A REVIEW PAPER ON THE EXCESS ENTHALPIES OF FEW BINARY FLUID MIXTURES FROM STATISTICAL THERMODYNAMIC CONSIDERATION

Dr. Naba Kumar Ghosh[1*]

Abstract:
Enthalpy of binary liquid mixtures of few systems is calculated from "Hard-Fluid" model using statistical thermodynamic consideration and using various thermodynamic parameters. This treatment is applied to few organic fluid mixtures. The calculated results are compared with the published experimental results and calculated results by other methods for certain cases and found to be satisfactory.

Keywords: Enthalpy, statistical thermodynamics, hard sphere, fluids, thermodynamic parameters.

[1*]Assistant Professor Department of Chemistry, Jangipur College, Jangipur, Mushidabed,West Bengal, India, Pin – 741235, Mail ID: naba1968@gmail.com

*Corresponding Author: Dr. Naba Kumar Ghosh
*Assistant Professor Department of Chemistry, Jangipur College, Jangipur, Mushidabed,West Bengal, India, Pin – 741235, Mail ID: naba1968@gmail.com

I.Introduction

Thermodynamic information for binary liquid mixtures such as cyclohexane + n-hexane, n-hexane+benzene, cyclohexane+carbontetrachloride, benzene+carbontetrachloride, cyclohexane+benzene, etc. should be very helpful for testing theories of solutions of non-electrolyte since the component liquids are made up of relatively simple molecules that can be prepared in high purity. Again, this helps chemists and engineers to get accurate data for design work, and it also gives physicists information on how the macroscopic characteristics of a mixture relate to the thermodynamic functions of these systems based on uncommon fundamental considerations that prevent the study of phase behavior.

(Colin et al., 1993) relationships were developed to calculate the excess thermodynamic functions of binary liquid combinations of polar and nonpolar substances; (Yosim& Owens, 1963) however, in this case, the system was particular to a mixture of benzene and acetonitrile, and no general theoretical equations that could be used to interpret experimental data had been developed. (Yosim, 1965)computed the excess entropy of a binary solution and the heat of vaporization of pure liquids using the findings of scale particle theory. (Huggins 1970)computed the heats of mixing of non-ionic binary solutions using the heat of vaporization data obtained. This study is an expansion of the author's earlier deductions regarding the thermodynamic properties of non-ionic liquid solutions (Huggins, 1937).

Our main goals are to create equations that will yield higher quantitative agreement with published experimental values than do existing theoretical equations, and to tie experimentally measured heats of mixing as closely as possible to molecular structure and intermolecular interactions. Here, we provide the findings of several systems' temperatures of mixing based on statistical thermodynamic analysis. Utilizing the hard sphere model for liquid mixtures, the contacts (a_i) have been computed based on a range of physico-chemical characteristics. Lastly, a discussion of the provided results based on intermolecular interactions and molecular structure has been held.

II. Calculations

The surface areas of the molecular groups, the interaction values per unit interaction, the constant for equilibrium, and the contact region of the different types of their contact values can all be used to determine the energy of intermolecular interactions in liquids like solutions. Equations based on vaporization of heat and mixing data of heat can be used to determine the magnitudes of the factors involved. Then, using these numbers, temperatures of vaporization for additional systems that have segments of the same kind can be predicted.

As the distance between two atoms increases, the interaction energy between those pairs decrease very quickly. The major portion of intermolecular liquid of energy is generated by interactions between atom pairs in adjacent molecules that are closest to one another.

All liquids have a structure that makes it impossible to the energy of atom-to-atom interactions can be directly added to determine the total intermolecular energy. With the exception of those that contain. Additionally, our current understanding of how these interaction energies vary on the distance between atoms, with the exception of simple ions, is inadequate (Huggins & Sakamoto, 1957)This is regrettably accurate, even in the crucial instance of H....H interactions.

This makes the use of a model imperative, with the hope that it will be straightforward enough to be used for experimental measurements on real solutions. The model that will be discussed must meet three requirements.

It is believed that each molecule has a molecular surface and other molecules' surfaces that come into interactions with one another have segments that differ chemically, meaning that different kinds of segments should interact with other segments of different molecules in different ways. These segments are thought to make up the molecular surface.

