

CHAPTER II

LITERATURE SURVEY

2.1 Ultrafiltration

Ultrafiltration (UF) technology is practiced in the laboratory and on the large scale industries. In laboratory, UF finds many clinical and biological uses for isolating proteins and other macromolecules from salts, metabolites and so on. In industries, UF finds applications in food processing, pharmaceutical, biological, medical, latex, oil-water emulsions, reduction of machining coolant wastes, electrophoretic paint, breaking of emulsion, textile size recovery and water scouring (Eykamp *et al.*, 1993). UF is a membrane process capable of retaining solutes as small as 1,000 daltons (1 dalton is 1/16 the mass of oxygen atom), while passing solvent and smaller solutes. UF is distinguished from reverse osmosis in that UF does not retain species for which bulk solution osmotic pressure is significant and distinguished from microfiltration in that UF exhibits some retention for soluble macromolecules regardless of pore size (Eykamp *et al.*, 1993). The useful ranges of common membranes separation processes are compared in Table 2.1. Figure 2.1 shows the relative sizes of some common materials and approximate molecular weights to the range of application for pressure driven membrane separation processes.

2.2 Ultrafiltration membrane

Ultrafiltration membranes are commonly asymmetric (skinned) polymeric membranes prepared by the phase inversion process (Eykamp and

Table 2.1 Characteristics of common membrane separation processes (Cheryan, 1986).

Process	Driving force	Permeate	Retentate	Operating Pressure (kPa)	Fluxes (L/m ² × h)
Osmosis	Chemical potential	Water	Solutes	-	-
Dialysis	Concentration difference	Water + Small molecule	Large molecules	-	-
Ultrafiltration	Pressure	Water + Small molecule	Large molecules	100-500	10-200
Reverse osmosis	Pressure	Water	Solutes	700-20,000	1-20
Electrodialysis	E.M.F	Water + Ionic solutes	Nonionic solute	-	-
Microfiltration	Pressure	Water + Dissolved organic	Large suspended particles	-	-

