

Thermodynamic Functions in 8-Hydroxyquinoline-Cinnamic Acid System

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(Received February 05, 2008)

Abstract: Thermodynamic investigation on realistic systems requires knowledge of thermodynamic properties of mixtures. The related data are very significant to formulate the condition of equilibrium between two different phases (especially reactions in process metallurgy) and heat treatment. The transparent organic systems due to transparency, minimized convection effect and low fusion temperature are being used as the model systems which provide deep and detailed insight about governing factors of properties in materials even in metallic systems. Thermodynamic studies on 8-hydroxyquinoline (HQ)-cinnamic acid (CA) system has been carried out. The phase diagram of HQ-CA system forms 1:1 molecular complex followed by two side by side eutectic alloys. The activity and activity coefficient of HQ and CA in HQ-CA alloys were computed with the help of the heat of fusion values obtained from DTA pattern of the materials. Using these values the partial and integral mixing and excess molar thermodynamic quantities have been calculated, which explain the structure, stability and ordering in liquid binary alloys. Higher heat of fusion value of alloys forecasts about their faceted (nonmetallic) growth of the interfaces.

Keywords: Phase diagram, activity, thermodynamic quantities, surface structure.

1. Introduction

The extensive investigation on metallic eutectics, noneutectics and intermetallic compounds^{1,2} are inadequate and incomplete as high transformation temperature, opacity, difficulty involved in purification and experimentation and density driven convection effect. The past paramount studies^{3,4} of most binary systems involving organic compounds exhibit the eutectic formation behavior. However some of the systems reveal the formation of monotectics and addition compounds. The organic compounds having special characteristics of low transformation temperature, transparency, ease in purification and experimentation, minimized convection effects and wider choice of materials have prompted the researchers to select organic systems having high enthalpy of fusion and solidify faceted or nonmetallic growth. 8-Hydroxyquinoline (HQ)-cinnamic acid (CA) system has been taken for detailed physicochemical investigation, such as, phase diagram, thermochemistry and internal structure of growing organic crystals.

2. Experimental

Phase diagram study

The phase diagram of HQ-CA system was determined by thaw-melt method⁵. Mixture of different compositions were made in glass tube by repeated heating followed by chilling in ice. The melting and thaw temperature were determined in a Toshniwal melting point apparatus using a precision Thermometer.

Materials and their purification

8-Hydroxyquinoline (E-Merck India Ltd., Bombay) and cinnamic acid (CDH, Delhi) were purified by fractional crystallization with ethanol. The purity of the compounds was confirmed by determining their melting points which were in good agreement with those quoted in literature.

Heat of fusion

Heat of fusion of organic compounds was measured by the DTA method⁶ using a Stanton Redcroft STA-780 series unit.

3. Results and Discussion

Phase diagram

The solid-liquid equilibrium data of HQ-CA system determined by thaw-melt method exhibit the formation of 1:1 molecular complex (at 107°C) followed by two side by side eutectic alloys E₁ (60°C) and E₂ (98°C) at 0.295 and 0.575 mole fraction of CA respectively, shown in Fig. 1.

Activity and activity coefficient

The activity coefficient of components for the systems under investigation may be calculated from the equation⁷ given below

$$(1) \quad -\ln X_i^l \gamma_i^l = \frac{\Delta H_i}{R} \left(\frac{1}{T_e} - \frac{1}{T_i} \right)$$

where X_i^l and γ_i^l are the mole fraction and activity coefficient of the component i in the liquid phase respectively, ΔH_i is the heat of fusion of component i at the melting point T_i . The value of activity and activity coefficient of the components in alloys are given in the Table1.

Mixing Functions

Integral free energy of mixing (ΔG^M), molar entropy of mixing (ΔS^M), molar enthalpy of mixing (ΔH^M) and partial thermodynamic mixing functions of the binary alloys when two components are mixed together were determined by using the following equations

$$(2) \quad \Delta G^M = RT(X_{HQ} \ln a_{HQ}^l + X_{CA} \ln a_{CA}^l)$$

$$(3) \quad \Delta S^M = -R(X_{HQ} \ln \gamma_{HQ}^l + X_{CA} \ln \gamma_{CA}^l)$$

