodevelopmental deficits (79).

Benzene is a proven human carcinogen. The toxicity of benzene has been known since the 19th century when aplastic anemia was first reported. Indeed the causal link between benzene and bone marrow toxicity in the form of hematoxicity and bone marrow suppression was described in 1897 (80). In addition to pure benzene, many other solvents contain from 1 to 3.5% benzene and these should also be considered dangerous in the context of hematopoietic cell-type toxicity of benzene (80).

Many organic solvents used in industry are neurotoxic, and may lead to a range of largely irreversible cognitive and psychological or psychiatric impairments in workers who are exposed over long periods of time, or who have had a peak exposure (an episode in which they were briefly exposed to a larger than normal level of solvent). The most vulnerable workers are those who work in the spray painting, boat building, printing, textile, plastic, agricultural and pharmaceutical industries (81).

The chronic, and often slow and insidious effects of occupational solvent neuro-toxicity (OSN) include psychological and psychiatric symptoms, impairments in cognitive functioning, and negative psychosocial consequences (81).

Many victims of OSN do not realize that their chronic fatigue, irritability, poor memory and other problems may be associated with solvents in their workplace (81).

Effects of trichloroethylene, xylene, toluene, styrene, and some other solvents on brain, lung, and heart functions were documented (82). Many allergic effects caused by solvents are well-known as ocular irritancy caused by solvents.

This short review of potential effects of solvents on health and safety only signalizes eventual problems caused by exposures to solvents. Extensive data and information can be found elsewhere (11,12).

8. Regulations

Several major regulations were enacted and amended (83), including the:

- Clean Air Act.
- Clean Water Act.
- Safe Drinking Water Act.
- Resource Conservation and Recover Act.
- Pollution Prevention Act.
- Toxic Substances Control Act.
- Occupational Safety and Health Act.

All these fundamental regulations have been impacting solvent use in the United States and are essential documents for industries using solvents.

In addition to regulatory functions, the need to form alliances with manufacturers and the public were recognized early and many programs and initiatives emerged encouraging voluntary participation. Some of these programs were very successful in reducing solvent-related pollution.

In addition to programs above, various resources have been developed to help those interested in solvent reduction or replacement by using data and information. These include (83):

- Solvent Alternatives Guide (SAGE).
- Coating Alternatives Guide (CAGE).
- Enviroene.
- Program for Assisting the Replacement of Industrial Solvents (PARIS).
- Computer-Aided Molecular Design (CAMD).
- Environmental Technology Verification (ETV).
- and many others.

These tools available to public help in technology conversion.

In Canada, Environment Canada, which was created in 1971, is the organization responsible for environmental regulations and protection. Its environmental services are administered through the Canadian Environment Protection Act (CEPA) which includes the Air Quality Act, the Canadian Water Act, the Ocean Dumping Act, the Environment Contaminant Act, and the Department of the Environment Act (83). As a result of these statutes, the federal government established objectives, guidelines, and emission standards for five national air quality pollutants (carbon monoxide, nitrogen oxides, ozone, sulfur dioxide, and suspended particulate matter) (83).

In Europe the environmental policy was structured as part of the formation of the integrated European states. This effort was extended and refined later with the Maastricht Treaty of 1992. Over the years, however, EU has taken steps to provide a better environment and health for its member states and citizens. Some of these steps have been through the implementation of comprehensive Environmental Action Programmes (EAPs) and specific legislative measures or directives. The fifth EAP started in 1993 with an emphasis on sustainable environmental development and a variety of environmental issues such as climate change, acidification and air pollution, depletion of natural resources and biodiversity, depletion and pollution of water resources, and deterioration of the urban environment and coastal zones, and waste (83).

Air legislation is targeting emissions from industrial operations, greenhouse gases, lead, motor vehicle emissions, nitrogen oxides, sulfur dioxide, and suspended particulate matter. Water legislation in the EU is divided into effect- and source-oriented directives. Four effect-oriented directives provide objectives for water with specific end uses: Bathing Water, Drinking Water, Fish Water and Shellfish Water, and Fresh Water Quality Information Exchange. Seven source-oriented directives focus on the elimination or reduction of pollution at the source: Asbestos, Dangerous Substances, Groundwater, Nitrate, Titanium Dioxide, Urban Wastewater, and Water Pollution Information Exchange (83).

