ELSEVIER Thermochimica Acta, 243 (1994) 17-25

thermochimica
acta

Thermochemical studies on the eutectics and addition compounds in the binary systems of benzidine with *p*-nitrophenol, *m*-aminophenol and resorcinol

U.S. Rai, * Santhi George

Department of Chemistry, Banaras Hindu University, Varanasi-221 005, U.P., India

(Received 19 November 1993; accepted 20 January 1994)

Abstract

The phase diagrams of the binary organic systems of benzidine with *p*-nitrophenol, *m*-aminophenol and resorcinol exhibit a double simple eutectic type phase diagram in each case, showing formation of one addition compound with a congruent melting point flanked by two eutectics. The values of the enthalpy of fusion of the pure components, the eutectics and the addition compounds, as determined by the DSC method, suggest that there is appreciable interaction between the two components forming the eutectic melts. Using enthalpy of fusion data, the enthalpy of mixing, entropy of fusion and excess thermodynamic functions were calculated and the results are explained with respect to interactions between the components.

Keywords: Aminophenol; Benzidine; Binary system; DSC; Entropy of fusion; Eutectic; Heat of fusion; Resorcinol

---

1. Introduction

The solidification processes and properties of polyphase alloys have been studied increasingly over the last decade [1,2]. An understanding of these processes can be applied to develop new materials with high strength, rigidity and ductility at high temperatures, in order to meet the demands of modern science. Although metallic eutectics and intermetallic compounds constitute an interesting area of investigation

---

* Corresponding author.

SSDI 0040-6031(94)01745-3

in metallurgy and materials science, studies on the various aspects of these system remain inadequate because of their difficult purification, high transformation temperature, opacity and associated convection effects. Transparent binary alloys involving organic compounds have become ideal model systems [3–6] for such studies as they permit visual observation of the phase transformations and processes involved in solidification. The low transformation temperature, ease of purification, transparency, wider choice of materials and minimized convection effects are additional advantages which have prompted a number of research groups [7–11] to undertake physicochemical investigations of organic eutectics and molecular complexes.

A critical survey of the existing literature [12,13] reveals that studies on binary organic systems forming molecular compounds are limited to a few systems only. As the organic eutectics and addition complexes are the respective analogues of metal eutectics and intermetallic compounds, a systematic thermochemical study of model systems involving organic compounds may be of potential importance in unravelling the mysteries of solidification and microstructure. In view of this, the phase diagrams and thermochemistry of three binary organic systems of benzidine with *p*-nitrophenol, *m*-aminophenol and resorcinol have been studied.

2. Experimental

2.1. Materials and purification

Analytical reagent grade benzidine (CDH, India) which is used as a reagent for the detection of blood, was used directly in the present investigation. *p*-Nitrophenol (SISCO-CHEM. Indus., India) and resorcinol (E. Merck, India) were purified by repeated distillation under vacuum and were stored in coloured bottles to avoid exposure to light. *m*-Aminophenol (S.d. Fine-Chem. Pvt. Ltd., India) was purified by a zone refining technique. The purities of benzidine, *p*-nitrophenol, *m*-aminophenol and resorcinol were 99.5%, 99%, 99.5% and 99%, respectively.

2.2. Phase diagram

The phase diagrams of benzidine(1) + *p*-nitrophenol(2), benzidine(1) + *m*-aminophenol(2), and benzidine(1) + resorcinol(2) were determined [14] by the thaw–melt method. In this method, mixtures of two components covering the entire range of composition in mole fraction (accuracy ±0.001) were prepared in different long-necked test tubes. These mixtures were homogenized by melting in silicone oil followed by chilling in ice, and their thawing and melting temperatures were determined using a Toshniwal melting point apparatus equipped with a precision thermometer which could read correctly up to ±0.5°C.

2.3. Enthalpy of fusion

The enthalpy of fusion (accuracy 1.5%) of the pure components, the eutectics and the addition compounds were determined [15] by the DSC method using a

Du Pont-9900 thermal analysis DSC apparatus. Indium was used as a standard sample to calibrate the DSC apparatus. The heating rate was 10 K min^{-1} and the sample mass was about 10 mg for each estimation.

