



Thermal and Interfacial Studies of Binary Alloys of Nicotinamide- β -Naphthol Drug System

H. SHEKHAR and VISHNU KANT*

Department of Chemistry, Veer Kunwar Singh University, Ara-802 301, India

*Corresponding author: E-mail: imvishnukant@gmail.com

(Received: 28 December 2011;

Accepted: 9 November 2012)

AJC-12377

The study reports the thermal and growth investigation of binary alloys represented by nicotinamide with β -naphthol. The solid-liquid equilibrium data determined by Thaw-melt method with their corresponding compositions construct the solid-liquid phase diagram which suggests simple eutectic behaviour is followed by the binary system. The activity coefficient model based on enthalpy of fusion was employed to calculate the excess thermodynamic properties that of g^E , h^E and s^E , which predict the nature of molecular interaction, ordering and stability between the components. The partial and integral mixing functions ΔG^M , ΔH^M , ΔS^M of the eutectic and noneutectic alloys were also computed. The driving force of nucleation during solidification (ΔG_v), critical size or radius (r^*) and the critical free energy of nucleation (ΔG^*) at different undercoolings have been determined. Using heat of fusion data the solid-liquid interface energy (σ), grain boundary energy (σ_{gb}), the Gibbs-Thomson coefficient (τ) and roughness parameter (α) of all the alloys are evaluated by numerical method. Interface morphology of the alloys follows the Jackson's surface roughness (α) theory and predicts the faceted growth proceeds in all the alloys.

Key Words: Phase diagram, Thermodynamic excess and mixing functions, Critical radius, Interfacial energy, Roughness parameter.

INTRODUCTION

It is well known that nicotinamide (niacinamide)/nicotinic acid (niacine) is useful in measuring pellagra preventive factors (PPF). It is a water soluble component of the vitamin B complex group. *In vivo*, nicotinamide is incorporated into nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). The physiological function and pharmaceutical action of NAD and NADP is to function as enzymes in a wide variety of enzymatic oxidation-reduction reactions essential for tissue respiration, lipid metabolism and glycogenolysis. It is mainly used in two principle forms together with niacin both as food nutrient and a drug. It may be beneficial in patients with inflammatory acne vulgaris, including but not limited to, suppression of antigen induced-lymphocytic transformation and inhibition of 3'-5' cycle AMP phosphodiesterase. It has demonstrated^{1,2} the ability to block the inflammatory actions of iodides known to precipitate or exacerbate inflammatory acne. It lacks the vasodilator, gastrointestinal, hepatic and hypolipemic action of niacin. As such nicotinamide has not been shown to produce the flushing, itching and burning sensations of the skin as is commonly seen when large doses of niacin are administered orally. Nicam gel is most effective when applied to the skin, which helps to reduce the inflammation and redness of inflammatory acne.

β -Naphthol is also employed in pharmaceutical, agricultural and rubber industries.

The process of solidification plays a vital role in obtaining homogeneous materials of high quality. It has been a great dream of scientists for a long time to find the techniques which control the properties of cast structures because the structure formed immediately after solidification determines the properties of the final products. Due to various difficulties encountered, while working with metallic systems, the interesting idea of observing the solidification phenomena using transparent model³⁻⁶ is being worked with great enthusiasm all over the world. It has been found that at small driving forces, the existence of rough interface leads the necessity for stepwise growth. Only at sufficiently high driving forces a surface can advance uniformly. Observation on melting and freezing of *p*-toluidine offered a direct demonstration of the validity of lateral mechanism. With view to achieve better drug products in binary form, the transparent and pharmaceutical active compound nicotinamide (NA) has been taken with β -naphthol (β N) as binary system for detailed thermal and solidification behaviours such as phase diagram, excess and mixing thermodynamic function, activity and activity coefficient, interfacial energy (σ), surface roughness (α), driving force of solidification (ΔG_v) and critical radius.

EXPERIMENTAL

Nicotinamide (Thomas Baker, Bombay) and β -naphthol (Loba, India) were directly taken for investigation. The melting point of nicotinamide was found 128 °C while for β -naphthol was found 119 °C, respectively.

Phase diagram: The solid-liquid equilibrium data of NA- β N system were determined by the thaw-melt method^{7,8}. Mixtures of different composition were made in glass test tubes by repeated heating and followed by chilling in ice. The melting and thaw temperatures were determined in a Toshniwal melting point apparatus using a precision thermometer which could read correctly up to ± 0.1 °C. The heater was regulated to give above 1 °C increase in temperature in every 5 min.