Solid and hazardous waste has received great attention in recent years, and directives have been developed to address their definition, classification, generation, management, and transport across frontiers. In 1993, the EU implemented the European Waste Catalogue which defines 15 categories of waste and a residual category intended to capture any materials, substances, or products not included in those categories. There are 27 substances defined as toxic and hazardous waste for which specific information must be provided during transport: nature, composition, quantity of waste, and sender's and receiver's name (83).

More information on the subject of health and safety in working with solvent can be found elsewhere (11,12).

9. Conclusion

This review of industrial solvents and their major properties shows that this group of materials offers many choices for industries which contemplate to use them. Solvents are very important technological substrates used by more than 30 segments of industry (12). Their use is currently restricted by many existing rules, initiatives, and regulations. Many technological processes were developed to reduce or eliminate the use of solvents. Many products, however, cannot be manufactured or used without solvents. Knowledge and data should therefore guide users to help them in the best selection of a solvent based on the chemical and physical properties of solvents and their influence on human health and environment.

Information on solvent storage conditions, equipment type, and engineering controls available to prevent solvent releases to soil, water and the atmosphere can be found elsewhere, as well as emerging groups of safer solvents which can be used as replacement (11,12).

BIBLIOGRAPHY

"Solvents, Industrial" in *ECT* 1st ed., Vol. 12, pp. 654–686, by A. K. Doolittle, Carbide and Carbon Chemicals Co., A Division of Union Carbide and Carbon Corp.; in *ECT* 2nd ed., Vol. 18, pp. 564–588, by J. W. Wyart, Celanese Chemical Co., and M. F. Dante, Shell Chemical Co.; in *ECT* 3rd ed., Vol. 21, pp. 377–401, by C. F. Parrish, Indiana State University; in *ECT* 4th ed., Vol. 22, pp. 529–571, by D. A. Sullivan, Shell Chemical Co.; "Solvents, Industrial" in *ECT* (online), posting date: December 4, 2000, by D. A. Sullivan, Shell Chemical Co.

CITED PUBLICATIONS

1. *The Exaggerated Demise of Solvents*, 2005, Eastman Web.
2. *World Solvents to 2007*, The Fredonia Group, Study #1715, 2003.
3. Ch. Reichardt, *Solvents and Solvents Effects in Organic Chemistry*, VCH, Weinheim, 1988.
4. V. Gutman and G. Resch, *Lecture Notes on Solution Chemistry*, World Scientific, Singapore, 1995.
5. G. Gritzner, *J. Mol. Liq.* **73**,**74**, 487–500 (1997).
6. Y. Marcus, *The Properties of Solvents*, John Wiley & Sons, Chichester, 1999.
7. L. R. Snyder, *J. Chromatographic Sci.* **16**, 223 (1978).
8. S. C. Rutan, P. W. Carr, J. Cheong, J. H. Park, and L. R. Snyder, *J. Chromatography* **463**, 21 (1989).
9. L. Rohrschneider, *Anal. Chem.* **45**, 1241 (1973).
10. U.S. Pat. 5,464,888 (1995), I. R. Owen (to 3M).
11. *Solvents Database*, ChemTec Publishing, Toronto, 2001.
12. G. Wypych, ed., *Handbook of Solvents*, ChemTec Publishing, Toronto, 2001.
13. V. Yu. Senichev and V. V. Tereshatov, "General Principles Governing Dissolution of Materials in Solvents," in Ref. 12.
14. I. H. Hildebrand, *J. Amer. Chem. Soc.* **38**, 1452 (1916).
15. G. Scatchard, *J. Amer. Chem. Soc.* **56**, 995 (1934).
16. Ch. M Hasen, *Hansen Solubility Parameters, A User's Handbook*, CRC Press, Boca Raton, 2000.
17. Ch. Wohlfarth, "Methods for the Measurement of Solvent Activity of Polymer Solutions," in Ref. 12.
18. E. Silla, A. Arnau, and I. Tunon, "Fundamental Principles Governing Solvents Use," in Ref. 12.
19. J. E. Lennard-Jones, *Proc. Phys. Soc. London* **43**, 461 (1931).
20. J. P. Daudey, *Int. J. Quantum Chem.* **b**, 29 (1974); J. L. Rivail, *Éléments de Chimie Quantique à l'usage des Chimistes*, InterÉditions-CNRS Éditions, Paris, 1994.
21. C. Sandorfy, R. Buchet, L. S. Lussier, P. Ménassa, and L. Wilson, *Pure Appl. Chem.* **58**, 1115 (1986); J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, San Diego, 1989.
22. W. Kauzmann, *Adv. Protein Chem.* **14**, 1 (1959).
23. H. S. Frank and M. W. Evans, *J. Chem. Phys.* **13**, 507 (1945).
24. W. Blokzilj and J. B. F. N. Engberts, *Angew. Chem. Int. Ed. Engl.* **32**, 1545 (1993).