3. Results and discussion

3.1. Phase diagram

The solid–liquid equilibrium data on the benzidine(1) + *p*-nitrophenol(2), benzidine(1) + *m*-aminophenol(2) and benzidine(1) + resorcinol(2) systems are given in Figs. 1–3. Each system exhibits a double simple eutectic type phase diagram showing the formation of an addition compound with a congruent melting point, flanked by two eutectics E_1 and E_2. While the phase diagram of benzidine(1) + *p*-nitrophenol(2) shows the formation of a 1:1 addition compound, those of benzidine(1) + *m*-aminophenol(2) and benzidine(1) + resorcinol(2) exhibit the formation of 1:2 molecular complex. It is evident from the figures that the melting point of benzidine decreases with the addition of the second component and it

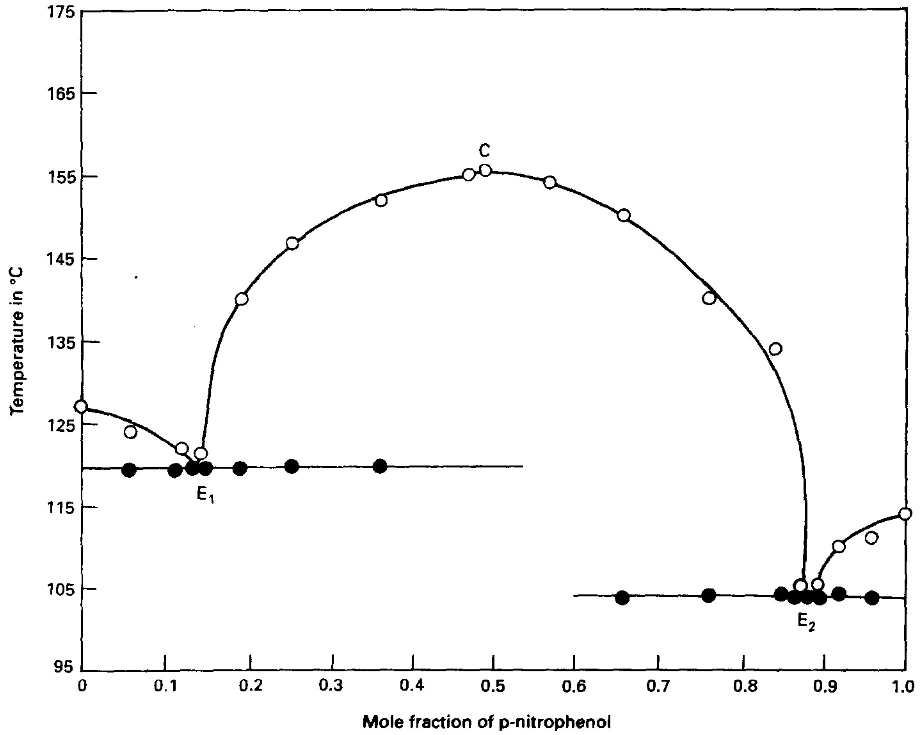

Fig. 1. Phase diagram of benzidine–*p*-nitrophenol system.

