Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 421 (2004) 161–169

thermochimica acta

www.elsevier.com/locate/tca

Quantitative essence of molecular interactions in binary organic eutectic melt systems

B.L. Sharma*, Sonika Tandon, Rajesh Kant, Ritu Sharma

Department of Chemistry, University of Jammu, Baba Saheb Ambedkar Road, Jammu 180006, India

Received 30 October 2003; received in revised form 25 February 2004; accepted 28 February 2004

Abstract

This manuscript presents thermodynamic analysis of some binary organic eutectic systems, which reveals the interactions between unlike phase molecules in the miscibility phenomenon. Computation of excess thermodynamic functions from experimentally investigated solidus–liquidus equilibrium data of a binary organic eutectic system in the condensed phase, comprehensively yields quantitative analysis of molecular interactions considered to be the cause of deviations from the molten state of the system over the entire mole fraction composition range. The excess functions are reliable, since all the parameters involved in their computation are experimentally determined. The obedience of spontaneity criteria, and Planck formulation, $S = k \ln w$ (k and w, respectively, being the Boltzmann constant and the complexion number of constituent phase molecules) by an eutectic system throughout its diagram of state accessible to it, authenticates the reliability of the functions. The application of Guggenheim lattice theory to the eutectic mixture at its liquidus temperature offers supporting evidence to the essence of molecular interactions. The aesthetics and motivation of the present work is that the excess thermodynamic functions, computed from experimentally determined enthalpies of fusion and consequently, from activity coefficients of eutectic phases, by variation in a mole fraction composition range provide an alternative tool to predict a schematic diagram of solidus–liquidus equilibrium curve of a binary system, particularly capable of forming eutectic mixture.

Keywords: Phase diagrams; Excess thermodynamic functions; Molecular interactions; Deviations; Thermal characterization

1. Introduction

An eutectic composite is a heterogeneous system consisting of two or more solidus phases in equilibrium with a single liquidus phase marked by the lowest liquidus temperature in the diagram of state. The growth of composite material from the eutectic melt has the disadvantage that the investigations must be carried out with eutectic systems provided by the nature [1–3]. The eutectic phases cannot be chosen arbitrarily. Nevertheless, eutectic growth covers a wide field, because eutectic reactions are very common in the sense that eutectic phases in many cases are miscible in the liquid state, but not in the solid state. Thermodynamic functions, namely, free energy and entropy are generally considered as major arguments for the miscibility criteria. Eutectic phenomenon by physical appearance seems to be very simple, but its crystallization remains to be elucidated [4–7]. In the present investigation, excess thermodynamic functions have been computed by using activity coefficients of constituent phases determined for different compositions from the thermodynamic analysis of solidus–liquidus phase equilibrium data of naphthalene-benzil, *m*-dinitrobenzene-acetanilide, *m*-dinitrobenzene-phenanthrene, 2,4-dinitrophenol-acetanilide, naphthalene-diphenylamine, naphthalene-vanillin and naphthalene-phenylacetic acid systems to exploring the nature of eutectic phenomenon. Since experimental determinations of excess functions inevitably involve the measurements of activity coefficients of the eutectic phases at various temperatures and pressures, this concerns the problems of practical realization by a highly skilled technique the design of which seems by no means simple. The interest in the excess thermodynamic functions in fact arises from their aesthetics ability, since they provide an alternative path for predicting the phase equilibrium curve of a binary system, particularly capable of forming eutectic mixture, by variation in a mole fraction composition.

---

* Corresponding author.

E-mail address: sharma_bl@rediffmail.com (B.L. Sharma).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.02.026

2. Experimental details

2.1. Materials and their purification

Naphthalene (Loba, SG; mp 353.20 K) and acetanilide (Nice, LR; mp 387.20 K) were respectively purified by slow sublimation method, and repeated distillation under vacuum. Vanillin (Ranbaxy, LR; mp 356.0 K), *m*-dinitrobenzene (Thomas Baker, LR; mp 363.0 K), and 2,4-dinitrophenol (Thomas Baker, LR; mp 363.30 K) were obtained by successive recrystallization with absolute ethyl alcohol. Phenanthrene (Loba, LR; mp 373.80 K) was purified in a manner as reported in Ref. [8]. Phenylacetic acid (Thomas Baker, LR; mp 350.0 K) was purified by repeated crystallization from ethyl acetate (AR), whereas diphenylamine (Reanal, AR; mp 326.50 K) and benzil (Thomas Baker, AR; mp 368.0 K) were used as supplied. The purity of materials was ascertained by the determination of their melting temperatures provided in the parentheses, which are found in good agreement with the recent literature values [9].

2.2. Diagrams of state

Enthalpies of fusion of constituent materials have been obtained by thermal analysis (Shimadzus DSC-60 Model), which are nearly approaching their literature values [9]. The solidus–liquidus equilibrium data for the aforementioned eutectic systems have been investigated by thaw-melt method.

2.2.1. Theory

Experimentally investigated solidus–liquidus equilibrium data of the systems have been subjected to thermodynamic analysis [10], which follow:

$$-\ln x_1^{\mathrm{l}}\gamma_1^{\mathrm{l}} = \frac{\Delta_{\mathrm{f}} H_i^{\circ}}{R}\left[\frac{1}{T} - \frac{1}{T_i^{\circ}}\right] \tag{1}$$

The computational procedure adopted for the essence of excess thermodynamic functions, namely, G^{E}, S^{E} and H^{E}, over the entire experimental range of mole fraction compositions of the systems together with the excess chemical potentials μ_i^{E} ($i = 1, 2$) of their respective eutectic phases is exactly the same as referred earlier [11,12]. The necessary expressions for the excess functions are:

$$G^{\mathrm{E}} = RT[x_1^{\mathrm{l}} \ln \gamma_1^{\mathrm{l}} + x_2^{\mathrm{l}} \ln \gamma_2^{\mathrm{l}}] \tag{2}$$

$$S^{\mathrm{E}} = -R\left[x_1^{\mathrm{l}} \ln \gamma_1^{\mathrm{l}} + x_2^{\mathrm{l}} \ln \gamma_2^{\mathrm{l}} + Tx_1^{\mathrm{l}}\left(\frac{\partial \ln \gamma_1^{\mathrm{l}}}{\partial T}\right)_P + Tx_2^{\mathrm{l}}\left(\frac{\partial \ln \gamma_2^{\mathrm{l}}}{\partial T}\right)_P\right] \tag{3}$$

$$H^{\mathrm{E}} = -RT^2\left[x_1^{\mathrm{l}}\left(\frac{\partial \ln \gamma_1^{\mathrm{l}}}{\partial T}\right)_P + x_2^{\mathrm{l}}\left(\frac{\partial \ln \gamma_2^{\mathrm{l}}}{\partial T}\right)_P\right] \tag{4}$$

$$\mu_i^{\mathrm{E}} = RT \ln \gamma_i^{\mathrm{l}} \tag{5}$$

where x_i^{l} and γ_i^{l} respectively are the mole fraction and activity coefficient of the eutectic phase i (=1, 2) rich in mixture of liquidus temperature, T with enthalpy of fusion $\Delta_{\mathrm{f}} H_i^{\circ}$ at the melting temperature T_i°. The superscript ‘l’ refers to the condensed phase of the system. The procedure for the evaluation of slopes $[\partial \ln \gamma_i^{\mathrm{l}}/\partial T]_P$ ($i = 1, 2$) is similar to that reported earlier [12].

