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Thermoanalysis of binary condensed eutectic phases evincing molecular interactions

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Abstract This article discusses the thermoanalytical model developed in the current work to study the influence of the molecular interactions between binary condensed eutectic phases in terms of excess thermodynamic functions that exhort the ability of providing quantitative idea of the interactions. Non-ideality of binary eutectic systems over the entire range of mole fraction composition is ascertained by subjecting the experimentally determined solidus–liquidus equilibrium data to thermodynamic analysis and thereby, apprehending quantitative idea about the nature of molecular interactions. The estimation of molecular interactions model of binary naphthalene–*o*-nitrophenol, α-naphthol–naphthalene, diphenylamine–α-naphthol, benzil–diphenyl, acenaphthene–antimonytrichloride and cadmium–bismuth eutectic systems authenticates the reliability of the excess functions, since the mixing of the eutectic phases either side of solidus–liquidus equilibrium curves of the systems is found to follow the criteria of spontaneity and Planck formulation $S = k\ln w$; where S, k and w, respectively, are the configurational entropy, Boltzmann constant and complexion number of constituent phase molecules. Moreover, the Guggenheim lattice theory applied to solidus mixtures at their liquidus temperatures offers supporting evidence to the essence of the excess functions and hence the thermomolecular interactions model.

Keywords Excess functions · Non-ideality · Deviation · Phase equilibrium · Eutectic

Introduction

The field of phase equilibria in materials science has become extensive, and a number of review articles have appeared and reported in the literature [1–6] but the nature and liquidus structure of eutectic phenomenon remain in quest. With a view to ascertain the behaviour of eutectic phenomenon in the phase equilibria, excess thermodynamic functions are thought to be the best tool to reveal the molecular interactions between the binary condensed phases (liquidus state) obtained by gradual mixing of one material with the other capable of forming eutectic mixture in the solid state. Thermodynamics restricts the number of experiments to define the state of a system [7–11], particularly, when the experimentation times are quite long or equipment is expensive or not possible to design. Since no conceptual or theoretical framework is available in the literature for understanding the changes in the thermodynamic functions: free energy, entropy, enthalpy, chemical potential, particularly, when attributed to specific changes in case of distinct changes in atomic or crystal structure, the excess functions can simply account for changes in these functions accompanying the formation of non-ideal solution models. Consequently, in the absence of accounting the crystal structure, the excess functions computed from lone enthalpy of fusion data of the constituent phases [7, 12–14] are enable to provide quantitative idea about the nature of molecular interactions which occur on the formation of non-ideal solutions including the non-isostructural solutions on the orthoenstatite-diopside solvus [15–18]. The derivation of Nernst distribution law by excess thermodynamic functions is based on the conventions of classical thermodynamics [19]. The excess functions also find their applications in the development of statistical theories based on fluid models, and play vital role in the formulation of an asymmetric solution model for multicomponent phase calculations [20–22].

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This study aims to three aspects, which are to: (a) ascertain the behaviour of a binary metallic eutectic system in comparison to its transparent analogs; (b) obtain quantitative idea of molecular interactions; and (c) combine this approach with standard equations to predict alternate procedure of binary phase diagram.

Experimental details

Materials and their purification

Homogeneous materials, diphenylamine (Reanal, AR); *o*-nitrophenol (Himedia, AR); benzil (Thomas Baker, AR); α-naphthol (E. Merck, AR); antimonytrichloride (Himedia, AR); and diphenyl (Himedia, AR), were used as supplied, whilst naphthalene (Aldrich, AR) and acenaphthene (Alpha Aesar) were, respectively, purified by sublimation method and repeated crystallization from ethyl acetate (AR). The melting temperatures of the aforementioned materials determined by thaw–melt technique are found on the order comparable to the literature values [23, 24]. The metals, bismuth (Merck, AR), and cadmium (Merck, AR), were also used as such, and their melting temperatures obtained by thermal analysis are found approaching the literature attributions [23, 24]. The enthalpies of fusion of the homogeneous materials were vouched at their respective melting temperatures by thermal analysis, which are in good agreement with the reported values [23, 24].

Diagrams of state

The variable compositional mixtures covering the entire mole fraction composition range of the experimental systems were prepared in Pyrex tubes of nearly the same dimensions. The experimental Pyrex tubes were sealed under vacuum to prevent the evaporation of the tubes'-content, and the homogeneity of the mixtures was attained by heat–chill method. The diagrams of state for binary naphthalene–*o*-nitrophenol, α-naphthol–naphthalene, diphenylamine–α-naphthol, benzil–diphenyl and acenaphthene–antimonytrichloride eutectic systems were studied by determining solidus–liquidus temperatures over their respective entire mole fraction composition range with thaw–melt technique, whereas the melting and liquidus temperatures of Cd–Bi eutectic system were likewise, obtained by thermal analysis.

Results

The experimental data comprising of melting temperatures, heat flows and enthalpies of fusion of the constituent materials are provided in Table 1. Tables 2, 3 and 4, respectively, record the solidus–liquidus equilibrium data of binary naphthalene–*o*-nitrophenol, α-naphthol–naphthalene and diphenylamine–α-naphthol eutectic systems. Likewise, the solidus–liquidus equilibrium curves drawn in Figs. 1, 2, and 3, respectively, represent the phase equilibrium data of binary benzil–diphenyl, acenaphthene–antimonytrichloride and cadmium–bismuth eutectic systems.