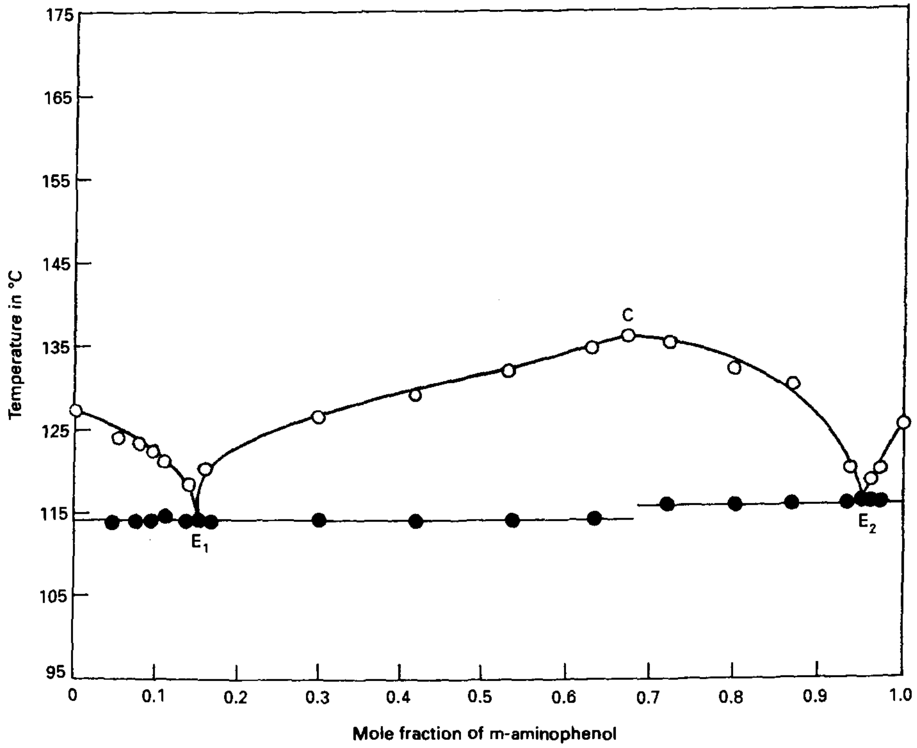

Fig. 2. Phase diagram of benzidine–*m*-aminophenol system.

attains a minimum value at the eutectic point E_1. From the first eutectic point E_1 onwards, on addition of the second component, the melting point rises and attains a maximum temperature at C where the compositions of the liquid and solid phases are identical. This maximum temperature is the congruent melting point of the addition compound [16,17]. A further increase in the mole fraction of the second component causes a decrease in the melting point of the mixture with a minimum at the second eutectic point E_2. The composition and melting points of the eutectics and the molecular complexes are reported in Table 1.

3.2. Thermochemical studies

Theories concerning the mode of crystallization, the structure of the eutectic melt and the nature of the interaction between the two components forming the eutectics and the addition compounds can be obtained from a knowledge of the entalpies of fusion of the pure components, the eutectics and the molecular complexes. Their enthalpies of fusion were determined and different thermodynamic parameters were calculated.

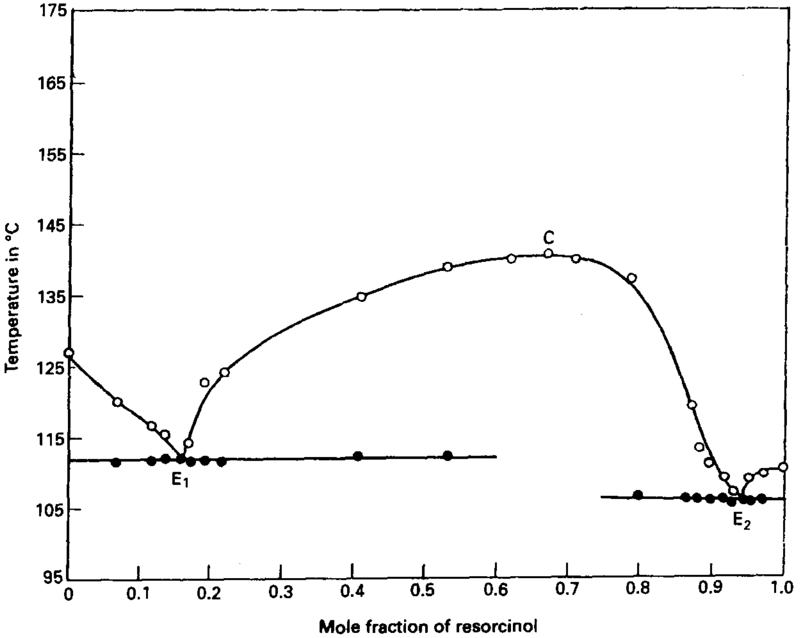

Fig. 3. Phase diagram of benzidine–resorcinol system.

Table 1
Mole fraction of benzidine x_2 and melting point T of eutectics and addition compounds of each system

Material	x_2	T/°C
Benzidine(1) + *p*-nitrophenol(2)		
Eutectic 1	0.873	120.0
Eutectic 2	0.118	104.0
1:1 Addition compound	0.514	155.5
Benzidine(1) + *m*-aminophenol(2)		
Eutectic 1	0.850	114.0
Eutectic 2	0.049	116.5
1:2 Addition compound	0.328	136.0
Benzidine(1) + resorcinol(2)		
Eutectic 1	0.845	112.0
Eutectic 2	0.063	106.0
1:2 Addition compound	0.329	140.5

3.2.1. Enthalpy of fusion of eutectics and addition compounds

If a eutectic is a simple mechanical mixture of two components involving no enthalpy of mixing or any type of association in the melt, the enthalpy of fusion can simply be given by the mixture law [18]

$$(\Delta_{\text{fus}}H)_{\text{e}} = x_1\Delta_{\text{fus}}H_1^{\ominus} + x_2\Delta_{\text{fus}}H_2^{\ominus} \tag{1}$$

