

Thermodynamic Investigation of Alloys of Phenanthrene-Benzidine System

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Abstract: The solid-liquid equilibrium data of phenanthrene (Ph)-benzidine (Bz) system determined by thaw-melt method show a simple regular behaviour in all alloys (A_1 to A_7) of the system. Heat of fusion data and activity coefficient obtained from liquidus curve for alloys of the system, evaluate the excess (partial and integral) thermodynamic functions (g^E , s^E and h^E). The mixing functions of binary alloys when two components are mixed together, such as, free energy of mixing or integral molar free energy of mixing (ΔG^M), integral molar entropy of mixing (ΔS^M) and integral molar enthalpy of mixing (ΔH^M) of alloys of Ph-Bz system are evaluated and reported. The Gibbs-Duhem equation gives the solution of the partial molar heat of mixing of specific constituents in the different binary alloys. Surface roughness (α) for each alloy of the system is found greater than two infers faceted growth proceeds in the alloys.

Keywords: Heat of fusion, entropy of fusion, interfacial energy, excess and mixing thermodynamic functions.

1. Introduction

The growing industrial activities create a continual demand for improved materials^{1,2} that satisfy more stringent requirements, such as, high tensile strength, modulus thermal conductivity, heat distortion temperature, lower thermal expansion and cost. These requirements are often satisfied by utilizing a composite material whose constituents act synergistically to solve the need of the pertinent utility. During the development of materials a need for the significant improvement in its cost, weight, efficiency (fuel consumption) and life cycle costs have been realized. Since last twenty five years the chemistry of organic materials³⁻⁵, its eutectics, noneutectics,

monotectics and molecular complexes have been the most active area of investigation due to their unusual anisotropic properties not normally shown by their parent components. The organic substances have recently been attracting the attention in connection with searches of new nonlinear materials for quantum electronics. These materials have considerably high nonlinearity, great possibility of varying the molecular structure, easier to engineer to fabricate instrument of high optical properties of the crystals, high resistance to high energy laser beams and are much cheaper than their inorganic counterparts. The eutectics, noneutectics, monotectics and molecular complexes of metal origin have a remarkable commercial and technological importance in modern age. The making idea behind efforts is to produce a material which consists of very strong but possibly brittle fibres embedded in a ductile matrix. In spite of great devotion to acquire the stronger and more reliable material to cater the ever-growing need and diversified demand of modern civilization the various studies on metallic eutectics, monotectics and intermetallic compounds are inadequate and incomplete as high transformation temperature, opacity, difficulty involved in purification and experimentation, density driven convection affect their solidification. The direct observation on solidification of transparent organic systems has been the most useful technique for unfolding the mysteries of solidification as it permits visual observation of the phase transformation and the processes during solidification which control the properties of material. In recent past extensive study has been developed in the use of eutectic solidification to produce materials having controlled two phase microstructures, forming the *in-situ* composites and thereby materials of desired properties.

Due to low transformation temperature, transparency, ease in purification and experimentation, minimized convection effects and wider choice of materials are the special features which have prompted a number of research groups^{6,7} to select the organic systems of model system for detailed physicochemical investigation of the parameters which control the mechanism of solidification which, in turn, control the properties of materials of technological importance. An another important objective of eutectic melt is to act as a catalyst because several organic and inorganic reactions which occur at very high temperature and are not possible in ordinary condition, have been successfully carried out in eutectic media. The flight experiment of these systems can give the clue of effect of gravity on solidification microstructure of faceted-faceted, faceted-nonfaceted, nonfaceted-nonfaceted and off eutectic systems. At present the low melting alloys are gaining prominence due to their practical and theoretical

importance. In liquid state it may be used as heat transfer media in high thermal plants, heat treatment bath, solders etc. In the solid state some of them find applications in superconductivity, thermoelectronic devices, besides their solid-liquid transition find many industrial application e.g. safety plugs in fire detection apparatus, alarm system precision casting, ultra refining of materials, design of gating, resering and continuous casting, production of composite materials etc.

In the present work thermochemistry, role of interfacial energy, roughness parameter during growth steps and excess and mixing functions of the binary alloys of phenanthrene(Ph)- benzidine(Bz) system have been highlighted.

