CHAPTER-II

Theoretical Aspects

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II.1  INTRODUCTION

The theoretical formalism to derive some of the physical, thermodynamic and acoustic parameters from the experimentally determined values of viscosity, density and ultrasonic velocity in liquid mixtures has been described in this chapter. The theoretical formalism is developed first by considering a pure liquid to derive the various parameters like isentropic compressibility, acoustic impedance intermolecular freellength, available volume, molar volume, molar sound velocity, molar compressibility, etc. Then the case of an ideal binary liquid mixture is considered and finally the effect of the interaction in non-ideal mixtures are related to the variation of these parameters with the concentration of their constituents in the liquid mixture.

II. 2  ACCURACY OF THE ULTRASONIC VELOCITY

An estimate of the maximum uncertainty in the velocity values can be made as follows: The accuracy of the wavelength depends on the distance over which the standing waves can be established and also on the accuracy of the measurement of the distance. The wavelengths were correct to ±0.05%. The error (1 part in 10^5) in the frequency measurements is negligible. Thus, using typical value of 0.21 mm for \(\lambda/2\) and 1300 m/s for velocity, the percentage of error in the velocity can be calculated as

\[
C = \Delta f
\]

\[
dc = \left( \frac{d\lambda}{\lambda} + \frac{df}{f} \right) C
\]

\[
= \left( \frac{0.0005}{0.21} + \frac{1}{10^5} \right) 1300
\]

\[
= 3 m/s \approx 0.2\%
\]
II.3 INTERMOLECULAR FORCE OF ATTRACTION

The intermolecular force of attraction between the nearby molecular is often expressed as a function of the intermolecular distance. To interpret the resultant effect in a liquid, the contribution to the interaction force is first visualised for one pair of molecules and the treatment is then extended to the generalised case of many pair of molecules. In binary and ternary liquid mixtures, the contribution to intermolecular interaction is generally of four types. These are

(i) Dipole-Dipole interaction:
This is due to the electrostatic forces existing between the molecules with permanent dipoles. For a pair of polar molecules, with permanent dipole movements $\mu$ and separated by a distance $r$, the potential energy of attraction between them varies directly as the square of $\mu$ and inversely as the sixth power of $r$.

(ii) The induction - interaction:
The dipole of a molecule polarizes the electrons of a neighbouring molecule such that the electrons of the second molecule are aligned, in a way so as to introduce a net attractive interaction with the dipole of the first. The potential energy, in this case, is a function of dipole moment as well as the polarisability.

(iii) London-dispersion force
The existence of this effect arises from consideration of the detailed motion of the electrons in the neighbouring molecules which result in an attraction between all the molecules. The potential energy is a function of polarisability and the intermolecular distance.
(iv) **Specific-dipolar interaction:**

This effect arises from asymmetric charge distribution in molecules. When an acidic hydrogen atom carrying a partial positive charge approaches an electron rich basic type of atom, an association occurs forming a bond between them. The contribution due to this short range electrostatic interaction is not significant but polarisation effect, specially the charge redistribution in the molecule affects the dipole moment and in certain specific cases, charge transfer interaction occurs. In these extreme cases, the electron rearrangement is no longer confined to the hydrogen-bonded site, but extends to the further ends of the molecules. Hence, a charge migration parallel to the hydrogen bounded axis results in a significant change in the dipole movement of the complex.

**II.4. DENSITY, COMPRESSIBILITY AND VISCOSITY OF LIQUIDS**

For the study of various properties molar volume $V_m$ of a liquid is considered here with the help of which available free space volume $V_a$ in that liquid can be defined.

$$V_m = \frac{M}{\rho}$$  \hspace{1cm} (2.1)

when $M$ is the relative molecular mass and $\rho$ is the density of the liquid

$$V_a = V_M - V_0$$  \hspace{1cm} (2.2)

where $V_M$ is the volume of the liquid at TK and $V_0$ is the volume of the liquid at OK.

In the case of liquid where available volume is only a fraction of the total volume, compressibility and viscosity of a liquid are generally influenced by the amount of space in which the molecules are free to move. According to vander Waals equations,

$$(P + P_0)(V_M - V_0) = RT$$  \hspace{1cm} (2.3)
the relative available volume should be same for all the liquids at their boiling point. $P^T$ is the pressure exerted by the fluid at $TK$, $P_0$ is the corrected pressure term, $V_0$ is the volume of occupied by the liquid at $OK$ and $R$ is the universal gas constant.