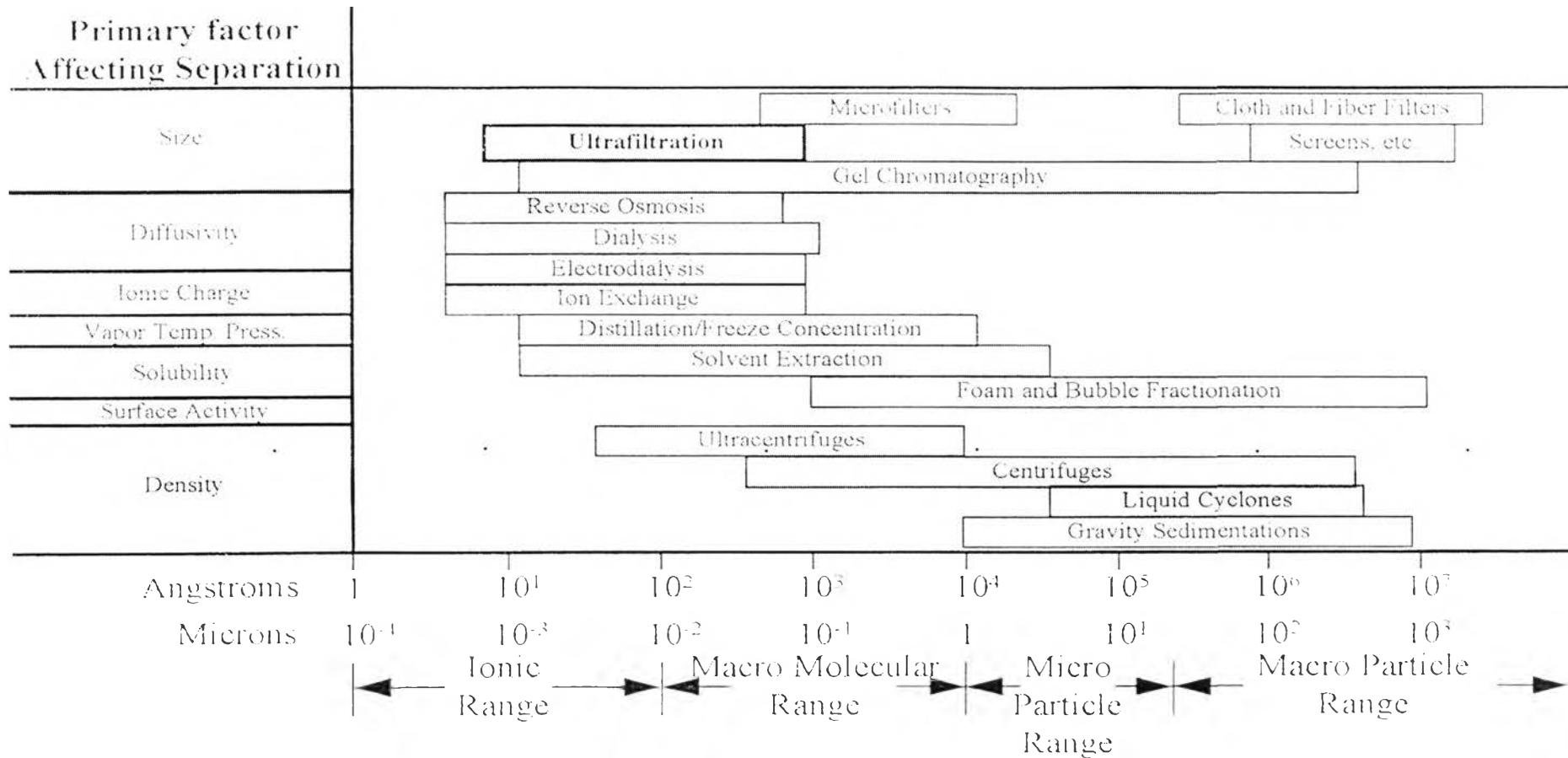


Figure 2.1 Overview of a variety of separation techniques, the range of separation and the primary factors affecting the separation (Cheryan, 1986).

Steen, 1987). Materials commercially made into membranes include cellulose acetate, cellulose nitrate, polysulfone, aramids, polyvinylidene fluoride, and acrylonitrile polymer and copolymers. Membrane manufacturers seek a variety of pore sizes and inherent flux characteristics to meet customer requirements. Resistance to temperature, pH, solvent, and aggressive chemicals has been a major goal. Because of its high residual stress and specific surface, a membrane is rarely as chemically resistant as is its parent polymer, and some caution is appropriate (Rousseau, 1987).

Molecular weight cutoff is a convenient fiction that provides a rough guide to a membrane's pore size. Most sources define the cutoff as the molecular weight of the substance to which the membrane shows 90% retention in very dilute solution. Molecular weight is one of many factors influencing retention. Shape near the membrane and affinity for the membrane are the determining factors in whether a molecule is retained. In general, UF membranes seldom exhibit "absolute" retention for any species near their rate pore size. Ideally, the membrane should be capable of retaining completely all solutes or particles above some specified molecular weight or size and passing completely all species below that size. Significant strides have been made in improving the "cutoff" characteristics of these membranes as shown in Figure 2.2, but the perfect "sharp-cutoff" membrane has not yet appeared.

The size, shape, charge and deformability of molecules determine their retentivity. The physical configuration and electrical charge of a molecule will also effect the separation characteristics of the membrane. As a general rule, linear, flexible molecules in solution ("free draining chains") tend to be retained to a lesser degree for a given molecular weight than do more highly structured molecules such as branched polymers.