2. Experimental Procedures

The solid-liquid equilibrium data for Ph-Bz system determined by thaw melt method was reported. The heat of fusion of pure components and binary alloys was determined by their DTA patterns obtained from Stanton Redcroft STA-780 series unit. All the runs were carried out with heating rate 2° C/min, chart speed 10 mm/min and chart sensitivity 100 $\mu\text{v}/10\text{ mv}$. The sample weight range was 5-20 mg for each estimation. Using benzoic acid as a standard substance the heat of fusion of unknown compound was determined using the following equations⁸:

$$(2.1) \quad \Delta H_x = \frac{H_s W_s A_x}{W_x A_s},$$

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 suffix x and s indicate the corresponding quantities for the unknown and standard substances, respectively. The heats of fusion of pure components determined by this method. The values of heat of fusion of the binary alloys were determined by using mixture law.

3. Results and Discussion

The solid-liquid equilibrium data for Ph-Bz system in form of temperature-composition curve (Table 1) determined by the thaw melt method is reported earlier⁹. On addition of one component into second the melting point of second decreases and attains a minimum temperature of the system. The maximum value of undercooling of parent components being of the same order in the most of alloys suggests that any of the components can

nucleate first during solidification. The various compositions and the corresponding temperature of alloys are reported in Table 1. An alloy is made to cool the liquid below the minimum temperature (T_e), it will cool only if one phase is vanished and the systems are univariant. In a homogenous binary liquid solution the two solid phases exists below the temperature T_e .

Table 1: Temperature-composition data, heat of fusion (ΔH), entropy of fusion (ΔS), roughness parameter (α) and interfacial energy (σ) of alloys of Ph-Bz system.

Alloys	Mole fraction of Ph	Temp °C	ΔH (kJ/mol)	ΔS (J/mol/K)	α	σ (erg/cm ²)
A ₁	0.105	121	18.99	48.21	5.79	26.25
A ₂	0.205	113	18.89	48.95	5.88	25.78
A ₃	0.305	108	18.79	49.33	5.93	25.31
A ₄	0.410	101	18.69	49.97	6.01	24.81
A ₅	0.510	97	18.59	50.24	6.04	24.34
A ₆	0.610	94	18.49	50.38	6.05	23.87
A ₇	0.700	90	18.40	50.69	6.09	23.45
Bz	0.000	99	18.10	48.66	5.85	22.03
Ph	1.000	127	19.10	47.75	5.74	26.75

4. Thermochemistry

The topology during phase transformation proceeds through nucleation and growth. The solid-liquid interfacial energy is responsible for nucleation which can be calculated from heat of fusion data. The interface structure of alloys has been decided by entropy of fusion. Using the heat of fusion data the entropy of fusion, interfacial energy, surface roughness, radius of critical nucleus, mixing and excess thermodynamic functions can be calculated to throw light on the behaviour of crystallization and nature of interaction between the components forming alloy.

5. Heat of fusion and entropy of fusion

The value of enthalpy of fusion of pure components and alloys are reported in Table 1. Theoretical studies on entropy of fusion of binary alloys predict the structure, stability and ordering in the binary melt. The entropy of fusion (ΔS) of pure components and alloys has been calculated using the following relation¹⁰:

$$(5.1) \quad \Delta S = \frac{\Delta H}{T},$$

where ΔH is the heat of fusion and T is the fusion temperature and given in table. In all the cases under investigations, ΔS values are positive indicating an increase of randomness during melting. In the case when the alloys have lower entropy of fusion as compared to the pure components, it can be inferred that the entropy factor is less effective in the melting process of a alloy in comparison to those of pure components.

6. Activity coefficient

For ideal mixture, the composition and temperature of alloy can be predicted the activity coefficient by solving the following equation

$$(6.1) \quad -\ln(x_{ph})_e = \frac{\Delta H_{ph}}{R} \left(\frac{1}{T_e} - \frac{1}{T_{ph}} \right),$$

$$(6.2) \quad -\ln(x_{Bz})_e = \frac{\Delta H_{Bz}}{R} \left(\frac{1}{T_e} - \frac{1}{T_{Bz}} \right),$$

where T_e is the temperature of the alloy and T_{Ph} and T_{Bz} are the melting points of components Ph and Bz, respectively. The activity coefficients of components Ph and Bz, for the systems under investigation may be calculated from the equation given below:

$$(6.3) \quad -\ln x_i^l \gamma_i^l = \frac{\Delta H_i}{R} \left(\frac{1}{T_e} - \frac{1}{T_i} \right),$$

where x_i^l and γ_i^l are the mole fraction and activity coefficient of the component i in the liquid phase respectively, ΔH_i is the heat of fusion of component i at the melting point T_i . The value of activity coefficient and activity of the components in alloys are given the Table 2.