Heat of fusion: Heat of fusion of materials was measured by the DTA method using NETZSCH Simultaneous Thermal Analyzer, STA 409 series unit. All the runs were carried out with heating rate 2 °C/min, chart speed 10 mm/min and chart sensitivity 100 μ V/10 mV. The sample weight was 5 mg for all estimation. Using benzoic acid was a standard substance, the heat of fusion of unknown compound was determined^{9,10} using the following equation:

$$\Delta H_x = \frac{\Delta H_s W_s A_x}{W_x A_s}$$

where ΔH_x is the heat of fusion of unknown sample and ΔH_s is the heat of fusion of standard substance. W and A are weight and peak area, respectively and suffices x and s indicate the corresponding quantities for the unknown and standard substances, respectively.

RESULTS AND DISCUSSION

Phase diagram: The phase diagram of nicotinamide- β -naphthol (NA- β N) system determined by the thaw melt method, is reported (Table-1) in the form of temperature-composition curve in Fig. 1. The system shows the formation of a simple eutectic. The melting point of NA (128 °C) decreases on the addition of second component β N (m.p. 116 °C) and further attains minimum and then increases. Eutectic alloy E (0.611 mol fraction of β N) are obtained at 65 °C. At the eutectic temperature two phases namely a liquid phase L and two solid phases (S_1 and S_2) are in equilibrium and the system is invariant.

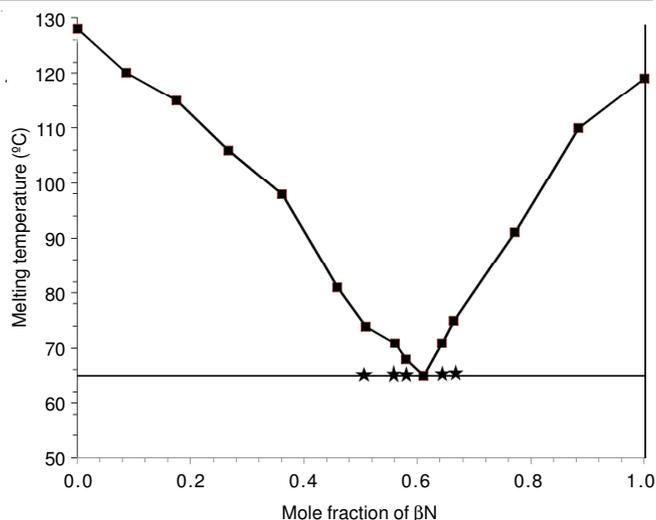


Fig. 1. Phase diagram of NA- β N system

In the region indicated by L a homogenous binary liquid solution exists while the two solid phases exist below the horizontal line. In the case, in region located on the left side of the diagram a binary liquid and solid NA exist while in a similar region located on the right side of the diagram a binary liquid and the second component of the system co-exist.



Heat of fusion: The values of heats of fusion of eutectic and non-eutectic alloys are calculated by the mixture law using equation

$$(\Delta H)_e = X_{NA} \Delta H_{NA} + X_{\beta N} \Delta H_{\beta N} \quad (1)$$

where X and ΔH are the mole fraction and the heat of fusion of the component indicated by the subscript, respectively. The value of heat of fusion of binary alloys A_1 - A_{12} , E is reported in Table-1.

Activity and activity coefficient: The activity coefficient of components for the systems under investigation has been calculated from the equation¹¹ given below

$$-\ln x_i^l \gamma_i^l = \frac{\Delta H_i}{R} \left(\frac{1}{T_e} - \frac{1}{T_i} \right) \quad (2)$$

where γ_i^l is activity coefficient of the component i in the liquid phase, respectively, ΔH_i is the heat of fusion of component i at

TABLE-1
PHASE COMPOSITION, MELTING TEMPERATURE, VALUES OF ENTHALPY OF FUSION (ΔH), ENTROPY OF FUSION (ΔS) AND ACTIVITY COEFFICIENT (γ)

Alloy	X_{NA}	m.p. (°C)	ΔS (kJ/mol)	ΔH (J/mol/K)	γ_{NA}	$\gamma_{\beta N}$
A ₁	0.116	110	18.425	48.108	6.026	0.997
A ₂	0.228	91	19.309	53.046	2.022	0.857
A ₃	0.336	75	20.161	57.934	0.933	0.764
A ₄	0.357	71	20.327	59.089	0.793	0.735
E	0.389	65	20.579	60.885	0.621	0.694
A ₅	0.42	68	20.824	61.067	0.623	0.772
A ₆	0.44	71	20.982	60.993	0.643	0.844
A ₇	0.491	74	21.384	61.625	0.622	0.979
A ₈	0.541	81	21.778	61.521	0.672	1.224
A ₉	0.639	98	22.552	60.786	0.845	2.044
A ₁₀	0.734	106	23.301	61.481	0.875	3.127
A ₁₁	0.825	115	24.019	61.905	0.939	5.406
A ₁₂	0.914	120	24.721	62.904	0.937	11.788

melting point T_i and R is the gas constant. T_e is the melting temperature of alloy. Using the values of activity and activity coefficient (Table-1) of the components in alloys mixing and excess thermodynamics functions have been computed.