3. Results

Solidus–liquidus equilibrium data and theoretically computed ideal temperatures for the systems in terms of their diagrams of state have been presented in Figs. 1–7. Enthalpies of fusion of the eutectic phases are recorded in Table 1. Table 2 represents the independent parameters of the systems. The activity coefficients and excess chemical potentials of the eutectic phases and the excess functions of the systems at different compositions have been provided in Table 3. Figs. 8–14 represent the variation of excess thermodynamic functions, G^{E} and S^{E} over the entire range of mole fraction compositions of the systems.

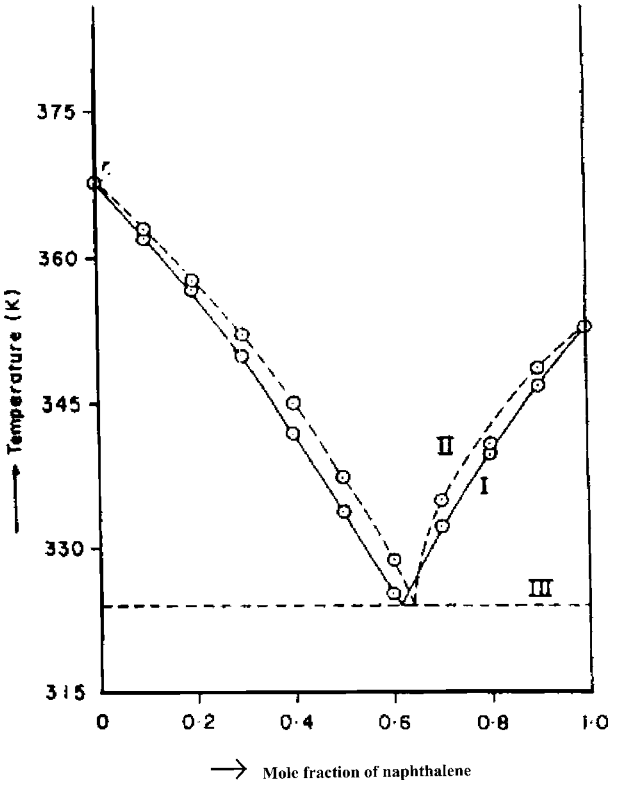

Fig. 1. Phase diagram for naphthalene-benzil system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

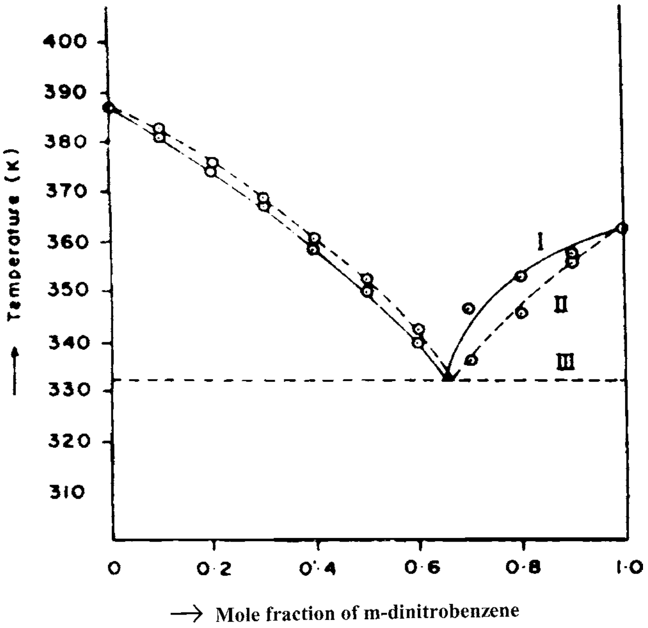

Fig. 2. Phase diagram for *m*-dinitrobenzene-acetanilide system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

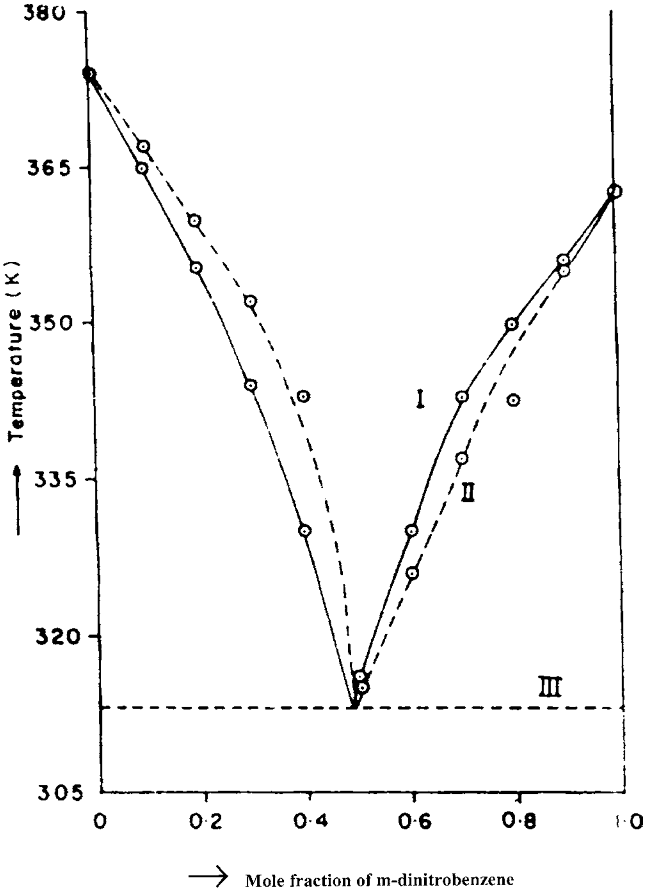

Fig. 3. Phase diagram for *m*-dinitrobenzene-phenanthrene system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