25. B. Lee, *Biopolymers* **24**, 813 (1985); **31**, 993 (1991).
26. W. L. Jorgensen, J. K. Bukner, S. Boudon, and J. Tirado-Rives, *Chem. Phys.* **89**, 3742 (1988); C. Pangali, M. Rao, and B. J. Berne, *J. Chem. Phys.* **71**, 2975 (1979); D. van Belle and S. J. Wodak, *J. Am. Chem. Soc.* **115**, 647 (1993); M. H. New and B. J. Berne, *J. Am. Chem. Soc.* **117**, 7172 (1995); D. E. Smith, L. Zhang, and A. D. J. Haymet, *J. Am. Chem. Soc.* **114**, 5875 (1992); D. E. Smith and A. D. J. Haymet, *J. Chem. Phys.* **98**, 6445 (1994); L. X. Dang, *J. Chem. Phys.* **100**, 9032 (1994); T. Head-Gordon, *Chem. Phys. Lett.* **227**, 215 (1994).
27. J. Pitarch, V. Moliner, J. L. Pascual-Ahuir, E. Silla, and I. Tuñçon, *J. Phys. Chem.* **100**, 9955 (1996).
28. M. Karelson, "Electronic and Electrical Effects of Solvents," in Ref. 12.
29. Z. Hrnjak-Murgic, J. Jelencic, and M. Bravar, *Angew. Makromol. Chem.* **242**, 85–96 (1996).
30. B. Hladik, S. Frahn, and W. Borchard, *Polym. Polym. Compos.* **3**(1), 21–28 (1995).
31. J. Frenkel, *Rubber Chem. Technol.* **13**, 264 (1940).
32. P. J. Flory and J. Rehner, *J. Chem. Phys.* **11**, 521 (1943).
33. P. J. Flory, *J. Chem. Phys.* **18**, 108 (1950).
34. H. J. Mencer and Z. Gomzi, *Eur. Polym. J.* **30**, 1, 33–36 (1994).
35. A. G. Webb and L. D. Hall, *Polymer* **32**(16), 2926–2938 (1991).
36. M. Ercken, P. Adriensens, D. Vanderzande, and J. Gelan, *Macromolecules* **28**, 8541–8547 (1995).
37. A. Ya. Malkin and A. I. Isayev, *Rheology, Concepts, Methods, and Applications*, ChemTec Publishing, Toronto, 2006.
38. Ch. W. Macosko, *Rheology, Principles, Measurements, and Applications*, VCH Publishers, New York, 1994.
39. M. L. Abel and M. M. Chehimi, *Synthetic Metals* **66**(3), 225–233 (1994).
40. H. Raval and S. Devi, *Angew. Makromol. Chem.* **227**, 27–34 (1995).
41. S. Alsoy and J. L. Duda, *Drying Technol.* **16**, 15 (1998).
42. R. Aust, F. Dust, and H. Raszillier, *Chem. Eng. Process.* **36**, 469 (1997).
43. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, New York, 1960.
44. D. Arnauld and R. L. Laurence, *Ind. Eng. Chem. Res.* **31**(1), 218–228 (1992).
45. D. E. Bornside, C. W. Macosko, and L. E. Scriven, *J. Appl. Phys.* **66**, 5185 (1989).
46. R. A. Cairncross, A. Limbert, L. F. Francis, and L. E. Scriven, *24th Annual Meeting of Fine Particle Society*, 24–28 August 1993, Chicago, Ill.
47. R. A. Cairncross, L. F. Francis, and L. E. Scriven, *AlChE J.* **42**, 55 (1996).
48. R. A. Cairncross, S. Jeyadev, R. F. Dunham, K. Evans, L. F. Francis, and L. E. Scriven, *J. Appl. Polym. Sci.* **58**, 1279 (1995).
49. R. A. Cairncross, Ph.D. thesis, University of Minnesota, Minneapolis, 1994.
50. J. D. Cary and E. B. Gutoff, *Chem. Eng. Prog.* **2**, 73 (1991).
51. E. Cohen and E. Gutoff, *Modern Coating and Drying Technology*, VCH Publishers, Inc., New York, 1992.
52. E. Cohen, E. J. Lightfoot, and K. N. Christodoulou, *Ind. Coating Res.* **3**, 45 (1995).
53. L. A. Errede, *Macromol. Symp.* **114**, 73–84 (1997).
54. L. A. Errede, P. J. Henrich, and J. N. Schroepfer, *J. Appl. Polym. Sci.* **54**(5), 649–667 (1994).
55. N. A. Peppas, J. C. Wu, and E. D. von Meerwall, *Macromolecules* **27**, 5626 (1994).
56. M. O. Ngui and S. K. Mallapragada, *J. Polym. Sci.: Polym. Phys. Ed.* **36**(15), 2771–2780 (1998).
57. S. Kojima and T. Moriga, *Polym. Eng. Sci.* **35**(13), 1098–1105 (1995).
58. R. A. Cairncross, S. Jeyadev, R. F. Dunham, K. Evans, L. F. Francis, and L. Scriven, *J. Appl. Polym. Sci.* **58**(8), 1279–1290 (1995).

