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A DSC STUDY FOR BINARY MIXTURE OF 2-CHLOROBENZOIC ACID WITH SALICYLIC ACID

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Solid-liquid equilibria (SLE) for binary mixture of 2-chlorobenzoic acid with salicylic acid were measured using differential scanning calorimetry (DSC) and corresponding activity coefficients were calculated. Simple eutectic behaviour for this system was observed. The excess functions: G^E and S^E for the pre-, post-, and eutectic composition, have been calculated by utilizing the computed activity coefficients data of the eutectic phase together with their excess chemical potentials μ_i^E (i=1,2). The experimental solid-liquid phase transformation temperatures were compared with predictions obtained from available eutectic equilibrium models. The results show the presence of non-ideality in this mixture.

INTRODUCTION

Solid-liquid phase equilibria (SLE) are important when separation and purification operation for a given mixture by crystallization is carried out. Although the measurement of SLE is very important, there is a little accumulation of these data, and the decisive measurement method is not yet established.[1] Various methods have been proposed[2] to measure solid-liquid equilibria. Recently, methods of using output data of differential scanning calorimetry (DSC) are suggested. Most of those researches adopted the method in which a liquidus and a solidus curves were estimated from the onset and peak temperatures obtained from the measured DSC curves.

Thermodynamic analysis of solidus-liquidus equilibrium data can yield important thermodynamic functions of binary mixtures in condensed phase.[3] In view of thermodynamic considerations, eutectic may be defined as the heterogeneous system[4] consisting of two or more solidus phases which are in equilibrium with a single liquidus phase and is the lowest liquidus temperature in the binary solidus-liquidus diagram of state. The eutectic phase cannot be chosen arbitrarily.

Activity coefficients of eutectic phases in their mixtures computed from thermodynamic analysis of the solidus-liquidus phase equilibrium data can readily be utilized in the determination of excess thermodynamic functions: G^E, S^E and μ_i^E. These functions have got considerable importance in the domain of quantitative analyses of molecular interactions.[5]

In the present paper the details studied concerning phase diagram, thermochemistry and microstructure of 2-chlorobenzoic acid with salicylic acid system are discussed.

RESULTS AND DISCUSSION

1. Phase diagram

The DSC curves measured with the different compositions for the 2-chlorobenzoic acid + salicylic acid system are shown in Fig. 1. The onset temperatures at each first peak almost show constant value for the simple eutectic system. The eutectic temperature was taken as the onset temperature at the solidus transition, as was applied by most researchers.[6] Since the onset temperature for the liquidus transition is difficult to be determined due to superimpose effect of the DSC curves, many authors[7, 8] report the liquidus temperature as the peak temperature in the liquidus transition.

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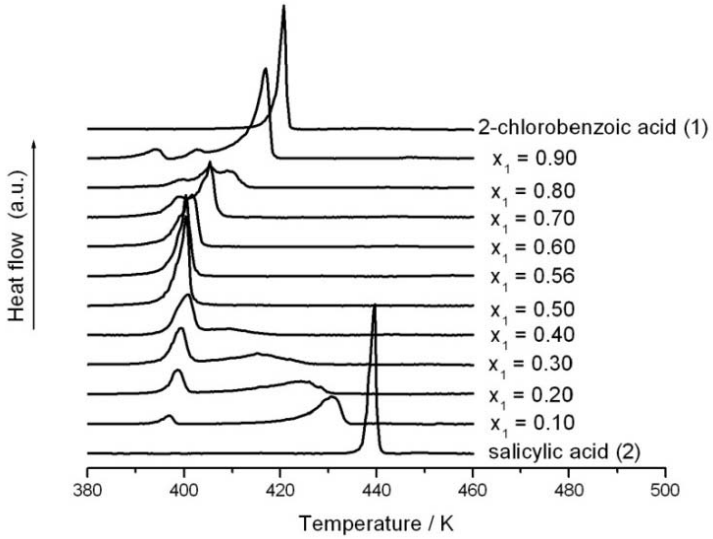

Fig. 1 – DSC curves at different composition for 2-chlorobenzoic acid + salicylic acid mixture.

