

A COMPREHENSIVE REVIEW OF THERMOPHYSICAL PROPERTIES AND MOLECULAR INTERACTIONS IN BINARY LIQUID MIXTURES

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ABSTRACT

Fluid mixtures of two components exhibit highly complex thermal and physical behaviors due to the interactions between different types of molecules. These behaviors vary with the chemical structures of the substances present in a mixture and other factors such as concentration and temperature. Understanding these nonideal behaviors is critical to many industrial processes involving two fluids, including chemical and pharmaceutical manufacturing and power and solvent production. This review provides a detailed overview of available information on the molecular and thermal properties of two-fluid mixtures. Topics discussed in detail include viscosity, speed of sound, refractive index, density, and excess thermal properties of these mixtures. Other topics include intermolecular forces such as dipole-dipole interactions, hydrogen bonding, steric effects, and London dispersion forces and their effects on fluid properties, as well as the influence of chemical structure, including functional groups and molecular size, on fluid properties. Several theoretical approaches used to describe these behaviors, including NRTL, UNIQUAC, Margules, Redlich-Kister, ERAS, and friction models, are described and evaluated for their predictive value. The review concludes that a combination of different thermal and physical properties provides the best information about intermolecular interactions and suggests that incorporating modern technologies such as artificial intelligence and molecular modeling techniques will help researchers develop powerful predictive tools to aid future research on fluid mixtures.

1. INTRODUCTION

Two-fluid systems are used widely in environmental science, medicine, and other industries. Their applications benefit from unique properties arising from interactions between the molecules in each fluid. Understanding molecular interactions in two-fluid systems is critical to other areas of study and application, including improving processes for separation, chemical production, and the development of other liquid products. Methods for measuring properties such as viscosity, density, refractive index, speed of sound, surface tension, heat capacity, and compressibility can help scientists learn more about the structure and other properties of two-fluid mixtures. Many factors cause departures of two-fluid mixtures from idealized models, including hydrogen bonding, steric effects, dipole-dipole attractions, London forces, and other structural variables that influence physical features of two-fluid mixes. . Temperature and relative concentrations of the components of a two-fluid mixture also affect microscopic and macroscopic properties. Systematic experimental measurement, including collection of data on excess and other functions, Can assist biologists in better understanding the macroscopic properties of two-fluid mixtures.

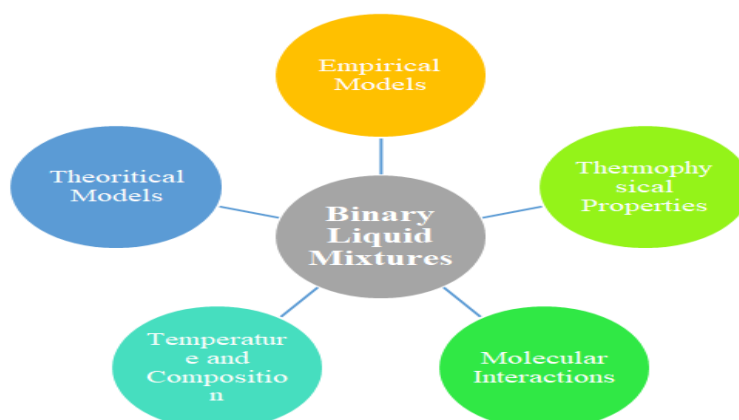


Figure 1: Understanding Binary Liquid Mixtures

This comprehensive review summarizes relevant research literature on the physical properties and intermolecular interactions of mixed-liquid systems. Key topics of discussion include the relationship of microscopic chemical interactions to macroscopic properties of mixed liquids. Other topics discussed are the influences of temperature and chemical structure on the properties of mixed liquids and reviews of theoretical and mathematical models for mixed liquids. Conclusions and future research directions include identification of knowledge gaps and new techniques to improve understanding and predictive capabilities for the physical properties and interactions of mixed liquids.

1.1 Molecular Interactions in Binary Liquid Mixtures

The thermal and physical properties of two-liquid mixtures mainly depend on the intermolecular forces between the constituents. Intermolecular interactions in a mixture of two liquids often differ from the interactions in each pure liquid. Important intermolecular forces in liquid mixtures include van der Waals forces, dipole interactions, specific donor-acceptor interactions, and especially hydrogen bonding. Hydrogen bonding is a strong interaction in liquid mixtures containing polar compounds such as water, amines, and alcohols. When unlike molecules attract each other strongly, the mixture packs more tightly than an ideal solution would. When the attraction between unlike molecules is weak or unfavorable, the mixture ends up less tightly packed than ideal behavior predicts. Intermolecular interactions in liquid mixtures can be grouped according to their type and strength. Table 1 lists the main intermolecular forces and describes how each affects the properties of liquid mixtures.

