THERMODYNAMICS PROPERTIES OF BINARY LIQUID MIXTURES OF ALKANOLS

Executive Summary submitted to

UNIVERSITY GRANTS COMMISSION
WESTERN REGIONAL OFFICE
PUNE

For the
MINOR RESEARCH PROJECT
In
CHEMISTRY

By

Dr. MIRGANE SUNIL RAMRAO
Associate Professor
P. G. Department of Chemistry, Jalna Education Society’s
R. G. Bagdia Arts, S. B. Lakhotia Commerce and R. Bezonji Science College,
Jalna-431 203 (M. S.)
THERMODYNAMICS PROPERTIES OF BINARY LIQUID MIXTURES OF ALKANOLS

EXECUTIVE SUMMARY

Studies on thermodynamic properties of liquid-liquid binary mixtures are gaining a lot of attention these days owing to their relevance in understanding the nature and extent of molecular interactions between the components of the liquid mixtures in developing the new theoretical models and carrying out engineering applications in the process industry. The knowledge of thermodynamic and physical properties of liquid-liquid systems is of considerable importance due to their wide range of applicability as solvent media in various physicochemical studies, in processing and product formation in many industrial applications. Measurements of some of the bulk properties like density, viscosity and ultrasonic velocity of liquids provide an insight into the investigation of the intermolecular arrangement of liquids and help to understand the thermodynamic and acoustic properties of the liquid mixtures. The study of thermodynamic properties involves challenges of interpreting the excess quantities as a means of understanding the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of characteristic departure from ideal behavior of some physical properties like density, volume, viscosity, compressibility and dielectric properties.

Accurate knowledge of thermodynamic properties of binary liquid mixtures has great relevance in theoretical and applied area of research. These data are needed for design process in chemical, petrochemical and pharmaceutical industries. Usually, for non-ideal mixtures, direct experimental measurements are performed over the entire composition range. Many times predictive methods for the excess quantities could be more useful than the direct experimental measurements especially when quick estimate are needed. Most empirical approach for calculating the excess properties attempts to explain solution non idealities, in terms of specific or non-specific intermolecular interactions.

Volume properties and evaluation of thermodynamic properties gives the better knowledge of the processes that occur in the mixture. In addition, the better understanding of these kinds of properties of fluids is essential in designing processes involving heat transfer,
mass transfer and fluid flow. The more information of magnitudes such as excess molar volume of a given component of a mixture, the more efficient the design of engineering processes in which these magnitudes are involved. However, during the mixing process new effects can affect the volume behavior, such as changes in the structure of components, repulsion or attraction between unlike molecules these effects can make. So a better understanding of the excess molar volume of a system is of considerable physicochemical interest. Binary liquid mixtures rather than single component liquid system are widely used in processing and product formulations in many industrial applications. Among the various properties considered in process and product design and optimization excess molar volumes is the most important. Although a number of predictive equations are available for estimating thermodynamic excess properties (excess volume, excess enthalpy, excess Gibb’s free energy, etc.) of multi component systems.

Study of viscous behaviour of liquid mixtures is of strategic importance in understanding the in-depth of their transport behavior. Recently, it has been applied in the study of mass transfer in a rotating packed bed with viscous Newtonian and non Newtonian fluids [8], on breakage parameters of quartz , on liquid-solid fluidization , diffusion and the mesoscopic hydrodynamics of super cooled liquids , in the use of nanoliter viscometer for analyzing blood plasma and other liquid samples , in the flow of viscous shear thinning fluids behind cooling coil banks in large reactors , on shear viscosity relaxation of liquid n-alkanes , etc. Besides this previous work, recently a large amount of work has been reported on the experimental measurements of viscosity of single components and that of binary liquid mixtures. Density and viscosity are important basic data used in process simulation, equipment design, solution theory and molecular dynamics. Knowledge of viscosity is widely used in processing and product formulations in many industrial applications.

