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Theoretical Formulation and Thermo–Optical Analysis on the Binary Acid-Acid Mixtures for the Identification of Eutectic Mixtures as a Function of Coefficient of Linear Thermal Expansion

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Abstract
A theoretical co-relation between coefficient of thermal expansion and melting point of the eutectic mixture has been developed. For the experimental verification of the developed co-relation, six different carboxylic acids namely; $CH_2(COOH)_2$, $(CH_2)_2(COOH)_2$, $(CH_2)_4(COOH)_2$, C_6H_5COOH, $C_6H_4(OH)COOH$, $(COOH)_2$ were taken. Their binary mixtures were prepared like Malonic Acid-Benzoic Acid, Succinic Acid-O-Salicylic Acid, Malonic Acid-Succinic Acid, Benzoic Acid-Oxalic Acid, Succinic Acid-Benzoic Acid and Adipic Acid-Benzoic Acid. For each Acid-Acid combination there were nine different compositions i.e. 1:9 or 10%, 2:8 or 20%, 3:7 or 30%, 4:6 or 40%, 5:5 or 50%, 6:4 or 60%, 7:3 or 70%, 8:2 or 80% and 9:1 or 90%. Each composition was then analyzed by thermo-optical method with the help of optical dilatometer to get their coefficient of linear thermal expansion. As a conclusion it was experimentally found that the composition which was having highest value of CLTE was the eutectic mixture because it was having the lowest melting point as well. This was the theoretical formulation and experimental verification for the identification of eutectic mixtures as a function of CLTE.
Key Words: *Eutectic Mixture, Oxalic acid ($C_2H_2O_4$), Malonic acid ($C_3H_4O_4$), Succinic acid ($C_4H_6O_4$), Salicylic acid ($C_7H_6O_3$), Benzoic acid ($C_7H_6O_2$), Adipic acid ($C_6H_{10}O_4$), CLTE (Coefficient of linear thermal expansion).*

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I. Introduction

In this chapter we have developed a co-relation between the eutectic mixture and coefficient of thermal expansion of that composition. In simpler form it has been said that in old and traditional methodology eutectic mixture has been determined by the lowest melting point of the particular composition only, however, in the present context eutectic mixtures can be identified from the value of coefficient of thermal expansion[1],[3]. This is very much useful rather because of its easy approach, time saving, energy saving and more accurate measurements. Unlike melting point determination of different compositions, determination of linear thermal expansion or coefficient of linear thermal expansion is an easy task to do. Melting point apparatus are generally renowned for giving inaccurate results or they are calibrated by using benzoic acid to get the accurate value of the melting point but optical dilatometer don't require such calibrations[2]. In this methodology or technique we don't need to go up to melting point of the particular composition, rather quite below the melting point of that composition we are able to find the coefficient of thermal expansion and hence identification of the eutectic mixture is simpler and easy[4],[5]. So, by eutectic mixture identification as a function of linear thermal expansion/coefficient of linear thermal expansion this target has been achieved.

II. Theoretical Formulation of The Relation Between Coefficient of Thermal Expansion And Eutectic Temperature

Coefficient of thermal expansion (α) is equal to the linear expansion (ΔL) during the unit degree increase in temperature in the unit length of the material. Mathematically it is expressed as follows:

$$\text{As,}\quad \alpha = \Delta L / L\,\Delta T \qquad \ldots (1)$$

In this relation, ΔL is the change in length of the sample i.e. $\Delta L = (L_f - L_i)$ and ΔT is the increase in temperature i.e. $\Delta T = (T_f - T_i)$. If the increase in length i.e. ΔL is taken as fixed e.g. 10×10^{-4}, and the length of the sample i.e. L is already taken as fixed e.g. 20 mm then equation (1) will change into a new equation in which coefficient of thermal expansion is a function of change in temperature only:

$$\text{i.e.}\quad \alpha \propto 1 / \Delta T \qquad \ldots (2)$$

This ΔT is the temperature that expands the substance by increasing kinetic energy of their molecules, which in turn increases the molecular vibrations. $ø_m$ is the melting temperature of the sample. When this $ø_m$ will have lowest value, that will be the eutectic temperature and that mixture will be the eutectic mixture. If for a particular material more temperature is needed to expand the molecules then the melting temperature of that sample would also be higher. So, ΔT will be directly proportional to $\varnothing_m$.