59. D. C. Shepard, *J. Coat. Technol.* **68**(857), 99–102 (1996).
60. L. Khal, E. Juergens, J. Petzoldt, and M. Sonntag, *Urethanes Technol.* **14**(3), 23–26 (1997).
61. J. S. Vrentas and C. M. Vrentas, *J. Polym. Sci., Part B: Polym. Phys.* **30**(9), 1005–1011 (1992).
62. J. S. Vrentas and C. M. Vrentas, *J. Appl. Polym. Sci.* **60**(7), 1049–1055 (1996).
63. J. Crank, *Proc. Phys. Soc.* **63**, 484 (1950).
64. Ch. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., Wiley-VCH, Weinheim, 2003.
65. Y. Marcus, *The Properties of Solvents*, Wiley, Chichester, 1998.
66. P. Knochel, ed., *Modern Solvents in Organic Synthesis*, Springer, Berlin, 1999.
67. R. Schmid, "Effect of Solvents on Chemical Reactions and Reactivity," in Ref. 12.
68. J. Catalan, "Solvent Effects Based on Pure Solvent Scales," in Ref. 12.
69. W. R. Roy, "The Environmental Fate and Movement of Solvents in Water, Soil, and Air," in Ref. 12.
70. G. Wypych, *Handbook of Materials Weathering*, 3rd ed., ChemTec Publishing, Toronto, 2003.
71. T. Hahn, K. Botzenhart, F. Schweinsberg, and G. Volland, "Indoor Air Pollution by Solvents Contained in Paints and Varnishes," in Ref. 12.
72. H. S. Rifai, Ch. J. Newell, and T. Wiedemeier, "Contamination Cleanup: Natural Attenuation and Advanced Remediation Technologies," in Ref. 12.
73. B. J. Spargo and J. G. Mueller, "Remediation Technologies and Approaches for Managing Sites Impacted by Hydrocarbon," in Ref. 12.
74. H. F. Calcote, C. A. Gregory, C. M. Barnett, and R. B. Gilmer, *Ind. Eng. Chem.* **44**, 2056 (1952).
75. T. Hahn, K. Botzenhart, and F. Schweinsberg, "Toxicokinetics, Toxicodynamics, and Toxicology," in Ref. 12.
76. N. Brautbar, "Hepatotoxicity," in Ref. 12; N. Brautbar and J. Williams II, *Int. J. Hyg. Env. Health* **205**, 479–491 (2002).
77. D. K. Bonauto, C. A. Brodkin, and W. O. Robertson, "Solvents and the Liver," in Ref. 12.
78. N. Brautbar, "Industrial Solvent and Kidney Disease," in Ref. 12; recent update in N. Brautbar, *Int. J. Occup. Environ. Health* **10**, 79–83 (2004).
79. K. I. McMartin and G. Koren, "Pregnancy Outcome Following Maternal Organic Solvent Exposure," in Ref. 12.
80. N. Brautbar, "Lymphohematopoietic Study of Workers Exposed to Benzene including Multiple Myeloma, Lymphoma, and Chronic Lymphatic Leukemia," in Ref. 12.
81. J. A. Ogden, "Cognitive and Psychosocial Outcome of Chronic Occupational Solvent Neurotoxicity," in Ref. 12.
82. K. H. Kilburn, "Toxicity of Environmental Solvent Exposure for Brain, Lung, and Heart," in Ref. 12.
83. C. M. Nunez, *Regulations in Handbook of Solvents*, ChemTec Publishing, Toronto, 2001.