Table 2
Experimental and calculated values of enthalpy of fusion $\Delta_{\mathrm{fus}}H$, enthalpy of mixing $\Delta_{\mathrm{mix}}H$, and entropy of fusion $\Delta_{\mathrm{fus}}S$ of eutectics and addition compounds

Material	$\Delta_{\mathrm{fus}}H/\mathrm{kJ\ mol^{-1}}$	$\Delta_{\mathrm{fus}}H(\mathrm{calc})/\mathrm{kJ\ mol^{-1}}$	$\Delta_{\mathrm{mix}}H/\mathrm{kJ\ mol^{-1}}$	$\Delta_{\mathrm{fus}}S/\mathrm{J\ K^{-1}\ mol^{-1}}$
Benzidine(1) + *p*-nitrophenol(2)				
Eutectic 1	16.8	21.8	−5.1	0.043
Eutectic 2	17.1	20.9	−3.8	0.045
1:1 Addition compound	20.4	36.8	−16.4	0.048
Benzidine(1) + *m*-aminophenol(2)				
Eutectic 1	20.3	23.7	−3.5	0.052
Eutectic 2	24.4	24.8	−0.4	0.063
1:2 Addition compound	24.8	38.2	−13.4	0.061
Benzidine(1) + resorcinol(2)				
Eutectic 1	18.0	23.3	−5.3	0.047
Eutectic 2	16.3	23.2	−6.9	0.043
1:2 Addition compound	23.1	33.1	−10.1	0.056

where x and $\Delta_{\mathrm{fus}}H^{\ominus}$ are the mole fraction and enthalpy of fusion, respectively, of the component indicated by the subscript. But when a solid eutectic melts there is considerable possibility of association and mixing, both causing violation of the mixture law.

The experimental values of the enthalpy of fusion, obtained by the DSC method, are given in Table 2. For comparative purposes, the enthalpies of fusion of the eutectics, calculated by the mixture law using Eq. (1), are also given in the same table. It is evident from the data reported in the table that the calculated values of enthalpy of fusion are higher than the experimental values. This difference may be attributed [19] to the formation of clusters in the eutectic melt. In eutectic systems, where one or both components contain a hydroxyl group, cluster formation will be favoured due to a tendency for hydrogen bond formation. This is one of the reasons why the experimental values of the enthalpy of fusion are lower than the calculated values.

The experimental values of the enthalpy of fusion of the addition compounds, determined by the DSC method, are reported in Table 2. Their theoretical enthalpy of fusion values are also given in the same table for the purpose of comparison. The theoretical values of the enthalpies of fusion of the addition compounds were calculated [19,20] using the equation

$$\frac{\Delta_{\mathrm{fus}}H}{R}\left[\frac{1}{T}-\frac{1}{T_{\mathrm{c}}}\right] = -\ln(x_{\mathrm{A}})^{m}(x_{\mathrm{B}})^{n} + \ln(x_{\mathrm{A}})_{\mathrm{c}}^{m}(x_{\mathrm{B}})_{\mathrm{c}}^{n} \tag{2}$$

where x_{A} and x_{B} are the mole fractions of the components A and B, respectively, T_{c} denotes the congruent melting temperature, and subscript c denotes the mole fraction corresponding to that which would exist in the molten addition compound with molecular formula $\mathrm{A}_m\mathrm{B}_n$; $\Delta_{\mathrm{fus}}H$ and R are the enthalpy of fusion of the addition compound and the gas constant, respectively.

From a plot of $(1/T - 1/T_c)$ versus $\ln(x_A)_c^m(x_B)_c^n/(x_A)^m(x_B)^n$ for each system, the values of the enthalpies of fusion of the addition compounds were calculated and are recorded in Table 2. The calculated values of the enthalpies of fusion are higher than the observed values.