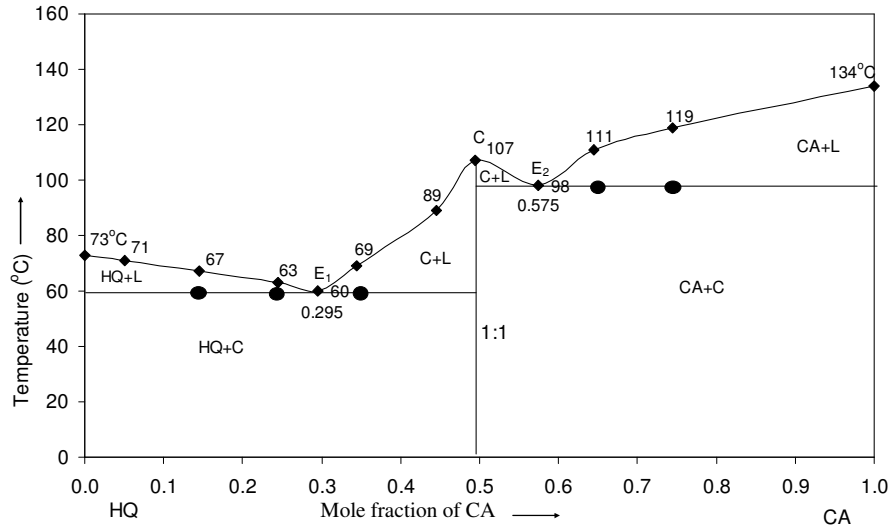


Fig.1 Phase diagram of 8-hydroxyquinoline (HQ)- cinnamic acid (CA) system.

● Thaw temperature.
◆ Melting temperature.

$$(4) \quad \Delta H^M = RT(X_{HQ} \ln \gamma'_{HQ} + X_{CA} \ln \gamma'_{CA})$$

$$(5) \quad G_i^{-M} = RT \ln a_i^l$$

where G_i^{-M} is the partial molar free energy of mixing of component i in binary mix and a_i is the activity of the component. The negative value of integral molar free energy of mixing (Table 2) in all cases is spontaneous. The integral molar enthalpy of mixing value corresponds to the value of excess integral molar free energy of the system favours the regularity in the binary solutions⁸. The positive value of ΔS^M of all alloys predicts the nature of molecular interaction between the components forming the binary melt.

Excess functions

The excess free energy of mixing (g^E), excess entropy of mixing (s^E) and excess enthalpy of mixing (h^E) have been calculated by the following equations

$$(6) \quad g^E = RT(X_{HQ} \ln \gamma'_{HQ} + X_{CA} \ln \gamma'_{CA}),$$

$$(7) \quad s^E = -R(X_{HQ} \ln \gamma'_{HQ} + X_{CA} \ln \gamma'_{CA} + X_{HQ} T \frac{\delta \ln \gamma'_{HQ}}{\delta T} + X_{CA} T \frac{\delta \ln \gamma'_{CA}}{\delta T}),$$

$$(8) \quad h^E = -RT^2(X_{HQ} \frac{\delta \ln \gamma'_{CA}}{\delta T} + X_{CA} \frac{\delta \ln \gamma'_{HQ}}{\delta T}),$$

where R is the gas constant and T is melting temperature of the alloy. The positive value of g^E (Table 3) predicts that molecular association between like molecules are stronger than unlike molecules. The negative value of excess free energy indicates the possibility of a

stronger association between like molecules while the positive value suggests⁹ on association of the weaker nature between unlike molecules and of stronger nature between like molecules.

Gibbs-Duhem Equation

The partial molar quantity, activity and activity coefficient can also be determined by using Gibbs-Duhem equation

$$\sum X_i dZ_i = 0, \text{ i.e.}$$

$$(9) \quad X_{HQ} dH_{HQ}^{-M} + X_{CA} dH_{CA}^{-M} = 0,$$

or

$$dH_{CA}^{-M} = \frac{X_{HQ}}{X_{CA}} dH_{HQ}^{-M}, \text{ i.e.}$$

$$(10) \quad [H_{CA}^{-M}]_{X_{CA}=y} = \int_{X_{CA}=y}^{X_{CA}=1} \frac{X_{HQ}}{X_{CA}} dH_{HQ}^{-M}.$$

Using equation (10), a plot between H_{HQ}^{-M} and x_{HQ}/x_{CA} gives the solution of the partial molar heat of mixing of a certain constituents in the binary alloys (Fig.2).

