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Dependence of Eutectic - Composition on Densities of Components of Binary Eutectic Mixtures of Solid Carboxylic Acids

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Abstract: *At eutectic point the composition was richer with that component which had lower density in comparison to the component of higher density, namely; Malonic acid(50%)-Succinic acid(50%) -stoichiometric ratio1:1, Malonic acid(40%)-Benzoic acid(60%) -stoichiometric ratio2:3, Succinic acid(30%)-Benzoic acid(70%) -stoichiometeic ratio 1:2.3, Salicylic acid(50%)-Malonic acid(50%) -stoichiometric ratio1:1, Salicylic acid(30%)-Benzoic acid(70%) -stoichiometric ratio 1:2.3, Benzoic acid(70%)-Oxalic acid(30%)-stoichiometric ratio 2.3:1.Components with similar densities were having stoichiometric ratio 1:1 whereas components with different densities were having different stoichiometric ratios and at the eutectic point the component with lower density could accommodate the other component with higher density into its empty sites, that's why at eutectic point the component with lower density was found to be present in higher proportions in comparisons to the other component with higher density. In this way, after mixing, the components were present in the free spaces of each other due to which old strong forces get weakened to the maximum extent and hence melting point of the eutectic mixture became lowest.*

Keywords: *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($C_7H_6O_2$).*

I. Introduction

In the present paper we have prepared some binary eutectic mixtures of carboxylic acids whose Eutectic-Compositions and Eutectic-Temperatures were determined from the phase diagram studies. We tried to find out that why Eutectic-Composition did not come to be 50% - 50% (or stoichiometric ratio 1:1) for both the components of Binary Eutectic Mixtures always, rather in most of the Eutectic Mixtures the Eutectic-Composition found to be different than stoichiometric ratio 1:1. Analysis showed that Eutectic-Composition found to be dependent on densities of both the components of Binary Eutectic Mixtures. Hence Eutectic-Composition is the function of densities of the components. So in this Paper we have studied the dependence of Eutectic-Composition on the densities of the "Components". We took some solid carboxylic acids namely oxalic acid, malonic acid, succinic acid, benzoic acid and ortho-salicylic acid whose melting points were within the oil-bath range and hence their melting can be easily attained. As their melting points were easily approachable so we could not get any difficulty to determine their Eutectic-Compositions and Eutectic Temperatures[1,2]. In this way we studied Eutectic–Composition of each Mixture w.r.t the densities of the components. Hence we came to know that when a component of lower density is present in higher proportions then lowest melting point (Eutectic Point) is achieved. Our next plan of action would be to determine the biological and thermodynamical properties[3-5] of these binary eutectic mixtures using DSC(or DTA) techniques.

Such low melting Eutectic-Compositions of carboxylic acids were found to be very useful in various fields.

For example, eutectic mixture of capric acid ($C_9H_{19}COOH$) and lauric acid ($C_{11}H_{23}COOH$) are applied in building wall boards for heat energy storage, these are known as Phase Change Materials (PCM).Similarly eutectic mixture of stearic acid($C_{17}H_{23}COOH$) and lauric acid($C_{11}H_{23}COOH$) is used in Thermal Energy Storage Systems (TES), such systems have the ability to store high or low- temperature energy for later use[6].

Eutectic mixtures of some carboxylic acids (selected from α-hydroxy acid, β-hydroxy acid and retinoic acid) are also used in cosmetic compositions. Such mixtures are liquid at room temperature and are relatively non-irritating and can be used to deliver higher levels of the principal acid than it would ordinarily be possible. A hair/scalp care composition in which the eutectic mixture further comprises an organic acid from the list consisting of salicylic acid, benzoic acid and mixture thereof[7-9].

II. Experimental

Experimental work was divided into different tasks:

TASK 1: Selection Of Materials For The Formation Of Eutectic Mixture:

1.1 This involved literature review[10-14]; identification of suitable material for eutectic mixture.

1.2 Materials are chosen in such a way that their melting point were within the range of oil-bath. For this purpose some solid acids were selected in Table(1):

Name of solid acid	Melting point (K)	Melting point(K) (Literature)
Oxalic acid	461	462-464
Malonic acid	407.5	408-409
Succinic acid	458	458-460
Benzoic acid	394	395
Salicylic acid	430.5	432

Table (1)

TASK 2: Methods Of Purification:

Benzoic acid, Malonic acid Succinic acid and Salicylic acid (ortho) were purified by repeated recrystallization from hot water . Oxalic acid was purified by sublimation. Adipic acid was recrystallized and purified from warm alcohols[15]. Then purification of the samples was verified by comparing melting points (experimental) with those of melting point (actual).

TASK 3: Preparation Of Different Mixture With Varying Composition:

For determination of phase diagram Acid-Acid samples were taken in the ratio varying from 0:10 to 10:0 (from 0% to 100%). The particular composition was mixed and taken in a boiling test tube and then heated above the melting point of higher melting component. This melting process was repeated three to four times to ensure uniform mixing of the given Acid-Acid components.

TASK 4: Determination Of Eutectic-Temperature And Hence % Composition Of The Eutectic Mixture:

For this purpose different compositions of a particular Acid-Acid mixture were taken (from 0:10 to 10:0 i.e. from 0% to 100%) and their melting points were noted for at least three times and their average was taken as given in table (2) to table (7).