Measurement of ultrasonic velocity ($C$) in liquids leads to an idea of size of he molecules which on the other hand determines $V_0$ [1-2] as

$$V_0 = \frac{M}{\rho} \left[ 1 - \frac{RT}{MC^2} \left( \sqrt{1 + \frac{MC^2}{3RT}} - 1 \right) \right]$$ (2.4)

It also leads to the determination of available volume of liquid which can be calculated from combined Jacobson and Schaff's equation [3-4] which assumes the form

$$V_a = V_m \left( 1 - \frac{C}{C_\infty} \right)$$ (2.5)

when $V_m$ is the major volume of the liquid and $C_\infty$ is equal to 1600 ms$^{-1}$. Ultrasonic velocity also leads to an idea of the isentropic compressibility defined as

$$\beta_s = \frac{1}{\rho C^2}$$ (2.6)

Isothermal compressibility $\beta_T$ is related to $\beta_s$ by

$$\beta_T = \beta_s + \frac{TV_M\alpha^2}{C_P}$$ (2.7)

where $\alpha$ is the coefficient of thermal expansion, $C_P$ is the molar specific heat at constant pressure of liquid.
According to Rao [5-6] in case of organic liquid the ratio of the temperature coefficient of the ultrasonic velocity to the expansion coefficient of volume is a constant i.e.,

\[
\frac{1}{C} \left( \frac{\partial c}{\partial T} \right)_P = -3
\]

(2.8)

From the equation (2.8) R is molar velocity known as Rao's constant which can be calculated as

\[ R = V_M C^{V/3} \]  

(2.9)

The constant R is independent of temperature for any liquid and can be used for finding molecular structure with the help of ultrasonic velocity [7-10]. Ultrasonic velocity is also influenced by acoustic impedance Z, which is defined as

\[ Z = \rho C \]  

(2.10)

Intermolecular free length \( L_f \) [3] and molar compressibility \( W \) of the liquid can be defined as

\[ L_f = K \beta_s^{1/2} \]  

(2.11)

and

\[ W = \left( \frac{M}{\rho} \right) \beta_s^{-1/7} \]  

(2.12)

where K is the temperature dependent constant.

The viscous flow of liquid involves both rotational and translational motion of molecules. Two major semiempirical theories used to predict viscosity are

(i) Free volume theory [11-13]
Absolute Reaction Rate Theory of Eyring and Coworkers [4]

The free volume theory relates the viscosity to the probability of occurrence of an empty neighbour site in which a molecule can jump. This probability is exponentially related to the free volume of the liquid.

According to Eyring et al., [15-17] viscous flow of liquid can be treated as a rate process in which the motion of one layer with respect to another involved passage of a molecule from one equilibrium position to another and for the passage to occur a suitable site or hole should be available. This process requires energy since work is to be done to push back other molecules. This type of movement is regarded as equivalent to the passage of the system over a potential energy barrier.

According to the theory of rate process [18] the number of times a molecule passes over the barrier in any direction per second is given by

\[ K = \frac{K_b T}{h} \cdot \frac{F^*}{F} e^{-\frac{E_o K_b T}{F}} \]  

where \( E_o \) is energy of activation at OK when no force is acting on the liquid, \( K_b \) is Boltzman constant, \( F^* \) and \( F \) are the partition function per unit volume in the activated and initial state respectively. In this derivation tunelling factor is neglected and transmission coefficient is unity.

Considering two layers of liquid at some distance apart from the definition of coefficient of viscosity (\( \eta \)).

\[ \eta = \frac{hN}{V_m} e^{-\frac{\Delta G}{RT}} \]
Where \( N \) is Avagadro's number, \( \Delta G^* \) is the standard free energy of activation per mole and \( V_M \) is the molar volume.

Taking the reciprocal of equation

\[
\Phi = \frac{V_M}{hN} e^{-\Delta G^*/RT}
\]  

(2.15)

Where \( \Phi \) is the fluidity of liquid.