GEORGE WYPYCH
ChemTec Laboratories, Inc.

Table 1. **Comparative Analysis of All Solvents**[a,b]

	Value		
Property	minimum	maximun	range
boiling temperature, °C	CFCs	PHA	−40.6−372
freezing temperature, °C	CFCs	amines	−189−142
flash point, °C	aliphatic HC	CFCs (none)	−104−350
autoignition temperature, °C	glycol ethers	phenols	174−715
refractive index	CFCs	halogenated	1.20−1.63
specific gravity, g/cm^3	aliphatic HC	CFCs	0.51−3
vapor density (air = 1)	aldehydes	CFCs	1−33.4
vapor pressure, kPa	many	CFCs	0.00−4000
viscosity, mPa.s	CFCs	PHA	0.02−114.6
surface tension, mN/m	CFCs	PHA	0.03−48.49
dissociation constant, pKa	ethers	alcohols	−8.3−19.00
pH	acids	amines	1−14
donor number, DN, kcal/mol	hydrocarbons	amines	0−61
acceptor number, AN	hydrocarbons	acids	0−105
polarity parameter, ET(30), kcal/mol	ethers	alcohols	16−65.3
coefficient of cubic expansion, 10^{-4}/°C	alcohols	ethers	7−14.5
specific heat, cal/K mol	CFCs	PHA	12.32−294
heat of vaporization, cal/g	CFCs	halogenated	3.76−81.2
heat of combustion, MJ/kg	CFCs	aliphatic HC	6.57−44.58
dielectric constant	CFCs	esters	1.0−64.9
Kauri-butanol number	aliphatic HC	esters	22−1000
aniline point, °C	aromatic HC	aliphatic HC	7−165
Hildebrand solubility parameter, cal$^{1/2}$ cm$^{-3/2}$	CFCs	alcohols	5.9−23
Henry's Law constant, atm/m^3 mol	amines	alcohols	1.7E-23−34.4
evaporation rate (butyl acetate = 1)	many	aliphatic HC	0−17.5
threshold limiting value −8 h average, ppm	several	several	0.1−1000
maximum concentration (15 min exp), ppm	aldehydes	CFCs	0.3−1250
LD50 oral, mg/kg	aldehydes	phenols	46−320000
LD50 dermal, mg/kg	amines	alcohols	64−225000
route of entry	absorption, contact, ingestion, inhalation		
target organs	blood, brain, bone marrow, central nervous system, eye, gastrointestinal tract, heart, kidney, lymphatic system, liver, lung, peripheral nervous system, respiratory system, skin, spleen, stomach, testes, thyroid		
carcinogenicity	representatives of the following groups: aromatic hydrocarbons, halogenated hydrocarbons, nitrogen-containing compounds, organic sulfur compounds, phenols, aldehydes, ethers, amines, esters		
mutagenic properties	each group contains some representatives		
theoretical oxygen demand, g/g	CFCs	aliphatic HC	0−3.56
biodegradation probability	days-weeks in the most cases		
ozone depletion potential		CFCs	
global warming potential		CFCs	
urban ozone formation	CFCs	aldehydes	0−1.55

[a] Adapted from Ref. 12.

[b] HC - hydrocarbons, PHA - polyhydric alcohols.

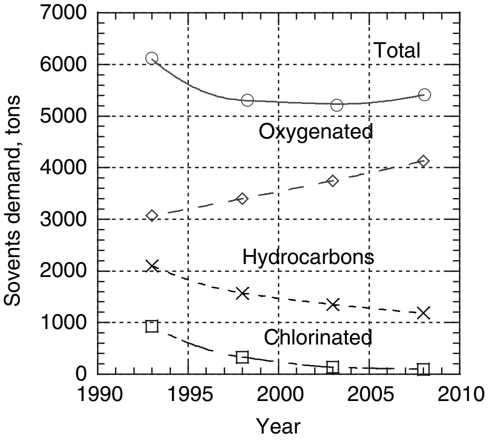

Fig. 1. Past, present, and future demand for various solvents in the United States (1).