$$\text{i.e.} \quad \Delta T \propto \varnothing_m \qquad \dots (3)$$

Using equations (2) and (3) we can write as follows:

$$[\ \alpha \propto 1 / \varnothing_m\ ] \qquad \dots (4)$$

In other words we can say that coefficient of linear thermal expansion (CLTE) is a function of melting temperature of the eutectic mixture or CLTE depends inversely on the melting temperature of the eutectic mixture.

$$\text{i.e.} \ \alpha = f(\varnothing_m) \qquad \dots (5)$$

From equation (4) we may conclude that for a particular change in length if increase in temperature is smaller then the coefficient of thermal expansion will have higher value i.e. that particular material under investigation is melting at lower temperature or melting point is lower. Similarly, highest value of coefficient of thermal expansion (α) will provide us the lowest melting temperature of the sample i.e. eutectic temperature. Once eutectic temperature is known then eutectic composition of the eutectic mixture would also be easily found out correspondingly.

III. Material And Methods

We had taken six different samples of Acid-Acid mixtures namely; Malonic Acid-Benzoic Acid, Succinic Acid-O-Salicylic Acid, Malonic Acid-Succinic Acid, Benzoic Acid-Oxalic Acid, Succinic Acid-Benzoic Acid and Adipic Acid-Benzoic Acid. For each Acid-Acid combination there were nine different compositions i.e. 1:9 or 10%, 2:8 or 20%, 3:7 or 30%, 4:6 or 40%, 5:5 or 50%, 6:4 or 60%, 7:3 or 70%, 8:2 or 80% and 9:1 or 90%. Every composition was initially mixed properly in pestle and mortar and then its sample of desired dimensions were prepared by simultaneous heating and stirring process.

The sample with length 20mm and height 10mm was positioned at the center of the disc-shaped furnace which was not subjected to external forces. Thin samples could also be easily analyzed with the sample holder, especially designed for this purpose [6], [7]. In this regards a high-performance LED was used to emit a planar broad width light beam over the sample. The shadow of the sample was detected by a high quality high-resolution charged-coupled device sensor i.e. "CCD Sensor" then the signal was evaluated by a digital edge-detection processor which as a result provided a sensitive & correct measurement of dimensional change of the material under investigation [8]. As in this technique shadow of the sample was used and detected, so this principle is also known as the "Shadowed Light Method" which provides absolute & accurate measurements of the sample dimensions with respect to change in temperature.

In this technique the sample size was taken with length ranging from 0.3mm to 30mm and maximum height 10mm. However whatsoever length of the sample was taken, the initial length of the sample was automatically determined and saved for the different calculations of the linear thermal expansion coefficient [9], [10]. The furnace of the DIL806 was capable of rapid heating speeds up to 100°C per minutes and cooling times from 1400°C to 50°C in less than 10 minutes.

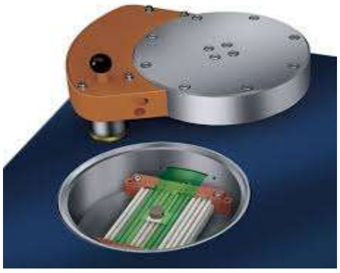
DIL806 provides uniform temperature across the sample i.e. horizontally as well as vertically. The sample was positioned at the center of a disc-shaped furnace with quick response. The design ensures uniform temperature homogeneity of the temperature across the entire sample over the entire temperature analytical range also at fast heating & cooling rates. DIL806 had highly effective control on the environmental conditions happening during a test which enables the users to analyze sample not only in air but also under vacuum and in an inert atmosphere which was a key requirements for the analysis of metals and metal-alloys[11], [12].

