Thermodynamics of eutectic mixtures. Addition compounds and associated mixtures

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Abstract

This paper reviews the earlier studies on thermodynamic and thermochemical properties of eutectic mixtures, addition compounds in the context of the binary mixtures of A and B where possibility of formation of molecular complexes of AB and AB$_2$ type exists. Solid-liquid equilibrium studies along with experimental measurements on phase diagrams and heats of fusion of eutectics (along with micro structure ) and molecular complexes have been examined together with experimental results on Associated fluid mixtures related to (i) equilibrium properties such as vapour pressure, volume of mixing, heat of mixing and isentropic compressibility and (ii) dielectric and electro-optical properties viz dielectric constant, refractive index and molar polarization. Current status of Ideal Associated Solution Model has been critically discussed in terms of statistical mechanical considerations keeping in view (i) nature of molecular interaction influencing the vibration or rotation of neighbouring molecules and (ii) size effect.

Some comments on the nature of stacking of A and B molecules in such complexes has been that complexation is so easy that formation of AB and AB$_2$ complexes can take place even by reaction in the solid state.

1. INTRODUCTION

In general, we can classify the molecules in a solution in three groups:

(a) molecules whose rotations and vibrations are not altered by the presence of the neighbouring molecules. These are called free molecules.

(b) molecules whose states of vibrations or rotations are altered by neighbouring like molecules. These are described as associated molecules. Self-association between similar molecules such as alcohols is an example.

(c) molecules whose state of vibration or rotation is altered by unlike molecules. These are supposed to form association complexes. Such complexes can be formed by dipole-dipole interaction, hydrogen bond interaction or charge transfer interaction. Complex formed between acetone and chloroform is a typical example.
Associated mixtures where such interaction is involved are a class by themselves and are comparatively simple from the viewpoint of thermodynamics interpretation. A useful review on thermodynamics of associated solutions has recently appeared (ref 2). However, this does not cover solid-liquid equilibrium studies. Further, since 1984, good amount of work has been reported on equilibrium and non-equilibrium properties of such mixtures and a critical assessment of these along with evaluation of solid-liquid equilibrium data is called for. This is attempted in the present communication.

2. EQUILIBRIUM PROPERTIES

Let us consider a general case of mixture of A and B components where both AB and AB₂ complexes are formed according to two equilibria represented by the equations.

$$K_1 \quad A + B \rightleftharpoons AB$$

and

$$K_2 \quad A + 2B \rightleftharpoons AB_2$$

$K_1$ and $K_2$ are the equilibrium constant of the two equilibria. Thus, one has four species $A$, $AB$, $AB_2$ and $B$ in mutual equilibrium provided it is assumed that $A$, $AB$, $AB_2$ and $B$ form an ideal mixture. The activities $a_A$ and $a_B$ of the species $A$ and $B$ are related to $K_1$ and $K_2$ by equation (1) as shown by McGlashan and Rastogi (ref 3).

$$1-a_A-a_B = K_1 + K_2 a_B a_{AB}$$

Equation (1) can be used for test of the theory and graphical evaluation of equilibrium constant $K_1$ and $K_2$. Equation (1) was originally applied to mixtures of 1,4-dioxane and chloroform and now a classic example. Recently very precise data (ref 4) on vapour pressures of mixtures of 1, dioxane with $\text{CH}_2\text{Cl}_2$, $\text{CH}_2\text{ClCH}_2\text{Cl}$ and $\text{CHClCCl}_2$ has been reported which is found to conform accurately to the above theory of ideal associated mixtures. The data on $K_1$ and $K_2$ for different mixtures have been recorded in table 1. The value of the equilibrium constant justify the behaviour that would be expected on the strength of hydrogen-bond or donor-acceptor interaction. Equation (1) does not hold for mixtures (1) of dioxane with cyclohexane and $\text{CCL}_2\text{CCl}_2$ since hydrogen-bond formation is not expected.

These studies give very strong evidence for interaction between molecules having $>\text{O}$ and $\text{H-C}<$ groups. It is expected that strong interaction should exist between $>\text{C}=\text{O}$ and $\text{H-C}$ groups of molecules of $A$ and $B$ also. Here again, total vapour pressure data (ref 5) for
TABLE 1. Equilibrium constants for mixtures of dioxane (A)
Molar volume of Dioxane= 85ml