Ultrasonic velocity measurement of liquid mixtures of non electrolytes provides an excellent tool to investigate inter and intermolecular interactions between unlike and like molecules. Alcohols exist in the form of aggregates. When they are mixed with other non electrolyte molecules, the aggregates of alcohol dissociate and form intermolecular complexes with unlike molecules.

The velocity of sound is very important for liquids to study molecular interactions and to elucidate internal structure of liquid mixture. The knowledge of sound velocity in liquids has been found very helpful in the study of high velocity interpartical collisions , ultra spectrometry
for liquids, in multiphase flows, crystal growth from solutions, aqueous fluids, convective flow electrochemistry, desorption of metal ions from activated carbon, gas phase RTD measurements in gas and gas-solid reactors, acoustical absorption spectrometry study, sonochemical removal of nitric oxide from flue gases, shear impedance spectrometry, ultrasonic spectrometry of polystyrene latex suspensions, structural isomerization and molecular motions of liquid n-alkanes. Density and ultrasonic velocity are important basic data used in process simulation, equipment design, solution theory and molecular dynamics.

Considering all these important aspects, studies on densities, viscosities, speeds of sound and other related properties of n-alkanes and their binary mixtures with alkan-1-01/ alka-2-ol have been undertaken in present investigation. This work will provide in depth understanding of molecular interactions and theoretical development of liquid and liquid mixtures.

The present work entitled “THERMODYNAMICS PROPERTIES OF BINARY LIQUID MIXTURES OF ALKANOLS”

Attempts have been made to probe the liquid structure through evaluation of density, viscosity and ultrasonic velocity data. Literature survey reveals that such type of study has been carried out for several liquid-liquid systems over the entire range of composition but at a limited range of temperature. We have thus undertaken the thermodynamic study of binary liquid-liquid systems containing many polar and non-polar liquids to investigate the molecular interactions.

Alcohols are a class of compounds with polar character. The dipole-dipole type van der Wall's forces are present. In addition to dipole-dipole forces alcohols are hydrogen bonded and thus involve strong intermolecular interactions. Alcohols are protic and have relatively high dielectric constants and are self associated with hydrogen bonding. Degree of association in them decreases with increasing carbon chain length; from hexanol to dodecanol. Alcohols serve as simple example of biologically and industrially important amphiphilic materials.

Alkanes are an important series of homologous, non-polar solvent. They have often used in study of solute dynamic because their physicochemical properties as a function of chain length are well-known. They are also employed in a large of chemical processes.

1-Hexanol is slightly soluble in water, but miscible with ether and ethanol. It is used in the perfume industry1-hexanol is believed to be a component of the odour of freshly mown grass. Alarm pheromones emitted by the Koschevnikov gland of honey bees contain 1-hexanol.

1-Heptanol is a clear colorless liquid that is very slightly soluble in water, but miscible with ether and ethanol. Heptanol is commonly used in cardiac electrophysiology experiments to block gap junctions and increase axial resistance between myocytes. Increasing axial resistance will decrease conduction velocity and increase the heart's susceptibility to reentrant excitation and sustained arrhythmias. 1-Heptanol has a pleasant smell and is used in cosmetics for its fragrance.
1-Octanol occurs naturally in the form of esters in some essential oils. The primary use of octanol is in the manufacture of various esters (both synthetic and naturally occurring), such as octyl acetate, which are used in perfumery and flavors. Other uses include experimental medical applications utilizing octanol to control essential Tremor and other types of involuntary neurological tremors.

1-Octanol and water are immiscible. The distribution of a compound between water and octanol is used to calculate the partition coefficient \( P \) of that molecule (often expressed as its logarithm to the base 10, \( \log P \)). Water/ octanol partitioning is a relatively good approximation of the partitioning between the cytosol and lipid membranes of living systems.