Theory

The important thermodynamic properties of any binary eutectic system can be extracted from the thermodynamic analysis of solidus–liquidus equilibrium data of that system in the condensed phase. In this investigation, it is initially attained that each experimental system is non-ideal and the

Table 1 Melting temperatures and heat flow of homogenous materials

Material	Melting temperature/°C		Heat flow/mW	Enthalpy of fusion/Jg^{-1}		Specific heat × 10^{-2}/ Jg^{-1} K^{-1}	
	Experimental value	Literature value [11]	Experimental value	Experimental value	Literature value [11]	Experimental values	Literature values
Naphthalene	80.50	80.26	75.300	149.2	148.5	42.21	42.04
o-Nitrophenol	45.50	44.80	69.479	156.5	143.9	49.14	45.28
α-Naphthol	95.0	95.0	80.809	163.3	160.4	44.38	43.59
Diphenylamine	53.50	53.20	64.661	109.4	108.8	33.50	33.35
Benzil	95.0	94.87	102.957	110.3	111.7	29.97	30.36
Diphenyl	70.20	68.93	73.011	120.6	120.5	35.14	35.24
Cadmium	323.0	323.50	217.045	55.3	55.4	9.28	9.29
Bismuth	272.0	272.67	122.458	53.6	53.3	9.83	9.77
Acenaphthene	94.0	94.50	88.292	136.3	139.5	37.14	37.96
Antimonytrichloride	74.0	75.0	67.072	55.7	55.8	16.05	16.03

Table 2 Solidus–liquidus equilibrium data for naphthalene (1)–*o*-nitrophenol (2) eutectic system

Mole fraction of component (1)	Solidus temperature T_s/°C	Liquidus temperature T_m/°C	Ideal temperature T_{id}/°C
0.0000		45.50	
0.1002	30.50	42.50	41.60
0.2003	30.50	38.50	36.60
0.3003	30.50	31.50	31.00
0.3250 (*e**)	30.50 (T_e)	30.50	31.90
0.4002	30.50	38.50	37.20
0.5001	30.50	48.50	46.50
0.5999	30.50	57.50	55.00
0.7002	30.50	63.50	62.20
0.8001	30.50	70.0	68.50
0.9003	30.50	76.0	75.10
1.0000		80.0	

Table 3 Solidus–liquidus equilibrium data for α-naphthol (1)–naphthalene (2) eutectic system

Mole fraction of component (1)	Solidus temperature T_s/°C	Liquidus temperature T_m/°C	Ideal temperature T_{id}/°C
0.0000		80.50	
0.1002	61.50	74.50	73.50
0.2003	61.50	68.50	68.50
0.3003	61.50	64.00	62.00
0.3950 (*e**)	61.50 (T_e)	61.50	61.50
0.4002	61.50	62.00	59.50
0.5001	61.50	67.50	65.50
0.6003	61.50	72.50	72.00
0.7004	61.50	78.50	78.50
0.8005	61.50	84.50	84.00
0.9003	61.50	90.00	90.00
1.0000		95.00	

Table 4 Solidus–liquidus equilibrium data for diphenylamine (1)–α–naphthol (2) eutectic system

Mole fraction of component (1)	Solidus temperature T_s/°C	Liquidus temperature T_m/°C	Ideal temperature T_{id}/°C
0.0000		95.00	
0.1002	44.50	89.50	90.00
0.2003	44.50	82.50	84.60
0.3003	44.50	76.50	78.70
0.4002	44.50	68.50	72.00
0.5001	44.50	61.50	64.50
0.5999	44.50	52.50	53.70
0.7002	44.50	42.50	45.10
0.7600 (*e**)	44.50 (T_e)	38.50	38.90
0.7999	44.50	41.50	43.90
0.8999	44.50	48.50	49.50
1.0000		54.00	

deviation from its ideal regions was ascertained by computing the activity coefficients of the eutectic phases, *i* (= 1, 2) depending on their richness in the pre- or post-binary mixtures vis–a-vis eutectic mixture, at respective liquidus temperature, *T* by the following equation [13, 25]:

$$-\ln x_i^{\ell}\gamma_i^{\ell} = \frac{\Delta_f H_i^0}{R}\left[\frac{1}{T}-\frac{1}{T_i^0}\right] \qquad (1)$$

where superscript ℓ refers to the condensed phase, whilst $x_i^{\ell}, \gamma_i^{\ell}$, $\Delta_f H_i^0$ and T_i^0, respectively, are the mole fraction, activity coefficient, enthalpy of fusion and melting temperature of eutectic phase, *i* (= 1, 2); *T* represents liquidus temperature of the phase mixture at mole fraction composition, x_i^{ℓ}, and *R* is the gas constant. Ideal liquidus temperatures of the binary naphthalene–*o*-nitrophenol, α-naphthol–naphthalene and diphenylamine–α-naphthol eutectic systems calculated by Eq. 1 putting $\gamma_i^{\ell} = 1$ are recorded in Tables 2, 3 and 4, whilst those of binary benzil–diphenyl, acenaphthene–antimonytrichloride and cadmium–bismuth eutectic systems are likewise obtained and plotted by dotted lines in Figs. 1, 2, and 3.

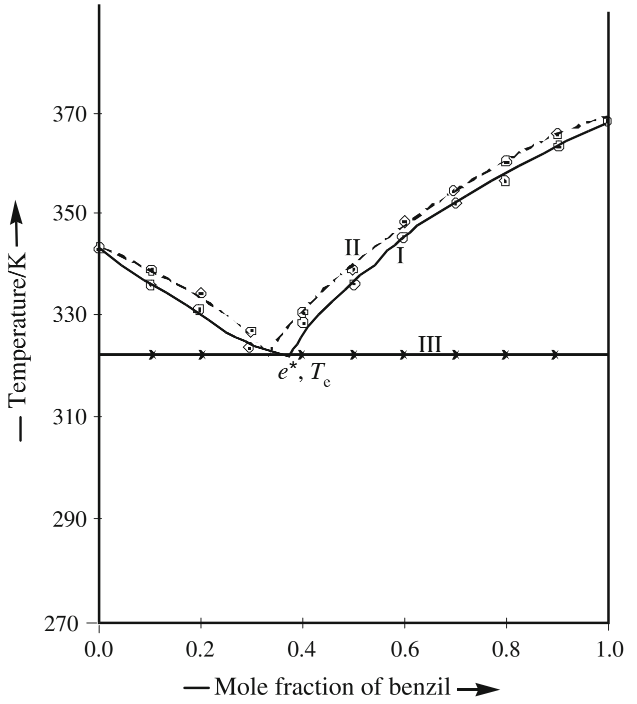

Fig. 1 Diagram of state for benzil–diphenyl system. *I* Liquidus temperatures curve; *II* Ideal temperatures curve; *III* Solidus temperatures; *e** eutectic composition T_e eutectic temperature