II. 5. DENSITY, COMPRESSIBILITY AND VISCOSITY OF BINARY AND TERNARY MISTURES

In case of an ideal mixture, where the component molecules are nonpolar and noninteracting, a linear variation of density, ultrasonic velocity and viscosity with the composition is expected. It is assumed that the two molecular species in the mixture do not interact with each other. Under the ideal condition, the viscous flow is considered to be the movement of one molecule at a time from one equilibrium position to the next. Fluidity of such a binary mixture is expected to be the sum of fluidity contribution of the two components. The theoretical value of various properties are obtained by the following relation.

\[
A_M = f_1 A_1 + f_2 A_2
\]  

(2.16)

Where \( A_M \) is the value of any property of the mixture and \( A_1 \) and \( A_2 \) are pure component properties, \( f_1 \) and \( f_2 \) are the mole fraction of first and second component respectively.

In the case of non-ideal mixture where the components are polar and interacting, there is a nonlinear variation of density \( (\rho) \), compressibility \( (\beta_s) \), ultrasonic velocity \( (C) \) and viscosity \( (\eta) \) with the concentration of the components. The experimental values deviate from the
theoretical values arising due to difference in size of the molecules and the strength of interaction between them. Those deviation are expressed as excess values of various properties. All the excess values are obtained by

\[ A^E = A_{\text{exp}} - A_{\text{theor}} \]  

(2.17)

where \( A_{\text{theor}} = f_1A_1 + f_2A_2 \), \( A^E \) is the excess value, \( A_1 \) and \( A_2 \) are pure component properties and \( f_1 \) and \( f_2 \) are the mole fractions of the components.

Information concerning the properties of solute and solute-solvent interaction is provided by the change in the ultrasonic velocity \( C \) with change in solute concentration i.e. \( \frac{dc}{df_m} \). From the equation \( \beta_s = \frac{1}{\rho C^2} \), we have,

\[ C = (\rho \beta_s)^{-1/2} \]  

(2.18)

From the above equation \( \frac{dC}{df_m} \) is related to the corresponding change in density and compressibility change in density and compressibility i.e.

\[ \frac{1}{C} \frac{dc}{df_m} = -\frac{1}{2} \left[ \frac{\beta_s}{df_m} \frac{d\beta_s}{df_m} + \frac{1}{\rho} \frac{d\rho}{df_m} \right] \]  

(2.19)

so the variation of isentropic compressibility bears an opposite sign to that of the ultrasonic velocity under the assumption that contribution due to the second term is neglected.

"Molar sound velocity" defined by Rao [5] as

\[ R = \frac{M}{\rho} C^{1/3} \]  

(2.20)
is a constant independent of temperature and is an additive function of constituting atoms [5] or bonds [19]. Grunberg and Nissan [20] proposed an expression for liquid mixtures exhibiting non-ideal behaviour by

$$l_n n_{m(a)} = f_1 l_n \eta_1 + f_2 l_n \eta_2 + f_1 f_2 d$$ (2.21)

where the factor d is regarded as an approximate measure of the strength of interaction between the components of the mixtures.

Katti and Choudhuri [21] deduced an equation for the viscosity of liquid mixtures, taking into account the variation of molar volume with composition by:

$$\Delta j_{m(\eta)} = f_1 l_n \eta_1 V_1 + f_2 l_n \eta_2 V_2 + f_1 f_2 W_{vis} / RT$$

where $W_{vis}$ represents the interaction energy between the components. The equation of Grunberg and Nissan and that of Katti and Choudhuri can be compared as follows:

Adding and subtracting $f_1 l_n V_1$ and $f_2 l_n V_2$ on the L.H.S. of equation (2.21) and adding and subtracting $f_1 l_n V_1$ and $f_2 l_n V_2$ on the R.H.S. of the same equation,

$$l_n n_{m(a)} V_m = f_1 l_n \eta_1 V_1 + f_2 l_n \eta_2 V_2 + l_n \frac{V_M}{V_1 V_2} + f_1 f_2 d$$ (2.23)

Comparing this with equation (2.22) one can see that the factor introduced to account for the nonideality is given as

$$f_1 f_2 \frac{W_{vis}}{RT} = \frac{l_n V_M}{V_1 V_2} + f_1 f_2 d$$ (2.24)

Thus using the equation (2.24) $W_{vis}$, the interaction energy term can be calculated. If, however, the volume $V_M$ is related to the volumes of the components $V_1$ and $V_2$ at different composition in such a way as to make

$$l_n \{ V_M(V_1 V_2) \}$$

exceedingly small, then from the equation (2.21)
\[ W_{\text{vis}} = d \ (RT) \]

Hence, using the equation (2.25), \( W_{\text{vis}} \) interaction energy can be calculated.