1-Decanol is a straight chain fatty alcohol and a colorless viscous liquid that is insoluble in water and has a strong odour. Decanol is used in the manufacture of plasticizers, lubricants, surfactants and solvents.

Dodecanol, also known by its IUPAC name 1-dodecanol or dodecan-1-ol and by its trivial name dodecyl alcohol and lauryl alcohol, is a fatty alcohol. Dodecanol is a colorless, water insoluble solid of melting point 24 °C and boiling point 259 °C. It has a floral odour. It can be obtained from palm kernel or coconut oil fatty acids and methyl esters by reduction. Dodecanol is used to make surfactants, lubricating oils and pharmaceuticals. In cosmetics, dodecanol is used as an emollient. It is also used to form a detergent called as sodium lauryl sulphate. This can be used in soft, hard water as well as in acidic solutions. It is also used in synthesis of mercaptant which finds applications in rubber processing and as an intermediate for various chemical derivatives. Highly refined graded 1-dodecanol used in tuberose violet and rose perfumes.

2-Hexanol has a chiral center and can be resolved into enantiomers.

2-octanol is nature colorless aromatic odour from the liquid fuel easily. It is used in polyethylene plastic used plasticizers, synthetic finishes, emulsifier’s toxicity of raw materials and low toxicity, slightly bactericidal. It has some unpleasant odour.

\( n \)-octane is used in organic syntheses, calibrations, and azeotropic distillations and is a common component of gasoline and other petroleum products. The engine fuel antiknocking properties of an isomer of \( n \)-octane (2,2,4-trimethylpentane or isooctane) are used as a comparative standard in the octane Rating System. Octane" is colloquially used as a short form of "octane rating" (named for the ability of octane's branched-chain isomers, especially isooctane, to reduce engine knock), particularly in the expression "high octane." However, components of gasoline other than isomers of octane can also contribute to a high octane rating, while some isomers of octane can lower it, and \( n \)-octane itself has a negative octane rating.

\( n \)-decane is used as a solvent in organic synthesis, as a hydrocarbon standard in jet fuel research, in the manufacturing of paraffin products, in the rubber industry, in the paper-processing
industry and in cleaning agents. n-decane is also found in several widely used petroleum distillates, such as Stoddard solvent and jet fuel. n-decane also represents 7.6-11% of white spirits, a mixture of saturated aliphatic and alicyclic, and alkyl aromatic C7-C12 hydrocarbons. Stoddard solvent, a form of white spirit, contains 30-50% of linear and branched alkanes (ATSDR, 1995a; World Health Organization, 1996). The source used to prepare the jet fuel JP-4 apparently affects the amount of n-decane present. N-decane was found at percentages of 11.25 or 2.24 in JP-4 fuel when the source was shale or petroleum, respectively.

n-dodecane is used as a solvent, in organic synthesis, distillation chaser, in jet fuel research, standardized hydrocarbon, manufacture of paraffin products; rubber industry, paper processing industry, and as a component of gasoline may result in its release to the environment through various waste streams. In recent years, n-dodecane has garnered attention as a possible surrogate for kerosene-based fuels such as Jet-A, S-8, and other conventional aviation fuels. It is considered a second-generation fuel surrogate designed to emulate the laminar flame speed, largely supplanting n-decane, primarily due to its higher molecular mass and hydrogen to carbon ratio which better reflect the n-alkane content of jet fuels.

n-Tetradecane is both a naturally occurring and an anthropogenic compound which is used as a solvent and a synthetic intermediate.

The materials and experimental techniques, which are being used in the present investigation. Purification process of liquid components used in the present investigation standard methods.

The densities were measured using a single capillary pycnometer made up of borosil glass with a bulb of 8 cm³ and capillary with internal diameter of 0.1 cm. The weights of empty pycnometer and pycnometer filled with experimental liquid were taken on a Mettler one pan balance, which can read up to fifth place of decimal, with an accuracy of ± 0.01 mg. The estimated uncertainty in mole fraction was <1 ×10⁻⁴.