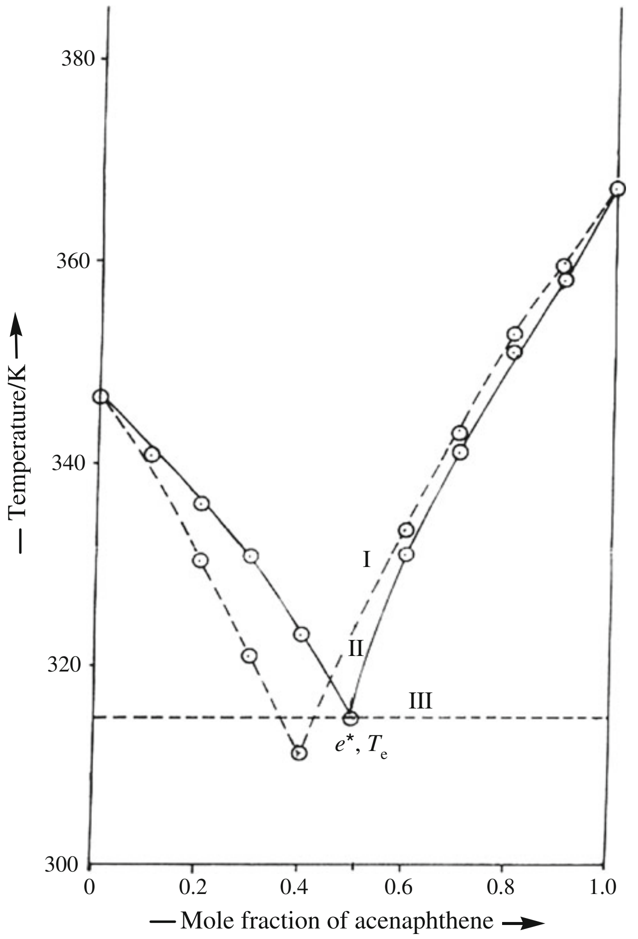

Fig. 2 Diagram of state for acenaphthene–antimonytrichloride system Liquidus temperatures curve. *I* Liquidus temperatures curve; *II* Ideal temperatures curve; *III* Solidus temperatures; *e** eutectic composition; T_e eutectic temperature

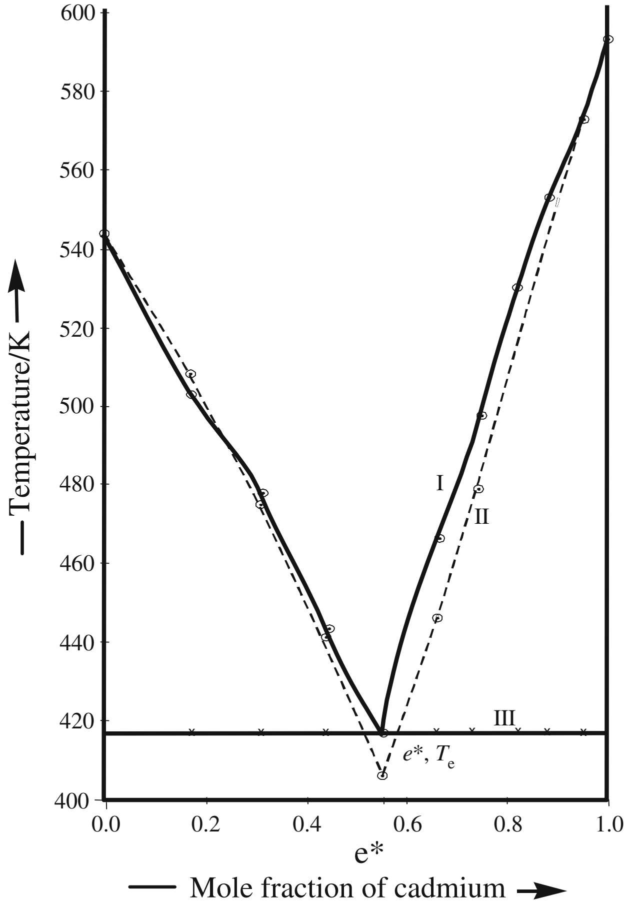

Fig. 3 Diagram of state of cadmium–bismuth system. *I* Liquidus temperatures curve; *II* Ideal temperatures curve; *III* Solidus temperature; *e** eutectic composition; T_e eutectic temperature

The experimental and theoretical solidus–liquidus equilibrium curves in each system evidentially do not coincide with each other confirming its deviation from ideality and the occurrence of molecular interactions between condensed phases as well. With a view to achieve physical understanding and the quantitative idea of molecular interactions, the activity coefficients of the eutectic phases either side of a solidus–liquidus equilibrium curve of each system are computed as a function of their respective temperature and composition from Eq. 1 and thereby, inserted in Eqs. 2 and 3 [12, 26]:

$$RT\ln\gamma_1^\ell = A(x_2^\ell) + B(x_2^\ell)^2 + C(x_2^\ell)^3 \tag{2}$$

$$RT\ln\gamma_2^\ell = A'(x_1^\ell) + B'(x_1^\ell)^2 + C'(x_1^\ell)^3 \tag{3}$$

The constants *A; B; C; A*′; *B*′ and *C*′ evaluated with the application of least-squares method are provided in Table 5. The application of Gibbs–Duhem transformation would determine ln γ_1^ℓ and ln γ_2^ℓ for each experimental

