Chapter - 4

Computational Aspects
Chapter - 4

COMPUTATIONAL ASPECTS

4.1 COMPUTATIONAL ASPECTS

4.1.1 Ultrasonic Parameters

As the distance between two successive maxima is $\lambda/2$, mean $\lambda$ is calculated from the readings of micrometer of interferometer and by using the relation,

$$u = f \lambda \quad ...... \quad 4.1$$

$f$ being the frequency equal to 2 MHz., $u$ was calculated for different compositions at different temperatures. In all the cases it was found that the ultrasonic velocity was linear with the temperature. Hence a method of least squares was applied to straight line fitting of ultrasonic velocity versus temperature. By extrapolating, $u_0$ velocity at 0°C was obtained.

If $(du/dt)$ denotes the slope, then velocity at any temperature can be obtained from

$$u = u_0 + (du/dt) t \quad ...... \quad 4.2$$

Similarly, density is given by

$$\rho = \rho_0 + (d\rho/dt) t \quad ...... \quad 4.3$$

The basic data of ultrasonic velocity and density at different temperature in presented in tables from IA-IH.
Adiabatic compressibility was calculated from

\[ \beta_a = \left( \frac{u^2}{\rho} \right)^{-1} \]  

Excess function is given by

\[ Y^E = Y_{\text{expt}} - Y_{\text{ideal}} \]  

where \[ Y_{\text{ideal}} = (1 - x) Y_1 + x Y_2 \]  

From this,

\[ V^E = V_{\text{expt}} - V_{\text{ideal}} \]

where, \[ V_{\text{expt}} = \frac{n_1 M_1 + n_2 M_2}{\rho} \], \( n_1 \) & \( n_2 \) being molar fraction and \( \rho \) is experimental density of mixture.

and Excess adiabatic compressibility

\[ \beta_a^E = (\beta_a)_{\text{expt}} - (\beta_a)_{\text{ideal}} \]  

were calculated.

Graphs of \( V^E \) and \( \beta_a^E \) against the volume fraction \( x \) were plotted for each binary system. The results of this computation are presented in figures 1-16 at the temperature 303 K.

### 4.2 SCALED PARTICLE THEORY

In each mixture which is experimented, molecules of two species are assigned one of the following shapes:

- a) Spherical
- b) Cubical
- c) Tetrahedral
Pure Liquid Parameters (Molecular Dimensions)

If R, S, v denote the Radius, Surface area and Volume of a molecule respectively, then shape factor denoted by X is given by.

\[
\frac{RS}{\nu} = X
\]

From an equation of state for pure liquids.

\[
\frac{\mu^2}{\gamma RT} = \frac{[1 + (X - 1) \eta]^2}{(1 - \eta)^4}
\]  
\[4.8\]

where, \(\eta = \nu \rho_N\), \(\rho_N\) being the number density, \(\nu\) = hard core volume and other quantities have their usual meaning.

Using experimental ultrasonic velocity \(u\), molecular weight \(M\) and \(\gamma\) calculated in Flory's calculations, \(\eta\) is determined for pure liquids, from equation 4.8.

Now \(\eta = \nu \rho_N\),

\[
\nu = \frac{\eta}{\rho_N} = \frac{\eta}{H/V}
\]  
\[4.9\]

\[
\nu = \frac{\eta M}{H \rho}
\]  
\[4.10\]

by knowing \(\eta\), molecular weight \(M\), molecular density \(\rho\) and Avogadro's number \(H\), hard core volume of a molecule is known.

(i) Spherical

For a spherical molecule, volume \(\nu = 4\pi R^3 / 3\),

Hence, \(R = \left(\frac{3\nu}{4\pi}\right)^{1/3} = \left(\frac{3}{4\pi}\right)^{1/3} \nu^{1/3}\)

and area of a molecule \(S = 4\pi R^2\)
(ii) Cubical

From Table VI, for a cubical molecule radius and surface area are given as $R = 3(l/4) & S = 6 l^2$, where ‘l’ is the side of the cube.