Malonic acid-Succinic acid:

Sr. No	Ratio (M.A : S.A)	% Composition	Melting Point(K)
1.	0:10	0	458.16
2.	1:9	10	441.16
3.	2:8	20	400.16
4.	3:7	30	398.66
5.	4:6	40	393.66
6.	5:5	50	392.16
7.	6:4	60	394.16
8.	7:3	70	397.66
9.	8:2	80	401.16
10.	9:1	90	403.16
11.	10:0	100	407.66

Table (2)

Malonic acid-Benzoic acid:

Sr. No	Ratio (M.A : B.A)	% Composition	Melting Point(K)
1.	0:10	0	394.16
2.	1:9	10	390.16
3.	2:8	20	387.33
4.	3:7	30	383.16
5.	4:6	40	378.16
6.	5:5	50	380.16
7.	6:4	60	382.66
8.	7:3	70	385.16
9.	8:2	80	388.33

10.	9:1	90	395.16
11.	10:0	100	407.66

Table (3)

Succinic acid-Benzoic acid:

Sr. No	**Ratio (S.A : B.A)**	**% Composition**	**Melting Point(K)**
1.	0:10	0	394.16
2.	1:9	10	392.16
3.	2:8	20	391.66
4.	3:7	30	389.16
5.	4:6	40	393.16
6.	5:5	50	395.16
7.	6:4	60	406.66
8.	7:3	70	428.16
9.	8:2	80	445.16
10.	9:1	90	453.66
11.	10:0	100	458.16

Table (4)

Salicylic acid-Malonic acid:

Sr. No	**Ratio (Sal.A : M.A)**	**% Composition**	Melting Point(K)
1.	0:10	0	407.16
2.	1:9	10	387.16
3.	2:8	20	375.66
4.	3:7	30	363.33
5.	4:6	40	362.66
6.	5:5	50	360.66
7.	6:4	60	373.33
8.	7:3	70	387.16
9.	8:2	80	407.16
10.	9:1	90	418.33
11.	10:0	100	430.66

Table (5)

Salicylic acid (o)-Benzoic acid:

Sr. No	**Ratio (Sal. A : B.A)**	**% Composition**	**Melting Point(K)**
1.	0:10	0	394.16
2.	1:9	10	390.16
3.	2:8	20	385.66
4.	3:7	30	380.33
5.	4:6	40	394.16
6.	5:5	50	405.33
7.	6:4	60	411.66
8.	7:3	70	417.33
9.	8:2	80	425.33
10.	9:1	90	428.16
11.	10:0	100	430.66

Table (6)

Benzoic acid-Oxalic acid:

Sr. No	Ratio (B.A : O.A)	% Composition	Melting Point(K)
1.	0:10	0	461.16
2.	1:9	10	443.16
3.	2:8	20	433.33
4.	3:7	30	414.66
5.	4:6	40	393.16
6.	5:5	50	388.33
7.	6:4	60	387.66
8.	7:3	70	391.16
9.	8:2	80	392.16
10.	9:1	90	392.66
11.	10:0	100	394.16

Table (7)

III. Results And Discussions

Eutectic-Compositions of different binary eutectic mixtures of carboxylic acids were summarized in table (8):

Sr. No	% COMPOSITION	EUTECTIC MIXTURE	Eutectic Temperature (K)
1.	Malonic acid(50%) Succinic acid(50%)	Malonic acid-Succinic acid	392.16
2.	Malonic acid(40%) Benzoic acid(60%)	Malonic acid-Benzoic acid	380.16
3.	Succinic acid(30%) Benzoic acid(70%)	Succinic acid-Benzoic acid	389.16
4.	Salicylic acid(50%) Malonic acid(50%)	Salicylic acid-Malonic acid	360.66
5.	Salicylic acid(30%) Benzoic acid(70%)	Salicylic acid-Benzoic acid	380.33
6.	Benzoic acid(60%) Oxalic acid(40%)	Benzoic acid-Oxalic acid	387.66

Table (8)

It was clear that the stoichiometric ratio for Malonic acid-Succinic acid Salicylic acid–Malonic acid eutectic mixtures were 1:1, whearas those of Malonic acid–Benzoic acid, Succinic acid–Benzoic acid, Salicylic acid–Benzoic acid and Benzoic acid–Oxalic acid were 2:3, 1:2.3, 1:2.3 and 3:2 respectively. The stoichiometric ratio; 1:1 indicated that both the components might have same densities whereas the stoichiometric ratio; 2:3 in case of Malonic acid–Benzoic acid showed that eutectic mixture was richer with Benzoic acid. Similarly stoichiometric ratio; 3:2 for Benzoic acid–Oxalic acid showed that eutectic mixture was richer with Benzoic acid. In case of Succinic acid–Benzoic acid and Salicylic–Benzoic acid the stoichiometric ratio was found to be 1:2.3 which again showed that both of these eutectic mixtures were richer with Benzoic acid.

IV. Conclusion :

The above discussion was in agreement with the densities of different acid-components as given in table (9). In the eutectic mixture the component which had higher density is present in the vacant spaces of the second component whose density is lower. In this way the component of lower density accommodated the component with higher density, so the component with lower density is present in more proportions in comparison to the component with higher density. In simple words we could say that some new interactions had weakened the old bonds of both the components during eutectic mixture formation due to which melting point of both the components had decreased to a lower value.

Acid component	Density (gm/ cc)
Oxalic acid	1.90
Malonic acid	1.62

Succinic acid	1.56
Benzoic acid	1.32
Salicylic acid	1.44

Table (9)

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