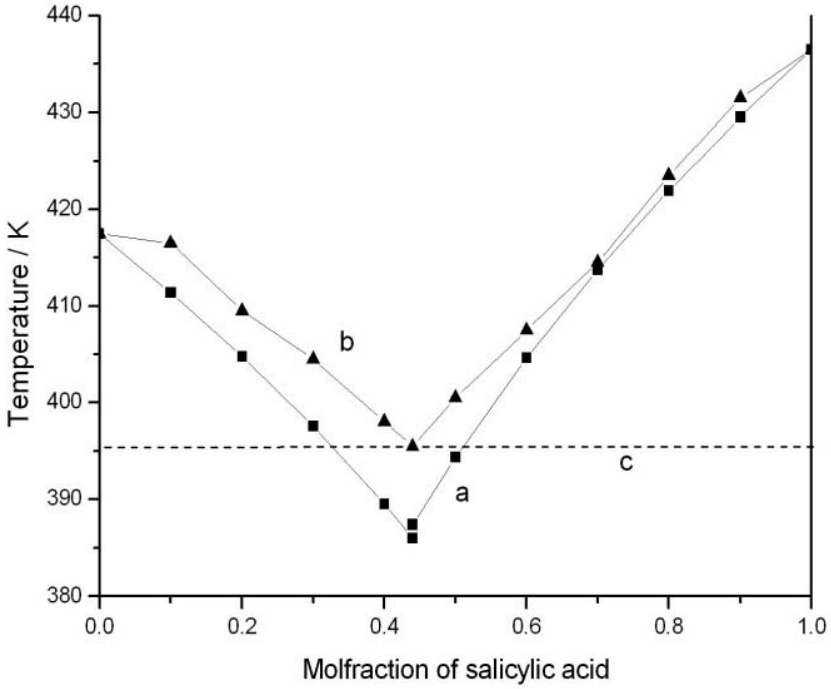

Fig. 2 – SLE phase diagram for 2-chlorobenzoic acid + salicylic acid system. a – ideal curve; b – liquidus curve; c – solidus temperature curve.

The phase diagram obtained from measured DSC curves is shown in Fig. 2 in the form of a temperature–composition plot.

The melting point of 2-chlorobenzoic acid is 417.5 K and its decreases with addition of salicylic acid and attains the minimum at 395.5 K when the mixture has 0.56 mole fraction of it.

2. Thermochemistry

The value of enthalpy of fusion determined by the DSC method and entropy of fusion for the pure components and for the binary system calculated with relation (1) is reported in Table 1:

$$\Delta_f S = \frac{\Delta_f H}{T} \qquad (1)$$

where $\Delta_f H$ is the heat of fusion and T is the fusion temperature on absolute scale.

Table 1

Heat of fusion, entropy of fusion, Jackson's roughness parameter and heat of mixing

Material	$\Delta_f H$ / kJ mol^{-1}		$\Delta_{mix}H$ / kJ mol^{-1}	$\Delta_f S$ / J mol^{-1}K^{-1}	α
	Exp.	Lit.			
2-chlorobenzoic acid (CBA)	24.67	25.25 [9]	-	59.08	7.1
Salicylic acid (SA)	23.52	24.62 [5]	-	53.88	6.5
CBA – SA eutectic (experimental)	21.10	-	- 3.06	53.33	6.4
CBA – SA eutectic (calculated)	24.16	-			

$\Delta_f S$ values are found to be positive for each compound, indicating an increase in randomness during melting of different phases.

If a eutectic is a simple mechanical mixture of two components not involving any type of association in the melt, the heat of fusion may simply be calculated by the mixture law:[10]

$$(\Delta_f H)_e = x_1 \Delta_f H_1^0 + x_2 \Delta_f H_2^0 \quad (2)$$

where x_i and $\Delta_f H_i^0$ are the mole fraction and enthalpy of fusion of the component indicated by the subscript, respectively.

The value of enthalpy of mixing, $\Delta_{mix}H$, of the eutectic is given by the following equation:[11]

$$\Delta_{mix}H = (\Delta_f H)_{exp} - (\Delta_f H)_{cal} \quad (3)$$

where $(\Delta_f H)_{exp}$ is the heat of fusion determined experimentally and $(\Delta_f H)_{cal}$ is corresponding calculated value.

Thermochemical studies[11] suggest that the structure of the binary eutectic melt depends on the sign and magnitude of heat of mixing. Three types of structure are suggested: quasieutectic for which $\Delta_{mix}H > 0$; clustering of molecules in which $\Delta_{mix}H < 0$, and molecular solutions, for which $\Delta_{mix}H = 0$. The negative value of $\Delta_{mix}H = -3.06\ kJ \cdot mol^{-1}$, for the 2-chlorobenzoic acid + salicylic acid system suggest that there is clustering of molecules in the binary eutectic melt.