Table 1: Major Molecular Interactions in Binary Liquid Mixtures

S. No.	Type of Interaction	Nature of Interaction	Commonly Involved Components	Influence on Thermophysical Behaviour
1	Hydrogen bonding	Strong directional attraction	Alcohols, amines, water, acids	Can increase association and produce significant deviations from ideality
2	Dipole–dipole interaction	Attraction between polar molecules	Polar solvents, amines, esters	Influences density, viscosity and excess properties
3	van der Waals interaction	Weak intermolecular attraction	Non-polar and polar molecules	Affects molecular packing and cohesive behaviour
4	Dispersion forces	Instantaneous dipole-induced attraction	Hydrocarbons and organic liquids	Influences mixing and structural arrangement
5	Donor–acceptor interaction	Specific molecular association	Amines, alcohols, esters, ketones	Can strongly modify excess thermodynamic properties
6	Solute–solvent interaction	Interaction between unlike molecules	Components of binary mixtures	Determines non-ideal mixing behaviour
7	Steric interaction	Spatial/size-related effect	Branched alcohols, amines, organic molecules	Affects molecular packing and free volume
8	Like-molecule interaction	Interaction between identical molecules	Pure components within mixture	Determines the reference behaviour for assessing deviations
9	Unlike-molecule interaction	Interaction between different molecules	Binary liquid components	Governs association, expansion/contraction and excess properties

The extent of structural organization and association in a mixture of liquids depends mainly on the physical and chemical nature of the components, such as molecular size and shape, polarity, and presence of particular functional groups or other steric hindrance to association. Physical properties of mixtures, such as density, viscosity, ultrasonic velocity, and changes in molar volume, offer qualitative information about the intermolecular associations of the components of the mixture. Understanding these associations is critical both to interpreting experimental results and to building predictive models of the thermodynamic properties of mixtures of two or more liquids.

1.2 Theoretical Models and Correlation Approaches

Mathematical relationships and correlations can be used to explain and predict experimental results for the thermophysical properties of binary liquid mixtures. Correlations between property deviations help quantify the nonideal behavior of a solution. The Redlich-Kister equation is a commonly used correlation for modeling excess properties of binary liquid mixtures as a function of composition. Other common models used to describe liquid-phase nonidealities and predict activity coefficients include UNIQUAC, NRTL, Wilson, and Margules models.

Both empirical and free-volume models can be used to model other transport properties, such as viscosity, based on fluid friction effects. Parameters in empirical models of binary liquid mixtures can be determined from experimental data and used to infer details of intermolecular interactions in the mixture. The reliability of a model can be evaluated by comparing its predictions with experimental data. Other applications of these models and correlations include studies of microscopic properties of binary liquid mixtures.

1.3 Fundamentals of Binary Liquid Mixtures

A binary fluid mixture consists of two different chemical liquids, called the main liquid and secondary liquid, mixed in various proportions. The properties and thermodynamic behavior of the mixture are influenced by the properties of each pure liquid and the interactions between the molecules of the two liquids in the mixture. Ideal binary fluid mixtures have similar interactions between molecules of different types as between molecules of the same type in their pure states, resulting in other ideal physical properties. Physical properties of binary fluid mixtures, including density, viscosity, ultrasonic velocity, heat capacity, and surface tension, can be measured and studied.

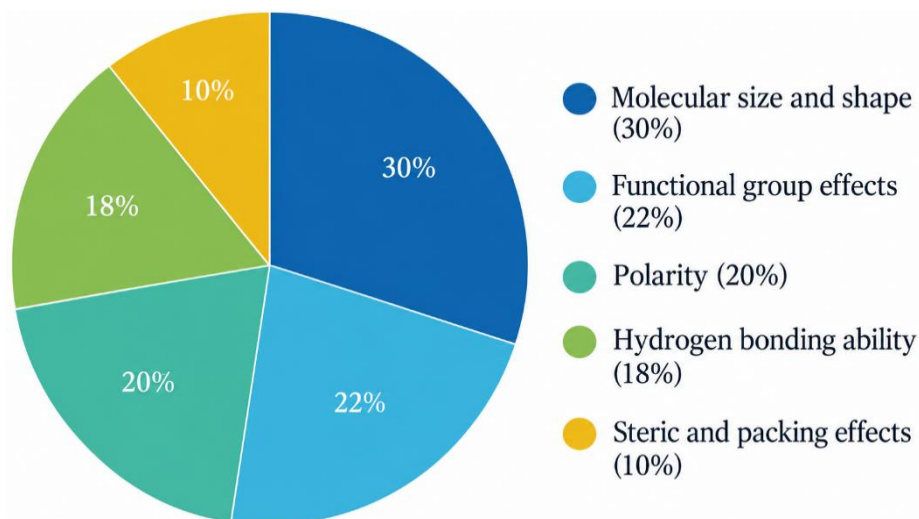


Figure 2: Factors Influencing Binary Liquid Mixture Behavior

Thermodynamic excess properties are valuable for judging how real fluids depart from ideal ones and for gaining insight into the structure and interactions of their molecules. Detailed investigation of binary mixtures across different compositions and temperatures can reveal how bulk properties relate to molecular structure. These relationships are essential for improving industrial operations such as chemical manufacturing and separation, and they also support the development of new solvent applications and alternative energy technologies.