Table 5 Independent parameters of the systems

System	*A*	*B*	*C*	*A*′	*B*′	*C*′
Naphthalene–*o*-nitrophenol	350.38	174.84	−49.025	1652.81	−17998	7313.87
α-Naphthol–naphthalene	197.90	1303.85	−50.00	63.33	159.37	−5908.41
Diphenylamine–α-naphthol	−2921.52	15100.00	−304.43	16291.64	−24345	−16428.57
Benzil–diphenyl	−4.0012	36.89	−62.50	−26268.43	−921.25	.071337
Acenaphthene–antimonytrichloride	−1570.66	−1304.79	2508.00	56.43	7400.02	11518.00
Cadmium–bismuth	5590.30	−17600	3245.28	−921.25	56.43	−345.40

composition comprising of mole fractions x_1^ℓ and x_2^ℓ, with liquidus temperature T of the same branch of the curve. This implies that the corresponding equations for Eqs. 2 and 3 at the same temperature could readily be obtained in the following forms:

$$RT\ln\gamma_1^\ell = (A' - 2B')x_1^\ell - A'\ln x_1^\ell + \left(B' - \frac{3}{2}C'\right)(x_1^\ell)^2 + C'(x_1^\ell)^3 + B' - A' + \frac{C'}{2} \tag{4}$$

$$RT\ln\gamma_2^\ell = (A - 2B)x_2^\ell - A\ln x_2^\ell + \left(B - \frac{3}{2}C\right)(x_2^\ell)^2 + C(x_2^\ell)^3 + B - A + \frac{C}{2} \tag{5}$$

The physical significance of the transformation is that Eqs. 4 and 5 can, respectively, predict quantitative values of ln γ_1^ℓ and ln γ_2^ℓ as functions of x_1^ℓ and x_2^ℓ for any composition at the same liquidus temperature, T. The computed activity coefficient data for the eutectic phases in various binary mixtures of the systems at respective liquidus temperatures are recorded in Tables 6, 7, 8, 9, 10 and 11. The activity coefficient data can further facile the process of reckoning the excess functions, viz., G^{E}, S^{E} and H^{E} of pre-, post-, and eutectic compositions along with the excess chemical potentials of the eutectic members, μ_i^{E} $(i = 1, 2)$ at the same liquidus temperature, T in all the systems at constant pressure using the following relations [9, 13]:

$$G^{\mathrm{E}} = RT[x_1^\ell\ln\gamma_1^\ell + x_2^\ell\ln\gamma_2^\ell] \tag{6}$$

$$S^{\mathrm{E}} = -R\left[x_1^\ell\ln\gamma_1^\ell + x_2^\ell\ln\gamma_2^\ell + Tx_1^\ell\left(\frac{\partial\ln\gamma_1^\ell}{\partial T}\right) + Tx_2^\ell\left(\frac{\partial\ln\gamma_2^\ell}{\partial T}\right)\right] \tag{7}$$

$$H^{\mathrm{E}} = -RT^2\left[x_1^\ell\left(\frac{\partial\ln\gamma_1^\ell}{\partial T}\right)_P + x_2^\ell\left(\frac{\partial\ln\gamma_2^\ell}{\partial T}\right)_P\right] \tag{8}$$

$$\mu_i^{\mathrm{E}} = RT\ln\gamma_i^\ell \tag{9}$$

The values of $[\frac{\partial\ln\gamma_i^\ell}{\partial T}]_P$ $(i = 1, 2)$ for any binary system can be determined from the slopes of the liquidus lines obtained by plotting the activity coefficients ln γ_1^ℓ and ln γ_2^ℓ of the eutectic phases in variable compositional mixtures against their liquidus temperatures T, for that system. The slopes for each system determined in this manner were utilized in computing the excess functions, viz., G^{E}, S^{E}, H^{E} and μ_i^{E} $(i = 1, 2)$ by Eqs. 6, 7, 8 and 9 which are recorded in Tables 6, 7, 8, 9, 10 and 11. The obtained excess functions for the binary benzil–diphenyl, acenaphthene–antimonytrichloride and cadmium–bismuth eutectic systems are also represented in Figs. 4, 5, and 6, with a definite purpose to reveal qualitative variation aspects of the excess functions over the entire mole fraction composition range in general and at the eutectic composition in particular (Table 5).

Discussion

The eutectic compositions (e*) and eutectic temperatures (T_{e}) of binary naphthalene–*o*-nitrophenol, α-naphthol–naphthalene, diphenylamine–α-naphthol and benzil–diphenyl, acenaphthene–antimonytrichloride and cadmium–bismuth systems manipulated from their respective diagrams of state and later experimentally verified are given numerically in Tables 2, 3 and 4 and theoretically indicated in Figs. 1, 2, and 3. The perusal of both quantitative (Tables 6, 7, 8, 9, 10 and 11) and qualitative (Figs. 4, 5 and 6) analyses explores that the excess free energy of mixing, G^{E} would decrease gradually either side of solidus–liquidus equilibrium curves (Figs. 1, 2, 3, 4, 5 and 6) and furnish minima at the eutectic compositions. Evidentially, the variation of G^{E} over the entire mole fraction composition range of each experimental

Table 6 Activity coefficient and excess thermodynamic functions for the binary system naphthalene(1)–*o*-nitrophenol (2)