Mixing functions: Integral molar free energy of mixing (ΔG^M), molar entropy of mixing (ΔS^M) and molar enthalpy of mixing (ΔH^M) and partial thermodynamic mixing functions of the binary alloys when two components are mixed together were determined by using the following equations

$$\Delta G^M = RT(x_{NA} \ln a_{NA}^1 + x_{BN} \ln a_{BN}^1) \quad (3)$$

$$\Delta S^M = -R(x_{NA} \ln x_{NA}^1 + x_{BN} \ln x_{BN}^1) \quad (4)$$

$$\Delta H^M = RT(x_{NA} \ln \gamma_{NA}^1 + x_{BN} \ln \gamma_{BN}^1) \quad (5)$$

$$G_i^{-M} = \mu_i^{-M} = RT \ln a_i^1 \quad (6)$$

where G_i^{-M} (μ_i^{-M}) is the partial molar free energy of mixing of component i (mixing chemical potential) in binary mix. and γ_i and a_i is the activity coefficient and activity of component, respectively. The negative value^{12,13} of molar free energy of mixing of alloys (Table-2) suggests that the mixing in all cases is spontaneous. The integral molar enthalpy of mixing value corresponds to the value of excess integral molar free energy of the system favours the regularity in the binary solutions.

Excess thermodynamic functions: In order to unfold the nature of the interactions between the components forming the eutectic and non-eutectic alloys, the excess thermodynamic functions such as integral excess integral free energy (g^E),

excess integral entropy (s^E) and excess integral enthalpy (h^E) were calculated using the following equations

$$g^E = RT(x_{NA} \ln \gamma_{NA}^1 + x_{BN} \ln \gamma_{BN}^1) \quad (7)$$

$$s^E = -R \left(x_{NA} \ln \gamma_{NA}^1 + x_{BN} \ln \gamma_{BN}^1 + x_{NA} T \frac{\delta \ln \gamma_{NA}^1}{\delta T} + x_{BN} T \frac{\delta \ln \gamma_{BN}^1}{\delta T} \right) \quad (8)$$

$$h^E = -RT^2 \left(x_{NA} \frac{\delta \ln \gamma_{NA}^1}{\delta T} + x_{BN} \frac{\delta \ln \gamma_{BN}^1}{\delta T} \right) \quad (9)$$

and excess chemical potential or excess partial free energy of mixing

$$g_i^{-E} = \mu_i^{-M} = RT \ln \gamma_i^1 \quad (10)$$

The values of $\delta \ln \gamma_i^1 / \delta T$ can be determined by the slope of liquids curve near the alloys form in the phase diagram. The values of the excess thermodynamic functions are given in Table-3. The value of the excess free energy is a measure of the departure of the system from ideal behaviour. The reported excess thermodynamic data substantiate the earlier conclusion of an appreciable interaction between the parent components during the formation of alloys. The negative value of excess free energy indicates the possibility of a stronger association

TABLE-2
VALUE OF PARTIAL AND INTEGRAL MIXING OF GIBBS FREE ENERGY (ΔG^M),
ENTHALPY (ΔH^M) AND ENTROPY (ΔS^M) OF NA- β N SYSTEM