Table 2: Values of activity and activity coefficient of components in binary melt of Ph-Bz system.

Alloys	$\ln\gamma_{Ph}$	$\ln\gamma_{Bz}$	γ_{Ph}	γ_{Bz}	$\ln a_{Ph}$	$\ln a_{Bz}$	a_{Ph}	a_{Bz}	X_{Ph}/ X_{Bz}
A ₁	2.581	0.042	13.205	1.043	0.327	0.069	1.386	0.933	0.117
A ₂	1.781	0.023	5.934	1.023	0.196	-0.207	1.216	0.813	0.257
A ₃	1.270	0.088	3.559	1.092	0.082	-0.276	1.086	0.759	0.438
A ₄	0.913	0.137	2.493	1.147	0.022	-0.391	1.022	0.677	0.694
A ₅	0.630	0.254	1.877	1.289	-0.043	-0.459	0.957	0.632	1.040
A ₆	0.407	0.436	1.503	1.546	-0.087	-0.506	0.917	0.603	1.564
A ₇	0.204	0.630	1.227	1.877	-0.152	-0.574	0.859	0.563	2.333

7. Mixing functions

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

$$(7.1) \quad \Delta G^M = RT (x_{ph} \ln \alpha_{ph}^l + x_{Bz} \ln \alpha_{Bz}^l),$$

$$(7.2) \quad \Delta S^M = -R (x_{ph} \ln x_{ph}^l + x_{Bz} \ln x_{Bz}^l),$$

$$(7.3) \quad \Delta H^M = RT (x_{ph} \ln \gamma_{ph}^l + x_{Bz} \ln \gamma_{Bz}^l),$$

$$(7.4) \quad \Delta G_i^{-M} = RT \ln a_i,$$

where ΔG_i^{-M} is the partial molar free energy of mixing of component i in binary mix.

The positive value¹¹ (Table 3) of molar free energy of mixing of all alloys suggests that the mixing in all cases is not spontaneous. The integral molar enthalpy of mixing value corresponds to the value of excess integral molar free energy of the system favors the regularity in the binary solution. The positive value of ΔS^M of all alloys predicts the nature of molecular interaction between the components forming the binary melt.

Table 3: Values of partial and integral thermodynamic mixing functions of alloys of Ph-Bz system.

Alloys	G_{ph}^{-M} J/mol	G_{Bz}^{-M} J/mol	ΔG^M J/mol	S_{ph}^{-M} J/mol/K	S_{Bz}^{-M} J/mol/K	ΔS^M J/mol/K	H_{ph}^{-M} J/mol	H_{Bz}^{-M} J/mol	ΔH^M J/mol
A ₁	1070.43	-202.05	-89.66	18.74	0.92	2.79	8453.24	161.32	1010.73
A ₂	628.68	-663.56	-398.65	13.17	1.91	4.22	5713.68	72.66	1229.24
A ₃	260.17	-864.88	-521.75	9.87	3.02	5.11	4021.41	287.63	1426.42
A ₄	67.69	-1214.89	-689.03	7.41	4.39	5.63	2840.06	425.74	1415.61
A ₅	-134.06	-1413.95	-761.21	5.60	5.93	5.76	1937.25	780.44	1370.39
A ₆	-256.84	-1544.30	-764.44	4.11	7.83	5.56	1242.38	2129.39	1277.02
A ₇	-460.20	-1733.85	-842.29	2.96	10.01	5.08	616.23	1899.80	1001.63

8. Excess thermodynamic functions

The activity coefficient of the components forming the binary melt deviate from unity which confirms a non-ideal character to the binary mixtures. The deviations from ideal behavior can best be expressed in terms of excess thermodynamic functions which give more quantitative idea about the nature of molecular interactions. The difference between the thermodynamic function of mixing for a real system and the corresponding value for an ideal system at the same temperature and pressure is called excess thermodynamic function. It is denoted by subscript E and represents the excess (positive or negative) of a given thermodynamic property of a solution over that in the ideal solution:

$$(8.1) \quad Y^E = \Delta Y_{mix}(\text{real}) - \Delta Y_{mix}(\text{ideal}),$$

where Y can be taken as any of the thermodynamic functions.