Mole fraction of component (1)	Liquidus temperature/K	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^{E}/kJ mol^{-1}	Excess entropy S^{E}/J mol^{-1} K^{-1}	H^{E}/J mol^{-1}	Chemical potential of component (1) μ_1^{E}/J mol^{-1}	Chemical potential of component (2) μ_2^{E}/J mol^{-1}
0.1	315.2	−0.0623	0.03532	0.12	−0.382	−0.406	−163.13	200
0.2	311.6	−0.0472	0.07509	0.079	−0.254	−0.146	−122.28	194.52
0.3	304.8	−0.0287	0.05626	0.077	−0.253	−0.114	−72.75	142.57
0.325 (e*)	303.7	−0.3006	0.02244	−0.314	1.035	0.329	−72.49	142.05
0.4	311.8	−0.3506	0.02618	0.263	0.844	0.159	92.26	58.17
0.5	321.3	0.04853	0.0371	−0.015	0.046	0.101	129.64	99.1
0.6	330.5	0.0643	0.0575	0.165	−0.5	−0.25	137.66	112.93
0.7	336.2	0.0274	0.0869	0.193	−0.575	−0.315	145.63	118.8
0.8	343.3	0.03458	0.1302	0.317	−0.925	−0.553	150.7	145.81
0.9	349	0.02566	0.2157	0.57	−1.636	−0.964	174	377.79

The values of G^{E} and S^{E} at eutectic point, e* by Guggenheim lattice theory, are −1.40 kJ mol^{-1} and 4.50 J mol^{-1} K^{-1}, respectively

Table 7 Activity coefficient and excess thermodynamic functions for the binary system α-naphthol (1)-naphthalene (2)

Mole fraction of component (1)	Liquidus temperature/K	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^{E}/kJ mol^{-1}	Excess entropy S^{E}/J mol^{-1} K^{-1}	H^{E}/J mol^{-1}	Chemical potential of component (1) μ_1^{E}/J mol^{-1}	Chemical potential of component (2) μ_2^{E}/J mol^{-1}
0.1	347.4	1.093	−0.00445	0.3	−0.864	−0.154	2888.28	−12.85
0.2	341.7	−1.202	0.0047	−0.67	1.961	0.07	−3414.75	13.35
0.3	337	−1.251	0.04504	−0.96	2.85	0.48	−3505.07	126.19
0.3250 (*e**)	334	−1.261	0.04624	−1.38	4.13	0.659	−3504.78	128.58
0.4	335	0.2394	−0.1686	−0.01	0.029	0.05	666.77	−469.58
0.5	340.6	−0.0818	−0.1419	−0.09	0.265	0.259	−231.75	−401.82
0.6	345.8	−0.0329	0.1968	0.17	−0.492	−0.134	−94.58	−565.79
0.7	351.8	−0.011	0.2627	0.2	−0.568	−0.526	−32.26	768.36
0.8	357.7	0.01294	0.344	0.24	−0.673	−0.732	38.48	1023.02
0.9	363.15	0.0159	0.673	0.25	−0.691	−0.936	48	2031.94

The values of G^{E} and S^{E} at eutectic point, *e** by Guggenheim lattice theory, are −1.42 kJ mol^{-1} and 4.30 J mol^{-1} K^{-1}, respectively

Table 8 Activity coefficient and excess thermodynamic functions for the binary system diphenylamine (1)–α-naphthol (2)

Mole fraction of component (1)	Liquidus temperature/K	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^{E}/kJ mol^{-1}	Excess entropy S^{E}/J mol^{-1} K^{-1}	H^{E}/KJ mol^{-1}	Chemical potential of component (1) μ_1^{E}/J mol^{-1}	Chemical potential of component (2) μ_2^{E}/J mol^{-1}
0.1	362.5	−4.84	−0.01	−1.47	0.00406	0.0018	−2.747	−14.589
0.2	355.7	−9.884	1.329	−2.7	0.0076	0.0033	−5.037	−29.229
0.3	349.7	−13.54	0.811	−10.15	0.0291	0.0262	−11.053	−39.372
0.4	341.7	−16.86	0.327	−18.59	0.545	0.0326	−35.421	−47.886
0.5	334.5	−20.04	−0.06	−27.95	0.084	0.148	−53.821	−55.731
0.6	325.4	−23.43	−0.5	−38.54	0.119	0.182	−75.32	−63.386
0.7	315.4	−27.15	−0.93	−50.57	0.161	0.209	−100.442	−71.193
0.7600 (*e**)	311.7	−29.34	0.052	−57.73	0.186	0.246	−115.394	−76.033
0.8	314.7	−0.045	2.737	0.25	−0.0008	−0.0017	0.496	−0.117
0.9	321.8	−0.002	5.102	0.3	−0.00094	−0.0025	0.589	−0.0053

The values of G^{E} and S^{E} at eutectic point, *e** by Guggenheim lattice theory, are −1516 kJ mol^{-1} and 4.87 J mol^{-1} K^{-1}, respectively

Table 9 Activity coefficient and excess thermodynamic functions for the binary system benzil (1)–diphenyl (2)

Mole fraction of component (1)	Liquidus temperature/K	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^{E}/kJ mol^{-1}	Excess entropy S^{E}/J mol^{-1} K^{-1}	H^{E}/J mol^{-1}	Chemical potential of component (1) μ_1^{E}/J mol^{-1}	Chemical potential of component (2) μ_2^{E}/J mol^{-1}
0.1	336.5	1.046	0.0032	0.3	−0.892	−0.158	2926.35	8.95
0.2	333.1	−0.746	0.055	−0.28	0.841	0.137	−2065.96	152.31
0.3	325.9	−0.59	−0.00622	−0.49	1.505	0.479	−1598.62	−16.85
0.3950 (*e**)	322	−0.69	−0.008	−0.57	1.773	0.906	−1847.2	−21.41
0.4	329.6	−0.3814	−0.00287	−0.42	1.275	0.24	−1044.87	−7.86
0.5	335.5	0.04823	0.00303	−0.06	0.179	0.05	134.53	8.45
0.6	344.8	−0.00329	−0.00199	−0.007	0.02	0.06	−9.43	−5.7
0.7	350.33	0.0281	−0.0353	0.026	−0.074	−0.274	81.83	−102.81
0.8	355.2	0.0509	0.0094	0.125	−0.353	−0.385	150.31	27.75
0.9	361	0.06261	0.00001	0.169	−0.47	−0.67	187.91	0.03

