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Excess thermodynamic functions: G^E and S^E of binary organic eutectic systems

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Abstract

Experimentally investigated solidus–liquidus equilibrium data for binary organic camphor–benzoic acid, α-chloroacetic acid–vanillin, benzoic acid–α-naphthylamine, naphthalene–*o*-nitrophenol, phenanthrene–naphthalene, α-naphthol–naphthalene and diphenylamine–α-naphthol eutectic systems have been subjected to thermodynamic analysis to compute activity coefficients for the components in the binary mixtures and the excess energy functions G^E and S^E for these mixtures. The computed data show the minimum value for G^E at the eutectic composition being the lowest liquidus temperature and the maximum value for S^E because of the most probable distribution of the component molecules at this composition in the solidus–liquidus phase diagram. The values of S^E at the pre-, post-, and eutectic compositions of binary composite systems show the applicability of Planck's formulation $S = k \ln w$ (k and w being respectively the Boltzmann constant and the weight of distribution) over the entire range of composition covered by the phase equilibrium curve. The excess functions ascertain the nonideal character of binary systems and predict their thermal nature. The result of Guggenheim's lattice theory for eutectic mixtures at their liquidus temperatures offers evidence to support the thermodynamic model for the eutectic phenomenon.

INTRODUCTION

Thermodynamic analysis of solidus–liquidus equilibrium data provides important thermodynamic properties of binary mixtures in the condensed phase. In spite of the simplicity of eutectic phenomena, the nature of the eutectic crystallization remains to be elucidated. Thermodynamics define the eutectic point in a binary mixture as the lowest liquidus temperature in the solidus–liquidus phase diagram, at which two solid phases are in equilibrium with a single liquid phase and the eutectic is generally considered to be a simple mechanical mixture. Activity coefficients for the components in the binary mixtures determined from the analysis of the

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solidus–liquidus equilibrium curve could be used in computing excess thermodynamic functions G^E and S^E. These excess functions are of great importance for their use in examining various theories of solutions [1] and in particular the lattice model theories for the mixtures [2]. The lattice model theory of Guggenheim could be more rigidly applicable for these mixtures near their liquidus temperature, since in the vicinity of this temperature, the structure of the liquid phase closely resembles its solid phase. With a view to showing the applicability of Planck's fomulation and to checking the validity of the Guggenheim lattice theory, phase equilibrium data for binary camphor–benzoic acid, α-chloroacetic acid–Vanillin, benzoic acid–α-naphthylamine, naphthalene–*o*-nitrophenol, phenanthrene–naphthalene, α-naphthol–naphthalene and diphenylamine–α-naphthol eutectic systems have been investigated and subjected to thermodynamic analysis.

EXPERIMENTAL

Materials

Camphor (Loba-chem., m.p. 448.20 K), benzoic acid (BDH, AR, m.p. 395.50 K), vanillin (AR, m.p. 354.90 K), α-naphthylamine (Merck, AR, m.p. 323.0 K), α-naphthol (Merck, AR, 368.0 K), α-chloroacetic acid (BDH, Pro Analysi, m.p. 336.20 K) and diphenylamine (Merck, AR, m.p. 327.0 K) were used as supplied. Naphthalene (Riedel, LR, m.p. 353.50 K) was purified by slow sublimation and phenanthrene (Fluka, AG, m.p. 373.0 K) was repeatedly distilled under reduced pressure at constant temperature and the distillate was further purified by fractional crystallization with absolute alcohol, whereas *o*-nitrophenol (Loba, LR, m.p. 318.0 K) was purified by successive steam distillation followed by crystallization with hot absolute alcohol. The purity of the materials was ascertained by the determination of the melting points (written against each sample) which are in good agreement with recent literature values [3–6].

Solidus–liquidus equilibrium data for binary mixtures of the aforementioned eutectic systems have been obtained by thaw–melt method and heats of fusion of the components of the mixtures were determined by DSC (Metler TA 3000 system) and found to be very close to their literature values [3,7].

RESULTS AND DISCUSSION

The results of phase equilibria are plotted in Figs. 1–7 to ascertain the eutectic compositions of the systems undertaken for investigation. Heats of fusion of the constituent materials are given in Table 1.