With subscripts i, j, etc. for segments ii, ij, jj, etc. for segment-segment contact, we can identify the different sorts of segments. Given a mole of substance on mixture, let a_i^o, a_j^o, etc. represent the intermolecular contacting surface areas. Assign the numbers a_j or a_i. To show the typical intermolecular surface area per mole of segment belonging to either i or j kinds. To show the average regions of the intermolecular interaction per mole, for each type of interaction, assign the numerals a_{ii}, a_{ij}, a_{jj} etc. For different types of intermolecular interaction, the average energies per unit contact area, are represented by letters ϵ_{ii}, ϵ_{ij}, and ϵ_{jj} respectively.

$$E_i = n_i a_i^o \frac{\epsilon_{ii}}{2}$$

$$1$$

$$E_j = n_j a_j^o \frac{\epsilon_{jj}}{2}$$

$$2$$

Where n_i(or n_j) is the number of (i or j) type of segment per molecule. In case of benzene,

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cyclohexane and carbon tetrachloride only one type of segment C-H (or $C - Cl$) is present and these molecules can be considered as a single segment. So, $n_i = n_j = 1$.

The surface tension of fluids γ has been expressed as follows by (Reiss&Schaaf, 1989) in the theory of rigid hand sphere liquids.

$$\gamma_i = \frac{KT}{4\pi\sigma_i^2}\left[\frac{12\eta}{1-\eta} + \frac{18\eta^2}{(1-\eta)^2}\right] - \frac{P\sigma_i}{2}$$

$$3$$

Where P is the pressure, η is pacting fractions and it is expressed as $\pi/6\,P\sigma_i^3$ & P_i is the number density, The Boltzmax constant K, the absolute temperature T and the hard sphere diameter (σ_i) of the fluid-containing molecule are rearranged Eq.3 we obtain

$$\gamma_i = \frac{1}{2}KT\sigma_i P_i\left[\frac{2-\eta-\eta^2}{(1-\eta)^3}\right] - \frac{1}{2}\,P\,\sigma_i$$

$$4$$

The rigid sphere model for fluids was used to determine the the power of vaporization for every hard-core particle.

$$E' = K\,T^2\,\alpha\left[\frac{(1+2\eta)^2}{(1-\eta)^3}\right]$$

$$5$$

Where α is the thermal expansivity is

$$\alpha = \frac{(1-\eta)^3}{T(1+2\eta)^2}$$

$$6$$

Substituting Eq.6 into Eq.5 yields

$$E' = KT\,\frac{(1+\eta^3)}{(1-\eta)^3}$$

$$7$$

Eliminating $(1-\eta)^3$ from Eq.4 and Eq.7

$$\gamma_i = \frac{1}{4}\sigma_i P_i\left[\frac{(2-\eta-\eta^2)}{(1-\eta)^3}\right]E' - \frac{1}{2}P\sigma_i$$

$$8$$

Since

$$P_i = \frac{N}{V_i} \text{ and } NE' = E_i$$

$$\gamma_i = \frac{1}{4}\sigma_i\left[\frac{(2-\eta-\eta^2)}{(1-\eta)^3}\right]\left(\frac{E_i}{V_i}\right) - \frac{1}{2}P\sigma_i$$

$$9$$

Where V_i is the molar volume. Thus Eq.9connects the surface tension with rigidity (γ_i)the cohesive energy liquid (E_i). The excess enthalpy per mole, sometimes referred to as the molar heat of mixing, is the difference between the mass of the components multiplied by their mole fractions in the solution and the actual mass of one mole of solution.

$$H^E = H - x_i H_i - x_j H_j$$
$$= E - x_i E_i - x_j E_j$$

$$10$$

Again the expressions for heat of mixing previously deduced by the author is,

$$H^E = \frac{a_i^0\Delta\epsilon}{2}\left[\frac{r\,(x_j - x_j^2)}{1 + x_j\,(r-1)}\right]$$

$$11$$

where $\triangle E$ is the attraction energy of the binary mixture and is given by the author is,

$$\Delta\epsilon = 2\epsilon_{i,j} - \epsilon_j - \epsilon_i$$

$$12$$

$$r = a_j^0/a_i^0$$

$$13$$

$$\epsilon_{i,j} = \sqrt{\epsilon_i, \epsilon_j}$$

$$14$$

and x_j is the mole fraction of one of the components.

The cohesion energy can be calculated from Eq.9 since other parameters are known. The attractive energies of the single component are known. So, from Eq.1 and 2 a_i^0 and a_j^0 can be calculated. Therefore, heats of mixing as a function of mole fraction can be calculated from Eq.11.