The values of G^{E} and S^{E} at eutectic point, e* by Guggenheim lattice theory, are −1.85 kJ mol^{-1} and 5.73 J mol^{-1} K^{-1}, respectively

Table 10 Activity coefficient and excess thermodynamic functions for the binary system acenaphthene (1)–antimonytrichloride (2)

Mole fraction of component (1)	Liquidus temperature/ K	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy $G^E \times 10^{-2}$/ kJ mol^{-1}	Excess entropy $S^E \times 10^{-1}$/ J mol^{-1} K^{-1}	H^E/ J mol^{-1}	Chemical potential of component (1) μ_1^E/ J mol^{-1}	Chemical potential of component (2) μ_2^E/ J mol^{-1}
0.1	341.00	0.19844	0.02781	1.27	−0.374	−0.534	562.59	78.85
0.2	336.00	−0.1174	0.07893	1.11	−0.331	−0.216	−328.07	220.49
0.3	331.00	−0.3013	0.14373	0.28	−0.085	−0.135	−828.29	395.53
0.4	323.00	−0.3837	0.18358	−1.16	0.36	0.28	−1030.39	492.99
0.5 (*e**)	315.00	−0.3843	0.18334	−16.00	5.09	3.35	−668.37	−2533.25
0.6	331.00	−0.2552	−0.9672	−14.86	4.492	0.85	−702.32	−2869.10
0.7	341.00	−0.1804	−1.0425	−12.44	3.65	0.65	−511.46	−3391.38
0.8	351.00	−0.0979	−1.1962	−9.27	2.642	0.30	−285.84	−3490.84
0.9	358.00	−0.0717	−1.5283	−6.47	1.808	0.26	−213.58	−4548.98

The values of G^E and S^E at eutectic point, *e** by Guggenheim lattice theory, are −21.08 kJ mol^{-1} and 6.69 J mol^{-1} K^{-1}, respectively

Table 11 Activity coefficient and excess thermodynamic functions for the binary system cadmium (1)–bismuth (2)

Mole fraction of component (1)	Liquidus temperature/ K	$\ln\gamma_1$	$\ln\gamma_2$	Excess Gibb's free energy G^E/ kJ mol^{-1}	Excess entropy S^E/ J mol^{-1} K^{-1}	H^E/ J mol^{-1}	Chemical potential of component (1) μ_1^E/ J mol^{-1}	Chemical potential of component (2) μ_2^E/ J mol^{-1}
0.171	503.00	0.0685	−0.013	0.00083	−0.00166	−0.005	286.50	−58.12
0.309	478.00	0.0723	0.0206	0.145	−0.304	−0.312	287.32	81.86
0.440	443.00	0.0770	0.0163	0.158	−0.358	−0.594	283.59	60.03
0.505 (*e**)	417.00	0.1530	−0.767	−1.24	2.978	1.826	530.44	−2660.52
0.656	466.00	0.0776	−1.057	−1.21	2.60	1.60	300.64	−4096.31
0.736	498.00	0.0597	−1.170	−1.09	2.19	0.62	247.18	−4844.64
0.815	530.00	0.0547	−1.211	−0.79	1.491	0.23	241.03	−5336.17
0.887	553.00	0.0294	−1.098	−0.45	0.814	0.14	135.17	−5050.04
0.952	573.00	0.0042	−0.563	−0.11	0.192	0.02	20.00	−2685.42

The values of G^E and S^E at eutectic point, *e** by Guggenheim lattice theory, are −2.19 kJ mol^{-1} and 5.25 J mol^{-1} K^{-1}, respectively

system is consistent with the miscibility criteria of spontaneity [27], because the mixing of the eutectic phases of any binary system would progress only if every infinitesimal change in the composition of that system is accompanied by a decrease in free energy. Obviously, the miscibility arguments favour the cause of most negative value of Gibbs free energy, G^E at the eutectic composition. On the contrary, the excess entropy of mixing, S^E would acquire maxima at the eutectic compositions of the experimental systems which should be there because of its obedience to the miscibility criteria. The explanation of the maximum value of S^E, at the eutectic composition, lies in the concept that the most probable configuration of the eutectic phase molecules in the condensed state, occurs at this very composition (*e**) and temperature (T_e) owing to the co-existence of three phases (two solidus and one liquidus) in equilibrium. Further, the minimum and maximum values of G^E and S^E, respectively, at the eutectic compositions, implicitly, predict that the experimental binary systems follow the criteria of spontaneity and Planck hypothesis, $S = k\ln w$ (where k and w, respectively, being the Boltzmann constant and weight of configuration which is estimated the most probable one at the eutectic composition.). It may be pertinent to mention here that the number of distinct arrangements of phase molecules in any compositional configuration do determine the weight of that configuration, and the most probable compositional configuration is characterized by optimum value of w. The excess chemical potentials, μ_i^E ($i = 1, 2$), of the eutectic phases numerically signify the equilibrium stages in the condensed states of the experimental binary systems. Likewise, the excess enthalpy of mixing, H^E, offers supporting evidence to strengthen the observations of G^E and S^E for the experimental binary systems to be far from being ideal, since H^E is found nontrivial for the systems. Further, the Tables 6, 7, 8, 9, 10 and 11 record positive and negative magnitudes of H^E which are, respectively, consistent with the positive and negative deviations from the ideal regions of the systems. Besides, the higher value of H^E for the eutectic composition in each system conforms to the most stable composition in the entire mole fraction compositional range at all liquidus