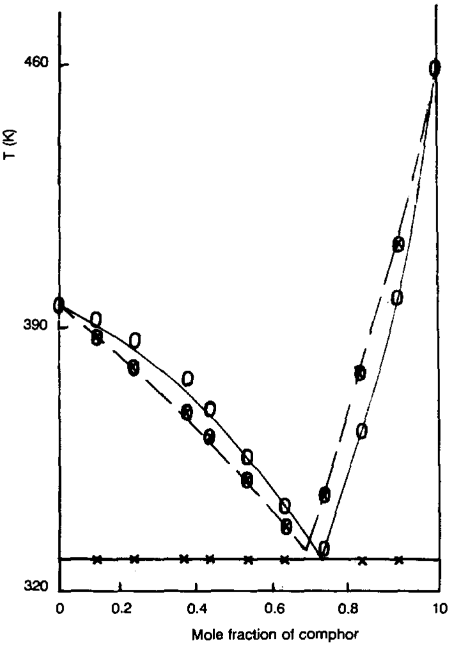

Fig. 1. Phase diagram for the system camphor + benzoic acid: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

Solidus–liquidus equilibrium data for a binary eutectic mixture obey the thermodynamic relation [5]

$$-\ln x_i^1 r_i^1 = \frac{\Delta_f H_i^\ominus}{R}\left[\frac{1}{T} - \frac{1}{T_i^\ominus}\right] \tag{1}$$

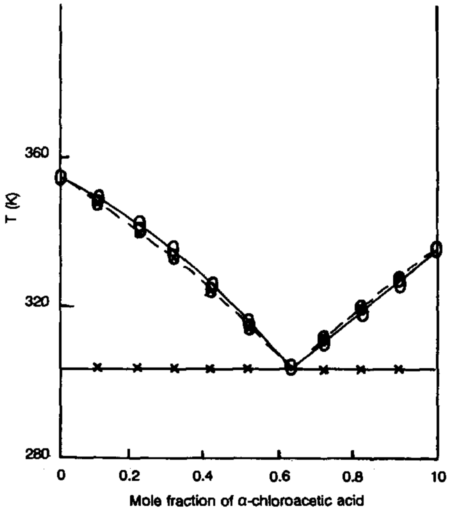

Fig. 2. Phase diagram for the system α-chloroacetic acid + vanillin: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

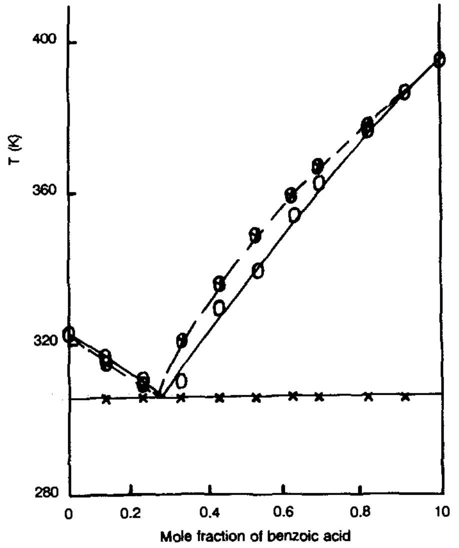

Fig. 3. Phase diagram for the system benzoic acid + α-naphthylamine: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

where x_i^1, r_i^1, $\Delta_f H_i^{\ominus}$ and $T_i^{\ominus}$ are respectively the mole fraction, activity coefficient, heat of fusion and freezing point of component i ($i = 1$, 2) depending upon whether a mixture is enriched in component 1 or 2. T is the liquidus temperature for the solidus–liquidus phase at mole fraction x_i^1. The ideal curve for the phase equilibrium can be obtained from eqn. (1) by

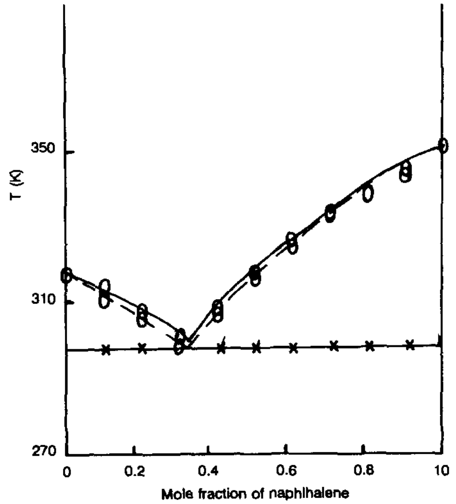

Fig. 4. Phase diagram for the system naphthalene + o-nitrophenol: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