1.4 Effect of Temperature and Composition

The basic properties of two-fluid mixtures are determined mainly by two factors: the composition of the mixtures and the temperature of the system. Increasing the temperature of a two-fluid mixture increases the kinetic energy of the molecules and reduces intermolecular attractive forces and other structural features of the fluid. These effects lead to reductions in density and viscosity and changes in other physical properties and sound wave propagation rates in the fluid. Differences in the composition of two-fluid mixtures affect the relative strengths of attractive forces between like and unlike molecules in the fluids. Variations in other molecular characteristics and properties, including particle arrangement and spacing and hydrogen bonding, due to changes in the composition of two-fluid mixtures result in positive or negative departures from ideal behavior. Studies of the physical properties of two-fluid mixtures over a range of temperatures and compositions help scientists understand the behavior of these fluids and confirm or refute existing theories. This information can be used by engineers for other purposes, such as predicting how two-fluid solvents will behave in industrial applications and designing or selecting binary solvent systems for specific industrial uses.

2. LITERATURE REVIEW

Chiu et al. (1999) studied the specific heats of various alkanolamines using differential scanning calorimetry, a very accurate technique. The results of their experimental study, which were highly reliable, demonstrated that certain structural and other characteristics of alkanolamines affect their specific heats. The information presented in their study helped other researchers understand the thermodynamic properties of alkanolamines and is useful to chemical engineers designing industrial processes or products involving alkanolamines. [1]

Majstorovic et al. (2020) investigated the thermophysical properties of binary mixtures of ethyl acetate with either 1-propanol or 1-butanol. The study set out to clarify how chemical composition relates to measurable properties of

the mixtures, and to supply data that can help predict how strongly the components interact. Its main conclusions were that mixture properties depend strongly on the carbon chain length of the alcohol, and that the departures from ideal thermodynamic behavior offer clues about the structure of these and comparable mixtures. [2]

Pandey et al. (2020) examined the optical properties, refractive index in particular, along with other physical properties, of binary mixtures of 2-diethylethanolamine with 1-butanol and 1-propanol. By measuring how these optical properties change across concentrations, the authors were able to draw useful conclusions about how macroscopic optical behavior reflects microscopic structure. Their results showed that optical methods are a helpful nondestructive way to follow changes in intermolecular interactions and other features of amine-alcohol mixtures. [3]

Dubey and Kumar (2012) measured the physical and thermal properties of binary alcohol-amine mixtures under a range of thermal conditions. Their work clarified how temperature and composition together influence the physical behavior of these mixtures. The authors tied the observed property changes to changes in molecular-level interactions, and they stressed the importance of physical property data for characterizing the thermodynamic behavior of nonideal amine-alcohol systems. [4]

Li et al. (2013) reviewed progress in carbon capture and storage and in other uses of carbon dioxide, paying particular attention to emerging technologies for cutting global greenhouse gas emissions. The role and properties of amine absorbents are among the main topics covered. The review also gives background on the uses of amines, including two-phase systems, which can help engineers and other readers understand the thermodynamic properties of amines that matter for carbon dioxide sequestration and related applications. [5]

Omrani et al. (2010) measured the density and related volumetric properties of binary mixtures of 1,4-dioxane with several amino alcohols and other alcohols at different temperatures. Their experimental results confirmed that temperature, molecular structure and the mole fraction of each component all play a significant part in determining the volumetric behavior of such mixtures. Measuring whether the mixtures contract or expand on mixing also gave useful information about the underlying intermolecular interactions. [6]

Omar and Sadeghi (2021) explored the thermal and physical properties, and the potential applications, of newly developed deep eutectic solvents based on nonanol. Their experiments showed that bulk properties such as viscosity and density are key factors in deciding how these solvents can be used in chemical extraction and analysis. They also found that the molecular-level properties of the components, and the interactions between them, influence both the bulk behavior of the resulting solvents and how they can be applied. [7]

Almasi (2015) measured the viscosity and density of binary solutions of ethyl formate with 2-alkanols. Free volume theory and fluid flow models were applied together to help explain how these solutions behave. The measured variations in viscosity and density allowed conclusions to be drawn about free volume and other molecular-level features and interactions in the solutions. Combined with mathematical modeling, the results help build a clearer picture of the intermolecular interactions in these binary mixtures. [8]

Bhagat and Maken (2021) studied optical and volume properties of binary mixtures of 2-amino-2-methylpropan-1-ol and several lower alkanols at various temperatures. Studies have shown that the temperature and composition of a binary mixture of 2-amino-2-methylpropan-1-ol and a lower alkanol strongly affect the mixture's properties. Bhagat and Maken (2021) observed changes in other properties, such as light refraction and volume, of the mixtures and used these observations to draw conclusions about the structure and aggregation of molecules in the mixtures. Findings from their study provide useful correlations between macroscopic properties and other phenomena that can be measured and molecular interactions. [9]