Alloy	ΔG_{NA}^{-M} (J/mol)	ΔG_{BN}^{-M} (J/mol)	ΔG^M (J/mol)	ΔH_{NA}^{-M} (J/mol)	ΔH_{BN}^{-M} (J/mol)	ΔH^M (J/mol)	ΔS_{NA}^{-M} (J/mol/K)	ΔS_{BN}^{-M} (J/mol/K)	ΔS^M (J/mol/K)
A ₁	-1193.73	-411.46	-502.21	-5988.07	9.84	-655.13	17.91	1.03	2.98
A ₂	-2581.87	-1346.92	-1628.49	-2347.02	515.13	-124.76	12.29	2.15	4.46
A ₃	-3868.39	-2213.91	-2769.81	232.28	899.59	586.11	9.07	3.40	5.31
A ₄	-4208.72	-2443.26	-3073.53	774.72	1027.06	803.79	8.56	3.67	5.42
E	-4734.32	-2797.46	-3550.90	1586.52	1219.20	1148.09	7.85	4.10	5.56
A ₅	-4469.21	-2618.80	-3395.97	1577.04	862.85	988.82	7.21	4.53	5.66
A ₆	-4208.72	-2443.26	-3220.06	1300.49	448.30	710.35	6.83	4.82	5.70
A ₇	-3952.74	-2270.75	-3096.61	1581.29	71.47	703.34	5.91	5.61	5.76
A ₈	-3372.32	-1879.60	-2687.16	1324.17	-673.38	359.56	5.11	6.47	5.73
A ₉	-2053.91	-991.13	-1670.25	560.81	-2382.96	-464.34	3.72	8.47	5.44
A ₁₀	-1474.41	-600.61	-1241.98	443.41	-3800.56	-647.88	2.57	11.01	4.82
A ₁₁	-851.03	-180.52	-733.69	209.68	-5626.25	-785.30	1.60	14.49	3.86
A ₁₂	-517.05	44.55	-468.75	217.25	-8225.03	-498.64	0.75	20.40	2.44

TABLE-3
VALUE OF PARTIAL AND INTEGRAL EXCESS GIBBS FREE ENERGY (g^E), ENTHALPY (h^E) AND ENTROPY (s^E) OF NA- β N SYSTEM

Alloy	g_{NA}^{-E} (J/mol)	g_{BN}^{-E} (J/mol)	g^E (J/mol)	h_{NA}^{-E} (J/mol)	h_{BN}^{-E} (J/mol)	h^E (J/mol)	s_{NA}^{-E} (J/mol/K)	s_{BN}^{-E} (J/mol/K)	s^E (J/mol/K)
A ₁	5719.276	-9.40	655.12	55473.52	3184.10	9249.67	129.91	8.34	22.40
A ₂	2130.464	-467.60	124.76	14861.96	1515.37	4558.39	34.98	5.45	10.20
A ₃	-201.577	-780.69	-586.11	-7772.93	-180.25	-2731.39	-21.76	1.72	-9.14
A ₄	-664.602	-881.07	-803.79	-25400	-7946.96	-14177.70	-71.91	-20.54	-42.17
E	-1337.26	-1027.66	-1148.09	5121.36	-9030.68	-3525.54	19.11	-23.68	-10.75
A ₅	-1341.07	-733.74	-988.82	-8136.42	3325.35	-1488.60	-19.93	11.90	-3.96
A ₆	-1262.46	-485.79	-827.52	-10493.2	-5797.55	-7863.65	-26.83	-15.44	-22.04
A ₇	-1368.35	-61.84	-703.34	85.75	-2759.31	-1362.38	4.19	-7.77	-2.08
A ₈	-1168.97	594.45	-359.56	-14895.4	10863.56	-3072.05	-38.78	29.01	-6.12
A ₉	-518.856	2204.68	464.34	-14207.2	-17510	-15399.54	-36.90	-53.14	-38.47
A ₁₀	-419.079	3592.06	647.88	-6805.51	8900.02	-2627.84	-16.85	14.01	-3.60
A ₁₁	-202.882	5443.85	785.30	-5171.8	42091.06	3099.20	-12.81	94.45	10.87
A ₁₂	-212.913	8060.94	498.64	-4326.33	97345.94	4417.48	-10.47	227.19	13.50

between unlike molecules while the positive value in the present system suggests an association of weaker nature between unlike molecules and of stronger nature between like molecules. The maximum negative g^E value for eutectic^{14,15} alloy E infers stronger interaction between NA and β N in the eutectic. The excess entropy is a measure of the change in configurational energy due to a change in potential energy and indicates an increase in randomness.

Gibbs-Duhem equation: Further the partial molar quantity, activity and activity coefficient can also be determined by using Gibbs-Duhem equation¹⁶

$$\sum x_i dz_i^{-M} = 0 \quad (11)$$

$$\text{or} \quad x_{NA} dH_{NA}^{-M} + x_{\beta N} dH_{\beta N}^{-M} = 0 \quad (12)$$

$$\text{or} \quad dH_{NA}^{-M} = \frac{x_{\beta N}}{x_{NA}} dH_{\beta N}^{-M} \quad (13)$$

$$\text{or} \quad [H_{NA}^{-M}]_{x_{NA}=y} = \int_{x_{NA}=y}^{x_{NA}=1} \frac{x_{\beta N}}{x_{NA}} dH_{\beta N}^{-M} \quad (14)$$

Using eqn. 14, a graph (Fig. 2) between $H_{\beta A}^{-M}$ and $x_{\beta N}/x_{NA}$ gives the solution of the partial molar heat of mixing of a constituent NA in NA/ β N alloy and plot between $x_{\beta N}/x_{NA}$ versus $\ln \gamma_{\beta N}$ determines the value of activity coefficient (Fig. 3) of component NA in binary alloys.

