JPEDAV (2008) 29:247–251
DOI: 10.1007/s11669-008-9283-2
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Thermodynamic Modeling of the Succinonitrile-Water System

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(Submitted August 2, 2007; in revised form November 21, 2007)

Succinonitrile-water (SCN-H_2O) system is a widely used transparent metallic alloy system due to its analog solidification behavior to metals. In the present work, Gibbs energy of pure succinonitrile was derived utilizing temperature as well as enthalpy of transformations, and temperature dependencies of heat capacity available in the literature. The phase diagram for the binary SCN-H_2O system was assessed via the CALPHAD approach using phase equilibrium data available in the literature. Self-consistent thermodynamic parameters were obtained. A good agreement between the experimental and calculated data for the phase diagram has been achieved. The present work contributes to the development of the thermodynamic database of the SCN-H_2O system that can be incorporated into thermodynamic and kinetic codes for computational simulations.

Keywords CALPHAD, succinonitrile-water, thermodynamic modeling

1. Introduction

Transparent metallic alloys have been used for the fundamental investigation of a large array of solidification phenomena because the solidification process of these alloys can be visually observed. Succinonitrile-water (SCN-H_2O) system is one of the transparent alloys and has received considerable attention.[1-5] The temperature versus composition phase diagram is an important tool for understanding and identifying the solidification morphologies in metallurgical studies. Although experimental work on the phase diagram of the SCN-H_2O system has been conducted by Schreinemakers[6] and by Smith et al.,[7] no work is available on the thermodynamic modeling of this system in the literature. The purpose of this research was to assess the experimental data on the phase diagram of the SCN-H_2O system, determine thermodynamic descriptions of all phases in the system, and develop a thermodynamic database for this system. The first step of this work was to derive the thermodynamic description of pure SCN. The phase diagram for the binary SCN-H_2O system was then modeled via the CALPHAD approach using thermodynamic and phase equilibrium data available in the literature. The thermodynamic database described in this article can be incorporated into the thermodynamic or kinetic codes for computational simulations of phase transformations of the SCN-H_2O system.

2. Experimental Data in the Literature

2.1 Pure SCN

Succinonitrile molecule has a symmetrical structure ($N \equiv C - (CH_2)_2 - C \equiv N$). Below the melting temperature (331 K), it crystallizes into a plastic phase with a bcc structure, which is stable between 233 and 331 K. A monoclinic phase becomes stable at a temperature lower than 233.3 K. Crystallographic data about SCN are listed in Table 1.

The transition temperatures and thermochemical properties of pure SCN were measured many times by different authors using various methods.[9-17] Transformation reactions and thermochemical properties of pure SCN are listed in Table 2. All these experimental data are in good agreement with each other. Very small differences come from the different purities of SCN and experimental errors. Given that the adiabatic method is the most precise, preference was given to the data reported by Wulff and Westrum.[9]

2.2 SCN-H_2O Binary System

The isobaric heat capacities of monoclinic, bcc, and liquid SCN were measured by Wulff and Westrum[9] by adiabatic calorimetry from 5 to 350 K.

The SCN-H_2O phase diagram was first determined by Scheinemakers.[6] However, the results lacked accuracy due to low purity of succinonitrile used. Smith et al.[7] redetermined the SCN-H_2O phase diagram using a laser aided

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Table 1 Crystallographic data for the pure SCN system

Compound	Molecular weight, g/mol	Phases	Temperature range, K	Space group	Reference
Succinotrile (SCN)	80.0890	Bcc Monoclinic	$233 < T < 331$ $T < 233$	$Im\bar{3}m$ $P2_1/a$	[8] [9]

Table 2 Transformation reactions and thermochemical properties of the pure SCN

Reactions	Temperature, K	ΔH_{tr}, J/mol	Method	Reference
Monoclinic → bcc	233.31	6200	Modeling	This work
	233.30 ± 0.20	6199 ± 20	Adiabatic	[9]
Bcc → liquid	331.30	3703	Modeling	This work
	331.60 ± 0.02	3703 ± 10	Adiabatic	[9]
	330.1 ± 0.6	11670 ± 80	Cryoscopic	[10]
	327.65	3920	...	[11]
	331.2305 ± 0.0015	...	Thermometer	[12]
	330.1	3730	DTA	[13]
	330.1	...	...	[14]
	334.0 ± 1.0	3704 ± 15	DSC	[15]
	329.9	...	DTA	[16]
	331.4 ± 0.3	3602 ± 80	DSC	[17]

optical approach. Both works show a eutectic, a monotectic and a large liquid miscibility gap in the system. Recently, Ashtari and Alizadeh[18] determined the liquid miscibility gap and consolute point again using a probe-type photometer. However, the results lacked accuracy owing to low purity of succinonitrile used without further treatment. The solubility of SCN and H_2O in each other is not determined. No thermochemical data are available in the literature.