Dubey and Rani (2021) performed many different thermodynamic, acoustic, and spectroscopic experiments on binary amine and alcohol mixtures. Combining the results from these different types of experiments allowed the authors to collect multiple types of data about the binary mixtures that provided greater insight into the behavior of molecules and intermolecular forces in the liquid mixtures. Acoustic and spectroscopic data together confirmed that structural changes occur in the liquids as they are mixed. Overall, research like that of Dubey and Rani shows that combining data from different physical and chemical experimental techniques can provide researchers with a more thorough understanding of complex liquid behavior than is possible using just one technique. [10]

Kumar et al. (2013) investigated the behavior of mixtures of alkoxypropanols and branched alkanols at various temperatures. Experimental results showed that the thermodynamic behavior of these binary mixtures depends strongly on temperature and molecular structure. Detailed experimental studies of binary mixture behavior revealed important thermodynamic deviations from ideal behavior. Insights gained about molecular interactions in these dissimilar mixtures advanced scientific knowledge of alkanol mixtures. [11]

Kumari and Maken (2021) studied the thermophysical and ultrasonic properties and density changes in binary mixtures of di-n-butylamine with isobutanol and n-butanol. The study was done to explore applications for carbon dioxide capture. A multidisciplinary study such as this one can help make connections between the macroscopic physical properties and microscopic chemical properties of a system. FTIR spectroscopy results for these mixtures were consistent with macroscopic ultrasonic and density measurement results and helped to determine chemical interactions in the mixtures. Overall, this type of in-depth thermophysical characterization is important in the development and testing of new solvent materials for carbon dioxide sequestration. [12]

Gahlyan et al. (2020) studied solid-liquid phase equilibria and other physical properties, including bulk density and viscosity, of mixtures of fatty acid methyl and ethyl esters. Combining experimental data with mathematical models, the authors demonstrated the importance of comprehensive thermophysical data and models for studying the properties and behavior of more complex fluid mixtures. Key findings of the study also include important information about the effects of temperature and chemical composition on the transport and phase behavior of these industrially important fluid mixtures. [13]

Dragoescu et al. (2021) investigated the thermophysical properties of binary mixtures of water with several alkanediols. Their experiments confirmed that the observable properties of these aqueous mixtures depend strongly on temperature, concentration and the molecular structure of the alkanediol. The data shed light on how water and alkanediols behave, including hydrogen bonding and molecular self-association. The results are also useful to researchers and engineers who build and test predictive models for other binary mixtures. [14]

Kikugawa et al. (2019) proposed a new machine learning method, based on clustering, for classifying and characterizing fluids that differ in physical and chemical properties. Their experiments showed that such techniques can pick out complex relationships among several fluid properties at once. One advantage of the approach is that it may be able to take the place of some conventional analytical methods for classifying and characterizing fluids. [15]

Estrada-Baltazar et al. (2015) measured the viscosity and density of binary mixtures of n-decane with alcohols, namely 1-pentanol, 1-hexanol and 1-heptanol, over a range of temperatures. Their results confirmed that both temperature and the carbon chain length of the alcohol strongly influence the flow behavior of alcohol-hydrocarbon mixtures. The changes seen in bulk properties helped clarify the molecular-level interactions and structural features of these mixtures. The findings improve understanding of the thermodynamics of such systems and provide equations that can help predict the behavior of related ones. [16]

Nayeem et al. (2016) studied molecular interactions in binary mixtures of benzyl benzoate and ethyl acetate at several temperatures, using ultrasonic velocity and density measurements. By combining the two datasets, they could draw conclusions about how the components interact. Their results indicate that analyzing ultrasonic velocity and density together is an effective way to examine deviations from ideal behavior and other molecular-scale effects in mixtures of this kind. [17]

Aminabhavi and Raikar (1993) studied thermodynamic properties of binary fluid mixtures consisting of bromoform and other fatty alcohols. In addition to other thermodynamic information, results from this study provide molecular-level information on interactions between halogenated and aliphatic-alcohol compounds. Analysis of the different thermodynamic behaviors of these two types of binary mixtures allowed Aminabhavi and Raikar to draw conclusions about the relationship of molecular and site-specific interactions to bulk properties of fluid mixtures. This study and others like it have helped increase understanding of the thermodynamic properties of nonideal binary mixtures of complex compounds. [18]

Chung, Roh, and Lee (2018) examined carbon dioxide capture technologies for industrial use, comparing newer amine-solvent processes with membrane-based alternatives. The study concentrated on the iron and steel industries and also considered the plant design and operating conditions needed to apply these technologies on an industrial scale. Although the work is aimed mainly at industrial practice, it provides useful background. It can support basic laboratory research on thermodynamic properties, which in turn helps in developing and improving amine solvents for large-scale carbon dioxide capture. [19]

Dubey, Saur, and Kaur (2017) investigated the thermodynamic behavior of binary mixtures of di-n-butylamine with other alkanols between 293.15 and 313.15 K. Their data confirmed that molecular association occurs in these mixtures and that their bulk properties vary with temperature. The results contribute to a better understanding of the intermolecular interactions and thermodynamic properties of amine-alcohol mixtures. [20]