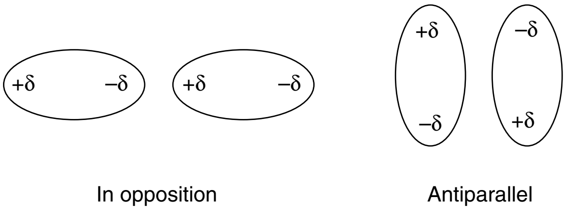

Fig. 2. The dipoles of two molecules can approach one another under an infinite variety of attractive orientations, among which these two extreme orientations stand out. Adapted from Ref. 18.

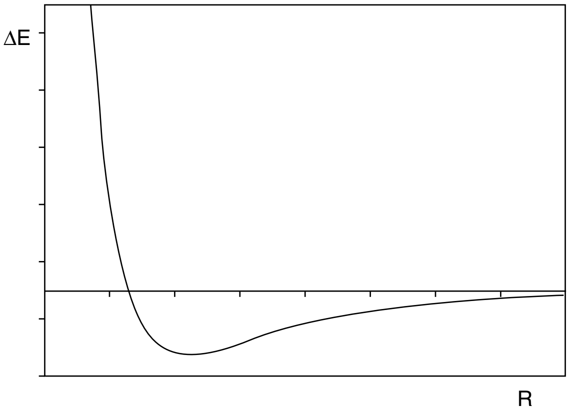

Fig. 3. Lennard-Jones potential between two atoms. Adapted from Ref. 18.

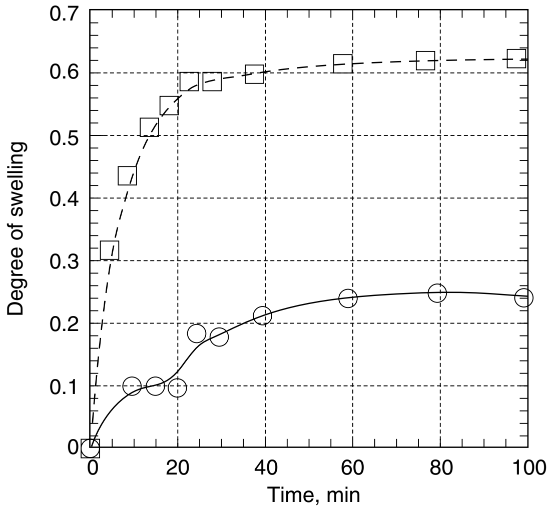

Fig. 4. Swelling kinetics of EVA in toluene and *i*-octane (34). -○- = *i*-octane; -□- = toluene.

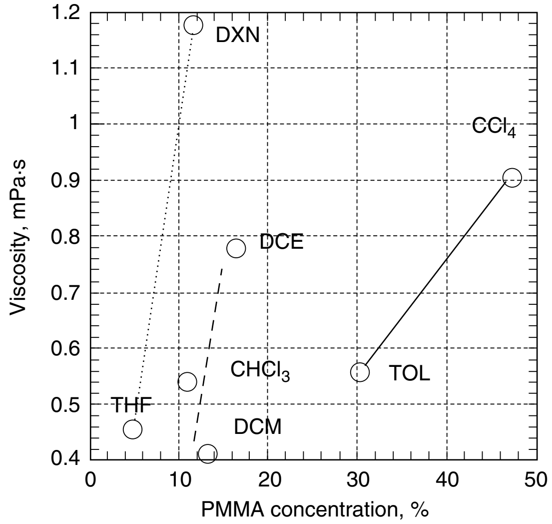

Fig. 5. Viscosity of PMMA solutions in different solvents vs. PMMA concentration. Basic solvents: tetrahydrofuran, THF, and dioxane, DXN; neutral: toluene, TOL and CCl_4; acidic: 1,2-dichloroethane, DCE, $CHCl_3$, and dichloromethane, DCM. Adapted from Ref. 39.