The deviation from ideal behavior can best be explained in terms of excess thermodynamic functions, which give more quantitative idea about the nature of molecular interactions. It is given by the difference between the thermodynamic functions of mixing for a real system at the same temperature and pressure. In order to know the nature of interaction between the components forming the eutectic melt, the excess thermodynamic functions: G^E and S^E of pre-, post-, and eutectic phase composition together with excess chemical potentials μ_i^E (i = 1, 2) of the eutectic phases at the same liquidus temperature, T, at constant pressure, have been computed by using the following relations: [5, 12]

$$G^E = RT\left[x_1^l \ln\gamma_1^l + x_2^l \ln\gamma_2^l\right] \quad (4)$$

$$S^E = -R\left[x_1 \ln\gamma_1^l + x_2 \ln\gamma_2^l\right] - RT\left[x_1 \frac{\partial \ln\gamma_1^l}{\partial T} + x_2 \frac{\partial \ln\gamma_2^l}{\partial T}\right] \quad (5)$$

$$\mu_i^E = RT \ln\gamma_i^l \quad (6)$$

The activity coefficient of a component i present in the eutectic melt, neglecting the difference for heat capacities of the liquid and solid phases, is given by:[5, 10-13]

$$\ln x_i^l \gamma_i^l = -\frac{\Delta_f H_i^0}{R}\left[\frac{1}{T} - \frac{1}{T_i^0}\right] \quad (7)$$

where x_i^l, γ_i^l, $\Delta_f H_i^0$ and T_i^0 are the mole fraction, activity coefficient, heat of fusion and the melting temperature of the component i, R is the gas constant and T is the liquidus temperature. The values of activity coefficients and excess functions are given in Table 2 and graphically drawn in Fig. 3.

Table 2

Activity coefficients and excess thermodynamic function data for binary mixture

x_{CBA}	T_{lq} (K)	$ln\gamma_1^l$	$ln\gamma_2^l$	G^E (J·mol^{-1})	S^E (J·mol^{-1}K^{-1})	μ_1^E (J·mol^{-1})	μ_2^E (J·mol^{-1})
0.1	431.5	2.5332	0.0303	1006.48	-2.33	9087.76	108.56
0.2	423.5	1.7101	0.0242	1272.43	-3.00	6021.34	85.20
0.3	414.5	1.1525	0.0127	1222.15	-2.95	3971.81	43.73
0.4	407.5	0.7419	0.0496	1106.21	-2.71	2513.45	168.04
0.5	400.5	0.3915	0.1106	835.85	-2.09	1303.48	368.22
0.56	395.5	0.1845	0.1491	555.43	-1.40	606.58	490.33
0.6	398	0.1626	0.2894	705.83	-1.77	538.06	957.48
0.7	404.5	0.1283	0.6913	999.35	-2.47	431.33	2324.72
0.8	409.5	0.0843	1.1821	1034.52	-2.53	286.99	4024.62
0.9	416.5	0.0883	1.9914	964.74	-2.32	305.75	6895.68

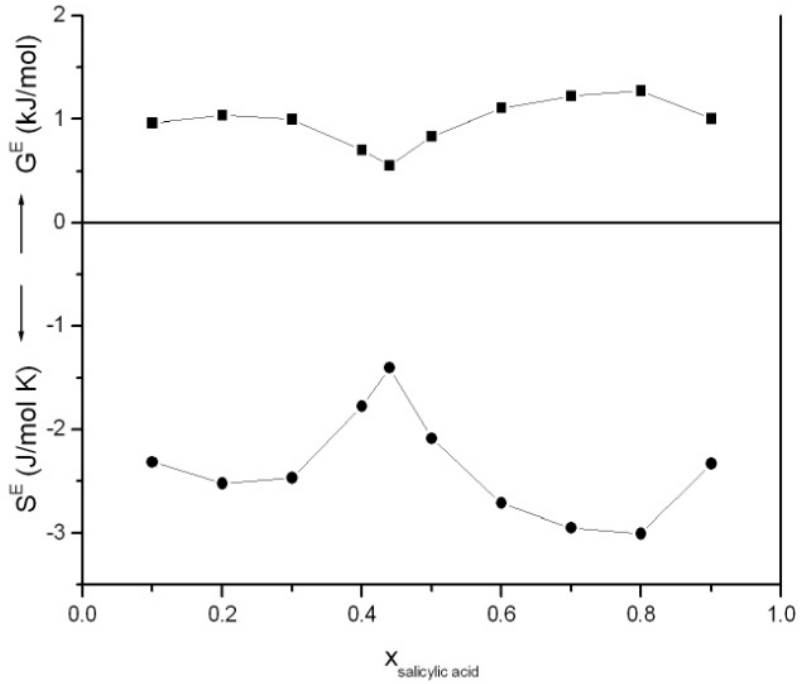

Fig. 3 – Excess functions G^E and S^E for 2-chlorobenzoic acid + salicylic acid system.