Jain et al. (2009) studied the liquid viscosities and excess molar volumes of binary mixtures of methanol with n-butylamine and di-n-butylamine at multiple temperatures. Techniques used by Jain et al. included the ERAS model to study the changes in molecular interactions and structure in these mixtures when they are combined. The authors used experimental data to identify specific interactions and structural changes in these mixtures, including hydrogen bonding and packing effects. The overall approach was very successful in measuring departures from ideal behavior in liquid mixtures of amines and alcohols and learning about their properties. [21]

Chowdhury and Saleh (2014) reported measurements of thermodynamic and transport properties, including deviations from ideal behavior for dynamic viscosity, for two-component systems of tert-butanol and several types of amines: n-butylamine, di-n-butylamine, and tri-n-butylamine. Comparison of the transport and thermodynamic properties of the different amine systems allowed the authors to show conclusively that factors such as amine substitution level and overall molecular structure significantly affect the transport and other properties of the two-component systems. Calculated viscosity deviations provided information that helped the authors understand intramolecular bonding and other structural interactions between the two types of molecules in the system shortly after mixing. Overall, the study demonstrated that measurements of viscosity deviations are a useful and reliable tool for investigating intramolecular interactions and other nonideal thermodynamic properties of systems containing amines and alcohols. [22]

Shakila et al. (2018) examined how temperature influences the thermal properties of binary mixtures of ethyl

acrylate with alkyl amines. Using experiments together with modeling, they showed that temperature affects several important properties of these mixtures, including the intermolecular interactions. The results and methods can help researchers understand and predict the behavior of mixtures containing alkyl amines and other components. [23]

Kumari and Maken (2021) explored the intermolecular interactions in binary mixtures of di-isopropylamine with three isomers of butanol, using volumetric and acoustic properties. By relating laboratory measurements of these properties to the molecular structure of the components, the researchers could draw conclusions about how the molecules interact. They found that molecular structure has a marked effect on both the thermodynamic and acoustic properties of these mixtures. The differences between the butanol isomers, for instance, produced clearly different volumetric and acoustic behavior, which shows that small local structural variations can strongly influence the thermodynamic behavior of a binary liquid mixture. [24]

Dubey and Kumar (2017) studied the spatial and volume properties and viscosity and other excess molar properties of binary solutions of diisopropylamine with 1-alkanols of chain length 6-10. Based on experimental data, they concluded that the thermodynamic properties of binary solutions of diisopropylamine and 1-alkanols depend systematically on temperature and the carbon chain length of the 1-alkanol. The researchers found other microscopic and macroscopic properties of binary solutions of diisopropylamine and 1-alkanols that depend on temperature and carbon chain length, such as intermolecular interactions and differences in spatial arrangement. Overall, their findings suggest that studying multiple macroscopic thermophysical properties of a substance can help scientists better understand interactions and spatial rearrangements of molecules in binary solvent systems. [25]

Zaitseva et al. (2011) used calorimetry to measure the enthalpy of cooperative hydrogen bonding in complexes formed between aliphatic alcohols and tertiary amines. Their calorimetric experiments gave direct thermodynamic evidence that cooperative hydrogen bonding occurs in these systems, and they quantified how much it contributes to the enthalpy of complex formation. The findings are important for understanding how aliphatic alcohol-tertiary amine solvent systems behave, since cooperative hydrogen bonding is one of the main factors shaping the thermodynamic and other properties of such nonideal mixtures. [26]

Wang et al. (2013) studied the bulk macroscopic properties, including volume, of mixtures of dimethyl sulfoxide with various amines at several temperatures. Detailed measurements of how the properties of these mixtures varied with temperature and other factors, such as composition and intermolecular interactions, allowed the researchers to better understand the changes in structure that take place when these mixtures are formed. Key findings from this study include increased understanding of the behavior of strongly polar, strongly interacting solvent mixtures and a set of data that can help other researchers interpret excess volume data and improve models for predicting the properties of mixtures. [27]

Table 2: Summary of Reviewed Literature on Thermophysical Properties and Molecular Interactions

S. No.	Author(s)	Year	Binary System / Material Studied	Properties / Approach	Major Focus / Contribution
1	Chiu, Liu & Li	1999	Alkanolamines	Heat capacity; DSC	Provided heat-capacity data and examined the thermal behaviour of alkanolamines.
2	Majstorovic et al.	2020	Ethyl acetate + 1-propanol/1-butanol	Thermophysical properties	Investigated the influence of composition and alcohol chain length on binary-mixture behaviour.
3	Pandey et al.	2020	2-Diethylethanolamine + 1-propanol/1-butanol	Refractive index and related properties	Related optical properties to composition and molecular interactions in amine-alcohol mixtures.
4	Dubey & Kumar	2012	Amine + alcohol systems	Thermophysical properties at different temperatures	Examined temperature and composition effects and their relationship with molecular association.
5	Li et al.	2013	CO ₂ capture systems	Review of CO ₂ capture, storage and utilization	Provided application-oriented background on CO ₂ capture and amine-based absorption technologies.
6	Omrani, Rostami & Mokhtary	2010	1,4-Dioxane + alcohol/amino-alcohol systems	Density and volumetric properties	Investigated temperature-dependent volumetric behaviour and molecular interactions.
7	Omar &	2021	Nonanol-based deep	Thermophysical	Examined thermophysical