<table>
<thead>
<tr>
<th>B</th>
<th>Molar Volume</th>
<th>Temperature K</th>
<th>K₁</th>
<th>K₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>80.5</td>
<td>323.15</td>
<td>1.11</td>
<td>1.24</td>
<td>3</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>63.67</td>
<td>298.15</td>
<td>1.140</td>
<td>0.900</td>
<td>4</td>
</tr>
<tr>
<td>CH₂ClCH₂Cl</td>
<td>78.86</td>
<td>303.15</td>
<td>0.760</td>
<td>0.285</td>
<td>4</td>
</tr>
<tr>
<td>CHClCCl₂</td>
<td>89.38</td>
<td>303.15</td>
<td>0.470</td>
<td>0.895</td>
<td>4</td>
</tr>
</tbody>
</table>

Binary liquid mixtures of acetone and CH₂Cl₂, CH₂ClCH₂Cl, CHClCCl₂ indicates that excess Gibbs free energy for these mixtures is negative and hence strong A-B interaction is indicated. Unfortunately detailed analysis from the viewpoint of equation (1) does not seem to have been carried out on these mixtures. Data on excess volume V^E for such mixtures do not give a clear picture (ref 6). Similarly the corresponding V^E data for mixtures of methyl ethyl ketone and CH₂Cl₂, CH₂ClCH₂Cl, CHClCCl₂, CCl₂CCl₂ are not decisive in this respect. Although extensive data on excess entropic compressibility Δk_s defined by

$$Δk_s = k_{s,m} = x_A k_{s,A} - x_B k_{s,AB}$$

(2)

from ultrasonic measurements have accumulated, this has also not yielded any clear-cut criteria for deciding the specific nature of interaction.

3. DIELECTRICAL, ELECTRO-OPTICAL AND NON-EQUILIBRIUM PROPERTIES OF SOLUTIONS OF NON-ELECTROLYTES

During recent years, there has been considerable interest in the study of electro-optical properties of such mixtures (ref 8-11) such as refractive index, relative permittivity ε and molar polarization P. Following parameters as defined below have been estimated from measurements on refractive index, dielectric constant and viscosity η of the above mixtures.

$$Δε = ε_m - x_A ε_A - x_B ε_B$$

(3)

$$Δg = g_m - x_A g_A - x_B g_B$$

(4)

$$Δη = η_m - x_A η_A - x_B η_B$$

(5)

$$x_A x_B = \ln η_m - x_A \ln η_A - x_B \ln η_B$$

(6)

where x_A and x_B denote the mole fraction of components A and B respectively. The subscript m denotes the two components. d is a parameter which is a measure of the strength of the interaction between the components 'g' is the Kirkwood correlation factor as defined by Hill et al. (ref 12). This factor gives useful
information about the degree of ordering in the solution. Three conditions arise:

1. \( g = 1 \), if fixing the position of one dipole does not influence the positions of the rest of the dipoles at all (except through long-range electrostatic forces).

2. \( g > 1 \), if fixing one dipole tends to make the neighbouring dipoles line up in a parallel direction.

3. \( g < 1 \), if fixing one dipole tends to line up the neighbours in an antiparallel direction.

Hence, the factor 'g' provides an indication of degree of alignment of molecules in pure liquids and their binary mixtures. However, one has to be aware of pitfalls in computation of 'g' when effect of distortion polarization is included (ref 12).

Molecular interaction can also be studied by Static Kerr Effect and Depolarised Rayleigh light scattering but this has not received adequate attention.

The electro-optical, dielectrical and other properties do not necessarily corroborate the conclusions drawn from the thermodynamic studies. However, these in most of the cases do indicate the presence of specific interaction, but information about the nature of interaction is difficult to extract. Nevertheless, the studies are useful from the data point of view.

Molar polarization results indicate formation of molecular complexes in mixtures of dioxane mentioned in Table I. However, whereas thermodynamic results indicate the magnitude of equilibrium constant \( K_1 \) in the order \( \text{CH}_2\text{Cl}_2 > \text{CH}_2\text{ClCH}_2\text{Cl} > \text{CHClCCl}_3 \), the order predicted by molar polarization is \( \text{CH}_2\text{ClCH}_2\text{Cl} > \text{CHClCCl}_3 > \text{CHClCCl}_3 \).

These complexes are supposed to be formed because chloro-compounds act as \( \sigma^- \) acceptor, whereas, 1,4 dioxane acts as strong \( n \)-donor towards these compounds on account of lone pair of electrons on two oxygen atoms. It is expected that if the above picture of interaction is correct, similar interaction of the chloro compounds should take place with the lone pair of electrons of carbonyl oxygen of ketones and the lone pair of electrons on nitrogen in \( \text{C}_9\text{H}_7\text{N} \) (Quinoline) (ref 8-10). Experimental studies partially justify this expectation on the basis of studies of electro-optical properties.