(iii) Tetrahedral

For a tetrahedral molecule,

Radius and Surface Area are given as $R = \frac{3l (\tan^{-1} \sqrt{2})}{2\pi}$ and $S = \sqrt{3} l^2$.

Now, molecular weight of the mixture is given as

$$M = M_1 + n [M_2 - M_1]$$

where $M_1$ and $M_2$ are molecular weights of two components and $n$ is molar fraction. Let $\rho_1$ and $\rho_2$ be the densities of pure liquids. Then from 4.10

$$v_1 = \frac{\eta_1 M_1}{H \rho_1} \text{ and } v_2 = \frac{\eta_2 M_2}{H \rho_2}$$

Volume of the mixture will be

$$V_0 = \frac{M_1}{\rho_1} + \left(\frac{M_2}{\rho_2} - \frac{M_1}{\rho_1}\right)x$$

For a mixture molecule, additive molecular dimensions become -

Average Radius $A = R_1 + [R_2 - R_1] n$ .......... 4.13

Surface Area $B = S_1 + [S_2 - S_1] n$ .......... 4.14

Square of Radius $C = R_1^2 + [R_2^2 - R_1^2] n$ .......... 4.15

& Average Volume $V = v_1 + [v_2 - v_1] n$ .......... 4.16
By substituting these values in an equation

\[
\frac{\mu^2}{\gamma RT} = \frac{1 + 2AB (\rho_N(1 - \rho_N)) + B^2C (\rho_N(1 - \rho_N))^2}{(1 - Y\rho_N)^2}
\]  

... ... 4.17

where, \( \rho_N = \frac{H}{V_0} \)

Ultrasonic velocity in a mixture is calculated. This gives the velocity \( u_{\text{SPT}} \) in a mixture at temperature \( T \) from the parameters of pure liquids.

The calculation of \( u_{\text{SPT}} \) are carried by considering different shapes of component molecules in a mixture as follows -

1. Spherical + spherical
2. Spherical + cubical
3. Spherical + tetrahedral
4. Cubical + spherical
5. Cubical + cubical
6. Cubical + tetrahedral
7. Tetrahedral + spherical
8. Tetrahedral + cubical
9. Tetrahedral + tetrahedral

The results of ultrasonic velocity calculated by using Scaled Particle Theory are presented in the Tables IIIA-IIIH. The comparison is made between experimental velocities \( u_{\text{expt}} \) and theoretical velocities \( u_{\text{SPT}} \). The deviation for each mole fraction in a given system is calculated by using the relation –

\[
\text{deviation} = \frac{u_{\text{expt}} - u_{\text{SPT}}}{u_{\text{SPT}}}
\]

Taking the sum of deviations for all mole fractions for a particular system, the total sum deviation is found out.

All the shape combinations are tried using equivalent radius, corresponding area and volume (Table VI) of molecules and that shape has been fixed which gives ultrasonic velocity values in close agreement with the experimental values (for which the total sum of the deviation is minimum).
4.3 FLORY’S THEORY

Starting with the reduced equation of state,
\[
\frac{\bar{p} \bar{v}}{\bar{T}} = \frac{\bar{v}^{1/3}}{(\bar{v}^{1/3} - 1)} - \frac{1}{\bar{v}} \quad \ldots \ldots \ldots 4.18
\]

where, \( p, v, T \) are reduced parameters given by \( \bar{p} = p/p^*, \bar{v} = v/v^*, \bar{T} = T/T^* \), \( p^*, v^*, T^* \) being characteristic parameters.