From the above experimentation the linear thermal expansion (ΔL) is calculated by the following relation:

$$\Delta L = CN/M \qquad \dots (6)$$

Where, 'C' is interval of CCD pixel,
'N' is the number of CCD pixels of two sample-edges,
'M' is the magnification of the optical system.

Then from ΔL, the coefficient of linear thermal expansion CLTE or 'α' was calculated by the relation; $\alpha = \Delta L / L\ \Delta T$. The experimental data was obtained and for every data, graphical representations were also obtained for proper understanding of the investigation conducted [13].



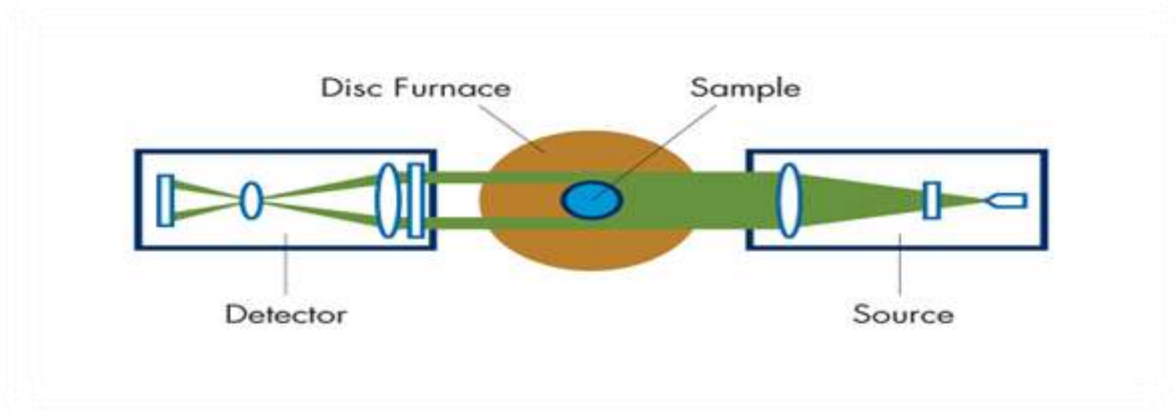


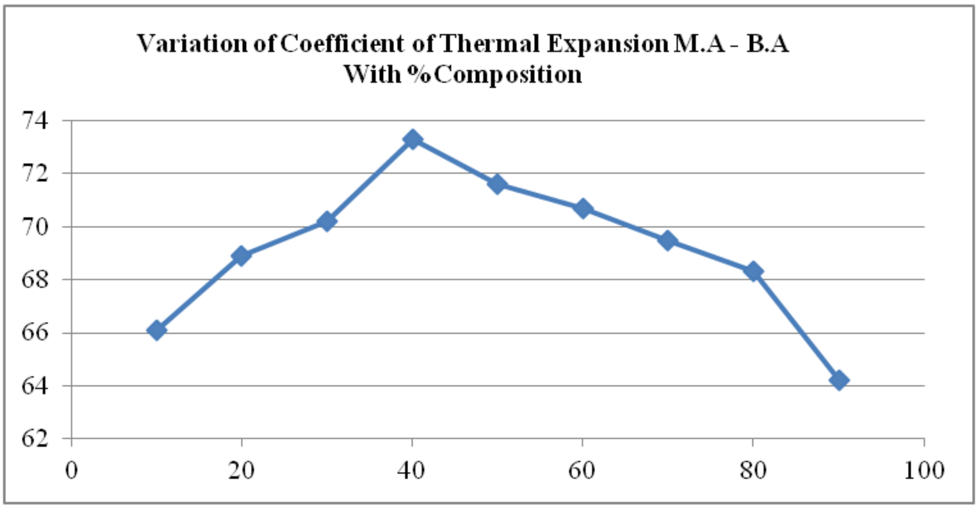
Fig 6.2: Working diagram of optical dilatometer DIL806