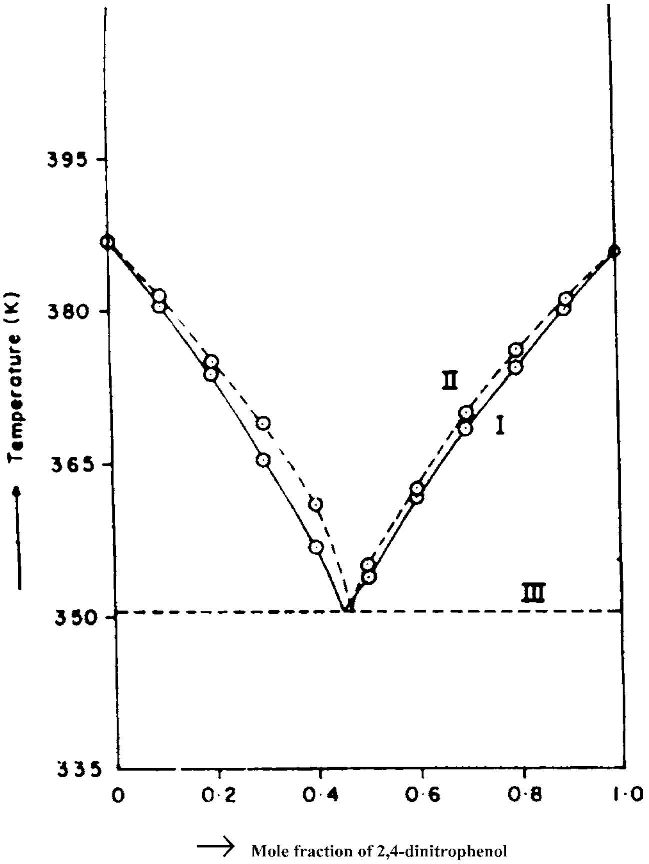

Fig. 4. Phase diagram for 2,4-dinitrophenol-acetanilide system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

Table 1
Enthalpies of fusion of eutectic phases

Eutectic phase	Heat of fusion (kJ mol^{-1})	
	Experimental value	Literature value
Vanillin	16.2	16.1
Naphthalene	18.8	19.0
Diphenylamine	18.2	18.5
Benzil	23.3	23.5
2,4-Dinitrophenol	25.3	–
Acetanilide	23.0	–
m-Dinitrobenzene	13.8	–
Phenanthrene	17.0	16.6
Phenylacetic acid	32.1	32.0

4. Discussion

Diagrams of state presented in Figs. 1–7 reveal the eutectic compositions and eutectic liquidus temperatures for naphthalene-benzil, *m*-dinitrobenzene-acetanilide, *m*-dinitrobenzene-phenanthrene, 2,4-dinitrophenol-acetanilide, naphthalene-diphenylamine, naphthalene-vanillin and naphthalene-phenylacetic acid eutectic systems. While, an insight analysis of the plots (Figs. 8–14) for excess thermodynamic functions, and of the value-pattern of these functions (Table 3), indicates the excess free energy of mix-

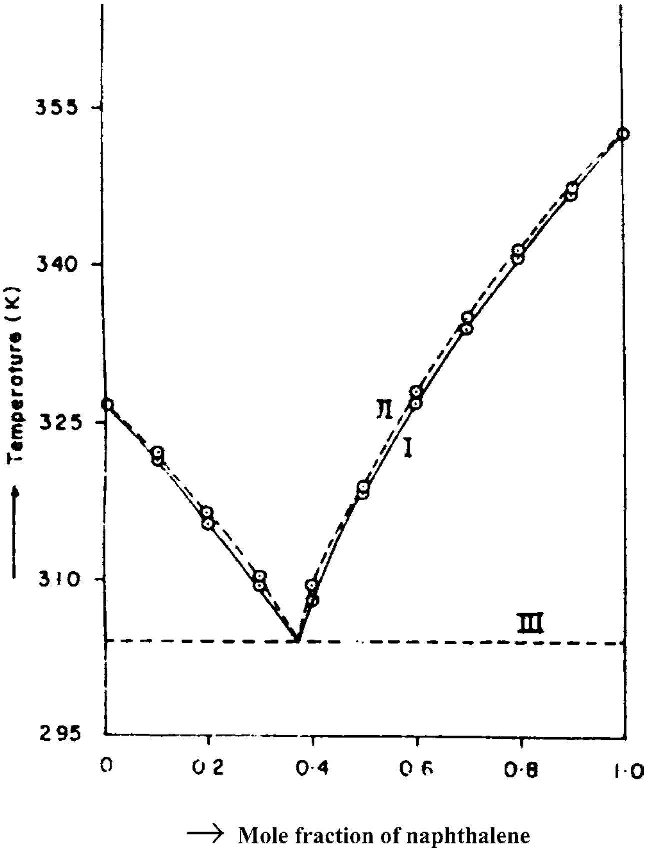

Fig. 5. Phase diagram for naphthalene-diphenylamine system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

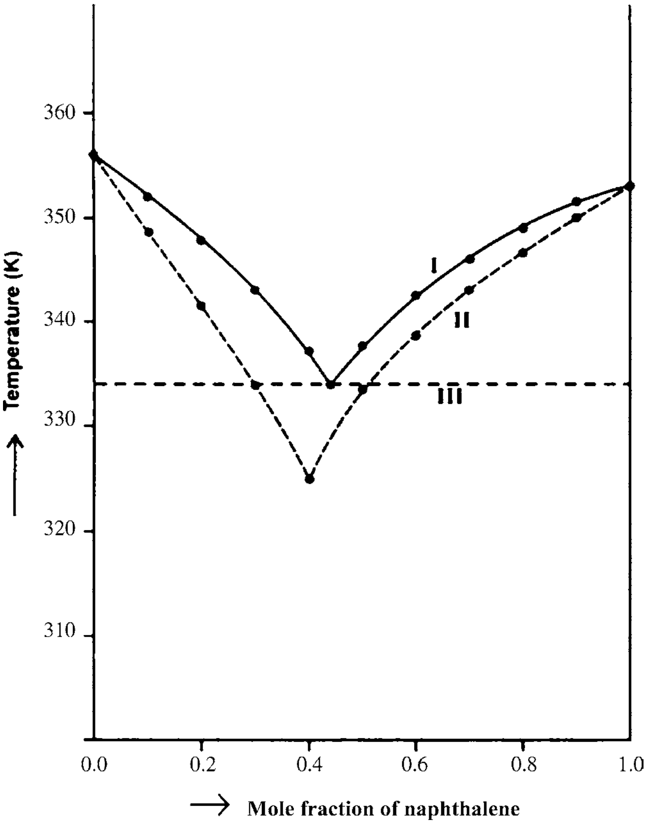

Fig. 6. Phase diagram for naphthalene-vanillin system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

ing, G^E rapidly decreases on either side of solidus–liquidus eutectic equilibrium curves and acquires minimal values at the eutectic compositions. Since an eutectic composition being the lowest liquidus temperature reached by the gradual addition of one of the eutectic phases into the other, obviously the behaviour of G^E is consistent with the miscibility criteria of spontaneity that the mixing of eutectic phases of the system would progress only if every infinitesimal change in the composition of a system is accompanied by a decrease in free energy. For this very reason, the most negative value of Gibbs free energy at the eutectic composition is expected. On the contrary, the excess entropy of mixing, S^E, progressively shows ascending order while tending towards eutectic composition whereat it attains maximal value in each system and thereafter follows the descending order. An eutectic composition by virtue of three phases in equilibrium is a seat of the most probable configuration of the phase molecules. The most probable configuration in any composition represents the maximum number of distinct arrangements of the constituent phase molecules in that composition. The explanation is consistent with the Planck formulation $S = k \ln w$ (k and w respectively being the Boltzmann constant and the configurational weight). The theoretical evidence for S^E to be maximum at the eutectic composition, is explicitly apparent, as thereat the most probable configuration occurs resulting in a maximum value of w compared to pre- and post-eutectic compositions whereat only two phases, one solidus and the other liquidus

