CHAPTER 1

INTRODUCTION

1.1 LIQUID MIXTURES

Liquid mixtures have attracted considerable attention due to their unusual behavior (Ewing et al 1970). In chemical process industries, materials are normally handled in fluid form and as a consequence, the physical, chemical, and transport properties of fluids assume importance. Fluid mixtures in process industries are often separated into their components by mass transfer operations such as distillation and extraction. Design of such operations requires quantitative estimates of the properties of fluid mixtures. Recently there has been considerable progress in the studies on intermolecular interactions and the internal structure of liquid mixtures. This is linked with the possibility of application of results for interpretation of problems connected with interactions of the ion – ion and ion-solvent type within the liquid system. Studies on determination of different thermophysical properties of liquid mixtures within wide ranges of composition and temperature are valuable sources of information that may be used to examine the relation between the internal structure of the system and its physical properties.

1.2 THERMOPHYSICAL PROPERTIES

Thermophysical properties of liquid mixtures have extensive practical applications in daily life. Any problem connected with heat, momentum and mass transfer entails knowledge of thermophysical properties.
and their variation with temperature. The data on some of the thermophysical properties associated with the liquids and liquid mixtures find applications in solution theory and molecular dynamics (Mchaweh et al 2004). These results are necessary for interpretation of data obtained from thermochemical, electrochemical, biochemical and kinetic studies (Kenart et al 2000). These are needed in many engineering problems such as process calculations, simulations and pipe design. The thermophysical properties of liquid mixtures like density, viscosity, refractive index, surface tension and ultrasonic velocities are often applied for calculations of other parameters characterizing binary and ternary liquid mixtures.

1.2.1 Density

Density ρ, belongs to the group of most useful intensive physicochemical properties widely applied in studies of pure liquids and liquid mixtures. It behaves as an additive volumetric property for ideal solutions. Results of many experimental works show that the analysis of deviation from ideality of density as a function of the composition of the mixture is more useful for studies of intermolecular interactions in liquid mixtures than the analogous examination of changes of density. The knowledge of density of liquid mixtures is necessary for calculations of other properties like viscosity and thermo acoustical parameters.

1.2.2 Viscosity

Viscosity η, is not a simple additive property. It is an important transport property for process design in petroleum, petrochemical and other chemical industries involving fluid transportation, mixing, agitation, filtration, heat exchange and concentration. The investigation of viscosity can be a powerful tool for characterization of intermolecular interactions present in the
mixtures. Many authors underlined the existing relationship between experimental data of viscosity of liquids and their internal structure. Rheology is the study of flow of fluids and deformation of solids. Resistance is offered when one part of fluid is moved over another as shown in Figure 1.1.

![Figure 1.1 Laminar shear of fluid between two plates](image)

The force required to slip one part of fluid over another is called shear stress while rate of movement is called rate of shear. Resistance to this movement is called viscosity. The viscosity of a liquid is defined as force per unit area necessary to maintain unit velocity gradient between two parallel planes of liquid separated by unit distance. The unit of viscosity is poise. But majority of the liquids have very low viscosity and hence it is often expressed in centipoises. Pure liquids often have constant viscosity at given temperature and pressure, such fluids are known as Newtonian fluids. The viscosity of these fluids increases with decrease in temperature. This suggests that molecular clustering or associations are prevailing in liquids. In the absence of experimental data on viscosity, it becomes necessary to predict or estimate viscosity data. An engineer frequently encounters fluids for which data may not be available in literature. To obtain the necessary data, extensive laboratory work is needed. Most of the liquid mixtures do not exhibit linear
This has attracted the idea to generate models which predict viscosity of liquid mixtures using the properties of pure components. Viscometer is the instrument used to measure the viscosity of liquid mixtures.

1.2.3 **Refractive index**

Refractive index measurements in combination with density are very useful industrially and also for common substances which include oils, waxes, sugar syrup etc. The refractive index $n_D$ is a physical property of the medium and it depends on the wavelength of the light and the temperature. The speed of light in vacuum is always the same, but when light moves through any other medium it travels more slowly since it is being constantly absorbed and reemitted by the atoms in the medium. The ratio of the speed of light in vacuum to the speed of light in another substance is defined as the index of refraction or refractive index of the substance. The ratio of the sine of the angle of incidence of a ray of light to the sine of the angle of refraction in the medium is equal to the ratio of the wave velocity of light to the wave velocity in the medium. Since refractive index is a physical property of a substance, it is often used to identify a particular substance, confirm its purity or measure its concentration. Most commonly it is used to measure the concentration of solute in an aqueous solution. A refractometer is the instrument used to measure the refractive index. The refractive index of a medium is a measure for how much the speed of light is reduced inside the medium. Whenever light changes speed as it crosses a boundary from one medium in to another its direction of travel also changes as shown in Figure 1.2.
In the special case where the light is traveling perpendicular to the boundary, there is no change in direction upon entering the new medium. The relationship between light speed in the two media $V_A$ and $V_B$, the angle of incidence, $\theta_A$ and refraction, $\theta_B$ and the refractive indices of the two media are shown below.