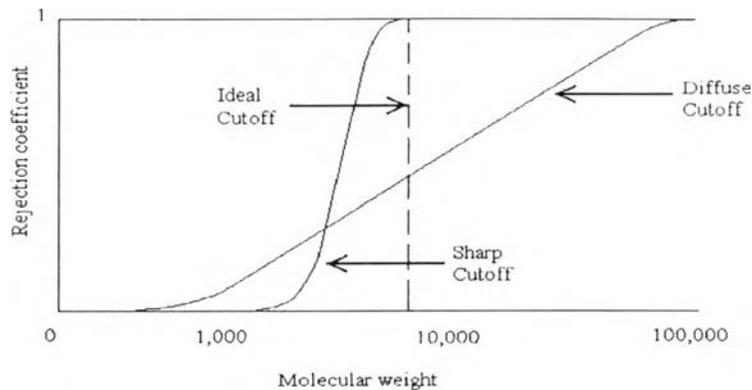


Figure 2.2 Typical rejection characteristics of ultrafiltration membranes showing ideal, sharp and diffuse molecular weight cutoffs (Spectrum Medical Inc.).

The rejection of a solute is defined as

$$R_b = 1 - (C_p/C_b) \quad (2.1)$$

where R_b is the rejection of the solute based on the bulk, C_b is retentate concentration of solute and C_p is the concentration of the solute in the permeate.

2.3 Gel Polarization

When a solute is rejected at an ultrafiltration membrane, the concentration of solute becomes higher in a region of the retentate solution adjacent to the membrane surface than in the bulk retentate solution (that is, a hydrodynamic boundary layer develops). This phenomenon is defined as concentration polarization. The development of concentration polarization in the retentate solution reduces the flux through the membrane due to the increase in resistance to flow caused by the highly viscous solution in the

boundary layer (called the gel layer) through which the permeate must pass to reach the membrane. Concentration polarization can be described by the gel polarization theory, which assumes that the concentration of solute at or near the membrane surface under these conditions of gel polarization is C_g , and the flux (J_w) varies with the bulk concentration of solute (C_b) as follows:

$$J_w = K_T \ln (C_g/C_b) \quad (2.2)$$

where K_T is mass transfer coefficient for back diffusion from the membrane surface. This expression indicates that the bulk concentration is equal to the gel concentration (C_g) when the corresponding flux is zero and that flux is linear with log of retentate solute concentration in the concentration polarization region. C_g is independent of membrane pore size and applied pressure for MEUF in removal of nonionic organic pollutants using an anionic surfactant (Scamehorn *et al.*, 1994). In the case of use of surfactant solutions without added polyelectrolyte, the gel layer formation concentration is higher than used polyelectrolyte-surfactant complexes in colloid-enhanced ultrafiltration (Guo *et al.*, 1997). The formation of a gel layer has been shown to be the major mechanism for reduced flux for ultrafiltration of colloids, such as those used in polyelectrolyte-enhanced ultrafiltration (PEUF). Others have theorized that gel layer formation affects ultrafiltration of colloidal suspensions. Recent work using polyelectrolyte supports the assumption that the gel layer mechanism is the primary mechanism affecting PEUF (Sasaki *et al.*, 1989 and Scamehorn *et al.*, 1990). The relative flux during PEUF removal of chromate from water is a function of retentate polyelectrolyte concentration (relative flux is solution flux divided by flux of pure water). Traditional concentration polarization behavior is observed with declining linearly with the logarithm of retentate concentration. An extrapolation of these data would result in a gel concentration (where flux equal 0) of approximately 0.55 M.

These gel concentration may be useful for setting a limited operating concentration of solution while running a PEUF process. Therefore, concentration polarization is not a severe problem in PEUF if the retentate concentration of polyelectrolyte is much lower than the gel polarization (Sriratana *et al.*, 1994).

2.4 Polyelectrolyte

The term "polyelectrolyte" (PEL) is employed for polymer systems consisting of a "macroion," i.e., a macromolecule carrying covalently bound anionic or cationic groups and low-molecular "counterions" securing for electroneutrality. Examples of an anionic and a cationic polyelectrolytes are presented in Figure 2.3 (Dautzenberg *et al.*, 1994).