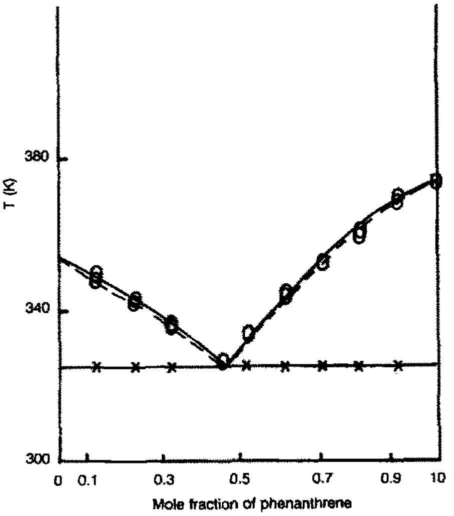

Fig. 5. Phase diagram for the system phenanthrene + naphthalene: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

substituting $r_i^1 = 1$. Experimental values of $\Delta_f H_i^{\ominus}$ were used in this computation. In Figs. 1–7, broken lines represent the ideal phase diagrams for the systems showing thereby their deviation from ideality. The activity coefficients for each branch of the experimental phase equilibrium curve were computed as a function of temperature and composition from eqn. (1). The computed activity coefficient data for constituent materials in

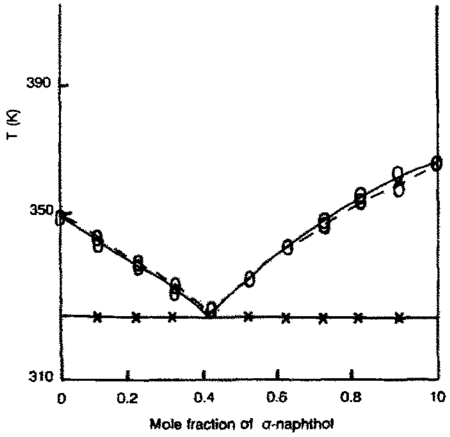

Fig. 6. Phase diagram for the system α-naphthol + naphthalene: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

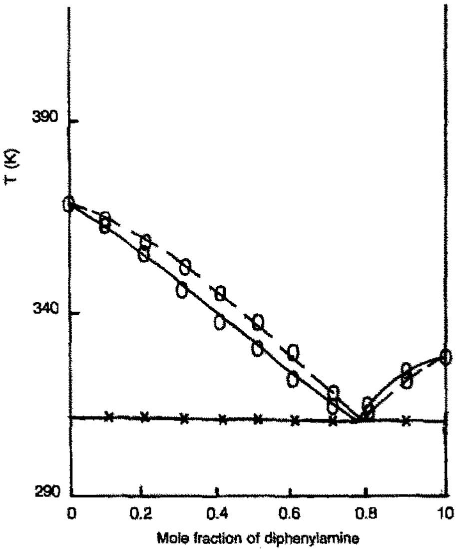

Fig. 7. Phase diagram for the system diphenylamine + α-naphthol: (———) experimental curve; (— — —) ideal curve; (×) thaw points (solidus temperatures).

various binary mixtures of the systems were fitted in eqns. (2) and (3).

$$RT \ln r_1^l = A(x_2^l) + B(x_2^l)^2 + C(x_2^l)^3 \tag{2}$$

$$RT \ln r_2^l = A'(x_1^l) + B'(x_1^l)^2 + C'(x_1^l)^3 \tag{3}$$

The constants A, A', B, B' and C, C' were determined by the least-squares method. Table 2 incorporates these constants. The Gibbs–Duhem transformation was used to determine ln r_2^l at the same temperature T for the same branch of curve at a composition, x_1^l. The correspond-

TABLE 1

Heats of fusion of components

Component	Heat of fusion (kJ mol^{-1})		Component	Heat of fusion (kJ mol^{-1})	
	Expt.	Lit. [a]		Expt.	Lit. [a]
Camphor	4.40		Naphthalene	19.11	19.30
Benzoic acid	17.30	17.33	o-Nitrophenol	17.88	18.05
α-Chloroacetic acid	12.35	12.30	Phenanthrene	18.23	18.13
Vanillin	16.13		α-Naphthol	23.93	23.70
α-Naphthylamine	13.30	13.37	Diphenylamine	17.72	17.85

[a] Refs. 3, 7.