Table 2
Independent parameters of the systems

System	A	B	C	A'	B'	C'
Naphthalene-benzil	−409.47	0.72	53.67	−330.29	−221.10	19.33
m-Dinitrobenzene-acetanilide	175.29	7810.62	−9178.20	−533.99	−1520.14	−1532.32
m-Dinitrobenzene-phenanthrene	3055.20	−6671.70	3469.60	−1520.62	−3642.03	−11283.49
2,4-Dinitrophenol-acetanilide	−969.11	3543.96	−3863.39	−379.95	−1250.73	1376.25
Naphthalene-diphenylamine	−16.23	−109.49	−122.91	−214.21	−174.32	−421.20
Naphthalene-vanillin	2169.50	6538.85	9134.73	794.45	−2497.11	−3.77
Naphthalene-phenylacetic acid	446.18	−1726.48	45.26	−409.07	−409.07	8.74

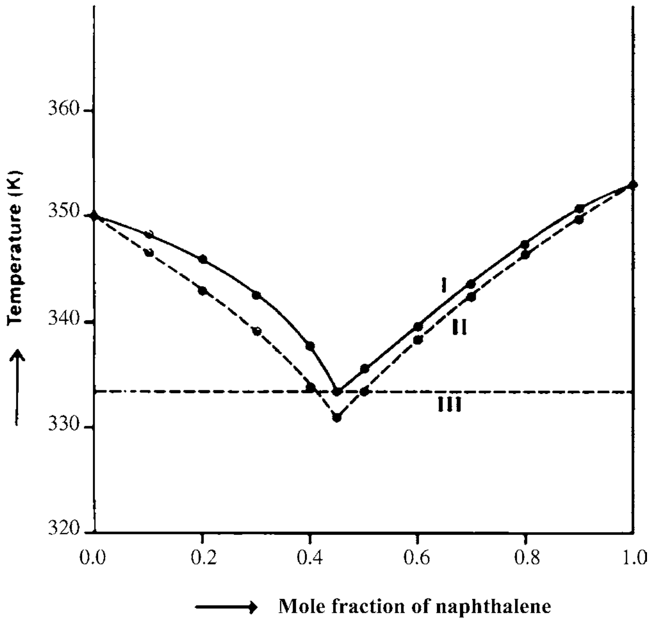

Fig. 7. Phase diagram for naphthalene-phenylacetic acid system: (I) liquidus temperatures; (II) ideal temperatures; (III) solidus temperatures.

coexist. Like G^E and S^E, excess enthalpy of mixing, H^E, also indicates the nonideal character of the systems, since it would otherwise have vanished. The positive and negative magnitudes of H^E (Table 3) respectively are consistent with the positive and negative deviations from the ideal regions of the systems. Moreover, the higher value of H^E for the

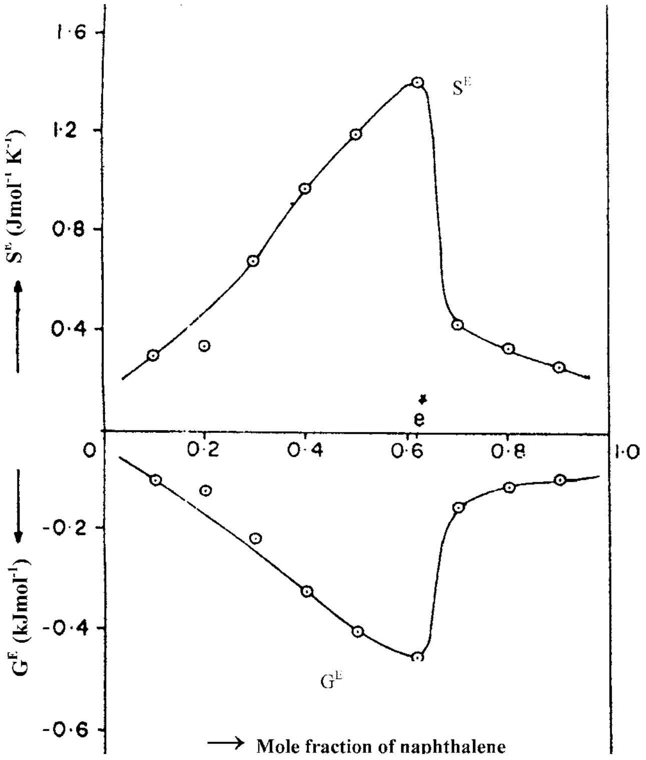

Fig. 8. Excess functions G^E and S^E for naphthalene-benzil system: e* denotes eutectic.

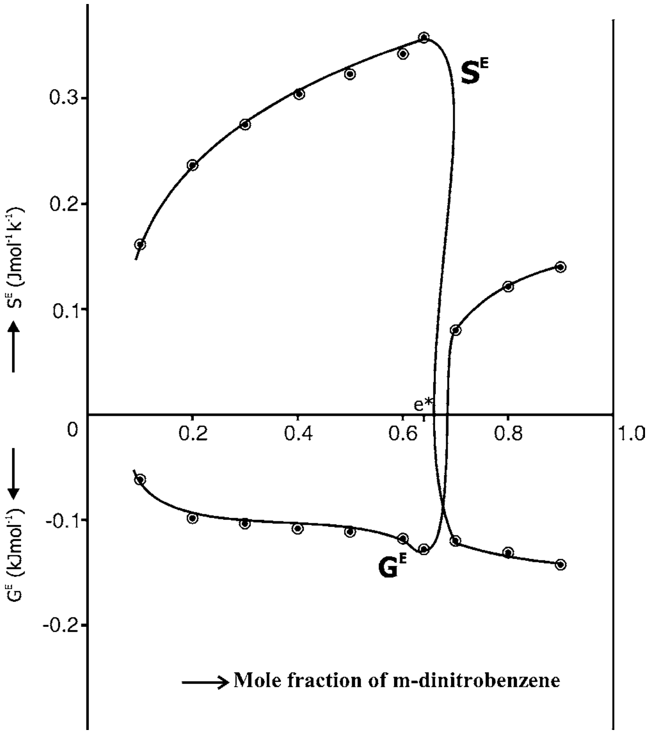

Fig. 9. Excess functions G^E and S^E for *m*-dinitrobenzene-acetanilide system: e* denotes eutectic.