3.2.2. Enthalpy of mixing of eutectics and addition compounds

The enthalpy of mixing $\Delta_{\text{mix}}H$ of the eutectics and addition compounds can be calculated very easily using the following equation [21,22], thus providing an insight into the structure of the melt in binary systems

$$\Delta_{\text{mix}}H = (\Delta_{\text{fus}}H)_{\text{expt}} - x_1\Delta_{\text{fus}}H_1^\ominus - x_2\Delta_{\text{fus}}H_2^\ominus \tag{3}$$

where $(\Delta_{\text{fus}}H)_{\text{expt}}$ is the experimental value of the enthalpy of fusion, and x and $\Delta_{\text{fus}}H^\ominus$ are the mole fraction and enthalpy of fusion of the component indicated by the subscript. Using this equation, values of the enthalpy of mixing of eutectics and addition compounds were calculated and are given in Table 2. For eutectics, the reported values of the enthalpies of mixing are negative in all cases. Thermochemical studies [23,24] suggest that the structure of a binary eutectic melt depends on the sign and magnitude of the enthalpy of mixing. Thus, three types of structures are suggested; quasi-eutectic for $\Delta_{\text{mix}}H > 0$, clustering of molecules for $\Delta_{\text{mix}}H < 0$ and molecular solutions for $\Delta_{\text{mix}}H = 0$. The negative values of $\Delta_{\text{mix}}H$ for all the eutectics under investigation suggest clustering of molecules in the binary eutectic melts. In the present investigation, an interesting observation is that the benzidine(1) + *m*-aminophenol(2) mixture has a very low enthalpy of mixing, which might be explained by formation of simple molecular solutions instead of weak interactions. These results [21] are quite different from those in simple eutectic systems where ordering of only the parent phases has been suggested as taking place in the melts. The values of the enthalpies of mixing of the addition compounds are also negative but they are very high in comparison to those of the eutectics. This may be due to exothermic reactions resulting from intermolecular interactions between the two components forming the addition compounds.

3.2.3. Excess thermodynamic function

The deviation from ideal behaviour which quantifies the nature of the molecular interactions can be expressed in terms of excess thermodynamic functions. It is defined [25,26] as 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. In order to determine the nature of the interaction between the two components forming the eutectics, some thermodynamic functions, such as the excess free energy G^E, excess enthalpy H^E, and excess entropy S^E were calculated using the equations

$$G^E = RT(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l) \tag{4}$$

$$H^E = -RT^2\left(x_1 \frac{\partial \ln \gamma_1^l}{\partial T} + x_2^2 \frac{\partial \ln \gamma_2^l}{\partial T}\right) \tag{5}$$

Table 3
Excess thermodynamic functions of eutectics of each system

Material	G^E/kJ mol^{-1}	H^E/kJ mol^{-1}	S^E/J K^{-1} mol^{-1}
Benzidine(1) + *p*-nitrophenol(2)			
Eutectic 1	1.0	4.0	7.7
Eutectic 2	0.6	5.2	12.2
Benzidine(1) + *m*-aminophenol(2)			
Eutectic 1	0.7	5.0	11.1
Eutectic 2	0.2	−9.5	−24.7
Benzidine(1) + resorcinol(2)			
Eutectic 1	0.4	−4.0	−11.4
Eutectic 2	0.5	4.3	10.1

$$S^E = -R(x_1 \ln \gamma_1^1 + x_2 \ln \gamma_2^1 + x_1 T \frac{\partial \ln \gamma_1^1}{\partial T} + x_2 T \frac{\partial \ln \gamma_2^1}{\partial T} \tag{6}$$

It is evident from Eqs. (4)–(6) that a knowledge of the activity coefficient and its variation with temperature is required to calculate the excess functions. The activity coefficient (γ_1^1) of a component *i* in the eutectic melt was calculated using the equation

$$-\ln x_1^1 \gamma_1^1 = \frac{\Delta_{\text{fus}} H_i^\ominus}{R} \left[\frac{1}{T} - \frac{1}{T_i^\ominus} \right] \tag{7}$$

where x_i, $\Delta_{\text{fus}} H_i^\ominus$ and $T_i^\ominus$ are the mole fraction, experimental enthalpy of fusion and melting temperature of component *i*, respectively, *R* is the gas constant and *T* is the melting temperature of the eutectic. The variation in the activity coefficient with temperature was calculated from the slope of the liquidus line near the eutectic point. Details of this calculation are reported in ref. 18. The values of the excess functions calculated in this way are recorded in Table 3. The positive values of G^E suggest [25] that the interaction between like molecules is stronger than that between unlike molecules. The excess entropy is a measure of the change in configurational energy due to a change in potential energy and indicates an increase in randomness. The excess enthalpy values correspond to the excess free energy and the excess entropy reported above.