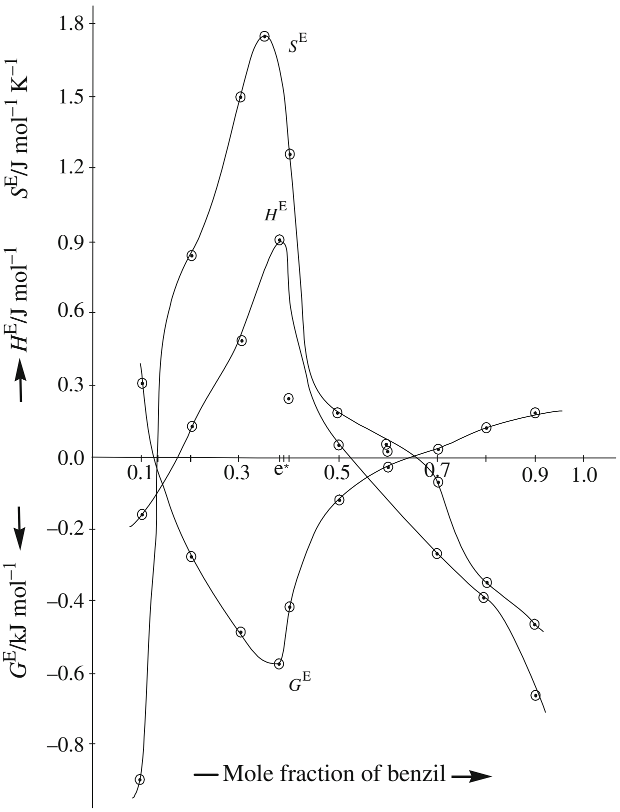

Fig. 4 Excess thermodynamics functions G^E, S^E and H^E for benzil–diphenyl system. *e** eutectic composition

temperatures covered by solidus–liquidus phase equilibrium curve. The computational procedure of the excess functions from enthalpies of fusion data of the eutectic phases confirms their reliability and authenticity in predicting the non-ideal nature of liquidus solutions of the binary systems, since the excess functions express their obedience to miscibility criteria and Planck formulation, thus provide quantitative idea of the molecular interactions.

Moreover, the Guggenheim lattice theory [28] would evidentially offer supporting evidence to the occurrence of molecular interactions in terms of excess thermodynamic functions. The theory speaks that the activity coefficients of the eutectic members can be computed from the following equation [9, 13, 21, 28]:

$$RT\ln\gamma_i^\ell = A(1 - x_i^\ell) + B(1 - x_i^\ell)^2 \tag{10}$$

The activity coefficient data accomplished by Eq. 10 inferred that the experimental systems are not regular. Imagine an equilibrium composition of a binary system which shows complete miscibility in solidus–liquidus regular solution at liquidus temperature, T at which applicability of the lattice theory is represented by Eq. 11:

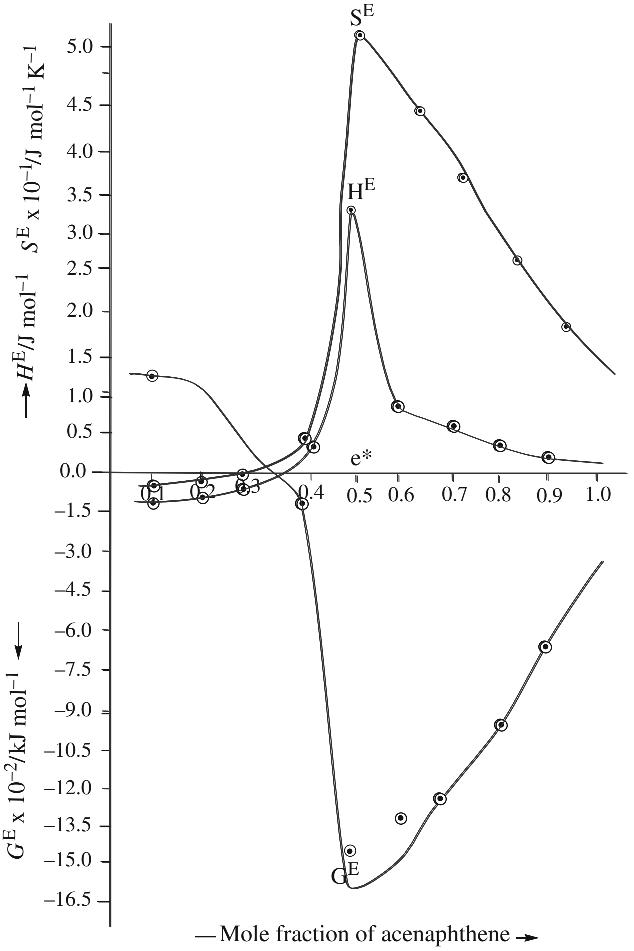

Fig. 5 Excess thermodynamics functions G^E, S^E and H^E for acenaphthene–antimonytrichloride system. *e** eutectic composition

$$-\ln\frac{x_i^\ell\gamma_i^\ell}{x_i^s\gamma_i^s} = \frac{\Delta_f H_i^0}{R}\left[\frac{1}{T} - \frac{1}{T_i^0}\right] \tag{11}$$

where x_i^ℓ, γ_i^ℓ, $\Delta_f H_i^0$ and T_i^0 are already defined for the eutectic phase i (= 1, 2) with mole fraction x_i^s and activity coefficient γ_i^s in the solidus phase in equilibrium with the liquidus phase at temperature T. The excess functions G^E and S^E calculated by Eqs. 6 and 7 for the eutectic compositions of the binary systems are not found in agreement with their values obtained by Eqs. 12 and 13, which are an extraction of Eq. 11 presuming the nature of eutectic mixture to be regular:

$$G^E = (x_1^\ell)_m\Delta_f H_1^0\left(\frac{T_m - T_1^0}{T_1^0}\right) + (x_2^\ell)_m\Delta_f H_2^0\left(\frac{T_m - T_2^0}{T_2^0}\right) \tag{12}$$

$$S^E = -\left[(x_1^\ell)_m\Delta_f H_1^0\left(\frac{T_m - T_1^0}{T_m T_1^0}\right) + (x_2^\ell)_m\Delta_f H_2^0\left(\frac{T_m - T_2^0}{T_m T_2^0}\right)\right] \tag{13}$$