	Sadeghi		eutectic solvents	properties; extraction applications	behaviour and demonstrated potential applications in liquid–liquid extraction.
8	Almasi	2015	Ethyl formate + 2-alkanols	Density and viscosity; friction/free-volume theories	Used theoretical models to interpret transport properties and molecular interactions.
9	Bhagat & Maken	2021	2-Amino-2-methylpropan-1-ol + C1–C3 alkanols	Volumetric and optical properties	Studied effects of temperature and composition on molecular association and structural changes.
10	Dubey & Rani	2021	Amine + alcohol systems	Thermodynamic, acoustic and spectroscopic properties	Combined experimental techniques to investigate molecular association and intermolecular interactions.
11	Kumar et al.	2013	Alkoxypropanols + branched alkanols	Mixing properties at different temperatures	Analysed temperature, molecular structure and deviations from ideal solution behaviour.
12	Kumari & Maken	2021	Di-n-butylamine + isomeric butanols	Volumetric, acoustic, transport and FTIR	Correlated macroscopic properties with molecular interactions for potential CO ₂ absorption.
13	Gahlyan, Maken & Park	2020	Fatty-acid methyl/ethyl esters	Solid–liquid equilibria, density, viscosity and modelling	Developed experimental data and modelling approaches for phase and transport properties.
14	Dragoescu, Sirbu & Almasy	2021	Aqueous alkanediols	Thermophysical properties	Examined effects of temperature, composition and molecular structure in water–alkanediol systems.
15	Kikugawa et al.	2019	Liquid substances	Multidimensional thermophysical data; machine learning	Applied clustering and machine learning to identify patterns in thermophysical-property datasets.
16	Estrada-Baltazar et al.	2015	n-Decane + 1-pentanol/1-hexanol/1-heptanol	Density and viscosity	Studied temperature and alcohol-chain-length effects on transport properties.
17	Nayeem et al.	2016	Benzyl benzoate + ethyl acetate	Ultrasonic velocity and density	Investigated molecular interactions through acoustic and volumetric measurements.
18	Aminabhavi & Raikar	1993	Bromoform + aliphatic alcohols	Mixing properties	Provided fundamental information on non-ideal mixing and specific molecular interactions.
19	Chung, Roh & Lee	2018	Industrial CO ₂ capture systems	Amine scrubbing and membrane separation	Evaluated CO ₂ -capture plant design and industrial application of amine-based technologies.
20	Dubey, Saur & Kaur	2017	Di-n-butylamine + alkanols	Mixing properties at 293.15–313.15 K	Investigated temperature-dependent mixing behaviour and molecular association.
21	Jain et al.	2009	Methanol + n-butylamine/di-n-butylamine	Viscosity and excess molar volume; ERAS model	Used excess properties and ERAS modelling to interpret molecular interactions and non-ideality.
22	Chowdhury & Saleh	2014	tert-Butanol + n-/di-/tri-n-butylamine	Viscosity and viscosity deviation	Examined effects of amine structure on transport behaviour and intermolecular interactions.
23	Shakila et al.	2018	Ethyl acrylate + alkyl amines	Thermophysical properties; experimental/theoretical analysis	Investigated temperature effects and developed theoretical interpretation of mixture behaviour.
24	Kumari & Maken	2021	Di-isopropylamine + isomeric butanols	Volumetric and acoustic properties; topological analysis	Related molecular topology and structural differences to intermolecular interactions.
25	Dubey & Kumar	2017	Diisopropylamine + C6–C10 1-alkanols	Volumetric, viscometric and molar properties	Investigated alcohol-chain-length and temperature effects on

					molecular association and transport behaviour.
26	Zaitseva et al.	2011	Tertiary amines + aliphatic alcohols	Calorimetry; hydrogen-bond enthalpy	Quantified cooperative hydrogen bonding and its energetic contribution to molecular interactions.
27	Wang et al.	2013	Dimethyl sulfoxide + amines	Volumetric properties at 293.15–363.15 K	Examined temperature, composition and molecular interactions through volumetric behaviour.

2.1 Research Gap

Although many experimental studies on the thermophysical properties of binary liquid mixtures have been conducted, there are many shortcomings in our understanding of the relationship between thermophysical properties and intermolecular forces. Most previous experimental studies have focused on a single thermophysical property of binary mixtures, including density, viscosity, speed of sound, refractive index, and excess molar volume. Lack of integrated studies of these properties has limited development of thermodynamic models for binary liquid mixtures.[28] While many experimental studies have reported nonideal behavior in various liquids, proposed molecular explanations for this behavior, such as hydrogen bonding, dipole-dipole forces, steric and packing effects, and London dispersion forces, have been inconsistent. Integrated studies comparing the effects of molecular structural features, including carbon chain length and branching and the presence and location of functional groups, on thermophysical properties over ranges of temperature and concentration are limited. Equations of state and other models for binary liquid mixtures are often accepted based on statistical, rather than physical, grounds. Few studies have used machine learning techniques in conjunction with traditional thermodynamic approaches. Future research to improve predictive thermodynamic models and knowledge of nonideal binary liquid mixtures should include the development of integrated models that incorporate diverse empirical and theoretical information.