4. SOLID-LIQUID EQUILIBRIA

Properties discussed in section 3 provide indirect evidence of molecular interaction. On the other hand, solid-liquid equilibrium data provide more reliable information about the state of such mixtures near the freezing point of the components.

Thus, in case of eutectic mixtures (ref 1,2) thermodynamic properties of the liquid eutectic mixture at the eutectic temperature and eutectic composition can be extracted from the phase-digram. Excess enthalpy \( h^e \), excess Gibbs function \( g^e \) and excess entropy \( s^e \) can easily be estimated by the procedure suggested by Rastogi et al. Data for a few liquid mixtures are recorded in Table I along with the heat of fusion \( \Delta h \) of eutectic mixtures.
Table-2 Excess of Thermodynamic functions of eutectics

<table>
<thead>
<tr>
<th>System</th>
<th>$h^E$/kj/mol</th>
<th>$g^E$/j/mol</th>
<th>$s^E$/j/mol/k</th>
<th>$\Delta f h$/kj/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene -phenanthrene</td>
<td>3.31</td>
<td>81</td>
<td>9.9</td>
<td>21 (23)</td>
</tr>
<tr>
<td>naphthalene -p-chloro nitro benzene</td>
<td>2.71</td>
<td>384</td>
<td>8.4</td>
<td>20.3 (18.6)</td>
</tr>
</tbody>
</table>

Figures in the parenthesis denote the value calculated on the basis of mixture law for the eutectic mixtures. The liquid mixtures have in general positive excess functions indicating that size effects are prominent. Heat of fusion of eutectic mixtures corresponds to the mixture law value if the uncertainties in measurements are taken into account. This is also supported by the nature of microstructure (ref 2).

Solid-liquid equilibrium data are equally informative about the state of associated mixtures near the freezing point of the components having congruent melting point or incongruent melting point. Rastogi and Girdhar (ref 15) obtained the low temperature phase diagram of mixtures of chloroform and dioxane which confirmed the existence of complexes of the AB and AB₂ in the mixture.

Thermodynamic treatment of such mixtures assuming ideal behaviour of the species A, B, AB₂ or A_mB^n, yields the relation (ref 1,16),

\[
\frac{\Delta_f h}{R} \left( \frac{1}{T} - \frac{1}{T_C} \right) = -\ln (\xi_{A}^1)^m(\xi_{B}^1)^n + \ln (\xi_{A}^1)^m (\xi_{C}^1)^n
\]

(7)

where the compound formed is A_mB^n, \(\xi_{A}^1\) and \(\xi_{B}^1\) are the mole-fraction of the species A and B respectively. These would be equal to the stoichiometric mole-fractions \(x_A\) and \(x_B\) if the compound is completely dissociated in the molten state. Subscript C represents the corresponding quantity at the congruent melting point \(T_C\).

Superscripts 1 denotes the liquid phase. An approximate idea of heat of fusion of the complex can be obtained from (7) by assuming complete dissociation of the complex and plotting \((1/T-1/T_C)\) against \(\ln(x_A^1)^n(x_B^1)^m\).

The values are for a few systems are given in table-3 along with the values directly determined by calorimetric technique. The latter are given in the parenthesis.

Heats of fusion obtained from phase diagrams are only approximate. Calorimetric measurements are more reliable. Values of entropy of fusion have also been calculated (ref 21) for some molecules including benzophenone-diphenylamine complex using statistical mechanics. Low value of entropy of fusion suggests that a tight complex is produced whereas high value of entropy of fusion suggests that a loose complex is produced.
Table 3. Heat of fusion and entropy of fusion of molecular complexes and components