Theoretical predictions of excess molar volumes of non ideal binary liquid mixtures have been satisfactory in explaining the sign and magnitude in terms of the extent of interactions between mixing components. For ternary mixtures, the predictive approach is more complex and thus empirical methods based on experimental methods based on experimental binary data have to be used. A search of literature on ternary mixtures suggest the availability of several empirical relations used to calculate the excess volume \((22-25)\). According to Davolio \textit{et al.} [26] the experimental densities and viscosities for the ternary system were obtained by adding the third component to a constant ratio of the other two i.e. \( x_1/x_2 = \text{constant} \). Molar excess volumes were calculated from

\[ V^E = x_1 M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 M_2 (\rho^{-1} - \rho_2^{-1}) + x_3 M_3 (\rho^{-1} - \rho_3^{-1}) \] (2.26)

where \( M_1, M_2 \) and \( M_3 \) are the molecular weight of the components respectively, \( \rho_1, \rho_2 \) and \( \rho_3 \) are the densities of the pure components and \( \rho \) the densities of the solution. The excess viscosity is defined by

\[ \eta^E = \eta - \exp(x_1/\eta_1 + x_2/\eta_2 + x_3/\ln \eta_3) \] (2.27)

where \( \eta, \eta_1, \eta_2 \) and \( \eta_3 \) are the viscosities of the mixture and of the pure components respectively.

Rastogi \textit{et al.} [27] suggested the following equation for prediction of excess volumes of ternary solutions.

\[ V_{123}^E = \frac{1}{2} \left[ (x_1 + x_2) \ V_{12}^E + (x_1 + x_3) \ V_{13}^E + (x_2 + x_3) \ V_{23}^E \right] \] (2.28)
in which \( V_{ij}^E \) represents the excess molar volume of the binary mixtures at composition \( x_i^0, x_j^0 \), such that

\[
x_i^0 = 1 - x_j^0 = \frac{x_j}{x_i + x_j} \tag{2.29}
\]

Radojović et al [28] considered an expression proposed by Redlich and Kister

\[
V_{123}^E = V_{12}^E + V_{23}^E + V_{13}^E \tag{2.30}
\]

where \( V_{12}^E, V_{23}^E \) and \( V_{13}^E \) represents the excess molar volumes with \( x_1, x_2 \) and \( x_3 \) mole fraction of the ternary system.

Kohler [29] proposed an equation for a ternary system of the form.

\[
V_{123}^E = (x_1 + x_2)^2 V_{12}^E + (x_1 + x_3)^2 V_{13}^E + (x_2 + x_3)^2 V_{23}^E \tag{2.31}
\]

Kohlers equation is symmetrical in that all three binary systems are treated identically. in this equation \( V_{ij}^E \) refers to the excess volumes of \( x_i^0, x_j^0 \) in the binary mixtures using Eqn. (2.29). Jacob and Fitzner [30] suggested an equation for estimating the properties of a ternary solution based on the binary data at composition nearest the ternary composition, taking the following form for the excess molar volume.

\[
V_{123}^E = \frac{x_1 x_2 V_{12}^E}{[x_1 + (x_3/2)] [x_2 + (x_3/2)]} + \frac{x_1 x_3 V_{13}^E}{[x_1 + (x_2/2)] [x_3 + (x_2/2)]} + \frac{x_2 x_3 V_{23}^E}{[x_2 + (x_1/2)] [x_3 + (x_1/2)]} \tag{2.32}
\]
so that for the binary system at composition

\[ x_i - x_j = x_i^0 - x_j^0 \]  

(2.33)

Tsao and Smith [31] proposed an equation for predicting the excess enthalpy of a ternary system. For excess molar volume, it becomes

\[ V_{123}^E = \left( \frac{x_2}{1-x_1} \right) V_{12}^E + \left( \frac{x_3}{1-x_1} \right) V_{13}^E + (1-x_1) V_{23}^E \]  

(2.34)

in which \( V_{ij}^E \) refers to the excess volume for the binary mixtures at composition \( x_i^0 \), \( x_j^0 \), such that \( x_i^0 = x_i \) for the 1,2 and 1,3 binary systems and

\[ x_2^0 = x_2(x_2 + x_3) \]  

for the 2,3 binary system.