$$\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A} \quad (1.1)$$

In the case shown, the speed of light in medium A is greater than the speed of light in medium B. It is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample quite accurately. Nearly all refractometers utilize this principle. It is also possible to design a refractometer based on the reflection of light from the boundary between the prism and the sample.
These types of refractometers are often used for continuous monitoring of industrial processes. Many refractometers are equipped with a thermometer and a means of circulating water through the refractometer to maintain a given temperature.

1.2.4 Surface tension

The existence of strong intermolecular forces of attraction in liquids gives rise to another property known as surface tension. Surface tension of liquid mixtures is also an additive property. However, it is necessary to mention that the composition of the surface of studied solutions is not the same as in bulk, especially for aqueous solutions of non-electrolytes. Surface tension shows the reflection of intermolecular interactions. The surface of the liquid remains in a state of tension because the molecules which are present in it are being constantly subjected to a force pulling them downwards as shown in Figure 1.3. Tension at the surface is known as surface tension.

![Figure 1.3 Forces on molecules of liquid](image)

It can be defined as the force in dynes acting on the surface at right angles to any line of unit length. It is well known that forces of attraction tend to decrease the energy of a system. The attractive forces are more predominant in the bulk of the liquid and associated with lower energy than
those in the bulk. It is the extra energy of surface molecules which gives rise to their tendency to move into the bulk. The molecules tend to move from the state of higher energy to state of lower energy. As a consequence of this transfer, the number of molecules at the surface becomes less than that in the bulk. The distance between any two surface molecules would decrease as they tend to move closer to one another in order to acquire normal distance between them as before. It is for this reason that drops of a liquid are spherical in shape. The surface tension of a liquid mixture is not a simple function of the surface tensions of the pure liquids. Also the composition of the bulk phase and the composition at the vapor – liquid interfaces are not always the same. At the interface there is migration of the species having the lowest surface tension or free energy per unit area at the temperature of the system. This migration at the interphase results in a liquid phase rich in the component with the highest surface tension and a vapor phase rich in the component with the lowest surface tension (Teixeira et al 1992, Carey et al 1980, Winterfield et al 1978). Interfacial tensiometer or surface tension meter are the instruments used to measure the surface tension.

1.2.5 Ultrasonic velocity

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interactions of liquid mixtures. Ultrasonic velocity $u$, of binary liquid mixtures could be related either to size and shape of the molecules or to the entropy effect because of volume and space filling effects with mixing processes. The review of literature on acoustical studies of solutions reveals that ultrasonic measurements are used to estimate different elastic properties. Ultrasonic interferometer is used to measure the ultrasonic velocity of liquid mixtures. It is a simple and direct device for determining ultrasonic velocity in liquids with a high degree of accuracy. The principle used in the measurement of
velocity is based on the accurate determination of the wavelength in the medium. The high frequency generator generates variable frequency, which excites the quartz crystals. The excited quartz crystals generate ultrasonic waves in the experimental liquid. The liquid will serve as an acoustical grating element. When ultrasonic waves pass through the rulings of grating, successive maxima and minima occur, satisfying the condition for diffraction. Ultrasonic velocity measurements combining with other physical quantities provide information of more than thirty parameters. Ultrasound waves are high frequency mechanical waves. Ultrasonic velocity in a medium depends inversely on density and the compressibility of the medium. The variation in ultrasonic velocity depends on the intermolecular free length on mixing. On the basis of a model for sound propagation proposed by Eyring and Kincaid (1938), ultrasonic velocity of the liquid mixtures increases on decrease of intermolecular free length of mixing and vice versa.

1.3 EXCESS PROPERTIES AND DERIVED PARAMETERS

Properties such as excess molar volume, deviations in viscosity, deviations in surface tension, deviations in refractive index and deviations in ultrasonic velocity have been used as qualitative and quantitative guides to understand the molecular interactions between the components of mixtures and carry out engineering applications in the process industries. Acoustic derived parameters like intermolecular free length, acoustical impedance, isentropic compressibility, molar compressibility and molar sound velocity were used to understand different kinds of association, molecular pacing, molecular motion and various types of intermolecular interactions.