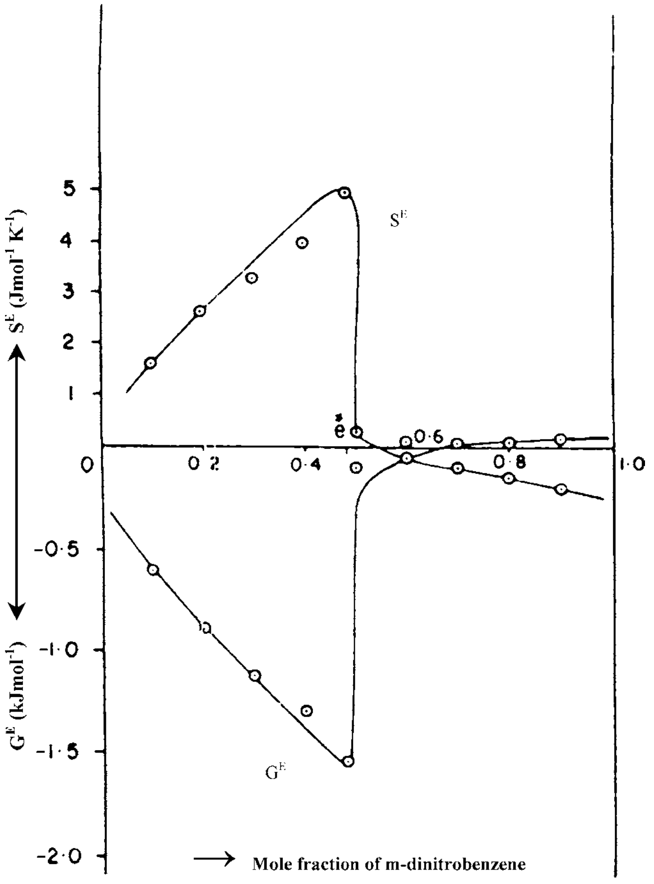

Fig. 10. Excess functions G^E and S^E for *m*-dinitrobenzene-phenanthrene system: e* denotes eutectic.

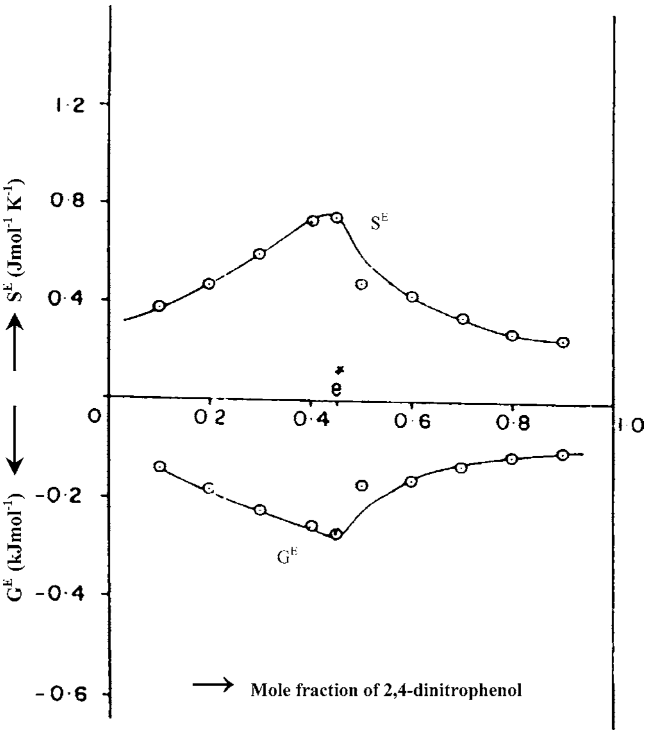

Fig. 11. Excess functions G^E and S^E for 2,4-dinitrophenol-acetanilide system: e* denotes eutectic.

eutectic composition in each of the systems reveals it as the most stable composition among all the compositions accessible to the system. This implies that the obedience of the Planck formulation by excess functions over the entire range of mole fraction compositions at all liquidus temperatures of an experimental solidus–liquidus equilibrium curve, authenticates the reliability of the functions. The results of Guggenheim lattice theory for the eutectic mixtures of the systems would offer supporting evidence to the essence of these functions. According to the theory [12], the activity coefficients of the constituent phases in the eutectic mixture can be determined by the following relation:

$$RT \ln \gamma_i^{\mathrm{l}} = A(1 - x_i^{\mathrm{l}}) + B(1 - x_i^{\mathrm{l}})^2 \tag{6}$$

The activity coefficients calculated in this manner confirmed that the systems do express deviations from their regular behaviour. The equilibrium composition of a binary system showing complete miscibility in solidus and liquidus phases (regular solution) at any liquidus temperature, T, is given by

$$-\ln \frac{x_1^{\mathrm{l}} \gamma_1^{\mathrm{l}}}{x_i^{\mathrm{s}} \gamma_i^{\mathrm{s}}} = \frac{\Delta_{\mathrm{f}} H_i^{\circ}}{R} \left[\frac{1}{T} - \frac{1}{T_i^{\circ}} \right] \tag{7}$$

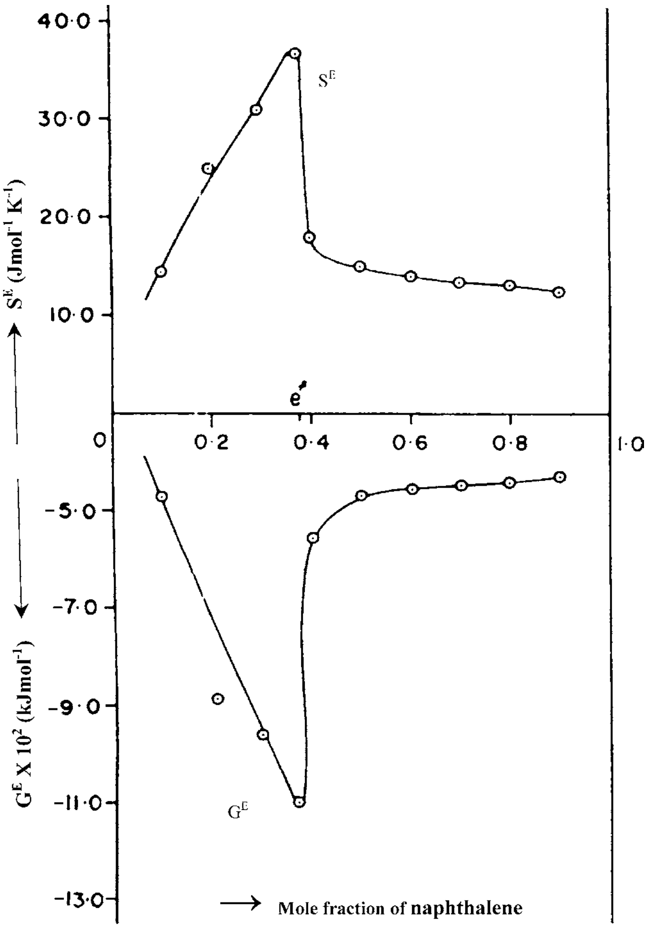

Fig. 12. Excess functions G^E and S^E for naphthalene-diphenylamine system: e* denotes eutectic.