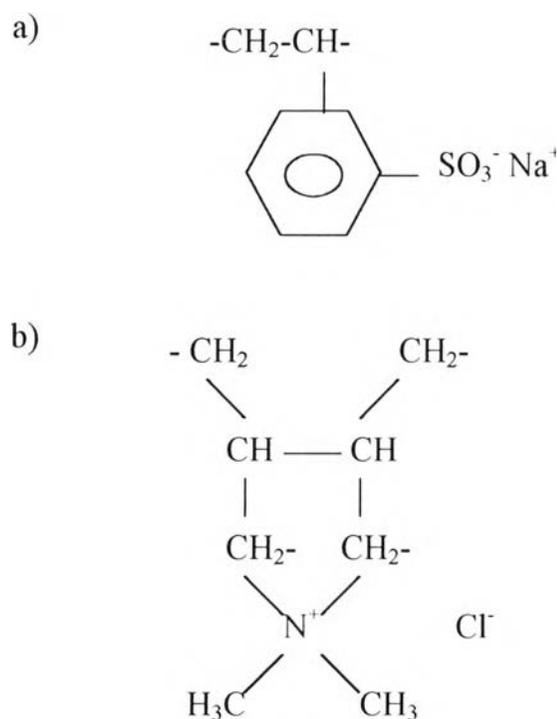


Figure 2.3 Chemical structure of (a) sodium polystyrene sulfonate and (b) poly(diallyldimethyl ammonium chloride) (poly-DADMAC).

Both Na-polystyrene sulfonate and poly(diallyldimethylammonium chloride) are dissociated into macroion and counterion in an aqueous solution in the total pH range between 0 to 14. Also polymers like poly(acrylic acid) or poly(ethylene imine) are usually classified as polyelectrolytes, in spite of the fact that they form a polyion-counterion system only in a limited pH range, and remain as an undissociated polyacid in the acid range or an undissociated polybase in the alkaline range, respectively (Figure 2.4) (Dautzenberg *et al.*, 1994).

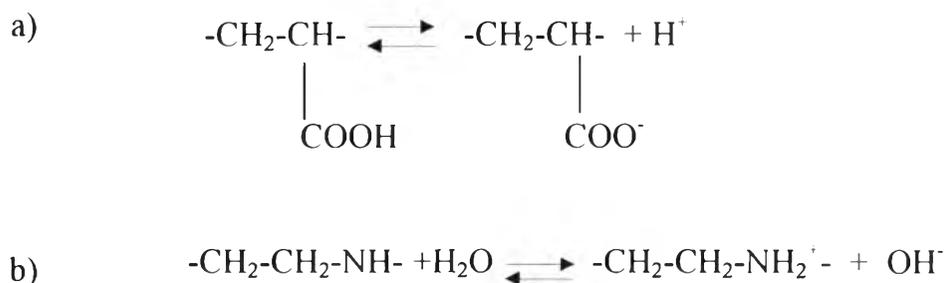


Figure 2.4 Dissociation equilibrium of the weak polyelectrolytes (a) poly(acrylic acid) and (b) poly(ethylene imine).

In principle, any macromolecular chemical structure can be transformed into a polyelectrolyte structure by covalently attaching a reasonable number of ionic groups to the polymer backbone, arriving with linear or branched macromolecules at a compound soluble in an aqueous medium of appropriate pH after introducing a sufficient number of ionic groups, while in the case of crosslinked polymer its swellability in aqueous media is enhanced by transferring into a PEL. A vast number of polyelectrolyte classes known today is selected and listed in Table 2.2 which demonstrates the remarkable variability of the polyelectrolyte chemical structure, resulting from the tremendous number of polymer backbone structures. A polymerization, polycondensation, or polyaddition process predominantly obtains today's

commercial polyelectrolytes, but numerous important PEL also originate from nature, such as gelatin, as a representative of the widespread class of proteins or pectins belonging to the group of anionic polysaccharides. Furthermore, some PEL of practical importance result from a chemical modification of nonionic natural polymers such as cellulose or starch.