Surface Structure

Surface structure behaviour related to the nature of the solid-liquid interface and can be predicted from the value of entropy of fusion. The type of growth from eutectic melt depends upon a factor α , defines as,

$$(11) \quad \alpha = \xi \frac{\Delta H}{RT} = \xi \frac{\Delta S}{R}$$

where ξ is a crystallographic factor depending upon the geometry of the molecules and has a value less than or equal to one, $\Delta S/R$ (α) is also known as Jackson's roughness parameter and R is the gas constant. All the alloys and compound have α (roughness parameter) value more than two, infer that the growth of solid-liquid interface of the alloys and compound leads through faceted growth mechanism.

Acknowledgement

Authors are thankful to the Head, Department of Chemistry, V.K.S. University, Ara-802301, India for providing research facilities.

Table 1 : Temperature-composition data, values of heat of fusion (ΔH), roughness parameter (α), activity and activity coefficient of component in binary melt of HQ-CA system.

Alloys and Compound	Mole Frection of CA	M.P. ($^{\circ}\text{C}$)	ΔH (kJ/mol)	α ($\Delta S/R$)	$\ln\gamma_{\text{HQ}}$	$\ln\gamma_{\text{CA}}$	$\ln a_{\text{HQ}}$	$\ln a_{\text{CA}}$	$X_{\text{HQ}}/X_{\text{CA}}$
A ₁	0.050	71	18.53	6.61	0.01	1.75	-0.04	-1.24	19.00
A ₂	0.145	67	19.38	6.70	0.04	0.60	-0.12	-1.35	5.90
A ₃	0.245	63	19.85	7.11	0.09	-0.02	-0.20	-1.43	3.10
E ₁	0.295	60	20.09	7.25	0.10	-0.28	-0.26	-1.51	2.40
A ₄	0.345	69	20.32	7.14	0.35	-0.22	-0.08	-1.27	1.90
A ₅	0.445	89	20.79	6.91	-0.48	-0.02	-1.08	-0.82	1.25
A _{1:1} (C)	0.495	107	21.03	6.65	1.26	0.24	0.58	-0.46	1.02
E ₂	0.575	98	21.41	6.94	1.29	-0.08	0.44	-0.63	0.74
A ₆	0.645	111	21.74	6.80	1.69	0.07	0.65	-0.37	0.55
A ₇	0.745	119	22.21	6.82	2.13	0.06	0.76	-0.23	0.34
CA	1.000	134	23.41	6.92					
HQ	0.000	73	18.70	6.50					

Table 2: Values of partial and integral thermodynamic mixing functions of alloys of HQ-CA system.

Alloys and Compound	G_{HQ}^{-M} (J/mol)	G_{CA}^{-M} (J/mol)	ΔG^M (J/mol)	S_{HQ}^{-M} (J/mol/K)	S_{CA}^{-M} (J/mol/K)	ΔS^M (J/mol/K)	H_{HQ}^{-M} (J/mol)	H_{CA}^{-M} (J/mol)	ΔH^M (J/mol)
A ₁	-114.40	-3546.42	-286.00	0.43	24.91	1.65	33.52	5022.62	277.42
A ₂	-339.21	-3816.13	263.31	1.30	16.05	3.44	102.79	1640.87	342.60
A ₃	-558.70	-3994.71	-1400.52	2.34	11.69	4.63	227.54	-66.87	176.13
E ₁	-719.83	-4180.53	-1740.73	2.91	10.15	5.05	249.20	-800.58	-33.50
A ₄	-227.47	-3611.10	-1394.82	3.52	8.85	5.36	976.37	584.40	436.03
A ₅	-3250.44	-2467.93	-2902.72	4.89	6.73	5.71	-1480.26	-31.67	-828.56
A _{1:1} (C)	1832.41	-1453.29	205.99	5.68	5.85	5.76	3990.81	769.71	2385.60
E ₂	1357.18	-1943.23	-540.56	7.11	4.60	5.67	3994.99	-236.63	1549.19
A ₆	2075.17	-1181.25	-25.22	8.61	3.65	5.41	5381.41	220.35	2059.53
A ₇	2476.91	-749.59	73.17	11.36	2.45	4.72	6930.30	210.81	1915.85