where x_i^{l}, γ_i^{l} and $\Delta_{\mathrm{f}} H_i^{\circ}$ have their usual meanings, and the superscripts 'l' and 's' respectively refer to liquidus and solidus phases. The excess functions, G^E and S^E, respectively computed by Eqs. (2) and (3) for nonideal eutectic mixtures of the systems in their condensed phases have significantly been found different from the values calculated for their ideal behaviour, for which Eq. (7) provides [12]:

$$G^E = (x_1^{\mathrm{l}})_{\mathrm{m}} \Delta_{\mathrm{f}} H_1^{\circ} \left(\frac{T_{\mathrm{m}} - T_1^{\circ}}{T_1^{\circ}} \right) + (x_2^{\mathrm{l}})_{\mathrm{m}} \Delta_{\mathrm{f}} H_2^{\circ} \left(\frac{T_{\mathrm{m}} - T_2^{\circ}}{T_2^{\circ}} \right) \tag{8}$$

$$\begin{aligned} S^E = -\Bigg[& (x_1^{\mathrm{l}})_{\mathrm{m}} \Delta_{\mathrm{f}} H_1^{\circ} \left(\frac{T_{\mathrm{m}} - T_1^{\circ}}{T_{\mathrm{m}} T_1^{\circ}} \right) \\ & + (x_2^{\mathrm{l}})_{\mathrm{m}} \Delta_{\mathrm{f}} H_2^{\circ} \left(\frac{T_{\mathrm{m}} - T_2^{\circ}}{T_{\mathrm{m}} T_2^{\circ}} \right) \Bigg] \end{aligned} \tag{9}$$

$$H^E = G^E - T_{\mathrm{m}} S^E = 0 \tag{10}$$

where subscript 'm' represents the minima in solidus–liquidus equilibrium curves. The Guggenheim lattice theory obeyed by Eqs. (8) and (9) provides lower value of G^E and higher value of S^E for regular eutectic mixture of each system compared to their values obtained for the nonideal counterpart by Eqs. (2) and (3), respectively. For example, values of G^E and S^E for nonideal eutectic mixture of naphthalene-benzil system computed by Eqs. (2) and (3) respectively are $-0.46\,\mathrm{k\,J\,mol^{-1}}$ and $1.41\,\mathrm{J\,mol^{-1}\,K^{-1}}$,

Table 3
Activity coefficients and excess thermodynamic functions of the eutectic phase systems

Eutectic phase system	Mole fraction of eutectic phase (1)	Liquidus temperature (K)	$\ln \gamma_1^l$	$\ln \gamma_2^l$	G^E (kJ mol^{-1})	S^E (J mol^{-1} K^{-1})	H^E (kJ mol^{-1})	μ_1^E (kJ mol^{-1})	μ_2^E (J mol^{-1})
Naphthalene(1)-benzil(2)	0.10	362.20	−0.24	−0.01	−0.11	0.30	−28.52	−709.47	−37.04
	0.20	357.50	−0.19	−0.30	−0.12	0.34	−27.27	−577.21	−8.92
	0.30	350.00	−0.18	−0.04	−0.24	0.68	−25.60	−532.51	−112.03
	0.40	342.10	−0.19	−0.07	−0.34	0.98	−23.96	−531.30	−205.64
	0.50	333.70	−0.20	−0.09	−0.41	1.22	−22.30	−550.16	−262.46
	0.60	325.50	−0.22	−0.09	−0.45	1.39	−20.77	−599.15	−234.36
	0.62 (e*)	324.00	−0.23	−0.05	−0.46	1.41	−20.49	−609.58	−132.13
	0.70	332.50	−0.05	−0.07	−0.15	0.44	−21.19	−129.37	−184.66
	0.80	340.20	−0.02	−0.11	−0.12	0.34	−21.69	−68.16	−306.60
	0.91	347.00	−0.02	−0.20	−0.96	0.28	−22.01	−46.16	−566.60
m-Dinitrobenzene(1)-acetanilide(2)	0.10	381.30	−0.15	−0.01	−0.06	0.16	−29.01	−428.81	−14.58
	0.20	374.60	−0.09	−0.02	−0.10	0.26	−26.83	−268.12	−55.74
	0.30	367.20	−0.03	−0.03	−0.09	0.27	−24.66	−94.02	−101.65
	0.40	359.00	−0.01	−0.05	0.11	0.30	−22.50	−37.91	−150.43
	0.50	350.00	−0.01	−0.07	−0.11	0.31	−20.36	−20.95	−192.63
	0.60	340.00	−0.01	−0.08	−0.11	0.32	−18.26	−40.42	−213.70
	0.65 (e*)	332.50	−0.01	−0.10	−0.12	0.36	−17.05	−41.19	−275.61
	0.70	348.00	0.16	0.10	0.86	−0.10	−17.61	463.79	331.63
	0.80	353.00	0.10	0.35	0.12	−0.13	−17.72	276.17	1024.85
	0.90	358.00	0.10	0.71	0.15	−0.14	−17.23	252.10	2107.89
m-Dinitrobenzene(1)-phenanthrene(2)	0.10	364.60	−1.52	−0.04	−0.58	1.60	−22.69	−0.15	−0.04
	0.20	355.50	−1.27	−0.08	−0.94	2.64	−21.22	−0.25	−0.06
	0.30	343.80	−0.97	−0.15	−1.14	3.32	−19.45	−0.29	−0.11
	0.40	329.60	−0.79	−0.27	−1.31	3.98	−17.52	−0.31	−0.16
	0.48 (e*)	313.00	−0.90	−0.32	−1.55	4.95	−15.54	−0.43	−0.22
	0.50	316.30	0.02	−0.08	−0.08	0.25	−15.80	0.01	−0.04
	0.60	329.60	0.05	−0.11	−0.04	0.13	−16.80	0.03	−0.46
	0.70	342.90	0.07	−0.13	0.05	−0.14	−17.08	0.05	−0.04
	0.80	349.60	0.05	−0.08	0.06	−0.18	−18.08	0.04	−0.02
	0.90	356.30	0.04	−0.09	0.08	−0.22	−18.36	0.04	0.01
2,4-Dinitrophenol(1)-acetanilide(2)	0.10	380.50	−0.28	−0.02	−0.14	0.38	−27.36	−877.15	−62.32
	0.20	373.80	−0.16	−0.03	−0.18	0.47	−26.67	−491.46	−96.66
	0.30	365.50	−0.09	−0.07	−0.22	0.60	−25.75	−264.85	−200.86
	0.40	357.20	−0.06	−0.10	−0.24	0.74	−24.84	−183.92	−286.25
	0.45 (e*)	350.50	−0.02	−0.15	−0.27	0.77	−24.03	−69.12	−431.24
	0.50	354.00	−0.03	−0.10	−0.17	0.49	−24.64	−77.41	−267.15
	0.60	361.70	−0.03	−0.10	−0.16	0.44	−25.97	−77.01	−282.58
	0.70	368.50	−0.02	−0.09	−0.13	0.36	−27.22	−75.06	−266.51
	0.80	374.60	−0.02	−0.08	−0.11	0.29	−28.39	−73.50	−247.32
	0.90	380.20	−0.02	−0.12	−0.10	0.27	−29.52	−71.71	−366.50
Naphthalene(1)-diphenylamine(2)	0.10	321.50	−0.14	−0.00	−4.68	14.56	20.42	−362.96	−11.49
	0.20	315.50	−0.10	−0.02	−8.89	28.20	−19.73	−249.82	−48.53
	0.30	309.50	−0.07	−0.02	−9.61	31.05	−19.04	−187.41	−56.87
	0.38 (e*)	304.20	−0.06	−0.04	−11.19	36.77	−18.44	−151.59	−88.01
	0.40	308.00	−0.03	−0.02	−5.64	18.31	−18.92	−79.92	−40.76
	0.50	318.50	−0.01	−0.02	−4.73	14.86	−20.29	−33.36	−61.28
	0.60	327.00	−0.01	−0.03	−4.69	14.35	−21.45	−21.94	−84.40
	0.70	334.20	−0.01	−0.04	−4.59	13.74	−22.45	−32.04	−110.04
	0.80	341.00	−0.01	−0.05	−4.51	13.22	−23.47	−25.49	−138.39
	0.90	347.00	−0.01	−0.06	−4.45	12.82	−24.38	−30.44	−171.26
Naphthalene(1)-vanillin(2)	0.10	352.0	−0.31	−0.03	−2.05	0.58	0.21	−910.20	−81.74
	0.20	347.5	−0.47	−0.03	−4.78	1.37	0.48	−1355.41	−72.04
	0.30	343.5	−0.29	−0.02	−5.63	1.64	0.56	−821.07	−56.11
	0.40	335.0	−0.12	−0.14	−5.75	1.68	0.68	−3432.24	−396.92
	0.44 (e*)	334.0	−0.06	−0.21	−6.15	2.00	0.69	−157.03	−576.87
	0.50	339.5	−0.21	−0.08	−4.12	1.21	0.41	−592.37	−228.92
	0.60	342.5	−0.14	−0.03	−2.05	0.59	0.20	−395.09	−080.41
	0.70	346.0	−0.11	−0.25	−0.09	0.02	0.01	−320.70	−716.60
	0.80	349.0	−0.08	−0.64	1.74	−0.49	−0.17	−244.07	−184.86
	0.90	351.5	−0.05	−1.33	2.49	−0.70	−0.25	−156.62	−390.00