3. PROBLEM STATEMENT

The physical and chemical properties of binary liquid mixtures are of interest to industry and have applications in areas including pharmaceutical and fine chemical production, separation and purification operations, and alternative energy and other green technologies. In these applications and others, important physical properties to measure include density, viscosity, speed of sound, refractive index, isentropic compressibility, and excess molar volume and viscosity.[29] Challenges to measuring and modeling the properties of binary liquid mixtures include the variety of interactions between different molecules in the mixture that can lead to significant thermodynamic nonidealities, such as hydrogen bonding and other dipole interactions, London dispersion forces, molecular complexation, steric effects, and differences in molar volume between the components.

One challenge in current thermophysical research is that available experimental data for many systems at limited temperatures and mole fractions do not allow for direct comparisons with data from other systems. Molecular understanding of observed trends in excess thermodynamic and transport properties, both positive and negative deviations from ideal behavior, is incomplete. Correlations of thermodynamic properties with experimental data can be statistically reliable but may provide little information about the interactions occurring in the systems tested. Transport properties are highly dependent on molecular characteristics and temperature. [30] Improved understanding of the molecular basis for fluid properties will likely result from literature reviews that combine information on thermophysical properties with other macroscopic and molecular information.

4. RESEARCH METHODOLOGY

To meet the goals of this comprehensive literature review, a systematic, thorough methodology was used to analyze published information on the thermodynamic and molecular properties of binary liquid mixtures. The purpose of this review was to combine and summarize information about binary liquid mixtures in the published literature to provide a more complete body of knowledge about the properties of these mixtures. The steps of the review process, which are designed to provide an objective, reproducible analytical approach, include targeted searches for published information on binary liquid mixtures and other related topics, as well as analysis and synthesis of the published information on binary liquid mixtures.

During the literature search, peer-reviewed journal articles on two-component fluids and related dynamic thermophysical properties were identified in databases. Both older and newer publications were identified for review. Literature search efforts were guided by a focus on studies with results for physical characteristics of two-component fluids, such as total system density, viscosity, ultrasonic velocity, refractive index, isentropic compressibility, excess molar volume, and viscosity differences. Other literature search priorities included identifying articles with detailed information on molecular interactions and other factors affecting two-component

systems, including hydrogen bonding, steric effects, and other thermodynamic changes related to temperature and molar ratios of components in the system.

After a rigorous selection process, the studies included in this review were categorized and grouped based on many features, including the types of binary systems studied, thermodynamic properties studied, temperatures used in the studies, concentration ranges studied, molecular structure effects, and modeling approaches used. This review comparison of favorable and unfavorable thermodynamic deviations from ideal solution behavior in binary systems provides insights into general trends in binary system behavior due to interactions between components. The review also discusses the usefulness and limitations of several thermodynamic modeling approaches, including polynomial models such as the Redlich-Kister model and local composition and related models such as the Margules, Wilson, NRTL, and UNIQUAC models and the ERAS, free-volume, and friction models.

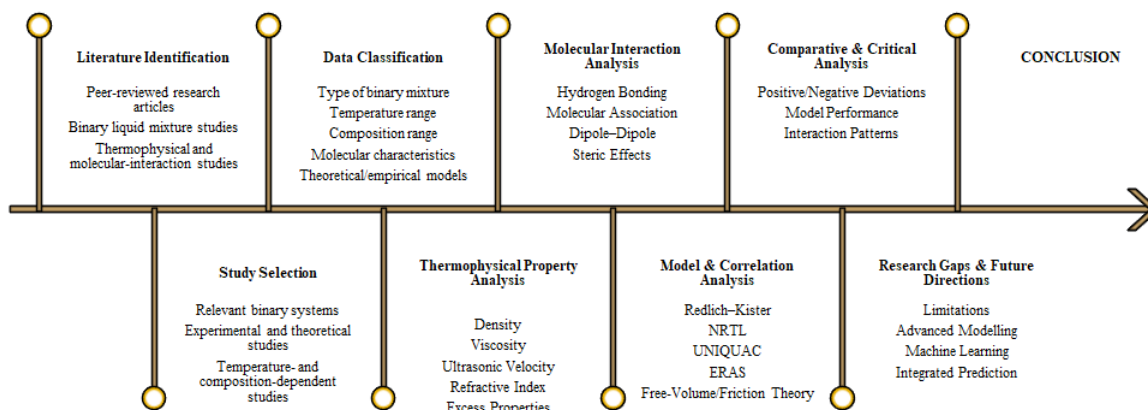


Figure 3: Research Methodology

In the final analysis stage, data and other findings from multiple studies were evaluated and compared to draw firm conclusions about relationships among bulk observations and molecular effects in binary liquid mixtures. A major advantage of the final analysis process is that it considers limitations of prior studies of binary liquid mixtures. Other benefits include the ability to assess knowledge gaps in the existing body of thermodynamic knowledge and to develop new research ideas to advance understanding of binary liquid mixtures.