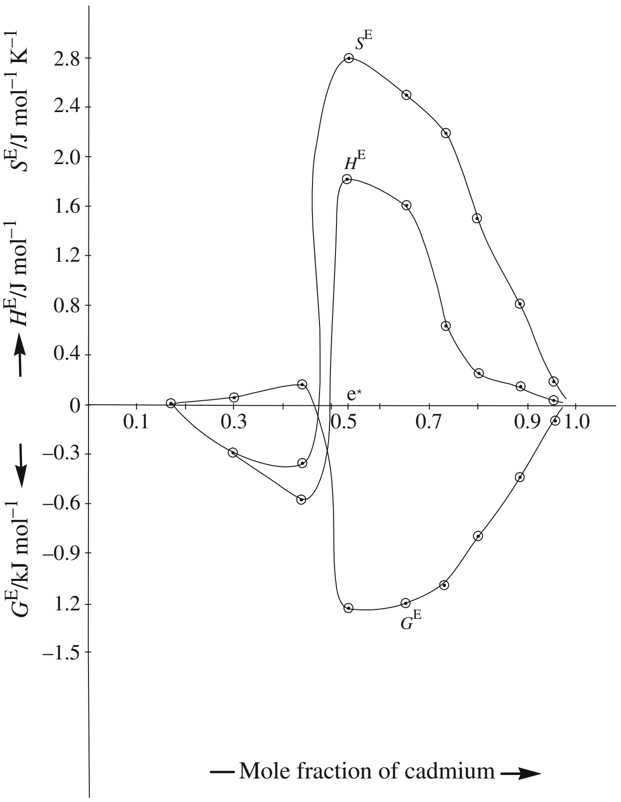

Fig. 6 Excess thermodynamics function G^E, S^E and H^E for cadmium–bismuth system. *e** eutectic composition

$$H^E = G^E - T_m S^E = 0 \tag{14}$$

the subscript 'm' represents the minima in solidus–liquidus equilibrium curves. Equations 12 and 13 expressing their obedience to the Guggenheim lattice theory, respectively, yield minimal value of G^E and maximal value of S^E for regular eutectic mixture presumed in each experimental system compared to the value attained by the non-ideal counterpart as revealed by Eqs. 6 and 7. For instance, G^E and S^E values for the nonideal eutectic mixture of naphthalene–*o*-nitrophenol system obtained by Eqs. 6 and 7, respectively, are -0.314 kJ mol^{-1} and 1.035 J mol$^{\mathbf{-1}}$ K^{-1}. On the contrary, the regular counterpart is explored to have respective values of the magnitude of -1.40 kJ mol^{-1} and 4.50 J mol$^{\mathbf{-1}}$ K^{-1} computed by Eqs. 12 and 13. An insight analysis indicates that the value of G^E obtained by Eq. 12 for regular eutectic melt is more negative than its value computed by Eq. 6, a physical phenomenon which is consistent with the criteria of spontaneity (miscibility) that the formation of regular eutectic mixture progresses only if every infinitesimal change in composition shows a decrease in Gibbs free energy implying certainly low in comparison to that of a non-ideal eutectic mixture. Contrarywise, Eq. 13 yields S^E which is more positive for the regular eutectic compositional melt because of the most probable configuration of the phase molecules that occur in the regular eutectic melt predominating the weight of phase molecules configuration in the non-ideal eutectic melt. This implies that molecular interactions exhibit the ability to uphold the inequality $w_{\text{reg}} > w_{\text{real}}$, where w_{reg} and w_{real}, respectively, represent the number of distinct arrangements of phase molecules in the regular and non-ideal eutectic melts. The conformity of all the experimental binary eutectic systems with the criteria of miscibility and Planck formulation explicitly evinces the reliability of thermodynamic analysis and thereby, the computational procedure of excess functions using lone enthalpy of fusion data of the constituent phases. Besides, the negative and positive numerical signs of the excess functions, viz., G^E is negative, and S^E and H^E are positive, for the eutectic compositions of binary naphthalene–*o*-nitrophenol, α-naphthol–naphthalene, diphenylamine–α-naphthol, benzil–diphenyl, acenaphthene–antimonytrichloride and cadmium–bismuth systems, predict that these compositions being endothermic in nature from thermochemistry view point, represent the most stable regions in the domain of temperature–composition range of phase equilibria spatial fidelity.

Conclusions

The present investigation explores that the molecular interactions in binary metallic eutectic systems, like any binary organic eutectic system, can be predicted by means of excess thermodynamic functions. Since no conceptual or theoretical framework is available in the literature for comprehensive understanding the changes in the thermodynamic functions, viz., free energy, enthalpy, entropy and chemical potential, specific to quantitative relevance of molecular interactions, the excess functions are only the exception that can predict the changes in these functions which accompany the formation of non-ideal liquidus structure. Implicit in the present approach is the concept of reliability of the excess functions that facilitates the thermomolecular interactions model. The excess functions express their obedience to the spontaneity criteria and Planck formulation throughout accessible phase equilibrium curve over the entire temperature–composition range in the condensed phase. The Guggenheim lattice theory applied to study the nature of eutectic mixtures at their liquidus temperatures offers supporting evidence to the essence of excess thermodynamic functions and hence, the thermomolecular interactions model. All these evidences not only evince the reliability of the excess functions but also authenticate the enabling authority of the lone enthalpy of fusion data obtained by the thermal analysis of the constituent phases to the accomplishment of the excess functions. Besides, this study emphasizes that the excess thermodynamic functions being prominent manipulators in the domain of solutions, evidentially, offer an alternative procedure to study the solidus–liquidus equilibrium curve of any binary system in general and especially, capable of forming eutectic mixture by variation of an excess thermodynamic quantity (G^E, S^E and H^E) over the entire composition range of that system, which is a significant contribution in phase equilibria.

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