At zero pressure,
\[
\text{i.e.} \quad \bar{v}^{1/3} - 1 = v^{4/3} T \quad \ldots \ldots \ldots 4.19
\]

If \( \alpha \) is coefficient of thermal expansion, then
\[
\bar{v}^{1/3} - 1 = \frac{\alpha T / 3}{1 + \alpha T} \quad \ldots \ldots \ldots 4.20
\]

from Eqn. 4.19,
\[
T = \frac{\bar{v}^{1/3} - 1}{\bar{v}^{4/3}} \quad \ldots \ldots \ldots 4.21
\]

\& \quad \beta_a = u^2 \rho^{-1}

From experimental values of adiabatic compressibility \( \beta_a \) and specific heat at constant pressure \( C_p \) (obtained from the literature), thermal pressure coefficient \( \gamma \) is calculated from
\[
\gamma = \frac{\alpha C_p}{\beta_a C_p + \alpha^2 T v} \quad \ldots \ldots \ldots 4.22
\]

and from \( p^* = \gamma T v^2 \), \( p^* \) is known \ldots \ldots \ldots 4.23

Isothermal compressibility is given by
\[
\beta_T = \alpha / \gamma
\]
Thus the parameters $v, T, v^*, T^*, p^*, \gamma, \beta_v, \beta_T$ etc. were calculated for pure liquids from above equations and the tables IVA-IVC in chapter no 5. show the values of these parameters.

### 4.3.1 Mixture Parameters

The following analysis is confined to binary mixtures, the components being indexed by subscripts $1$ & $2$.

From ideal molar volume of the mixture $v_{\text{ideal}}$, reduced volume of the mixture is given by

$$\overline{V} = \frac{v_{\text{ideal}}}{x_1 v_1^* + x_2 v_2^*} \quad \ldots \ldots \ 4.24$$

**Characteristic volume of the mixture**

$$v^* = x_1 v_1^* + x_2 v_2^*$$

where, $x_2 = x$ and $(1 - x_2) = x_1$

Segment fractions $\phi_1$ and $\phi_2$ are given by

$$\phi_1 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*} \quad \text{&} \quad \phi_2 = \frac{x_1 v_1^*}{x_1 v_1^* + x_2 v_2^*} \quad \ldots \ldots \ 4.25$$

Number of sites $r_S$ per molecule are taken proportional to the surface area of a sphere of the same core volume.

Thus,

$$\frac{r_1 S_1}{r_2 S_2} = \left(\frac{v_1^*}{v_2^*}\right)^{2/3} \quad \text{&} \quad \frac{v_1^*}{v_2^*} = \frac{r_1}{r_2}$$

which gives

$$\frac{S_1}{S_2} = \left(\frac{v_2^*}{v_1^*}\right)^{1/3} \quad \ldots \ldots \ 4.26$$
Site fraction is given by

\[ \theta_2 = \frac{\phi_2}{(S_1/S_2) \phi_1 + \phi_2} \]  

...... 4.27

Interaction parameter is given by,

\[ X_{12} = p_1^* \left( 1 - \left( \frac{S_1}{S_2} \right)^{1/2} \left( \frac{p_2^*}{p_1^*} \right)^{1/2} \right)^2 \]  

...... 4.28

And \( p^* \) is calculated from this value of \( X_{12} \) by using an equation

\[ p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \theta_2 X_{12} \]  

...... 4.29

for the mixture.

Then proceeding in the same manner as explained in chapter two, adiabatic compressibilities and ultrasonic velocities are calculated.

In above considerations, \( (S_1/S_2) \) is calculated as follows from different shapes.

(i) Considering molecules of two species spherical \((sph + sph)\)

\[ \frac{r_1 S_1}{r_2 S_2} = \frac{4\pi R_1^2}{4\pi R_2^2} = \frac{R_1^2}{R_2^2} \]

\[ \frac{S_1}{S_2} = \frac{R_1^2}{R_2^2} \cdot \frac{r_2}{r_1} \]

But ratio of segments taken proportional to volume, hence

\[ \frac{r_1}{r_2} = \frac{v_1^*}{v_2^*} \]  

and radius of sphere \( R = \left( \frac{3v}{4\pi} \right)^{1/3} \)

\[ \frac{S_1}{S_2} = \left\{ \left( \frac{3v_1^*}{4\pi} \right)^{2/3} \left( \frac{3v_2^*}{4\pi} \right)^{2/3} \right\} \frac{v_2^*}{v_1^*} \]

\[ \frac{S_1}{S_2} = \left( \frac{v_2^*}{v_1^*} \right)^{1/3} \]  

...... 4.30
ii) Spherical + Cubical

As cited earlier.