Singh et al. [32] proposed an equation of the form

\[ V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 [A + B x_1 (x_2 - x_3)] + C + x_1^2 (x_2 - x_3)^2 \]  

(2.35)

where \( A \), \( B \) and \( C \) are parameters characteristic of the mixtures and are evaluated by fitting this equation by the least squares method with a standard deviation. Finally Cibulka [33] proposed the equation.

\[ V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 (A + B x_1 + x_2) \]  

(2.36)

Nomoto empirical relation for ultrasonic velocity, \( C_m \) in ternary liquid mixture [34] yields the following expression:

\[ C_{mix} = \left( \frac{X_1 R_1 + X_2 R_2 + X_3 R_3}{X_1 V_1 + X_2 V_2 + X_3 V_3} \right)^3 = \left( \frac{R_{mix}}{V_{mix}} \right) \]  

(2.37)

where \( R_m = X_1 R_1 + X_2 R_2 + X_3 R_3 \)  

(2.38)
\begin{equation}
V_m = X_1V_1 + X_2V_2 + X_3V_3
\end{equation}

\(X_1, X_2 \text{ and } X_3\) being the mole fraction of respective compounds in the mixture. \(R_1, R_2, R_3 \text{ and } V_1, V_2 \text{ and } V_3\) are respectively the molar sound velocities and molar volumes of components 1, 2 and 3. Molar sound velocity, \(R\), is given by

\begin{equation}
R = \left(\frac{M}{\rho}\right) C^{1/3} = VC^{1/3}
\end{equation}

where \(M\) and \(\rho\) are respectively the molecular weight and density of liquid.

According to the theory of ideal mixing \[35\] ultrasonic velocity in ternary liquid mixture \[36-38\] is given by

\begin{equation}
\frac{1}{X_1M_1 + X_2M_2 + X_3M_3} = \frac{X_1}{M_1C_1^2} + \frac{Y_2}{M_2C_2^2} + \frac{X_3}{M_3C_3^2}
\end{equation}

The collision factor theory of Schaffs \[39\] on the other hand, yields the following relation for ultrasonic velocity in ternary liquid mixtures.

\begin{equation}
C_m = \frac{C_n (X_1S_1 + X_2S_2 + X_3S_3)}{X_1V_1 + X_2V_2 + X_3V_3}
\end{equation}

where \(C_n = 1600 \text{ ms}^{-1}\) and \(S_1, S_2 \text{ and } S_3\) are the collision factors for respective pure components. Junjie \[40\] developed an equation for estimating ultrasonic velocity in ternary liquid mixtures starting from the relation.

\begin{equation}
C^{-2} = \frac{\rho}{V} \left(\frac{\partial V}{\partial \rho}\right)
\end{equation}

Molar volumes, \(V_m\) and excess Volumes \(V^E\) for ternary mixtures were obtained from the expression.
\[ V_m = \frac{X_1 M_1 + X_2 M_2 + X_3 M_3}{\rho_{\text{mix}}} \] (2.44)

\[ V^E = V_m - (X_1 V_1 + X_2 V_2 + X_3 V_3) \] (2.45)

\[ V_i = \frac{M}{\rho_i} \] (2.46)

From the above equations

\[ C_m = \frac{X_1 V_1 + X_2 V_2 + X_3 V_3}{(X_1 M_1 + X_2 M_2 + X_3 M_3)^{1/2}} \left( \frac{X_1 V_1 + X_2 V_2 + X_3 V_3}{\rho_1 C_1^2 + \rho_2 C_2^2 + \rho_3 C_3^2} \right)^{1/6} \] (2.47)

The expression has been obtained by neglecting excess molar volume and its derivatives.
REFERENCES