Table 3: Values of partial and intergal excess thermodynamic functions of alloys of HQ-CA system

Alloys and Compound	$g_{\text{HQ}}^{-\text{E}}$ (J/mol)	$g_{\text{CA}}^{-\text{E}}$ (J/mol)	g^{E} (J/mol)	$S_{\text{HQ}}^{-\text{E}}$ (J/mol/K)	$S_{\text{CA}}^{-\text{E}}$ (J/mol/K)	S^{E} (J/mol/K)	$h_{\text{HQ}}^{-\text{E}}$ (KJ/mol)	$h_{\text{CA}}^{-\text{E}}$ (KJ/mol)	h^{E} (KJ/mol)
A ₁	33.52	5022.62	277.42	5.77	2207.69	115.87	2.01	763.67	40.09
A ₂	102.79	1640.87	342.60	10.69	705.66	111.45	3.75	241.72	38.25
A ₃	227.54	-66.87	176.13	91.71	158.73	108.13	31.03	53.21	36.46
E ₁	249.20	-800.58	-33.50	-17.72	-21.05	-18.70	-5.62	-7.78	-6.26
A ₄	976.37	584.40	436.03	-35.83	-25.38	29.66	-11.28	-9.32	10.59
A ₅	-1480.26	-31.67	-828.56	-20.53	-30.66	-25.03	-8.89	-11.17	-9.90
A _{1:1} (C)	3990.81	769.71	2385.60	-44.02	0.22	-22.12	-12.76	0.84	-6.02
E ₂	3994.99	-236.63	1549.19	-24.70	-35.54	-30.97	-5.24	-13.46	-9.96
A ₆	5381.41	220.35	2059.53	-17.75	-12.02	-14.06	-1.43	-4.40	-3.35
A ₇	6930.30	210.81	1915.85	62.37	-16.46	3.64	31.40	-6.26	3.34

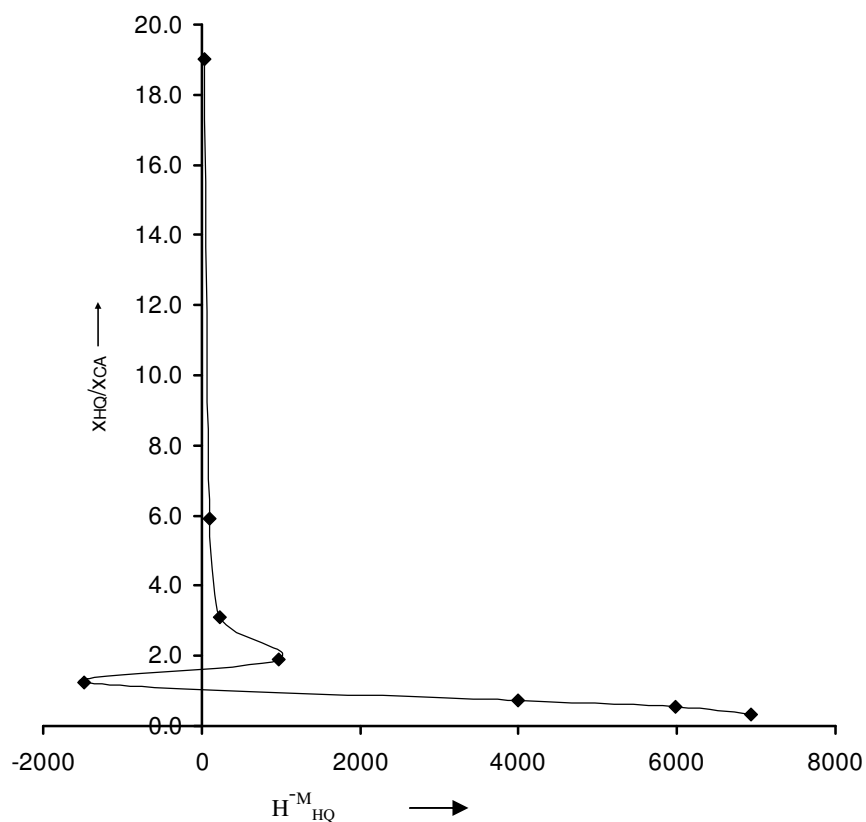


Fig. 2. Graphical solution of partial molar heat of mixing of CA in binary mix.

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