5. SIGNIFICANCE OR RESEARCH

A detailed knowledge of the thermodynamic and molecular properties of binary mixtures is important for understanding the behavior of more complex multicomponent mixtures. The most valuable information about these properties includes experimental data on density, viscosity, speed of sound, refractive index, and isentropic compressibility and derived excess molar volume and viscosity data for binary mixtures. These and other properties of binary mixtures provide information about molecular interactions and structures that help explain departures from Raoult's law and other ideal behaviors in multicomponent systems. Advantages of studying binary mixtures include their relevance to applications and the insight they offer about molecular interactions. Excess thermodynamic properties of positive or negative magnitude convey information about attractive and repulsive interactions among molecules in a mixture as well as steric and hydrogen bonding effects and phase transitions. These insights can be applied by scientists and chemical engineers to develop improved solvent mixtures for industrial-scale applications. Comparative studies of current mathematical theories and models can help evaluate their ability to describe experimental findings and other properties of binary mixtures. Strategies for enhancing the predictive capabilities of thermodynamic models of binary mixtures at various temperatures and compositions include integration of conventional equations of state with data analysis techniques based on machine learning. This review provides an overview of current thermodynamic knowledge of binary mixtures and areas for future research in experimental and computational thermodynamics. Knowledge of binary mixture thermodynamics is important for applications in chemical manufacturing, pharmaceuticals, separations, energy storage, and solvent design.

6. SCOPE OF RESEARCH

This review provides a comprehensive overview of the existing literature on thermophysical properties and molecular interactions in binary liquid mixtures. Both experimental and theoretical studies of various binary mixtures at different temperatures and concentrations are summarized. Thermophysical properties discussed in this review include density, dynamic viscosity, speed of sound, refractive index, and isentropic compressibility; excess and related properties include excess molar volume and deviations in dynamic viscosity. Key topics of the review include the effects of temperature and concentration and molecular properties such as size, shape, polarity, and

functional group position on thermophysical properties. Molecular interactions discussed include hydrogen bonding, dipole-dipole interactions, London dispersion forces, van der Waals forces, and molecular crowding; both positive and negative deviations from Raoult's law are discussed. Correlations between molecular and macroscopic properties are explored.

The review discusses the pros and cons of existing mathematical methods for estimating or predicting thermophysical properties. Methods reviewed include empirical thermodynamic models, such as Redlich-Kister and Margules, and other models based on thermodynamic theory, including Wilson, NRTL, and UNIQUAC. The review also provides some specific applications of other thermodynamic and physical models, including ERAS and modified free-volume and friction models. Key points of the review include gaps in thermophysical property data. Potential strategies include combining empirical thermodynamic models with computational and data-based machine learning approaches. Relevant disciplines include thermodynamics and physical chemistry, chemical engineering, and molecular modeling and prediction of thermophysical properties.

7. FUTURE SCOPE

Additional experimental studies of binary liquid systems at different temperatures and with different formulations would help scientists better understand and model the properties of these systems. Other research topics of interest include studies of greener alternative formulations, such as biofluids, ionic liquids, and deep eutectic and green solvent mixtures. Scientists should study multiple properties of these and other systems, in addition to individual properties, such as mass and volume, viscosity, speed of sound, refractive index, heat capacity, and excess properties, to learn more about the behavior of binary liquid systems. Information about hydrogen bonding and other interactions and associations in binary liquid systems can be obtained through a combination of bulk measurements and spectroscopic techniques, such as FTIR and NMR spectroscopy. Modeling techniques for binary liquid systems are expected to advance through the development of hybrid approaches that combine conventional thermodynamic modeling techniques with molecular simulations and machine learning approaches. Ways to promote advances in modeling techniques include the creation of reference data sets and other tools to help scientists evaluate and report errors and other information needed to reproduce their findings. Uses of these advances could include improved selection and design of solvents and other applications in the industrial and pharmaceutical sectors that use green chemical engineering approaches.

8. CONCLUSION

This review shows that macroscopic properties of liquids, including density, viscosity, speed of sound, refractive index, isentropic compressibility, and associated excess properties, can provide useful information about the behavior of binary mixtures. Deviations from ideal-solution behavior in binary mixtures result from several intermolecular forces, such as hydrogen bonding and dipole-dipole and London dispersion interactions, as well as steric effects. Temperature and composition affect the macroscopic and structural properties of binary mixtures. The magnitudes and signs of excess and related properties for binary mixtures can help evaluate and compare intermolecular forces and structural differences in these mixtures.

Traditional mathematical and thermodynamic methods are commonly used to model and interpret nonideal liquid properties. Examples of traditional methods include the Redlich-Kister and other empirical methods and detailed local composition and structural methods, such as Margules, Wilson, NRTL, UNIQUAC, ERAS, free-volume, and friction models. Literature shortcomings suggest opportunities for integrated experimental, computational, thermodynamic, and machine learning studies to improve connections between macroscopic and molecular understandings of liquids. Benefits of these opportunities include improvements in the development of liquid solvents and other products and processes by industry and others.

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