An Ubbelhode viscometer was selected for the measurement of viscosity, having a flow time of approximately 300 seconds at 298.15K. The uncertainty of viscosity measurements was ± 0.3 %. The pycnometer and viscometer were clamped vertically in thermostatically controlled water bath, whose temperature was maintained constant by circulating water, capable of maintaining constant temperature (± 0.02°C).

A variable path single crystal interferometer (model F-8I, Mittal's Enterprises, New Delhi) o was used for the measurement of ultrasonic velocity. The error in velocity measurements is ± 0.1 %.

The above measurements have been carried out at 298.15, 303.15, 308.15, and 313.15 K
and at atmospheric pressure over the entire composition range for the following binary systems


The measurement of density, viscosity and ultrasonic velocities at temperatures 298.15, 303.15, 308.15 and 313.15 K and at atmospheric pressure over the entire range of composition for liquid-liquid binary mixtures of n-alkanes with l-alkanols and 2-alkanols. From the measured data of density (ρ), viscosity (η) and ultrasonic velocity (u); derived thermodynamic functions such as excess molar volumes (V_m^E), deviations in viscosity (Δη), excess isentropic compressibility (K_E^s), excess intermolecular free length (L_E^f), excess specific acoustic impedance (Z_E^f), excess available volume (V_a^E), excess energy of activation of viscous flow (ΔG^E) and excess internal pressure (π_int^E) have been evaluated and their variation with temperature and concentration is discussed. All the excess derived thermodynamic properties of these parameters at 298.15K have been represented graphically for comparison purpose. Furthermore, the excess thermodynamic properties such as excess molar volume, deviation in viscosity and deviation isentropic compressibility have been fitted to Redlich-Kister [33] polynomial equation to obtain the binary coefficients and standard percentage deviation at all the temperatures.

For the of n-octane + hexan-1-ol/ hexan-2-ol V_m^E shows negative deviation for lower mole fraction (x_1<0.25) of hexan-1-ol/hexan-2-ol and become positive for remaining mole fraction of hexan-1-ol/ hexan-2-ol. The V_m^E curve for (n-octane + heptane-1-ol/ heptan-2-ol, +octan-1-ol/ octan-2-ol) are sigmoidal and tend to changes from negative to positive values at higher mole fraction of (x_1>0.50) for heptane-1-ol/ heptan-2-ol and (x_1>0.65) for octan-1-ol/
octan-2-ol. For (n-octane + decan-1-ol, +doedcan-1-ol) $V_m^E$ values show a negative variation for the entire range of mole fraction of decan-1-ol and doedcan-1-ol. Similar plots are obtained at other temperatures.

The excess molar volumes were found to be positive for (n-decane + hexane-1-ol/hexan-2-ol, +heptan-1-ol/heptan-2-ol and octan-1-ol/octan-2-ol) at all temperatures. The $V_m^E$ curve for the mixture of n-decane + decan-1-ol, they were sigmoidal and tend to change to positive values at higher mole fractions ($x_1 \geq 0.50$) of n-decane. For n-decane + dodecan-1-ol $V_m^E$ curve shows negative curve. The excess molar volume seems to be symmetric in (n-decane + hexane-1-ol/hexan-2-ol, +heptan-1-ol/heptan-2-ol and octan-1-ol/octan-2-ol) all these systems.

The excess molar volumes were found to be positive in (n-dodecane + hexan-1-ol/ hexan-2, +heptan-1-ol/ heptan-2-ol, +octan-1-ol/octan-2-ol and decan-1-ol) at all temperatures. The $V_m^E$ curve for the mixture of n-dodecane +dodecan-1-ol, they were sigmoidal and tend to change to positive values at higher mole fractions ($x_1 \geq 0.30$) of n-dodecane.

The excess molar volumes were found to be positive in this case n-tetradecane with alkan-1-ols and alkan-2-ols at all temperatures.