Ratio of surface areas of two molecules \( = r_1 S_1 / r_2 S_2 \), from Table 6, for equivalent dimensions.

\[
\frac{S_1}{S_2} = \frac{4\pi r_1^2}{6 l_2^2} \frac{r_2}{r_1}
\]

hence,

\[
\frac{S_1}{S_2} = \frac{4\pi (3/4\pi)^{2/3} v_1^{2/3}}{6 v_2^{2/3}} \frac{v_2^*}{v_1^*}
\]

\[
= 0.805866 \left( \frac{v_2^*}{v_1^*} \right)^{1/3}
\]

\[\text{... ... 4.31}\]

(iii) Cubical + Spherical

\[
\frac{S_1}{S_2} = \frac{6 l_1^2}{4\pi R_2^2} \frac{r_2}{r_1}
\]

\[
= 1.2409 \left( \frac{v_2^*}{v_1^*} \right)^{1/3}
\]

\[\text{... ... 4.32}\]

(iv) Spherical + Tetrahedral

\[
\frac{S_1}{S_2} = \frac{4\pi R_1^2}{\sqrt{3} l_2^2} \frac{r_2}{r_1}
\]

For sphere, \( v_1^* = 4\pi R_1^3 / 3 \) and for tetrahedral, \( v_2^* = \sqrt{2} l_2^3 / 12 \)

hence,

\[
\frac{S_1}{S_2} = \frac{4\pi R_1^2}{\sqrt{3} l_2^2} \frac{r_2}{r_1}
\]
\[
= (\pi/2)^{1/4} \frac{1}{\sqrt{3}} \left( \frac{v_2^*}{v_1^*} \right)^{1/3}
\]
\[
= 0.671026 \left( \frac{v_2^*}{v_1^*} \right)^{1/3} 
\]

(v) In a similar manner, for tetrahedral + spherical

\[
\frac{S_1}{S_2} = \frac{\sqrt{3} l_1^2}{4\pi R_2^2} \frac{r_2}{r_1}
\]
\[
= \sqrt{3} \frac{2}{\pi} \left( \frac{v_2^*}{v_1^*} \right)^{1/3}
\]
\[
= 1.49025 \left( \frac{v_2^*}{v_1^*} \right)^{1/3} 
\]

(vi) Cubical + Tetrahedral

\[
\frac{S_1}{S_2} = \frac{6 l_1^2}{\sqrt{3} l_2^2} \frac{r_2}{r_1}
\]
\[
= 0.83268 \left( \frac{v_2^*}{v_1^*} \right)^{1/3} 
\]

(vii) Tetrahedral + Cubical

\[
\frac{S_1}{S_2} = 1.20093 \left( \frac{v_2^*}{v_1^*} \right)^{1/3}
\]

In this theory, \( (S_1/S_2) \) for molecules of same shapes, spherical + spherical, cubical + cubical, tetrahedral + tetrahedral

\[
\frac{S_1}{S_2} = \left( \frac{v_2^*}{v_1^*} \right)^{1/3}
\]
Same as the first combination Spherical + Spherical and so there are seven combinations of behavioural shapes of molecules as illustrated above.

Using the above shape combinations, $S_1/S_2$ value is substituted to get interaction parameter $X_{12}$ and $p^*$. These values are used to calculate $u_{110}$ according to the details given in Flory’s theory. For a particular binary system, shapes of constituent species are considered for all mole fractions. These results are presented in Tables VA-VH. Particular shape combination giving minimum sum deviation i.e. producing the ultrasonic velocities in close agreement with the experimental ones is treated as predicting the behavioural shapes of those molecules in that particular mixture at 303 K.