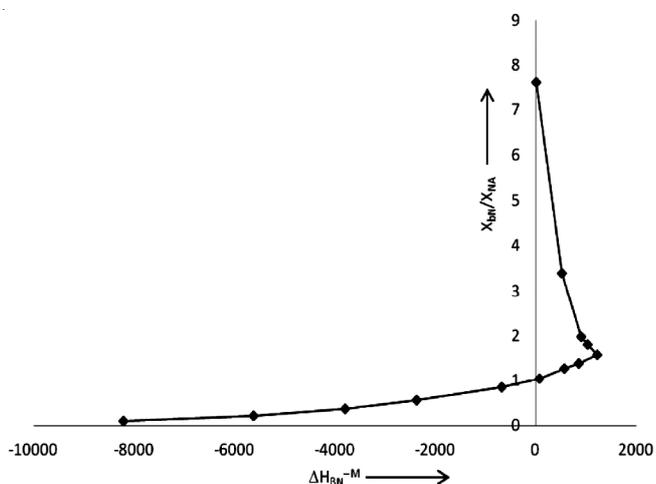


Fig. 2. Graphical solution of partial molar enthalpy of mixing of nicotinamide in binary mix

Effective entropy change (ΔS_v): It is obvious that the effective entropy change and the volume fraction of phases in the alloy are inter-related to decide the interface morphology during solidification and the volume fraction of the two phases depends on the ratio of effective entropy change of the phases. The entropy of fusion ($\Delta S = \Delta H/T$) value (Table-1) of alloys is calculated by heat of fusion values of the materials. The effective entropy change per unit volume (ΔS_v) is given by

$$\Delta S_v = \frac{\Delta H}{T} \cdot \frac{1}{V_m} \quad (15)$$

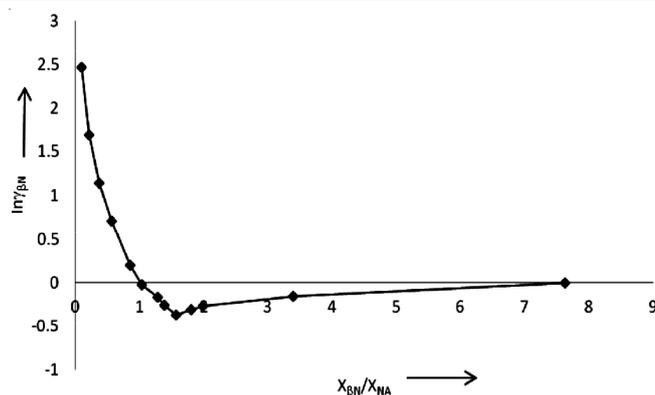


Fig. 3. Graphical solution of activity coefficient of NA in binary mix

where ΔH is the enthalpy change, T is the melting temperature and V_m is the molar volume of solid phase. The entropy of fusion per unit volume (ΔS_v) for NA and β N was found 0.726 and 0.377 JK⁻¹ cm⁻³, respectively. Values of ΔS_v for alloys are reported in Table-4.

Solid-liquid interfacial energy (σ): It has been found that the experimental observed value of interfacial energy ' σ ' keeps a variation of 50-100 % from one worker to other. However, Singh and Glickman¹⁷ were calculated the solid-liquid interfacial energy (σ) from melting enthalpy change and values obtained are found in good agreement with the experimental values. Turnbull empirical relationship¹⁸ between the interfacial energy and enthalpy change provides the clue to determine the interfacial energy value of alloy and is expressed as:

$$\sigma = \frac{C\Delta H}{(N)^{1/3}(V_m)^{2/3}} \quad (16)$$

where the coefficient C lies between 0.33-0.35 for nonmetallic system, V_m is molar volume and N is the Avogadro's constant. The value of the solid-liquid interfacial energy of nicotinamide and β -naphthol was found to be 5.046×10^{-6} and 2.83665×10^{-6} J cm⁻², respectively and σ value of alloys was given in Table-4.