The $\Delta \eta$ values for all the mixtures are negative for all systems over the entire mole fraction range.

$\kappa_c^E$ and $L_f^E$ shows same trends as given by excess molar volume for all binary mixtures.

The $\eta \alpha^E$ values show a positive variation for all systems over entire range of mole fraction at all temperatures.

The $Z^E$ and $P_{int}^E$ values show a positive variation for all systems over entire range of mole fraction at all temperatures.

Several empirical and semi-empirical relations have been used to represent the dependence of viscosity on concentration of components in binary liquid mixtures and these are classified according to the number of adjustable parameters used to account for the deviation from some average. We will consider here some of the most commonly used semi-empirical models for analyzing viscosity of liquid mixtures based on one, two and three parameters. An attempt has been made to check the suitability of equations for experimental data fitted by taking into account the number of empirical adjustment coefficients. From experimental values of viscosity various interaction parameters have been evaluated along with their standard errors using semi-empirical equations such as Grunberg-Nissan, Hind, Choudhary-Katti and Tamura-Kurata.
which were single parameter equations; Heric-Bewer, McAllister three body model which were two parameter and McAllister four body model which was three parameter empirical equations. Heric and brewer accounted for molecular interactions by dividing the free energy of activation into two parts. One part accounts for the excess free energy of activation, while the other accounts for the ideal free energy of activation. Their discussion of the effect of molecular size on excess functions gives insight into solution non-ideality and molecular interactions.

Measured values of ultrasonic velocities were compared using different types of theories proposed by Nomoto, Van deal theory, free length theory and collision factor theory. These theories have been described and used to calculate the speed of sound in the present mixtures and compared with the experimental results.

The Jouyban-Agree model was introduced to correlate the physicochemical properties of the solution in mixed solvents including the dielectric constants, viscosity solvatochromic parameter, and density, speed of sound and more recently molar volumes. The model uses the physicochemical properties of the mono-solvents as input data and a number of curve-fitting parameters representing the effects of solvent-solvent interactions in the solution. It is basically derived for representing the solvent effects on the solubility of non-polar solutes in nearly ideal binary solvent mixtures at isothermal conditions. Experimentally measured fundamental thermodynamic properties such as density, viscosity and ultrasonic velocity were correlated using Jouyban-Agree model.

The excess molar volume data have been analyzed by using Flory and Prigogine-Flory-Patterson theories (PEP Theory) at $T = 298.15$ K. The theoretical values of the speed of sound, $u$ and isentropic compressibility $k_s$ for both the liquid components and the liquid mixtures have been estimated using the Van der Waals (VdW) potential energy model in the Prigogine–Flory–Patterson [47–49] (PFP) theory. The comparison between experimental and theoretically calculated values of speed of sound and isentropic compressibility for the studied binary mixtures at $T = 298.15$ K has been graphically represented. The values of $\Delta \ln \eta$ have also been analyzed using Bloomfield and Dewan model [50]. The experimental and calculated quantities are used to study the nature of mixing behavior between the mixtures.

Nomoto’s empirical equation and Schaffs CFT succeeds in accurately predicting the ultrasonic velocities of all the binary mixtures.

The PFP theory and van der Waals (vdW) potential energy model in the Prigogine–
Flory–Patterson (PFP) theory is quite successful in predicting the trend of the dependence of $V_m^E$, $u$ and $k_s$ on composition for the present binary systems.

Jouyban-Acree model and Bloomfield and Dewan shows that the good agreement between the estimated and experimental curves occurs for all binary systems studied.

The present work represents an overview of the systematic experimental and theoretical research work on the physicochemical properties of associated liquid mixtures. The characteristic feature of the present work was that it involves the study of thermodynamic properties of liquid-liquid mixtures involving strongly polar alkanols, weakly non-polar alkanes.

Dr. Mirgane S.R.
Principal Investigator