Table 2.2 Selected classes of polyelectrolytes

Anionic and cationic polysaccharides and polysaccharidic derivatives

Nucleic acid

Gelatin

Lignosulfonic acids

Polyacrylic and poly methacrylic acid and its copolymers

Maleic acid anhydride copolymers

Polystyrene sulfonic acid

Polyethylene imine

Polyamines and polyamidamines

Ionenenes

Poly(diallyldimethylammonium chloride)

Homo- and copolymers of cationic acrylic acid esters

In contrast to the huge variability of the polymer backbone structure, the number of different chemical structures of anionic or cationic sites responsible for the peculiar behavior of PEL in solution is rather small (Table 2.3).

Table 2.3 Structure of ionic site of PEL

$-\text{COO}^-$	$-\text{NH}_3^+$
$-\text{CSS}^-$	$=\text{NH}_2^+$
$-\text{O}\cdot\text{SO}_3^-$	$-\text{NR}_3^+$
$-\text{SO}_3^-$	
$-\text{OPO}_3^{2-}$	

These ionic groups are usually classified as anionic and cationic; a further subdivision into weakly and strongly acid and basic groups is reasonable in analogy to “strong” and “weak” acid and bases of low molecular chemistry, with the sulfonate, the sulfate half-ester, and the tetraalkylammonium group being representative for the so-called “strong PEL” (Dautzenberg *et al.*, 1994).

Besides the acid or base strength of the ionic site, the average distance between adjacent anionic or cationic charges along the polymer chain is decisive parameter determining PEL behavior, especially in the dissolved state. This charge carrier density or charge density is defined as the average distance between ionic sites, taking into account chain bond geometry, or as the average number of ionic sites per monomer unit in a case of copolymers, with the latter definition yielding comparable data only within the same class of copolymers with ionic component. In addition, the regularity of distribution of ionic sites along the chain can also influence PEL properties significantly, for example, with regard to solubility. As a rule, typical PEL behavior can be expected if more than one ionic site per 10 monomeric unit is present in a copolymer (Dautzenberg *et al.*, 1994).

In addition to acid or base strength and charge density a third important point determining PEL properties is the location of the charge sites within the molecular geometry of the macroion. It is principally distinguished between an integral type of PEL with the ionic sites being part of the polymer backbone, and the pendant type with the ionic site being attached to the

backbone as a site chain with a broad variability in spacer length. The geometric position of the charged sites is relevant especially in polyanion-polycation complex formation (Dautzenberg *et al.*, 1994).

Besides these three parameters characterizing the macroion, the species of low molecular counterions has strong influence on the properties of the whole system in solution, especially on solubility and structure formation. The example may illustrate this and demonstrate that the counterion is not just an anonymous particle securing electroneutrality: the chloride of the poly(diallyl dimethylammonium) polycation is easily soluble in water, while the corresponding iodide is rather insoluble. The potassium salt of some water-soluble high molecular cellulose sulfates forms a stiff, cuttable thermoreversible gel at a polymer concentration between 1 and 2%, while the sodium salt of the same sample at the same concentration give quite a normal polymer solution of the expected viscosity (Dautzenberg *et al.*, 1994).

2.5 Chromate and Other Anions

The chromium plating industries use a wide variety of processes and chemistry to apply surface finish to metallic and non-metallic substrates. The sequence of routing parts through cleaning, surface treatment, and plating processes are varied. Each facility has unique processing parameters such as cleaning method, bath operating conditions, plating times, rinsing methods, and other operations to achieve customer-specified surface characteristics. Following mechanical surface preparation, acids (i.e. nitric, sulfuric and hydrochloric) are used to remove rust, scales and oxides and to activate the metal surface for plating (Bennett, 1996). Although chromic acid is a strong oxidizing agent by chemical means, a solution of pure chromic acid is not directly reduced by electrolysis. A deposit of chromium can only be obtained in the presence of anion such as SO_4^{2-} , which serves as a catalyst (Morisset *et*

al., 1954). Therefore plating waste from metal industries generally contains toxic chromate ions and other anionic species and metal ions in wastewater (Bennett, 1996).