Table 3 (*Continued*)

Eutectic phase system	Mole fraction of eutectic phase (1)	Liquidus temperature (K)	$\ln \gamma_1^l$	$\ln \gamma_2^l$	G^E (kJ mol^{-1})	S^E (J mol^{-1} K^{-1})	H^E (kJ mol^{-1})	μ_1^E (kJ mol^{-1})	μ_2^E (J mol^{-1})
Naphthalene(1)-phenylacetic acid(2)	0.10	348.5	−0.76	−0.06	−3.71	1.00	0.35	−2205.82	−168.13
	0.20	346.0	−0.57	−0.10	−5.46	1.50	0.52	−1626.99	−276.19
	0.30	342.5	−0.42	−0.11	−6.00	1.72	0.59	−1197.88	−329.93
	0.40	338.5	−0.30	−0.14	−6.45	2.20	0.74	−0853.88	−384.47
	0.45 (e*)	333.5	−0.14	−0.25	−6.50	2.40	0.80	−0385.70	−700.18
	0.50	336.0	−0.08	−0.12	−3.00	1.80	0.60	−0221.86	−334.13
	0.60	339.0	−0.01	−0.17	−2.02	0.59	0.20	−0279.18	−467.12
	0.70	343.5	−0.00	−0.21	−1.87	0.54	0.19	−0086.57	−605.13
	0.80	347.0	−0.01	−0.25	−1.75	0.50	0.17	−0038.71	−724.55
	0.90	351.0	−0.05	−0.26	−1.50	0.45	0.16	−0157.11	−749.57

whereas these values from Eqs. (8) and (9) have been found to be −2.04 kJ mol^{-1} and 6.44 J mol^{-1} K^{-1}. The lower value of G^E for a binary system capable of forming regular eutectic mixture compared to its counterpart yielding non-ideal eutectic mixture, is consistent with the spontaneity criteria of miscibility, since the mixing of eutectic phases of the system progresses only if every infinitesimal change in the composition is accompanied by a decrease of free energy. By contrariety, the higher value of S^E for a regular eutectic mixture determines the extent of randomness of phase molecules predominating their randomness in a non-ideal eutectic mixture. In consequence thereof, $w_{\text{reg}} > w_{\text{real}}$, where w_{reg} and w_{real} respectively are the configurational weights of the phase molecules for regular and nonideal eutectic phase mixtures. The excess enthalpy of mixing, H^E, for such solidus–liquidus equilibrium does vanish which is very apparent by Eqs. (8) and (9). These observations evidently authenticate the reliability of the procedure adopted for computing the excess thermodynamic functions from experimentally determined solidus–liquidus equilibrium data and effectuate an alternative method to studying the diagrams of state of binary systems, particularly capable of forming eutectic mixtures. The magnitude signs of the