IV. Result

From the varying compositions of every acid-acid sample, coefficient of thermal expansion has been recorded with the help of optical dilatometer (DIL806). The requisite experimental data and their graphical representations are being provided in this section:

1. "Malonic Acid - Benzoic Acid" Mixtures

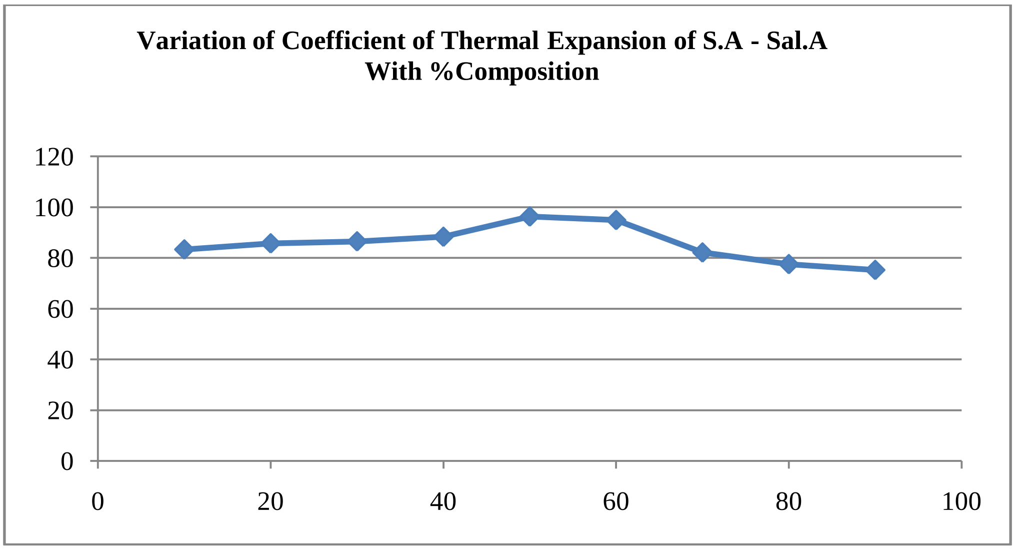
Sr. No.	Ratio (M.A : B.A)	Composition (%)	Coefficient of Thermal Expansion ($\times 10^{-6} K^{-1}$)
1	1:9	10	66.1
2	2:8	20	68.9
3	3:7	30	70.2
4	4:6	40	73.3
5	5:5	50	71.6
6	6:4	60	70.7
7	7:3	70	69.5
8	8:2	80	68.3
9	9:1	90	64.2



Coclusion: At "40% Malonic Acid – 60% Benzoic Acid" CTE is maximum, so this is the Eutectic Mixture.