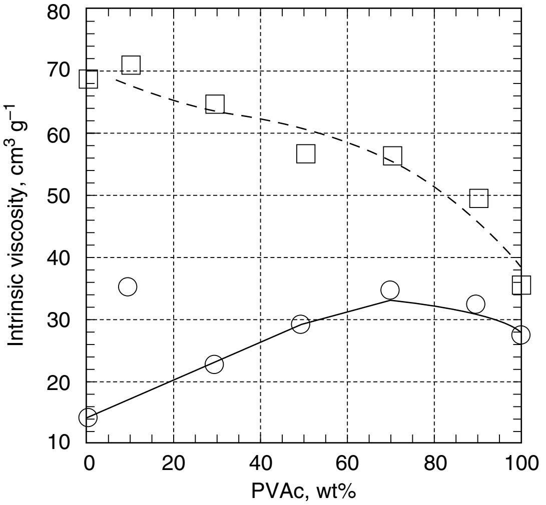

Fig. 6. Intrinsic viscosity of PS/PVAc mixtures in methyl ethyl ketone, MEK, and toluene . -○- = MEK; -□- = toluene (40).

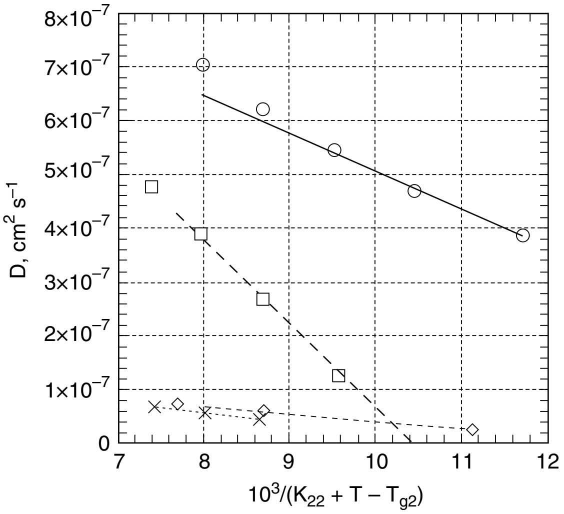

Fig. 7. Free-volume correlation data for various solvents (44). -○- = methanol; -□- = acetone; -◇- = methyl acetate; --×-- = benzene.

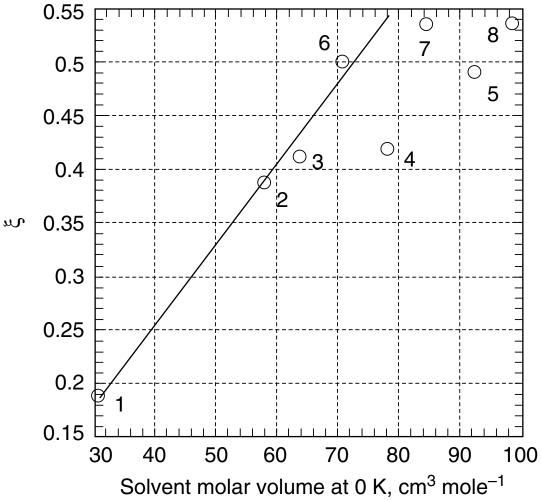

Fig. 8. Parameter ξ vs. solvent molar volume. 1, methanol; 2, acetone; 3, methyl acetate; 4, ethyl acetate; 5, propyl acetate; 6, benzene; 7, toluene; 8, ethylbenzene. Adapted from Ref. 44.

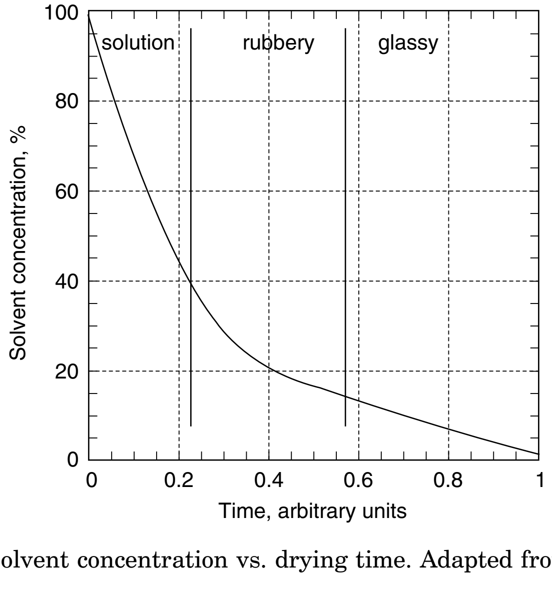

Fig. 9. Solvent concentration vs. drying time. Adapted from Ref. 12.