TABLE 2

Constants for the system

System	A	B	C	A'	B'	C'
Camphor–benzoic acid	−689.51	3498.91	−5797.69	405.16	−487.61	1.57
α-Chloroacetic acid–vanillin	−389.19	744.24	−443.50	−270.20	1799.08	−2425.61
Benzoic acid–α-naphthylamine	−1945.31	7756.03	−7743.41	222.74	−548.75	0.00
Naphthalene–*o*-nitrophenol	4.70	17.03	24.22	−182.78	588.34	−1103.20
Phenanthrene–naphthalene	−59.68	264.88	−211.25	2.48	452.24	−1225.25
α-Naphthol–naphthalene	19.21	−82.96	45.36	2934.41	−10856.23	8695.00
Diphenylamine–α-naphthol	599.04	−1485.02	710.84	−161.74	229.62	−428.49

ing equations for eqns. (2) and (3) at the same temperature T can readily be obtained as

$$RT \ln r_2^1 = (A - 2B)x_2^1 - A \ln x_2^1 + \left(B - \tfrac{3}{2}C\right)\left(x_2^1\right)^2 + C\left(x_2^1\right)^3 + B - A + \tfrac{1}{2}C \tag{4}$$

$$RT \ln r_1^1 = (A' - 2B')x_1^1 - A' \ln x_1^1 + \left(B' - \tfrac{3}{2}C'\right)\left(x_1^1\right)^2 + C'\left(x_1^1\right)^3 + B' - A' + \tfrac{1}{2}C' \tag{5}$$

Equations (4) and (5) provide ln r_1^1 and ln r_2^1 corresponding to x_1^1 and x_2^1 for any mixture at a temperature T. The computed activity coefficient data for the components in binary mixtures of all undertaken systems at their different liquidus temperatures are provided in Table 3. The excess thermodynamic functions, free energy and entropy of mixing of the components at the same liquidus temperature T at constant pressure, have been determined from eqns. (6) and (7) [8]

$$G^{\mathrm{E}} = RT\left[x_1^1 \ln r_1^1 + x_2^1 \ln r_2^1\right] \tag{6}$$

$$S^{\mathrm{E}} = -R\left[x_1^1 \ln r_1^1 + x_2^1 \ln r_2^1\right] \quad \text{(condensed phase)} \tag{7}$$

The values of these functions for each system are recorded in Table 3 and were plotted graphically. It has been found that three common types of curves are possible in these systems as represented in Figs. 8–10. The excess functions of eutectic systems camphor–benzoic acid and benzoic acid–α-naphthylamine (Table 3) exhibit identical patterns before and after the eutectic point (Fig. 8); Fig. 9 is for the excess functions of the α-chloroacetic acid–vanillin eutectic system and Fig. 10 denotes the excess

TABLE 3

Activity coefficient and excess thermodynamic function data for different binary mixtures

Mixture	Mole fraction of component (1)	Liquidus temperature (K)	$\ln r_1$	$\ln r_2$	G^E (kJ mol^{-1})	$S^E \times 10^{-3}$ (kJ mol^{-1} K^{-1})
Camphor (1) + benzoic acid (2)	0.1092	393.00	0.2217	0.0529	0.25	−0.67
	0.2000	385.50	0.0196	0.0878	0.24	−0.62
	0.3000	377.00	−0.0477	0.0995	0.17	−0.46
	0.4000	367.50	−0.0664	0.1108	0.12	−0.33
	0.5001	355.80	−0.0634	0.1067	0.06	−0.18
	0.6003	342.70	−0.0505	0.1060	0.03	−0.10
	0.6750(E) [a]	329.60	−0.0320	−1.3684	−1.29	3.91
	0.6997	330.00	−0.0731	−1.3790	−1.27	3.84
	0.8001	361.50	−0.0646	−1.2755	−0.85	2.34
	0.9000	397.70	−0.0470	−1.2030	−0.38	1.18
α-Chloroacetic acid (1) + vanillin (2)	0.1000	349.00	−0.1684	0.0130	−1.00	0.40
	0.1997	341.50	−0.2458	0.0087	−1.20	0.35
	0.3000	333.50	−0.3248	0.0060	−2.5	0.87
	0.4000	324.80	−0.3578	0.0044	−3.80	1.10
	0.5000	315.10	−0.3415	0.0030	−4.40	1.40
	0.6000(E) [a]	303.20	−0.2858	−0.0154	−4.50	1.50
	0.7000	310.20	−0.1002	−0.0086	−2.00	0.60
	0.8000	318.10	−0.0816	−0.0592	−2.00	0.64
	0.9000	362.30	−0.0493	−0.2446	−1.80	0.57
Benzoic acid (1) + α-naphthylamine (2)	0.1000	317.00	0.0501	0.0119	0.41	−0.13
	0.2000	310.40	−0.0245	0.0220	0.33	−0.11
	0.2460(E) [a]	306.20	−1.4049	0.0106	−8.59	2.80
	0.3000	310.00	−1.3180	0.1490	−7.50	2.42
	0.4000	329.40	−0.1384	−0.2745	−6.03	1.83
	0.5000	340.00	−0.1646	−0.1750	−4.65	1.41
	0.6000	354.10	−0.1031	−0.1004	−3.00	0.84
	0.6684	363.00	−0.0611	−0.0366	−1.60	0.44
	0.8000	376.20	−0.0366	−0.0331	−0.70	0.19
	0.9000	387.60	−0.0053	−0.0010	−0.17	0.04