Driving force of nucleation (ΔG_v): The theories of solidification process in past have been discussed on the basis of diffusion model, kinetic characteristics of nucleation and on thermodynamic features. The lateral motion of rudimentary steps in liquid advances stepwise/ nonuniform surface at low driving force while continuous and uniform surface advances at sufficiently high driving force. The driving force of nucleation during solidification (ΔG_v) is determined at under cooling (ΔT) by using the following equation¹⁹

$$\Delta G_v = \Delta S_v \Delta T \quad (17)$$

It is opposed by the increase in surface free energy due to creation of a new solid-liquid interface. By assuming that solid phase nucleates as small spherical cluster of radius arising due to random motion of atoms within liquid. The value of ΔG_v is shown in the Table-5.

Critical radius (r^*): During liquid-solid transformation embryos are rapidly dispersed in unsaturated liquid and on undercooling liquid becomes saturated and provide embryo of a critical size with radius r^* for nucleation which can be expressed by the Chadwick relation²⁰

TABLE-4
VALUES OF ENTHALPY (ΔH_v) AND ENTROPY OF FUSION PER UNIT VOLUME (ΔS_v), INTERFACIAL ENERGY (σ),
GRAIN BOUNDARY ENERGY (σ_{gb}), GIBBS-THOMSON COEFFICIENT (τ) AND ROUGHNESS PARAMETER (α)

Alloy	ΔH_v (J/cm ³)	ΔS_v (J/cm ³ /K)	α	$\sigma \times 10^6$ (J/cm ²)	$\tau \times 10^6$	$\sigma_{gb} \times 10^6$ (J/cm ²)
A ₁	160.44	0.419	5.8	3.047	7.27	5.89
A ₂	173.42	0.476	6.4	3.260	6.84	6.30
A ₃	186.73	0.536	7.0	3.474	6.48	6.71
A ₄	192.70	0.560	7.1	3.558	6.35	6.87
E	198.79	0.588	7.3	3.647	6.20	7.05
A ₅	202.88	0.595	7.3	3.712	6.24	7.17
A ₆	203.75	0.592	7.3	3.732	6.30	7.21
A ₇	216.70	0.625	7.4	3.913	6.26	7.56
A ₈	224.04	0.633	7.4	4.025	6.36	7.78
A ₉	250.69	0.676	7.3	4.389	6.50	8.48
A ₁₀	267.05	0.705	7.4	4.628	6.57	8.94
A ₁₁	283.37	0.730	7.4	4.864	6.66	9.40
A ₁₂	300.90	0.766	7.6	5.112	6.68	9.87

TABLE-5
VALUE OF VOLUME FREE ENERGY CHANGE (ΔG_v)
DURING SOLIDIFICATION FOR NA- β N SYSTEM
AT DIFFERENT UNDER COOLINGS (ΔT)

Alloy	ΔG_v (J/cm ³)					
	ΔT					
	1.0	1.5	2.0	2.5	3.0	3.5
A ₁	0.419	0.628	0.838	1.047	1.257	1.466
A ₂	0.476	0.715	0.953	1.191	1.429	1.667
A ₃	0.536	0.805	1.073	1.341	1.610	1.878
A ₄	0.560	0.840	1.120	1.400	1.681	1.960
E	0.588	0.882	1.176	1.470	1.764	2.058
A ₅	0.595	0.892	1.190	1.487	1.785	2.082
A ₆	0.592	0.888	1.184	1.481	1.777	2.073
A ₇	0.624	0.937	1.249	1.561	1.873	2.186
A ₈	0.633	0.949	1.266	1.582	1.899	2.215
A ₉	0.676	1.014	1.351	1.689	2.027	2.365
A ₁₀	0.705	1.057	1.409	1.762	2.114	2.466
A ₁₁	0.730	1.096	1.461	1.826	2.191	2.556
A ₁₂	0.766	1.148	1.531	1.914	2.297	2.680

TABLE-6
CRITICAL SIZE OF NUCLEUS (r^*)
AT DIFFERENT UNDERCOOLINGS (ΔT)