An insight analysis of the plot (Fig. 3) for excess thermodynamic functions indicate that the excess free energy of mixing, G^E, decreases on either side of the phase equilibrium curves and acquires minimal values at the eutectic composition, which is expected, since eutectic being the lowest liquidus temperature reached by the gradual addition of an eutectic phase into the

other.[5.12] The type of the behavior is consistent with the criteria of spontaneity according to which the mixing of eutectic phases of the system would progress only if every infinitesimal change in the composition is accompanied by a decrease in the Gibbs free energy. On the contrary, the excess entropy of mixing, S^E, shows the maximal value at the eutectic composition because the most probable distribution of the eutectic phase molecules occurs in a eutectic composition owing to the co-existence of three phases: two solidus phases and a liquisus phase in equilibrium at eutectic liquidus temperature in the condensed phase.

The excess free energy, G^E, being positive suggests[10] that there is weak interaction among the components forming the eutectic melt, and strong association between like molecules.

3. Microstructure

The growth morphology[14] developed by a eutectic system is governed by the growth characteristics of the individual constituent phases. Depending on interface morphology they can solidify with either a faceted or with a non-faceted interface. This behavior is related to the nature of the solid-liquid interface and can be predicted for pure materials from the entropy of fusion value. The predicted structure is related to roughness factor (α) which is closely related to entropy of fusion by the equation:

$$\alpha = \xi \frac{\Delta^f H}{RT} = \xi \frac{\Delta^f S}{R} \qquad (8)$$

The crystallographic factor ξ is usually less than but almost one and represents the fraction of total number of neighbors situated in the newly formed layer, while $\Delta^f S/R$ is the entropy of fusion in dimensionless units.

Since α values of eutectic phases distinguish three possible eutectic structures:[15] regular structures are formed when both the eutectic phases have $\alpha < 2$; irregular structures, when $\alpha > 2$ for both the phases; and complex regular structures crop out when one phase has $\alpha > 2$ and the other has $\alpha < 2$.

Microstructure of eutectic phase is presented in Fig. 4.

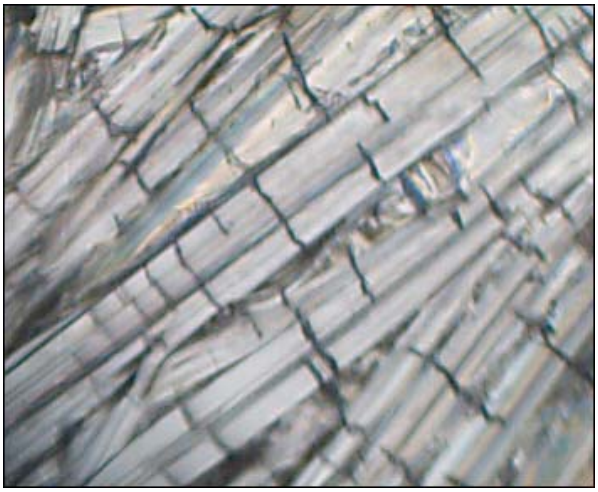

Fig. 4 – Microstructures of eutectic 10 X.

The value of α (Table 1) being higher than 2 suggest a faceted morphology for the system. The growth front of a faceted crystal has a sharp shape.

Since $\alpha > 2$, the solid-liquid interface is atomically smooth and advances into the liquid by the propagation of atomic steps across the interface. This process requires considerable kinetic undercooling.

EXPERIMENTAL

2-chlorobenzoic acid (Loba-Chemie, m.p. 417.5 K) and salicylic acid (Reactivul; m.p. 436.5 K) was used without further purification. Mixtures of known concentration were prepared by weighing and dissolving in absolute ethanol.

The melting temperature and enthalpy of fusion of eutectic phases were determined by differential scanning calorimetry

(DSC Perkin Elmer) under a heating rate of 10 K/min over a temperature range (323–473) K. The apparatus was calibrated for temperature and enthalpy by melting high purity indium. The instrument was flushed with argon. Sample of 2 to 4 mg were transferred into aluminium crucibles which were sealed and weighed with the Partner XA balance with a precision of 10μg.

The microstructure of pure components and eutectic was recorded by placing a drop of molten compound on a hot glass slide. The melt was covered with cover-slip and it was solidified unidirectionally. The slide was put on the platform of an optical microscope (BioLux Al, Bresser) and interesting regions were photographed.

CONCLUSIONS

The negative value of enthalpy of mixing for the 2-chlorobenzoic acid+ salicylic acid system suggest that there is clustering of molecules in the binary eutectic melt.

The 2-chlorobenzoic acid + salicylic acid system is endothermic in nature, since G^E is positive and S^E is negative, indicating positive deviations of the system from its ideal behavior.

The value of α being higher than 2 suggest a faceted morphology for the system.

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