3.2.4. Entropy of fusion

Theoretical studies on the entropy of fusion and calculation of some excess thermodynamic functions of eutectics predict the structure, stability and ordering in the eutectic melt. The values of the entropy of fusion $\Delta_{\text{fus}} S$ of the pure components, the eutectics and the addition compounds were calculated [13] using the equation

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T} \tag{8}$$

where $\Delta_{fus}H$ is the enthalpy of fusion and T is the fusion temperature, and are given in Table 2. In all the systems under investigation, the $\Delta_{fus}S$ values are positive indicating an increase in randomness during melting. In general, the eutectics have lower entropies of fusion than the pure components. From this observation, it can be inferred that entropy factors are less effective in the melting process of a eutectic than the pure components.

Acknowledgements

Thanks are due to Dr. (Mrs.) Veena Choudhary, Centre for Materials Science and Technology, IIT, Delhi, New Delhi for determining the enthalpy of fusion data. Thanks are also due to UGC New Delhi for financial assistance.

References

[1] R. Elliott, Eutectic Solidification Processing, Butterworths, London, 1983.
[2] R. Elliott, Cast Iron Technology, Butterworths, London, 1988.
[3] W.F. Kaukler and D.O.J. Frazier, Cryst. Growth, 71 (1985) 340.
[4] M.E. Glicksmann, N.D. Singh and M. Chopera, Manufacturing in Space, 11 (1983) 207.
[5] R.N. Grugel and A. Hellawell, Metall. Trans., 15A (1984) 1626.
[6] K.A. Jackson and J.D. Hunt, Trans. Metall. Soc. AIME, 236 (1966) 1129.
[7] R.P. Rastogi, D.P. Singh, N. Singh and N.B. Singh, Mol. Cryst. Liq. Cryst., 73 (1981) 7.
[8] K. Pigon and A. Krajewska, Thermochim. Acta, 58 (1982) 58.
[9] A. Togashi and Y. Matsunga. Bull. Chem. Soc. Jpn., 69(b) (1987) 1171.
[10] P.S. Bassi, N.K. Sharma and M.K. Sharma, Cryst. Res. Technol., 18 (1983) 1191.
[11] W. Kruz and R. Trivedi. Proc. 3rd Int. Conf. on Solidification Processing, Sheffield, Inst. Metals, London, 1987, p. 1.
[12] N.B. Singh and K.D. Dwivedi, J. Sci. Ind. Res., 41 (1982) 98.
[13] U.S. Rai and K.D. Mandal, Mol. Cryst. Liq. Cryst., 182 (1990) 387.
[14] N.B. Singh, U.S. Rai and O.P. Singh, J. Cryst. Growth, 71 (1985) 353.
[15] U.S. Rai, K.D. Mandal and N.P. Singh, J. Therm. Anal., 35 (1989) 1687.
[16] R.P. Rastogi, J. Chem. Educ., 41 (1964) 443.
[17] M. Radomska and R. Radomski, Thermochim. Acta, 40 (1980) 415.
[18] U.S. Rai, G.P. Singh, N.P. Singh and N.B. Singh. Thermochim. Acta, 71 (1983) 373.
[19] R.P. Rastogi, N.B. Singh and K.D. Dwivedi, Ber. Busenges. Phys. Chem., 85 (1981), 85.
[20] U.S. Rai and S. George, Thermochim. Acta, 191 (1991) 271.
[21] N.P. Singh, B.M. Shukla, N. Singh and N.B. Singh, J. Chem. Eng. Data, 30 (1985) 49.
[22] U.S. Rai and S. George, Thermochim. Acta, 186 (1991) 131.
[23] N. Singh, N.B. Singh, U.S. Rai and O.P. Singh, Thermochim. Acta, 95 (1985) 291.
[24] U.S. Rai and K.D. Mandal, Bull Chem. Soc. Jpn., 63 (1990) 1496.
[25] J. Wisniak and A. Tamir, Mixing and Excess Thermodynamic Properties (a Literature Source Book), Phys. Sci. Data, Elsevier, New York, 1978.
[26] R.P. Rastogi and R.R. Mishra, An Introduction to Chemical Thermodynamics, 4th edn., Vikash Publishing House Pvt. Ltd., New Delhi, 1978, p. 319.