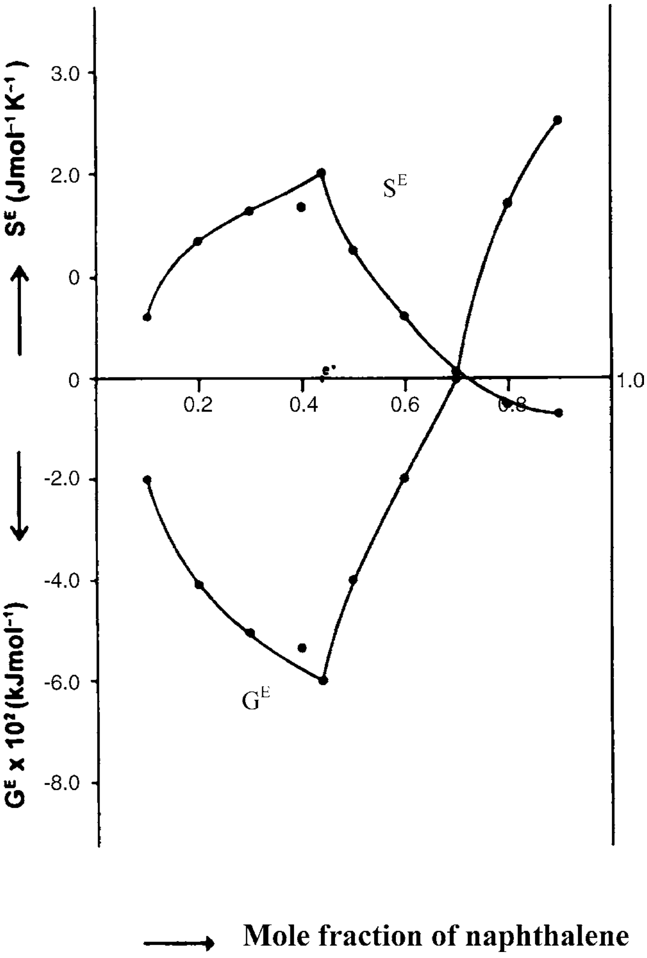

Fig. 13. Excess functions G^E and S^E for naphthalene-vanillin system: e* denotes eutectic.

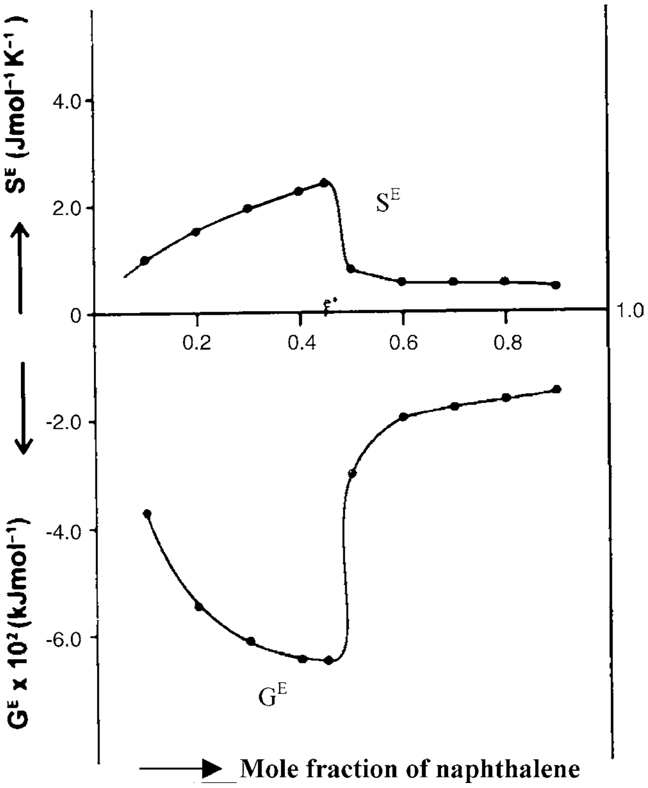

Fig. 14. Excess functions G^E and S^E for naphthalene-phenylacetic acid system: e* denotes eutectic.

computed excess thermodynamic functions predict the thermonature of the investigated systems. For instance, the signs of both G^E and H^E are negative while that of S^E is positive for naphthalene-benzil, naphthalene-diphenylamine and 2,4-dinitrophenol-acetanilide eutectic systems, predicting them to be exothermic in nature, whereas naphthalene-phenylacetic acid is endothermic, since it has both H^E and S^E positive and G^E negative, while other systems, namely, *m*-dinitrobenzene-phenanthrene, *m*-dinitrobenzene-acetanilide and naphthalene-vanillin show mixed thermal nature as the magnitude signs of the excess functions are alternatively positive and negative.

5. Conclusion

The aesthetics and motivation of the present work was to develop an auxiliary device by the variation of excess thermodynamic functions over the entire range of mole fraction compositions as the positional co-ordinates for diagrams of state of binary organic eutectic systems. The excess functions computed from experimentally determined solidus–liquidus equilibrium data of the investigated binary eutectic systems essentially different from their ideal counterparts, provide an alternative procedure for studying their phase diagrams. These functions have attained great importance in the domain of solution studies, since they provide quantitative idea about the nature of molecular interactions occurring at various compositions of binary eutectic melt systems. Direct experimental techniques to measuring excess thermodynamic functions are firstly not developed and secondly their design seems to be by no means simple. To overcome this limitation, a comprehensive theoretical model for excess thermodynamic functions is developed. The excess functions are reliable, as all the parameters involved in their computation are experimentally determined. Moreover, the reliability of excess functions has essentially been authenticated by their obedience to the miscibility criteria of spontaneity and Planck formulation over the entire range of mole fraction compositions of the systems. The applicability of Guggenheim lattice theory to eutectic mixtures of the systems at their respective liquidus temperatures apparently furnishes a supporting evidence to the reliability of excess thermodynamic functions. These functions also express their aesthetics ability in predicting the thermal nature of the systems.

References

[1] W. Albers, in: H. Muller (Ed.), Preparative Methods of Solid State Chemistry, Academic Press, New York, 1972, p. 365.

[2] D.E. Ovesienko, G.A. Alfintsev, in: T. Arizumi (Ed.), Crystals Growth, Properties and Applications, vol. 2, Springer-Verlag, Berlin, 1980, p. 119.

[3] D. Hull, An Introduction to Composite Materials, Cambridge University press, Cambridge, 1985.

[4] B.L. Sharma, Mater. Sci. Eng. B 25 (1994) 11.

[5] R. Derebail, W.R. Wilcox, J. Cryst. Growth 119 (1992) 98.

[6] C.T. Rios, R. Caram, J. Cryst. Growth 174 (1997) 65.

[7] L. Vocadio, G.D. Prince, I.G. Wood, Acta Cryst. B 55 (1999) 484.

[8] B.L. Sharma, N.K. Sharma, M. Rambal, Thermochim. Acta 206 (1992) 71.

[9] D.R. Lide, CRC Handbook of Chemistry and Physics, 80th ed., CRC Press, London, 1999.

[10] B.L. Sharma, N.K. Sharma, P.S. Bassi, Z. Phys. Chem. Leipzig 265 (4) (1984) S769.

[11] J.G. Kirkwood, I. Oppenheim, Chemical Thermodynamics, McGraw-Hill Book Company, New York, 1961, p. 120.

[12] B.L. Sharma, R. Kant, R. Sharma, S. Tandon, Mater. Chem. Phys. 82 (2003) 216.