2. "Succinic Acid - O-Salicylic Acid" Mixtures

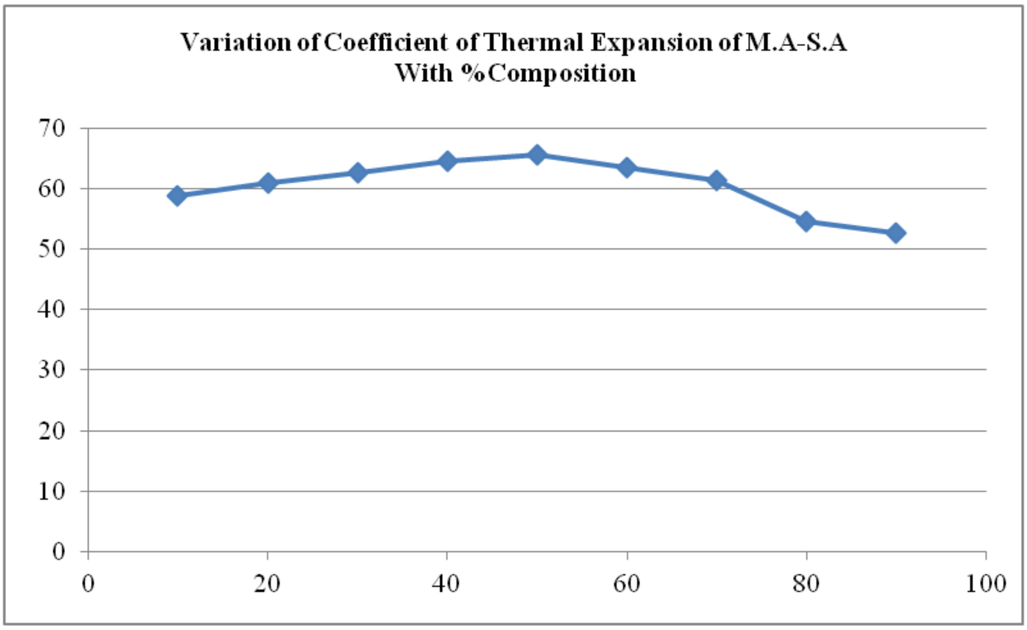
Sr. No.	Ratio (S.A : Sal.A)	Composition (%)	Coefficient of Thermal Expansion ($\times 10^{-6}$ K^{-1})
1	1:9	10	83.3
2	2:8	20	85.7
3	3:7	30	86.5
4	4:6	40	88.3
5	5:5	50	96.3
6	6:4	60	94.9
7	7:3	70	82.1
8	8:2	80	77.5
9	9:1	90	75.2



Coclusion: At "50% Succinic Acid – 50% O-Salicylic Acid" CTE is maximum, so this is the Eutectic Mixture.

3. "Malonic Acid - Succinic Acid" Mixtures

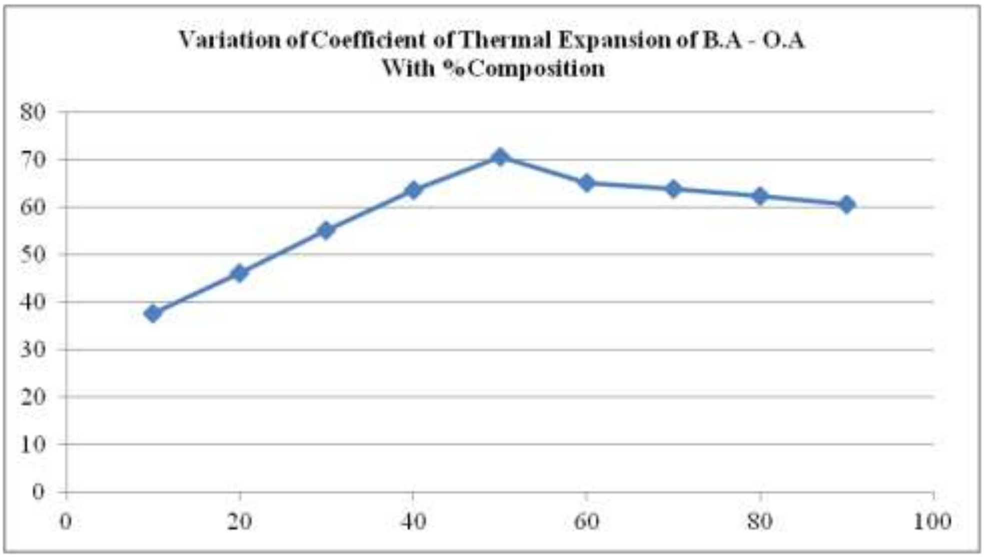
Sr. No.	Ratio (M.A : S.A)	Composition (%)	Coefficient of Thermal Expansion ($\times 10^{-6}$ K^{-1})
1	1:9	10	58.8
2	2:8	20	60.9
3	3:7	30	62.7
4	4:6	40	64.5
5	5:5	50	65.6
6	6:4	60	63.4
7	7:3	70	61.3
8	8:2	80	54.6
9	9:1	90	52.7



Coclusion: At "50% Malonic Acid – 50% Succinic Acid" CTE is maximum, so this is the Eutectic Mixture.