Alloy	r^* (cm) $\times 10^6$					
	ΔT					
	1.0	1.5	2.0	2.5	3.0	3.5
A ₁	14.5	9.70	7.27	5.82	4.85	4.16
A ₂	13.7	9.12	6.84	5.47	4.56	3.91
A ₃	13.0	8.63	6.47	5.18	4.32	3.70
A ₄	12.7	8.47	6.35	5.08	4.23	3.63
E	12.4	8.27	6.20	4.96	4.13	3.54
A ₅	12.5	8.32	6.24	4.99	4.16	3.56
A ₆	12.6	8.41	6.30	5.04	4.20	3.60
A ₇	12.5	8.35	6.26	5.01	4.18	3.58
A ₈	12.7	8.48	6.36	5.09	4.24	3.63
A ₉	13.0	8.66	6.50	5.20	4.33	3.71
A ₁₀	13.1	8.76	6.57	5.25	4.38	3.75
A ₁₁	13.3	8.88	6.66	5.33	4.44	3.80
A ₁₂	13.4	8.90	6.68	5.34	4.45	3.81
NA	13.9	9.26	6.95	5.56	4.63	3.97
β N	15.0	10.00	7.52	6.02	5.02	4.30

$$r^* = \frac{2\sigma}{\Delta G_v} = \frac{2\sigma T}{\Delta H_v \Delta T} \quad (18)$$

where σ is the interfacial energy and ΔH_v is the enthalpy of fusion of the compound per unit volume, respectively. The critical size of the nucleus for the components and alloys was calculated at different undercoolings and values are presented in Table-6. It can be inferred from Table-6 that the size of the critical nucleus decreases with increase in the undercooling of the melt. The existence of embryo and a range of embryo size can be expected in the liquid at any temperature.

Critical free energy of nucleation (ΔG^*): To form critical nucleus, it requires a localized critical free energy of nucleation (ΔG^*) which is evaluated²¹ as

$$\Delta G^* = \frac{16 \pi \sigma^3}{3 \Delta G_v^2} \quad (19)$$

The value of ΔG^* has been found in the range of 10^{-15} - 10^{-16} J at different undercoolings and has been reported in Table-7.

Gibbs-Thomson coefficient (τ): For a planar grain boundary on planar solid-liquid interface the Gibbs-Thomson coefficient (τ) for the system can be calculated by the Gibbs-Thomson equation is expressed as

$$\tau = r\Delta T = \frac{TV_m\sigma}{\Delta H} = \frac{\sigma}{\Delta S_v} \quad (20)$$

TABLE-7
VALUE OF CRITICAL FREE ENERGY OF NUCLEATION
(ΔG^*) FOR ALLOYS OF NA- β N SYSTEM AT
DIFFERENT UNDERCOOLING (ΔT)

Alloy	ΔG^* (kJ/mol) $\times 10^6$					
	ΔT					
	1.0	1.5	2.0	2.5	3.0	3.5
A ₁	27.0	12.0	6.76	4.32	3.00	2.21
A ₂	25.6	11.4	6.40	4.09	2.84	2.09
A ₃	24.4	10.8	6.10	3.91	2.71	1.99
A ₄	24.1	10.7	6.01	3.85	2.67	1.96
E	23.5	10.4	5.88	3.76	2.61	1.92
A ₅	24.2	10.8	6.05	3.87	2.69	1.98
A ₆	24.8	11.0	6.21	3.97	2.76	2.03
A ₇	25.8	11.4	6.44	4.12	2.86	2.10
A ₈	27.3	12.1	6.82	4.37	3.03	2.23
A ₉	31.0	13.8	7.76	4.97	3.45	2.53
A ₁₀	33.5	14.9	8.37	5.36	3.72	2.73
A ₁₁	36.2	16.1	9.04	5.79	4.02	2.95
A ₁₂	38.2	17.0	9.55	6.11	4.24	3.12

where τ is the Gibbs-Thomson coefficient, ΔT is the dispersion in equilibrium temperature and, r is the radius of grooves of interface. The theoretical basis of determination of t was made for equal thermal conductivities of solid and liquid phases for some transparent materials. It was also determined by the help of Gunduz and Hunt numerical method²² for materials having known grain boundary shape, temperature gradient in solid and the ratio of thermal conductivity of the equilibrated liquid phases to solid phase ($R = K_L/K_S$). The Gibbs-Thomson coefficient for NA, β N and their alloys are found in the range of $7.274\text{--}6.202 \times 10^{-6}$ km and is reported in Table-4.

Interfacial grain boundary energy (σ_{gb}): Grain boundary is the internal surface which can be understood in a very similar way to nucleation on surfaces in liquid-solid transformation. In past, a numerical method²³ is applied to observe the interfacial grain boundary energy (σ_{gb}) without applying the temperature gradient for the grain boundary groove shape. For isotropic interface there is no difference in the value of interfacial tension and interfacial energy. A considerable force is employed at the grain boundary groove in anisotropic interface. The grain boundary energy can be obtained by the equation:

$$\sigma_{gb} = 2\sigma \cos \theta \quad (21)$$

where θ is equilibrium contact angle precipitates at solid-liquid interface of grain boundary. The grain boundary energy could be twice the solid-liquid interfacial energy in the case where the contact angle tends to zero. The value of σ_{gb} for solid NA and β N was found to be 13.14×10^{-2} and 4.79×10^{-2} Jm⁻², respectively and the value for all alloys is given in Table-4.