Various methods have been used to remove chromium from industrial wastewater, including conventional chemical precipitation which is a common technique for removal of heavy metals. Chromium (VI), existing as chromate (CrO_4^{2-}) must first be reduced to chromium (III) before precipitation with lime, caustic soda, or sodium carbonate (Beszedit *et al.*, 1988). The cost for both chemicals and sludge removal are quite high because such large volumes are involved. Micellar-enhanced ultrafiltration can be used to remove chromate ion (CrO_4^{2-}). The cationic surfactant, hexadecylpyridinium chloride is added to the solution and the chromate ions preferentially adsorb at the surface of the highly charged surfactant micelles. The permeate solution has a chromate concentration less than 0.1% that in the original stream (Christain *et al.*, 1988).

Nitrate are one of the most problematic and widespread of the vast number of potential ground water contaminants (Canter, 1997). Nitrate test results can be expressed as either nitrate-nitrogen ($\text{NO}_3\text{-N}$) or as nitrate (NO_3). The drinking water quality standard in the U.S. for $\text{NO}_3\text{-N}$ is 10 mg/l, whereas, for NO_3 it is 45 mg/l (Chandler, 1989). Nitrate itself is relatively non-toxic, however the toxicity of nitrate to humans is due to the body's reduction of nitrate to nitrite, which poses several health threats to human including methemoglobinemia (heme Fe^{2+} of hemoglobin is incapable of binding oxygen which mostly occurs in infant) (Canter, 1997), liver damage, and cancers.

Current technologies to remove nitrate from water include ion exchange, reverse osmosis, biological denitrification, and chemical reduction. Removal of nitrate ions from tap water by means of combined membrane process - reverse osmosis (RO) and nano-filtration (NF) were investigated (Bohdziewicz *et al.*, 1999). First the water was filtered on NF membranes which resulted in an absence of bivalent ions in the permeate obtained and

nitrate ion was filtered by RO membrane (Bohdziewicz *et al.*, 1999). Reverse osmosis and ion exchange are not selective for nitrate and required frequent regeneration of the media. Both processes did not destroy nitrate, but generate secondary brine waste. Biological denitrification is unfavorable because it requires intensive maintenance and constant supply of organic substrates. Additional drawbacks include biomass sludge disposal and treatment (aeration and disinfection) of denitrified water. Moreover, these microbial processes are generally slow and sometime incomplete compare to chemical reduction. Chemical reduction of nitrate using ferrous iron as bulk reducing agent has been investigated (Young *et al.*, 1964; Buresh and Moraghan, 1976; Van Hecke *et al.*, 1990).

Generally sulphate is found in manufacture of the kraft paper, paperboard and glass, filler in synthetic detergents, sodium salts, ceramic glazes, processing textile, fibers, dyes, tanning, pharmaceuticals, freezing mix, laboratory reagent, food additive and metal plating industries (Eykramp *et al.*, 1993). In general the toxic properties of substance containing the sulphate radical is that of the material (cation) with which the sulphate (anion) is combined (Eykramp *et al.*, 1993). For example, multivalent cations (Cu^{2+} , Zn^{2+} and Pb^{2+} , etc) and anion (SO_4^{2-}) were used in industrial processes. Therefore, precipitates such as copper sulphate (CuSO_4) would have been forms. The toxicity of sulphate compound (ZnSO_4 , PbSO_4) to humans is a strong irritant to skin, eyes and mucous membranes (Sax and Lewis, 1987).

Several techniques are used to remove sulphate from wastewaters. Biological desulphurisation of wastewater is of growing interest. In biotechnological processes, anaerobic treatment of such wastes has been already evaluated. The sulphate and other oxidized compounds of sulfur (SO_4^{2-} , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, etc.) are reduced anaerobically to sulfide ($\text{HS}^- + \text{H}_2\text{S}_{(\text{aq})} + \text{H}_2\text{S}_{(\text{g})}$) by the sulphate reducing bacteria (SRB) which can utilize various substrates, such as alcohols, fatty acids, dicarboxylic acid and aromatic

compounds (Hansen *et al.*, 1998). It is well know that hydrogen sulfide causes significant damage to treatment facilities.