In order to know the nature of interaction between the components forming the binary alloy some thermodynamic functions such as the excess free energy of mixing (g^E), excess entropy of mixing (s^E) and excess enthalpy of mixing (h^E) and have been calculated by the following equation :

$$(8.2) \quad g^E = RT (x_{ph} \ln \gamma_{ph}^l + x_{Bz} \ln \gamma_{Bz}^l),$$

$$(8.3) \quad s^E = -R \left(x_{ph} \ln \gamma_{ph}^l + x_{Bz} \ln \gamma_{Bz}^l + x_{ph} T \frac{\delta \ln \gamma_{ph}^l}{\delta T} + x_{Bz} T \frac{\delta \ln \gamma_{Bz}^l}{\delta T} \right),$$

$$(8.4) \quad h^E = -RT^2 \left(x_{ph} \frac{\delta \ln \gamma_{ph}^l}{\delta T} + x_{Bz} \frac{\delta \ln \gamma_{Bz}^l}{\delta T} \right),$$

where R is the gas constant and T is melting temperature of the alloy. The values of $\left(\frac{\delta x}{\delta T} \right)$ can be determined by the slope of the liquidus curve in the phase diagram, on differentiating equation (4)

$$(8.5) \quad \frac{\delta \ln \gamma_i^l}{\delta T} = \frac{\Delta H_i}{RT^2} - \frac{1}{x_i} \frac{\delta x_i}{\delta T}.$$

Since the liquidus curves in phase diagrams are virtually straight lines in the present system, the value of $\left(\frac{\delta x_i}{\delta T} \right)$ can be calculated by taking their slope

near the binary melt. The variation of mole fraction with temperature $\left(\frac{\delta x_i}{\delta T} \right)$ can also be calculated with accuracy by taking two points near the binary temperature and using the relationship

$$(8.6) \quad x_i = \alpha + \beta T,$$

where α and β are constants, and $\beta = \left(\frac{\delta x_i}{\delta T} \right)$. The value of $\frac{\delta \ln \gamma_i^l}{\delta T}$ for different systems,

calculated from equation (8.5) is reported in Table 2 . It is evident from the Table 4 that the values of all thermodynamic functions are positive. The positive value of g^E predicts¹² that molecular association between like

molecules are stronger than unlike molecules. The value of s^E measures change in configurational energy due to change in potential energy and increase in randomness. The negative value of excess free energy in the case of Ph-Bz system indicate the possibility of a stronger association between unlike molecules while the positive value in the Ph-Bz system suggests an association of weaker nature between unlike molecules and of stronger nature between like molecules. Its sign provides information regarding a change in density of the alloy during the phase transformation.

Table 4: Values of partial and integral excess thermodynamic functions of alloys of Ph-Bz system.

Alloys	g_{ph}^{-E} J/mol	g_{Bz}^{-E} J/mol	g^E J/mol	S_{ph}^{-E} J/mol/K	S_{Bz}^{-E} J/mol/K	S^E J/mol/K	h_{ph}^{-E} kJ/mol	h_{Bz}^{-E} kJ/mol	h^E kJ/mol
A ₁	8453.24	161.32	1010.73	244.57	28.02	50.75	104.82	11.18	21.01
A ₂	5713.68	72.66	1229.24	94.83	31.06	44.14	42.32	12.06	18.27
A ₃	4021.41	287.63	1426.42	149.65	-5.29	42.01	61.04	-1.73	17.41
A ₄	2840.06	425.74	1415.61	19.85	52.46	39.52	10.26	20.32	16.20
A ₅	1937.25	780.44	1370.39	58.37	71.82	69.10	26.53	27.36	26.94
A ₆	1242.38	2129.39	1277.02	47.32	100.79	68.18	18.61	38.33	26.30
A ₇	616.23	1899.80	1001.63	34.66	143.34	67.27	13.20	53.94	25.42

9. Gibbs-Duhem equation

The partial molar quantity, activity and activity coefficient can also be determined by using Gibbs Duhem equation

$$(9.1) \quad \sum x_i dz_i^- = 0,$$

$$(9.2) \quad x_{ph} dH_{ph}^{-M} + x_{Bz} dH_{Bz}^{-M} = 0,$$

$$(9.3) \quad dH_{Bz}^{-M} = x_{ph} / x_{Bz} dH_{ph}^{-M},$$

$$(9.4) \quad \left[H_{Bz}^{-M} \right]_{x_{Bz}=y}^{x_{Bz}=1} = \int_{x_{Bz}=y}^{x_{Bz}=1} \frac{x_{ph}}{x_{Bz}} dH_{ph}^{-M}.$$

Using equation (9.4), a graph between $\frac{x_{ph}}{x_{Bz}}$ and H_{ph}^{-M} (fig1) gives the solution of the partial molar heat of mixing of a certain constituents in the binary alloys and plots between $\frac{x_{ph}}{x_{Bz}}$ vs $\ln \alpha_{ph}$ and $\ln \gamma_{ph}$ (fig 2 and fig 3) determine the value of activity and activity coefficient of specific components in binary alloys respectively.