1.4 APPLICATIONS OF LIQUID MIXTURES

The applications of liquid mixtures under investigation are listed below. Anisaldehyde (CAS:123-11-5] is chemically known as 4-methoxy
benzaldehyde. Its molecular formula is \( \text{C}_8\text{H}_8\text{O}_2 \). It is an organic compound that consists of a benzene ring substituted with an aldehyde and a methoxy group. It is a clear colorless liquid with a strong aroma. It comes in three varieties, ortho, meta, and para. The unmodified term anisaldehyde generally refers to the para isomer. Anisaldehyde is used as an intermediate in the synthesis of organic compounds used in pharmaceuticals and perfumery, particularly has a scent of licorice. A solution of para anisaldehyde in acid and ethanol is frequently used to stain thin layer chromatography plates. It is particularly a useful stain because different spots on the plate can be stained different colors allowing easy distinction. A mixture of para anisaldehyde and benzene acts as an antibacterial agent and is used in pharma industries. Para anisaldehyde and chlorobenzene mixture is used as insecticide, comprising gel formulations for vapor producing systems and also in the preparation of a polymer containing pendant unsaturation. Para anisaldehyde and bromobenzene mixture is used as antibacterial agent. Para anisaldehyde and nitrobenzene mixture is used in the preparation of antineoplastic agents. Para anisaldehyde and ethylbenzene mixture is used as pesticides. The ternary mixtures of para anisaldehyde with bromobenzene, chlorobenzene and para anisaldehyde with bromobenzene, nitro benzene can be used as an antibacterial and antifungal agents (Kubendran et al 2007 a).

Diacetone alcohol (CAS:123-42-2) is chemically known as 4-hydroxy 4-methyl 2-pentanone and used as antifungal and antibacterial coating solvents. Its molecular formula is \((\text{CH}_3)_2\text{C}($OH$)$\text{CH}_2\text{COCH}_3\). Diacetone alcohol and benzene mixture is used in the preparation of tetramethyl oxopiperidine and also acts as pigments. Diacetone alcohol and chlorobenzene mixture is used in the preparation of polymeric photonic crystals which is used for producing switches. Diacetone alcohol and bromobenzene mixture is used as fluorotech coatings. Diacetone alcohol and
nitrobenzene mixture is used in the preparation of triazine carbamates and in the production of pigments. Diacetone alcohol and ethylbenzene mixture is used in the extraction of aromatic sulphonic acids in the presence of surfactant as well as in the industrial production of water proof material called Blair Matte Spray.

1.5 ARTIFICIAL NEURAL NETWORK

There are currently increasing demands on the accuracy of prediction techniques of thermophysical properties of liquid mixtures for implementation in industrial property prediction computer routines. In many real world applications, one expects computer to solve complex problems. Our conventional computers are obviously not suited to this type of field, therefore borrow features from the physiology has come to be known as Artificial Neural Systems (ANS) technology or neural networks. Artificial neural network is a branch of artificial intelligence (AI) that attempts to achieve human brain like capability. Traditional approaches of solving chemical engineering problems frequently have their limitations, as for example in the modeling of highly complex and nonlinear systems. ANN has proved to be able to solve complex tasks in a number of practical applications. The utility of artificial neural network models lies in the fact that they can be used to infer a function from observations. This is particularly useful in applications where the complexity of the data or task makes the design of such a function by hand impractical. ANN provide good empirical models of complex nonlinear processes useful for a wide variety of purposes. The applications of ANN include detection of medical phenomena, stock market prediction, credit assignment, monitoring the condition of machinery, engine management, Robotics, image processing, character recognition, voice recognition, and optimization.
1.5.1 Analogy of human brain

The brain is principally composed of a very large number of neurons, massively interconnected (with an average of several thousand interconnects per neuron, although this varies enormously). Basically, a biological neuron receives inputs from other sources, combines them in some way, performs a generally nonlinear operation on the result, and then outputs the final result. All natural neurons have the same four basic components. These components are known by their biological names - dendrites, soma, axon, and synapses. Dendrites are hair-like extensions of the soma which act like input channels. These input channels receive their input through the synapses of other neurons. The soma then processes these incoming signals over time. The soma then turns that processed value into an output which is sent out to other neurons through the axon and the synapses. Figure 1.4 shows the relationship of these four parts.