III. Results and Discussion

The parameter required for pure components in Table 1.

Table 1 : Parameters for pure components at 25° C

Component	γ (dynes/cm)	σ (Å)	E/K (°k)	E (kcal/mol)
CCl_4	25.5	5.18	497	7.18
C_6H_6	27.5	5.02	308	6.81
$c - C_6H_{12}$	23.7	5.33	313	6.21
$n - C_6H_{14}$	17.4	5.81	413	6.35

The surface tension of pure liquids has been used to compute cohesion energy values. The system under study is made up of tiny, roughly spherical molecules. As a result, the mixture's molecular interactions should be accurately represented by the Lennard-Jones potential. This makes these mixtures seem appropriate for the theory's crucial assignment. The computation of the results shown in Table 3 was done assuming the validity of the (Calvin & Reed, 1971) combining rules, which

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means that the Lennard-Jones parameters for the interaction between dissimilar molecular species are provided by,

$$\epsilon_{i,j} = \sqrt{\epsilon_i, \epsilon_j}$$

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We see an unsatisfactory concordance between our values and the experimental results. Specifically, there is a relatively slight difference in the extra enthalpies, which can be partly explained by not following the Lorentz-Bertholet equations and partly by inaccuracies in the selected potential values. Regarding the former, it may be said that these combining rules for the realistic molecules have no compelling evidence to support their validity. Therefore, it would seem to be beneficial to look at how these rules' exceptions affect mixing's characteristics$\epsilon_{i,j}$, the depth of a system's potential energy curve, is given in eq.15. The relationship mentioned above is valid for gaseous states that obey the Lennard-Jones potential. However, unlike in the case of gases, interactions between molecules are more complex in liquids. Thus, the depth of the mixture's potential differs from the relation when the two fluids are mixed. It will be necessary to thoroughly examine the interactions between molecules I and J using the principles of quantum mechanics in order to determine the relationship. The ad hoc linkages listed below are therefore suggested.

$$\epsilon_{i,j} = \sqrt{\epsilon_i, \epsilon_j} \, (1 + \beta)$$

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Where β is a changeable parameter in this case. It is permitted to vary by $\pm 5\%$. Table 2 provides approximate values of β, and Table 3 provides the enthalpies of mixing for equimolar mixtures in order to achieve good results for various systems.

Table 2 : Parameters for different mixtures

System	r	β	σ_i/σ_j	$a_i^\circ \Delta \in$
$C_6H_6 + CCl_4$	1.53	0.037	1.032	0.1706
$c\text{-}C_6H_{12} + CCl_4$	1.37	0.037	1.03	0.250
$C_6H_6 + c\text{-}C_6H_{12}$	1.131	0.05	1.055	1.2127
$C_6H_6 + \eta - C_6H_{14}$	1.44	0.05	1.097	0.8580
$\eta - C_6H_{14} + c - C_6H_{12}$	1.29	0.027	1.033	0.3823

In each system A,B and C three pets of data, which represent respectively the enthalpies of mixing calculated Eq.11. from various physic-chemical properties, calculate by the Huggin's and experimental data (Chung &Espenscheid, 1967)

Table 3 : Enthalpy of mixing at $25^\circ C$

System	Enthalpy of mixing (cal/mol) at x_2=0.5		
	A	B	C
$C_6H_6 + CCl_4$	27.4	27.4	27.0
$c\text{-}C_6H_{12} + CCl_4$	35.05	35.1	35.0
$C_6H_6 + C - C_6H_{12}$	181.1	185.7	195$\pm$5
$C_6H_6 + \eta - C_6H_{14}$	128	-	205.0
$\eta\text{-}C_6H_{14} + CC_6H_{12}$	52.8	-	51$\pm$1

IV. Conclusion

It is possible to choose a combination rule that produces findings that are in good agreement with experiments. It is interesting to note that optimum choice of $(1 + \beta)$ in Eq.16 for all systems, approximately correspond to the diameter ratios of hand sphere in the mixture. We can then write Eq.16 in the form

$$\epsilon_{i,j} = \sqrt{\epsilon_i \epsilon_j} \, (\sigma_i/\sigma_j)$$

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Where $\sigma_i > \sigma_j$

But here the results are not so satisfactory as with the results obtained, from eq.16. Approximate choice of hard cord diameters may give satisfactory results.

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