Naphthalene (1) + o-nitrophenol (2)	0.1000	315.60	−0.3512	0.0494	−0.24	0.80 [b]
	0.2000	309.90	−0.4314	0.0383	−1.43	4.63 [b]
	0.3000	302.00	−0.3935	0.0352	−2.34	7.77 [b]
	0.3250(E) [a]	300.50	−0.3770	0.0360	−2.45	8.15 [b]
	0.4000	310.00	0.0048	0.0119	0.22	−7.00 [b]
	0.5000	320.00	0.0131	0.0175	0.40	−1.26 [b]
	0.6000	328.00	0.0058	0.0236	0.35	−1.41 [b]
	0.7000	355.60	0.0123	0.0303	0.48	−1.47 [b]
	0.8000	342.00	0.0047	0.0376	0.31	−0.92 [b]
	0.9000	348.70	0.0159	0.0464	0.54	−1.59 [b]
Phenanthrene (1) + naphthalene (2)	0.1000	349.30	−0.3250	0.0151	−0.40	0.12
	0.1989	341.90	−0.3566	−0.0220	−2.50	0.74
	0.3000	334.80	−0.3869	−0.0131	−3.40	1.03
	0.4000	327.20	−0.3733	−0.0025	−4.20	1.27
	0.4328(E)	325.20	−0.3633	0.0018	−4.30	1.31
	0.5000	333.00	−0.0085	0.0148	0.10	−0.03
	0.6100	344.30	0.0179	0.0202	0.50	−0.15
	0.7000	351.50	0.0183	0.0242	0.60	−0.17
	0.8000	359.35	0.0229	0.0295	0.80	−0.22
	0.9100	369.80	0.0344	0.0384	1.00	−0.29
α-Naphthol (1) + naphthalene (2)	0.1000	347.30	−0.6578	−0.0106	−2.18	0.63
	0.2000	341.00	−0.6019	−0.0149	3.75	1.10
	0.3000	334.60	−0.6501	−0.0226	−5.93	1.76
	0.3950(E)	328.00	−0.5988	−0.0031	−6.50	1.98
	0.4000	328.50	−0.0100	−0.0005	−1.00	0.03
	0.5000	337.50	−0.0090	0.0006	−1.21	0.03
	0.6000	345.00	−0.0046	0.0004	−0.97	0.02
	0.7000	351.80	−0.0065	−0.0006	−0.18	0.04
	0.8000	358.00	0.0047	−0.0037	0.09	−0.03
	0.9000	364.00	0.0169	−0.0132	0.42	−0.01

Mixture	Mole fraction of component (1)	Liquidus temperature (K)	ln r_1	ln r_2	G^E (kJ mol^{-1})	$S^E \times 10^{-3}$ (kJ mol^{-1} K^{-1})
Diphenylamine (1) + α-naphthol (2)	0.1000	362.50	−0.3457	−0.0153	−1.45	0.40
	0.2000	355.70	−0.2489	−0.0465	−2.57	0.72
	0.3000	345.70	−0.1994	−0.0650	−3.03	0.80
	0.4000	336.70	−0.1666	−0.0885	−3.40	1.00
	0.5000	329.50	−0.1532	−0.1044	−3.57	1.07
	0.6000	321.40	−0.1551	−0.1617	−4.24	1.31
	0.7000	314.90	−0.1721	−0.2351	−4.92	1.59
	0.7660(E)	311.70	−0.1873	−0.3087	−6.12	1.99
	0.8000	316.70	0.0154	−0.0365	0.26	−0.08
	0.9000	323.00	0.0258	−0.0274	0.40	−0.02

[a] Eutectic.