10. Surface roughness

Nature of the solid-liquid interface and can be predicted from the value of the entropy of fusion. According to Hunt and Jackson¹³ the type of growth from a binary melt depends upon a factor α , defined as

$$(10.1) \quad \alpha = \xi \frac{\Delta H}{RT} = \xi \frac{\Delta S}{T},$$

where ξ is a crystallographic factor depending upon the geometry of the molecules and has a value less than or equal to one. $\frac{\Delta S}{R}$ (also known as Jackson's roughness parameter) is the entropy of fusion (dimension less) and R is the gas constant. When α is less than two the solid-liquid interface is atomically rough and exhibits non-faceted growth. The value of Jackson's roughness parameter $\left(\frac{\Delta S}{R}\right)$ are given in Table1. In all the alloys under investigation the $\frac{\Delta S}{R}$ values are greater than two, which indicates that they exhibit faceted growth¹⁴.

11. Interfacial energy

The magnitude of heat of fusion is affected by the interfacial tension. The solid-liquid interface plays an important role in determining the kinetics of phase transformation. During the growth of a crystal the radius of critical nucleus is influenced by undercooling as well as the interfacial energy of surface involved. The interfacial energy (σ) is given by the expression,

$$(11.1) \quad \sigma = \frac{C \Delta H}{(N)^{1/3} (V_m)^{2/3}},$$

where N is Avogadro number, V_m is the molar volume and C lies between 0.33 to 0.35 Measurement of the solid-liquid interface energy is extremely difficult and in unfortunately its magnitude varies from 50-100 % from one worker to other. However, Glicksman¹⁵ have proposed the above method for the calculation of interfacial energy from the heat of fusion and the value obtained agree well with experimental values. The same method was used to calculate the interfacial energy in the present investigation. The calculated value of interfacial energy for all the systems are reported in Table 1.

12. Critical-nucleus size

According to Chadwick¹⁶ the critical size of the nucleus (r^*) is related to the undercooling (ΔT) by the following relationship:

$$(12.1) \quad r^* = \frac{2\sigma T_m}{\Delta H_v \Delta T},$$

where σ is the interfacial energy and T_m and ΔH_v are the melting temperature and 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 5. It can be concluded from Table 5 that the size of the critical nucleus decreases with increasing undercooling values.

Table 5: Critical size of nucleus at different undercoolings.

Undercooling ΔT (°C)	Critical radius x 10 ⁶ (cm)								
	Ph	Bz	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇
2.0	8.23	8.26	8.18	8.07	8.01	7.92	7.89	7.88	7.85
2.5	6.59	6.61	6.56	6.45	6.41	6.34	6.31	6.30	6.28
3.0	5.49	5.50	5.46	5.38	5.34	5.28	5.26	5.25	5.23
3.5	4.71	4.72	4.68	4.61	4.58	4.53	4.51	4.50	4.48
4.0	4.12	4.13	4.09	4.03	4.01	3.96	3.95	3.94	3.92
4.5	3.66	3.67	3.64	3.59	3.56	3.52	3.51	3.50	3.49