Interface morphology: The solid-liquid interface morphology can be predicted from the value of the entropy of fusion. According to Hunt and Jackson²⁴, the type of growth from a binary melt depends upon a factor α , defined as:

$$\alpha = \xi \frac{\Delta H}{RT} = \xi \frac{\Delta S}{R} \quad (22)$$

where ξ is a crystallographic factor depending upon the geometry of the molecules and has a value less than or equal to one. $\Delta S/R$ (also known as Jackson's roughness parameter α) is the entropy of fusion (dimensionless) and R is the gas constant. When α is less than two the solid-liquid interface is atomically rough and exhibits nonfaceted growth. The value

of Jackson's roughness parameter ($\Delta S/R$) is given in Table-4. For all the alloy the a value was found greater than 2 which indicates the faceted²⁵ growth proceeds in all the cases.

ACKNOWLEDGEMENTS

Thanks are due to Head Department of Chemistry, Veer Kunwar Singh University, Ara, India for providing necessary research facilities.

REFERENCES

1. M. Knip, I.F. Douek and W.P. Moore, *Diabetologia*, **43**, 1337 (2000).
2. T. Hakoziaki, L. Minwalla and J. Zhung, *Br. J. Dermatol.*, **147**, 20 (2002).
3. S. Akbulut, Y. Ocak, K. Keslioglu and N. Marasli, *Appl. Surf. Sci.*, **255**, 3594 (2009).
4. R. Kumar, V. Ulagendran, V. Kannappan and S. Jayakumar, *Fluid Phase Equilibria*, **307**, 113 (2011).
5. Y. Dwivedy, S. Kant, U.S. Rai and R.N. Rai, *J. Fluorescence*, **21**, 1255 (2011).
6. B.L. Sharama, S. Tandon and S. Gupta, *Cryst. Res. Technol.*, **44**, 258 (2009).
7. R.P. Rastogi and K.T. Rama Verma, *J. Chem. Soc.*, 2097 (1956).
8. H. Shekhar, K.B. Pandey and V. Kant, *J. Natl. Acad. Sci. Lett.*, **33**, 153 (2010).
9. A. Krajewska-Cizio, *Thermochim. Acta*, **158**, 317 (1990).
10. U.S. Rai and H. Shekhar, *Asian J. Chem.*, **11**, 453 (1999).
11. J. Sangester, *J. Phys. Chem. Ref. Data*, **23**, 295 (1994).
12. R. Nieto, M.C. Gonozalet and F. Herrero, *Am. J. Phys.*, **67**, 1096 (1999).
13. H. Shekhar and S.S. Salim, *J. Nat. Acad. Sci. Lett.*, **34**, 117 (2011).
14. J. Wisniak and A. Tamir, *Mixing and Excess Thermodynamic Properties (A Literature Source Book)*, Phys. Sci. Data 1, Elsevier, New York (1978).
15. T. Agarwal, P. Gupta, S.S. Das, A. Gupta and N.B. Singh, *J. Chem. Eng. Data*, **55**, 4206 (2010).
16. M. Shamsuddin, S.B. Singh and A. Nasar, *Thermochim. Acta*, **316**, 11 (1998).
17. N.B. Singh and M.E. Glicksman, *J. Cryst. Growth*, **98**, 573 (1989).
18. D. Turnbull, *J. Chem. Phys.*, **18**, 768 (1950).
19. J.D. Hunt and S.Z. Lu, in ed.: Ed. D.T.J. Hurle, *Hand Book of Crystal Growth*, Elsevier, Amsterdam (1994).
20. G.A. Chadwick, *Metallography of Phase Transformation*, Butterworths, London, p. 61 (1972).
21. W.R. Wilcox, *J. Crystal Growth*, **26**, 153 (1974).
22. M. Gunduz and J.D. Hunt, *Acta Metall.*, **37**, 1839 (1989).
23. Y. Ocak, S. Akbulut, K. Keslioglu and N. Marasli, *J. Colloid Interf. Sci.*, **320**, 555 (2008).
24. J.D. Hunt and K.A. Jackson, *Trans. Metall. Soc. AIME*, **236**, 843 (1966).
25. H. Shekhar and V. Kant, *J. Indian Chem. Soc.*, **88**, 947 (2011).