[b] $S^E \times 10^{-4}$.

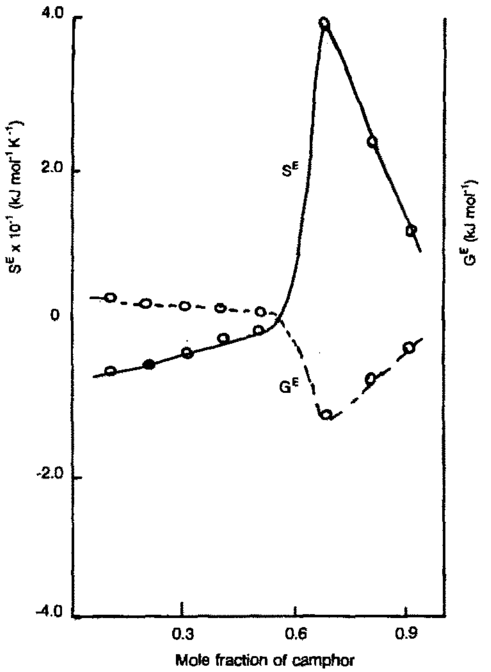

Fig. 8. Excess functions for the system camphor + benzoic acid.

functions of the phenanthrene–naphthalene system which is identical in behaviour to the naphthalene–*o*-nitrophenol, α-naphthol–naphthalene and diphenylamine–α-naphthol systems. On examining Table 3 and Figs. 8–10, it is noted that the function G^E decreases along either branch of the phase equilibrium curve (Figs. 1–7) approaching the eutectic composition where it shows minima for each system, which is expected, since the eutectic (being the lowest liquidus temperature reached by the gradual addition of one component into the other) should therefore be accompanied by a decrease in G^E. On the contrary, the function S^E exhibits maxima at the eutectic composition which would occur because at this composition three phases coexist, namely, two solid phases and one liquid phase, inevitably causing the most probable distribution of the molecules of the components in the eutectic mixture of the solidus–liquidus phase diagram. The number of distinct arrangements of the component molecules in any binary mixture determines the weight w of that mixture. Since w for the eutectic mixture is higher than any other composition of the solidus–liquidus equilibrium curve, this results in the function S^E being maximal at this composition. This shows the applicability of Planck's formulation, $S = k \ln w$ over the entire composition range covered by the phase equilibrium curve. Besides

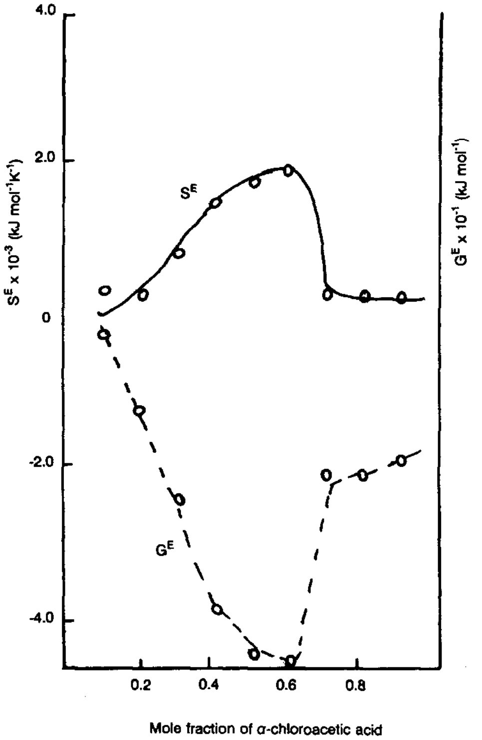

Fig. 9. Excess functions for the system α-chloroacetic acid + vanillin.

the excess energy functions, activity coefficient data for each component in the eutectic mixtures given by

$$RT \ln r_i^l = A\left[1 - x_i^l\right] + B\left(1 - x_i^l\right)^2 \tag{8}$$

confirmed that the systems are far from being regular.