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point (K)</th>
<th>( \Delta_f^h ) (J/mol)</th>
<th>( \Delta_f^S ) (Exp) (J/mol/k)</th>
<th>( \Delta_f^S ) (Theory) (J/mol/k)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>209.6</td>
<td>-</td>
<td>41.4</td>
<td>40.6</td>
<td>*</td>
<td>19</td>
</tr>
<tr>
<td>Dioxane</td>
<td>284.6</td>
<td>-</td>
<td>45.2</td>
<td>46.4</td>
<td>*</td>
<td>20</td>
</tr>
<tr>
<td>CHCl₃(A) - Dioxane(B)</td>
<td>244.4</td>
<td>5.55</td>
<td>22.2</td>
<td>-</td>
<td>**</td>
<td>15</td>
</tr>
<tr>
<td>AB₂</td>
<td>215.7</td>
<td>27.2</td>
<td>126.0</td>
<td>-</td>
<td>**</td>
<td></td>
</tr>
<tr>
<td>Benzophenone</td>
<td>321.35</td>
<td>16.9ₜ±2</td>
<td>52.7ₜ±0.5</td>
<td>51.0</td>
<td>**</td>
<td>18</td>
</tr>
<tr>
<td>-Diphenylamine</td>
<td>326.25</td>
<td>18.7ₜ±2</td>
<td>57.3ₜ±1.0</td>
<td>55.6</td>
<td>**</td>
<td>18</td>
</tr>
<tr>
<td>Benzophenone-Diphenylamine</td>
<td>341.05</td>
<td>25.5</td>
<td>80.8</td>
<td>-</td>
<td>**</td>
<td>17</td>
</tr>
<tr>
<td>Dibenzophenone</td>
<td>314.35</td>
<td>(32.3ₜ±0.2)</td>
<td>(102.9ₜ±1)</td>
<td>-</td>
<td>*</td>
<td>18</td>
</tr>
<tr>
<td>p-nitro toluene</td>
<td>324.33</td>
<td>13.3ₜ±0.2</td>
<td>41.0ₜ±0.5</td>
<td>-</td>
<td>*</td>
<td>18</td>
</tr>
<tr>
<td>p-toluidine</td>
<td>326.53</td>
<td>18.9ₜ±0.2</td>
<td>59.8ₜ±0.5</td>
<td>-</td>
<td>*</td>
<td>18</td>
</tr>
<tr>
<td>p-nitrotoluene-p-toluidine</td>
<td>3.05</td>
<td>10.0</td>
<td>-</td>
<td>*</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Urea(A)-phenol(B)</td>
<td>332.35</td>
<td>31.8</td>
<td>95</td>
<td>-</td>
<td>*</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>335.15</td>
<td>(54.9ₜ±2)</td>
<td>(164ₜ±5)</td>
<td>-</td>
<td>*</td>
<td>18</td>
</tr>
</tbody>
</table>

* indicates calorimetric method and ** estimation from phase diagram.

Thus, solid-liquid equilibrium data as well as liquid-vapour equilibrium data support the hypothesis of complex formation. The thermodynamic data for the latter can be quantitatively explained on this basis. In the next section we shall examine to what extent Ideal Associated Solution model is theoretically justified.

5. STATISTICAL MECHANICS OF ASSOCIATED MIXTURES

In order to get some justification for equation (2), attempts have been made to develop a statistical theory (ref 22) using a lattice model taking into account the orientation of the molecules. Each A and B molecule is supposed to occupy one site while \( A_m B_n \) species are supposed to occupy \( m+n \) sites similar to the theory of Flory and Higgins for polymer solutions. It may be noted that with one or two exceptions, the molar volume of A and B in the above mixtures are similar. An alternative theory (ref 22) involving cell model has also been developed. The sign of the excess thermodynamic functions is correctly predicted by the theory for dioxane + CHCl₃ and acetone + CHCl₃ mixture but the quantitative agreement is rather poor.

The major criticism of Ideal Associated Solution model has been associated with "the basic assumption that all solution
non-ideality is caused by the formation of new chemical species" and neglect of physical interaction. It may be noted that physical interaction is expected to be negligible if molar volume of A and B have similar magnitude. In the examples cited above, this is so. It may be noted that such complexes can be formed easily since reaction between A and B can even occur easily in such cases as exemplified by certain typical systems during recent years.

6. GEOMETRY OF COMPLEXES AND COMPLEXATION REACTION IN THE SOLID STATE

In reaction of the type being considered in the present communication, the complex may be formed by a) dipole-dipole interaction, b) dipole induced dipole interaction, c) charge-transfer interaction, and d) hydrogen bond interaction. It may be noted that (a) and (b) are involved in the formation of picrates of hydrocarbons and naphthols. In several complexes, A and B are stacked in parallel. Interplanar distances in several cases is found to range between 3 to 3.4 Å. In CBr₄-p-xylene and ferrocene-tetracyanoethylene complexes (ref 30,32), this distance is 3.36 and 3.14 Å. Parallel stacking has also been observed in hydrogen-bonded complexes such as 8-hydroxyquinoline-chloranil complex on the basis of X-ray studies.

In view of the simple geometry of such complexes, the process of complexation is an easy affair and even in the case of dipole-dipole interaction or dipole-induced dipole interaction distinct species (coloured) can be formed even by solid (A)- solid (B) interaction such as in the case of picrates of naphthalene and naphthols (ref 25-27).

Acknowledgements

Thanks are due to Indian Council of Scientific and Industrial Research for financial support. Author is also grateful to Director, Central Drug Research Institute Lucknow for providing necessary facilities.

REFERENCES