Figure 1.4 Simplified biological neuron
1.5.2 Artificial neurons

To capture the essence of biological neural systems, an artificial neuron can be defined as follows:

- It receives the number of inputs (either from original data, or from the output of other neurons in the neural network). Each input comes via a connection that has a strength (or weight); these weights correspond to synaptic efficacy in a biological neuron. Each neuron also has a single threshold value. The weighted sum of the inputs is formed, and the threshold subtracted, to compose the activation of the neuron (also known as the post-synaptic potential). The activation signal is passed through an activation function (also known as a transfer function) to produce the output of the neuron. In Figure 1.5, various inputs to the network are represented by the mathematical symbol, x(n).

![Figure 1.5 A Basic Artificial Neuron.](image-url)
Each of these inputs is multiplied by a connected weight. These weights are represented by \( w(n) \). In the simplest case, these products are simply summed, fed through a transfer function to generate a result, and then output. This process lends itself to physical implementation on a large scale in a small package.

1.5.3 Architecture of neural network

Neural networks are the simple clustering of the primitive artificial neurons. This clustering occurs by creating layers which are then connected to one another. How these layers connect is the other part of the "art" of engineering networks to resolve real world problems. The common type of artificial neural network consists of three groups or layers of units: input, hidden and output as shown in Figure 1.6.

![Figure 1.6 A simple neural network design](image)

The layer of input neurons receives the data either from input files or directly from electronic sensors in real-time applications. The output layer sends information directly to the outside world, to a secondary computer process, or to other devices such as a mechanical control system. Between
these two layers can be many hidden layers. These internal layers contain many of the neurons in various interconnected structures. The inputs and outputs of each of these hidden neurons simply go to other neurons. The major components which make up an artificial neuron are weighting factors, summation function, transfer function, scaling and limiting.

### 1.5.4 Learning and training process

Learning is the process by which the weight and biases are initialized randomly and error is used to modify the weights so that the network gives a more correct answer next time. Network training is the matter of adjusting weights, such that the network is capable of reproducing the target output within specific error margin for respective input pattern. The learning ability of a neural network is determined by its architecture and by the algorithmic method chosen for training. The training or learning method can be classified into two major categories.

- Supervised learning
- Unsupervised learning

The vast majority of artificial neural network solutions have been trained with supervision which is shown in Figure 1.7.

![Supervised learning](image_url)
In this mode, the actual output of a neural network is compared to the desired output. Weights, which are usually randomly set to begin with, are then adjusted by the network so that the next iteration or cycle will produce a closer match between the desired and the actual output. The learning method tries to minimize the current errors of all processing elements. This global error reduction is created over a period of time by continuously modifying the input weights until acceptable network accuracy is reached. For an unsupervised learning rule, the training set consists of input training patterns only. The network learns to adapt, based on the experiences collected through the previous training patterns. Unsupervised learning is sometimes called self-supervised learning or self organization. These networks use no external influences to adjust their weights instead, they internally monitor their performance.

1.5.5 Feed forward back propagation training algorithm

This back-propagation architecture is the most popular, effective, and easy to earn model for complex, multi-layered networks. Its greatest strength is in non-linear solutions to ill-defined problems. The typical back-propagation network has an input layer, an output layer and at least one hidden layer. There is no theoretical limit on the number of hidden layers but typically there is just one or two. Each layer is fully connected to the succeeding layer, as shown in Figure 1.8.

![Feed Forward network](image)

**Figure 1.8 Feed Forward network**
The number of layers and the number of processing elements per layer are important decisions. These parameters to a feed-forward back-propagation topology are also the most ethereal. They are the art of the network designer. As the complexity in the relationship between the input data and the desired output increases, then the number of the processing elements in the hidden layer should also increase. If the process being modelled is separable into multiple stages, then additional hidden layers may be required. If the process is not separable into stages, then additional layers may simply enable memorization and not a true general solution. The amount of training data available sets an upper bound for the number of processing elements in the hidden layers. To calculate this upper bound, use the number of input output pair examples in the training set and divide that number by the total number of input and output processing elements in the network. Then divide that result again by a scaling factor between five and ten. It is important that the hidden layers have few processing elements. Typical feed forward, back propagation applications include speech synthesis from text, robot arms, evaluation of bank loans, image processing, knowledge representation, forecasting and prediction and multi-target tracking. In the absence of experimental data on thermophysical properties of liquid mixtures, it becomes necessary to resort to generalizations like artificial neural network to predict or estimate the data.