4. "Benzoic Acid - Oxalic Acid" Mixtures

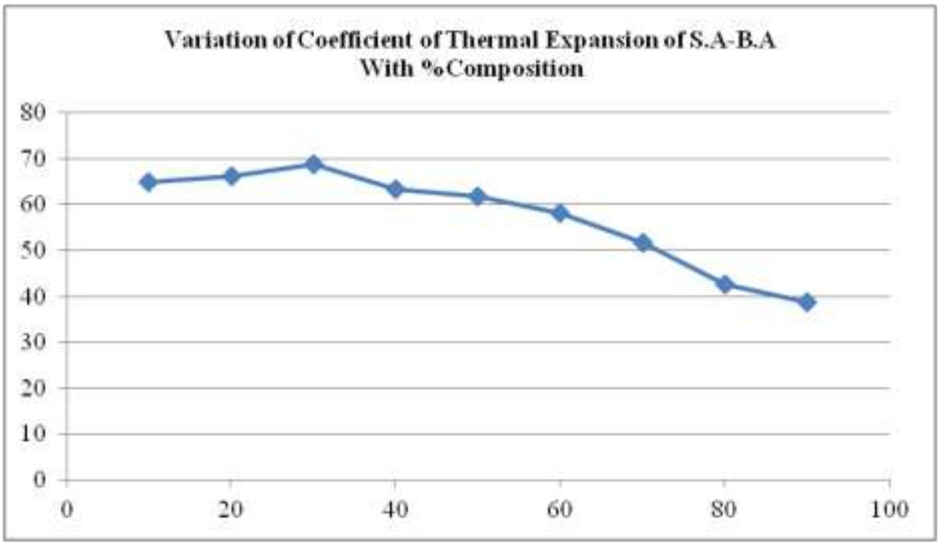
Sr. No.	Ratio (B.A : O.A)	Composition (%)	Coefficient of Thermal Expansion ($\times 10^{-6}$ K^{-1})
1	1:9	10	37.8
2	2:8	20	46.3
3	3:7	30	55.1
4	4:6	40	63.6
5	5:5	50	70.6
6	6:4	60	65.2
7	7:3	70	64.0
8	8:2	80	62.5
9	9:1	90	60.7



Conclusion: At "50% Benzoic Acid – 50% Oxalic Acid" CTE is maximum, so this is the Eutectic Mixture.

5. "Succinic Acid - Benzoic Acid" Mixtures

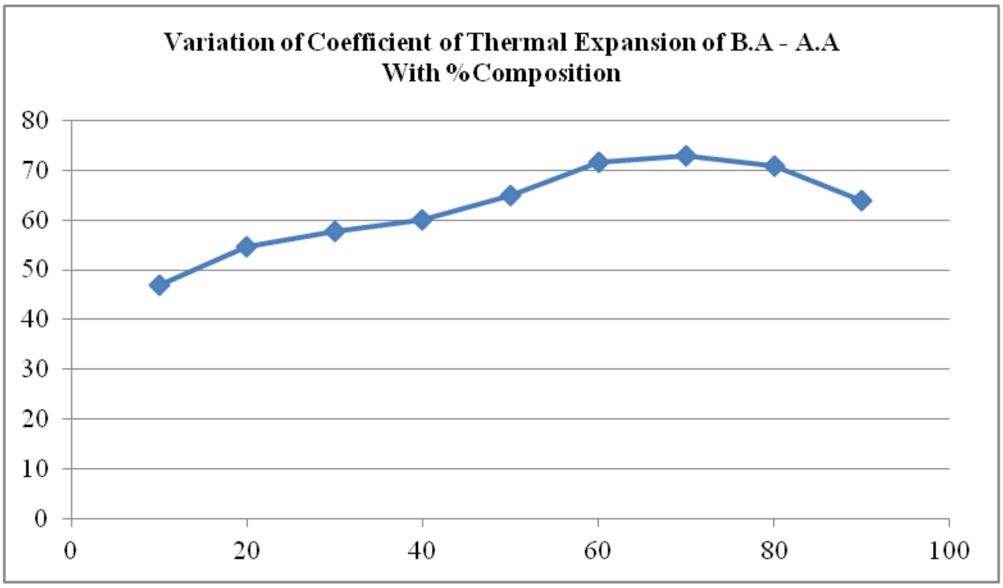
Sr. No.	Ratio (S.A : B.A)	Composition (%)	Coefficient of Thermal Expansion ($\times 10^{-6} K^{-1}$)
1	1:9	10	64.8
2	2:8	20	66.3
3	3:7	30	68.8
4	4:6	40	63.3
5	5:5	50	61.9
6	6:4	60	58.2
7	7:3	70	51.8
8	8:2	80	42.5
9	9:1	90	38.7