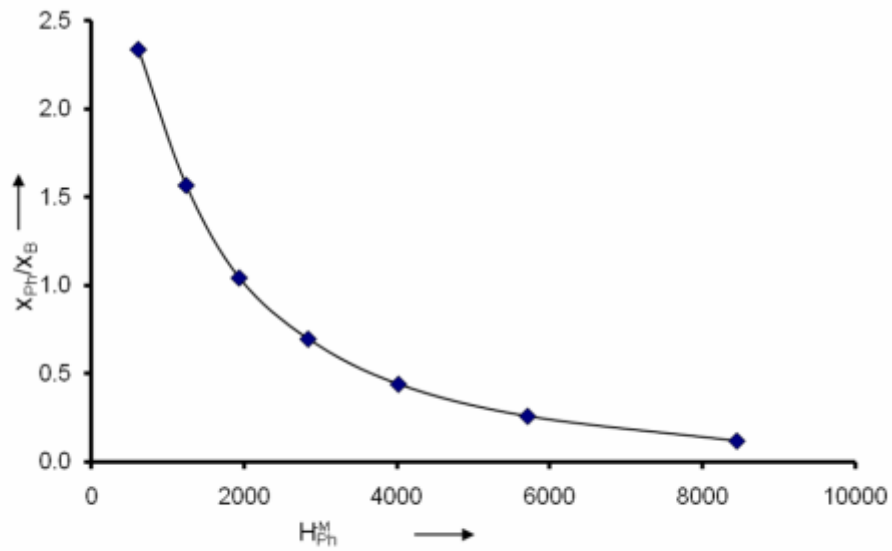


Fig1 Graphical solution of partial molar heat of mixing of Bz in

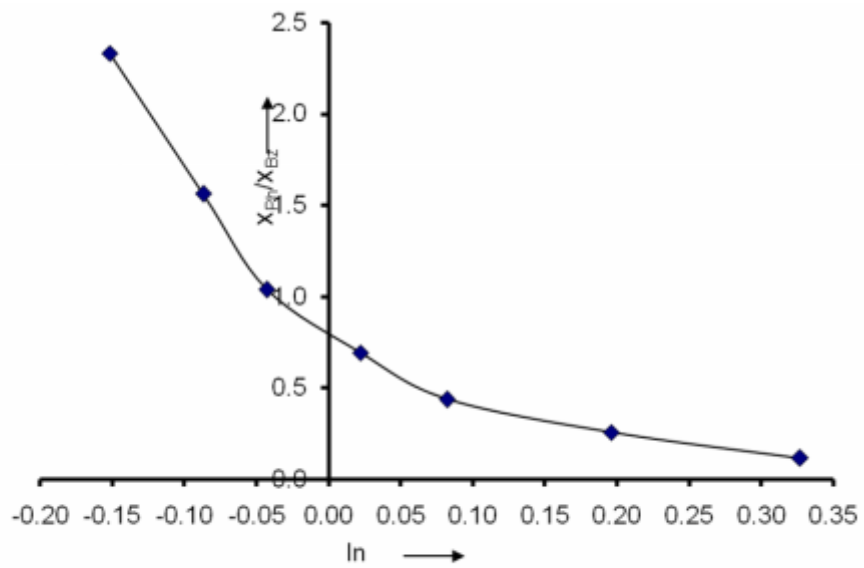


Fig.2 Graphical solution of activity of Bz in

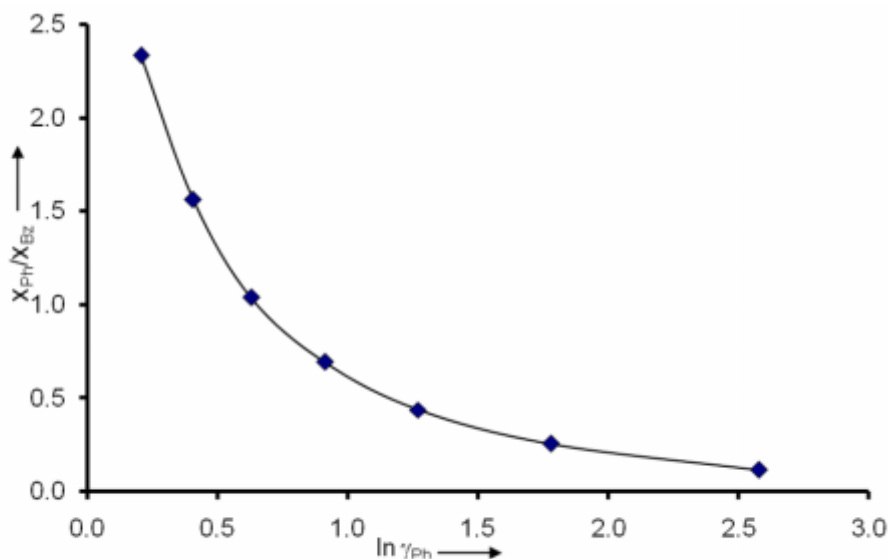


Fig.3 Graphical solution of activity coefficient of Bz

13. Conclusions

The excess and mixing thermodynamic functions have not yet been experimentally determined. These functions in the present work have been determined from analysis of solidus-liquids equilibrium curve as well as the value of heat of fusion of the materials. These functions have great importance in the area of solution studies, since quantitative picture about the nature of molecular interaction can be expressed. These functions infer that there is stronger molecular association between the like molecules. High surface roughness gives indication about faceted growth in the alloys. The observation of crystal growth indicates that a binary melt only solidifies spontaneously below its equilibrium temperature, when a cluster of molecules gets the critical size of a crystal.

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