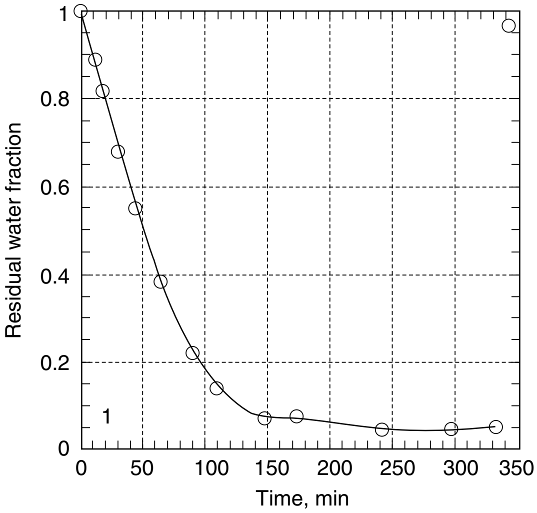

Fig. 10. Fraction of water remaining in PVA as a function of drying time at 23°C (56).

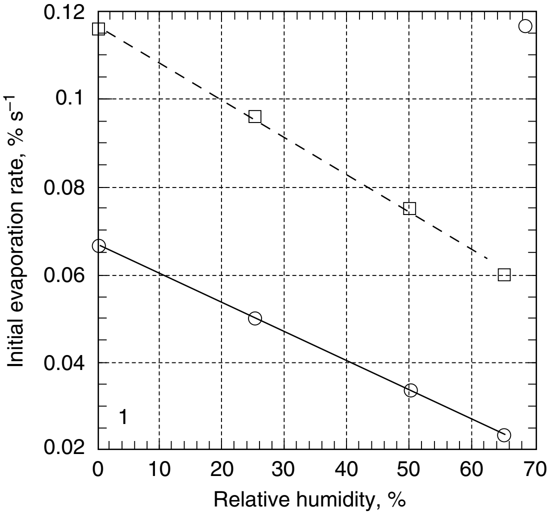

Fig. 11. Initial evaporation rate from waterborne coating vs. relative humidity for two solvent systems (57). -○- = H_2O; -□- = $H_2O + BuOH$.

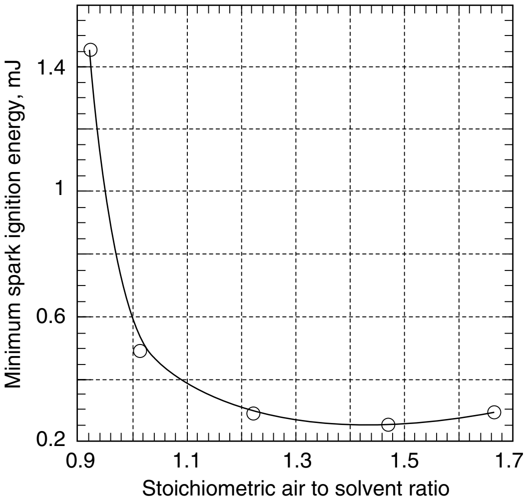

Fig. 12. Minimum ignition energy vs. stoichiometric ratio of air to methyl ethyl ketone (74).

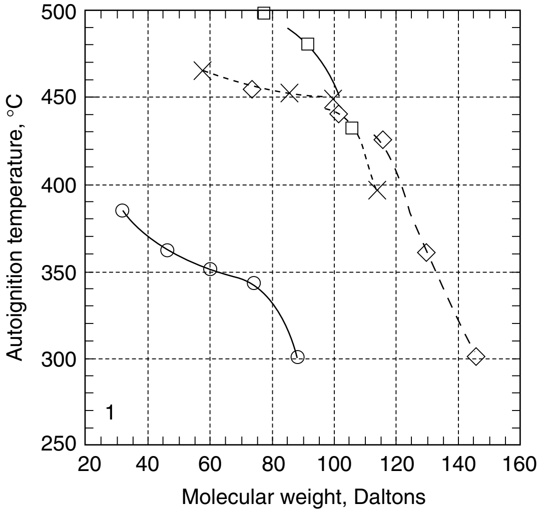

Fig. 13. Autoignition temperature of selected solvents vs. their molecular weight. -○- = alcohols; -□- = aromatic CH; -◇- = esters; --×-- = ketones. Adapted from Ref. 12.