Conclusion: At "30% Succinic Acid – 70% Benzoic Acid" CTE is maximum, so this is the Eutectic Mixture.

6. "Benzoic Acid – Adipic Acid" Mixtures

Sr. No.	Ratio (B.A : A.A)	Composition (%)	Coefficient of Thermal Expansion ($\times 10^{-6} K^{-1}$)
1	1:9	10	46.8
2	2:8	20	54.6
3	3:7	30	57.8
4	4:6	40	60.0
5	5:5	50	64.9
6	6:4	60	71.7
7	7:3	70	72.9
8	8:2	80	70.8
9	9:1	90	64.0



Conclusion: At "70% Benzoic Acid – 30% Adipic Acid" CTE is maximum, so this is the Eutectic Mixture.

V. Discussion

All the results obtained from the above experimentation showed that the composition which showed maximum value of coefficient of linear thermal expansion (CLTE) was the eutectic composition or eutectic mixture. This data was also verified from the eutectic temperatures calculated by differential scanning calorimetry, shown in table (1). Lowest temperature was showing highest CLTE value in every composition/eutectic mixture. This clearly indicated that at eutectic composition the intermolecular interactions are weakened due to which melting point becomes lowest and hence coefficient of thermal expansion value becomes highest. The theoretical formulation in this paper has also proved that CLTE is inversely proportional to melting temperature of the eutectic mixtures. Due to high efficacy of the instrument and its digital edge-detection processor the results provided were absolutely correct and sensitive. Though in certain cases thermo-optical analysis also show negative linear thermal expansion i.e. contraction of the material takes place with temperature, this might be due to bending of bonds which absorbs the lattice expansion by changing the position of atoms in the sample, however, in these acid-acid mixtures we always found the positive linear thermal expansion, which clearly indicated the lowering in temperature with the expansion of the sample under thermal investigation.

VI. Conclusion

Coefficient of linear thermal expansion (CLTE) of the binary acid-acid eutectic mixtures under investigation has been found to be dependent on melting temperature. CLTE was verying inversely with respect to melting temperature of eutectic mixtures. As lowest melting point represents the eutectic mixture. So it has been finally concluded that from highest value of CLTE corresponding eutectic mixture can be easily identified. This was the thermo-optical analysis of eutectic mixtures as a function of CLTE.

Table 1.

Sr. No.	Name of Eutectic mixture	Mole fraction	Eutectic Temp (k)
1.	Malonic acid + Succnic acid	0.530	392.33
2.	Malonic acid + Benzoic acid	0.401	378.16
3.	Succinic acid + Salicylic acid (ortho)	0.532	310.66
4.	Succinic acid + Benzoic acid	0.301	389.16
5.	Benzoic acid + Oxalic acid	0.501	388.16
6.	Benzoic acid + Adipic acid	0.701	378.16

Table 1: *Showing eutectic temperatures and eutectic compositions determined by DSC*

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