According to Guggenheim's lattice theory [9], the equilibrium composition of binary systems showing complete miscibility in solid and liquid phases (regular solution) at any liquidus temperature is given by

$$-\ln \frac{x_i^l r_i^l}{x_i^s r_i^s} = \frac{\Delta_f H_i^{\ominus}}{R}\left(\frac{1}{T} - \frac{1}{T_i^{\ominus}}\right) \tag{9}$$

where x_i, r_i and $\Delta_f H_i^0$ have their usual meanings and the superscripts l and s refer to liquid and solid phases. The functions G^E and S^E determined by eqns. (7) and (8) at the eutectic compositions of binary systems at constant pressure were found to differ appreciably from their calculated values assuming the eutectic mixtures to be regular, for which eqn. (9) provides

$$G^E = \left(x_1^l\right)_m \Delta_f H_1^{\ominus}\left(\frac{T_m - T_1^{\ominus}}{T_1^{\ominus}}\right) + \left(x_2^l\right)_m \Delta_f H_2^{\ominus}\left(\frac{T_m - T_2^{\ominus}}{T_2^{\ominus}}\right) \tag{10}$$

$$S^E = -\left(x_1^l\right)_m \Delta_f H_1^{\ominus}\left(\frac{T_m - T_1^{\ominus}}{T_m T_1^{\ominus}}\right) - \left(x_2^l\right)_m \Delta_f H_2^{\ominus}\left(\frac{T_m - T_2^{\ominus}}{T_m T_2^{\ominus}}\right) \tag{11}$$

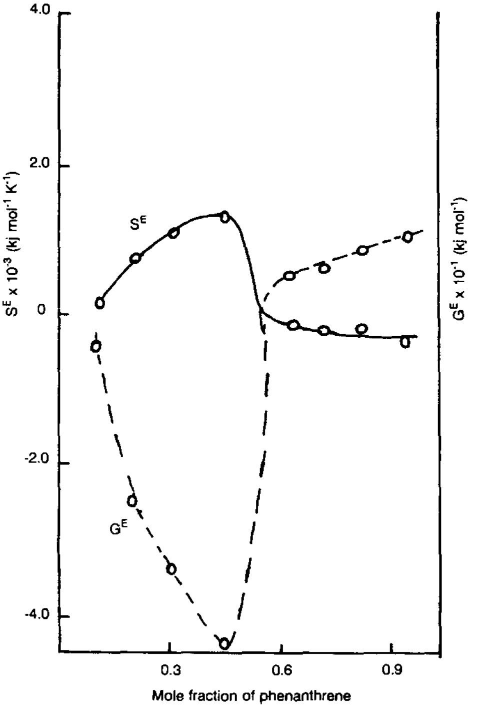

Fig. 10. Excess functions for the system phenanthrene + naphthalene.

where subscript m represents the minima in the solidus–liquidus equilibrium curves. For instance, the values of G^E and S^E for the eutectic mixture of the camphor–benzoic acid system determined from eqns. (7) and (8) are -1.29 kJ mol^{-1} and 3.91×10^{-3} kJ mol^{-1} K^{-1} respectively (Table 3), whereas these values have been found from eqns. (10) and (11) to be -1.72 kJ mol^{-1} and 5.22×10^{-3} kJ mol^{-1} K^{-1}. Since the value of G^E obtained from eqn. (10) is less than its value determined from eqn. (7), which is expected because the formation of a regular mixture is accompanied by low free energy in comparison with that of a non-ideal eutectic mixture. This result thus confirms the reliability of the procedure for computing the excess thermodynamic functions from the phase diagram and offers evidence supporting the thermodynamic model for the eutectic phenomenon. The excess functions also predict the thermal nature of the systems; that is, Fig. 8 shows that the pre-eutectics of the camphor–benzoic acid system are endothermic whereas the eutectic and post-eutectics are exothermic, Fig. 9 indicates exothermic mixing of components α-chloroacetic acid and vanillin throughout the temperature range covered by the solidus–liquidus phase diagram, and Fig. 10 signifies that the system is exothermic until the eutectic point is reached and is endothermic thereafter.

CONCLUSIONS

Direct experimental methods for measuring the excess thermodynamic functions at the freezing points of mixtures are firstly not developed and secondly by no means simple. The excess functions determined from the analysis of solidus–liquidus equilibrium curves are reliable because all the quantities used in the various equations for such a computation were experimentally determined; the applicability of Planck's formulation offers supporting evidence as to their reliability and hence can frequently be used to examine various theories of solutions and in particular the lattice theories of the mixtures.

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