3. Thermodynamic Models

The Gibbs energy in per mole of formula of SCN was obtained using the model suggested by the Scientific Group Thermodata Europe (SGTE) as follows.

$$^{o}G_i^m - H_i^{\mathrm{SER}} = a + bT + cT\ln T + \sum d_n T^n \qquad \text{(Eq 1)}$$

The left side of the equation is defined as the Gibbs free energy of the phase i (i = monoclinic, bcc or liquid) relative to a standard element reference state (SER), with H_i^{SER} being the enthalpy of the substance in its stable state at 298.15 K. Coefficients a, b, c and d_n are the parameters to be evaluated and n represents a set of integers.

The liquid phase is modeled as a substitutional solution, with the molar Gibbs energy expressed as[19]:

$$G_m^{\Phi} = \sum_i x_i {}^{o}G_i^{\Phi} + RT\sum_i x_i \ln x_i + {}^{xs}G_m^{\Phi} \qquad \text{(Eq 2)}$$

where ${}^{o}G_i^{\Phi}$ is the molar Gibbs energy of the pure substance i with the structure Φ. R is the gas constant. ${}^{xs}G_m^{\Phi}$ is the excess Gibbs energy, expressed in the Redlich-Kister polynomial[20] as:

$${}^{xs}G_m^{\Phi} = \sum_i \sum_{j>i} x_i x_j \sum_{k=0}^{n} {}^{k}L_{i,j}^{\Phi}(x_i - x_j)^k \qquad \text{(Eq 3)}$$

where, ${}^{k}L_{i,j}^{\Phi}$ is the kth binary interaction parameter between i and j and may depend on temperature as $A + BT$, where A and B are model parameters to be evaluated.

4. Results and Discussions

All model parameters were evaluated using the Parrot module in Thermo-Calc.[21] This program is able to take various kinds of experimental data in one operation. It works by minimizing an error of sum with each of the selected data given a certain weight. The weight was chosen and adjusted based upon the data uncertainties given in the original publications and upon the authors' judgment by examining all experimental data simultaneously. All thermodynamic calculations were carried out using Thermo-Calc. The complete and self-consistent thermodynamic descriptions for the pure SCN, pure H_2O and SCN-H_2O binary systems thus obtained are listed in Table 3.

The thermodynamic properties of the water phase are taken from the SGTE substance database.[23] The thermodynamic property of the ice phase was provided by Dinsdale[22] and was obtained in the concentrated aqueous modeling projects.

The evaluation procedure started with the pure SCN phase. The reference states of the three components, C, H, and N forming the pure SCN are graphite, hydrogen, and nitrogen in their stable states at 298.15 K. The isobaric heat capacity data by Wulff and Westrum[9] were used to evaluate the model parameters c and d_n in Eq. 1. The temperature and the enthalpy of transformation between bcc, monoclinic, and liquid phases were then used to evaluate the parameters a and b in Eq. 1 for these three phases.

The relative standard deviations, calculated by the formula as follows, are included in each figure caption.

$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left[(x_i^{\mathrm{cal}} - x_i^{\mathrm{exp}})/x_i^{\mathrm{exp}}\right]^2} \qquad \text{(Eq 4)}$$

where x_i^{cal} is the calculated result, x_i^{exp} the experimental datum, and n the number of experimental data.

The calculated heat capacities are compared with the experimental data in Fig. 1. The heat capacities of the bcc and monoclinic phases above their transformation temperature were modeled in such a way that they approach the heat capacity of the liquid phase at high temperatures based on the SGTE recommendation, and maintains the same values of entropy, enthalpy, and heat capacity at the transformation temperature when approached from both higher and lower temperatures. The calculated Gibbs energies of the monoclinic, bcc, and liquid phases are shown in Fig. 2.

Table 3 The Gibbs energy functions of pure SCN and H_2O as well as thermodynamic parameters of the binary SCN-H_2O system in SI unit (100 < T < 400)

System	Phase	Gibbs energy function/thermodynamic parameter	Reference
SCN	Monoclinic	$109361.36 – 13.799961T + 7.07832T\ln(T) – 0.451575T^2 – 3.15\times10^{4}T^3$ $+ 5.9746500\times10^{-6}T^4 – 2.1968300\times10^{-8}T^5 + 3.4871\times10^{-11}$ $T^6 – 2.06836\times10^{-14}T^7$	This work
	Bcc	$109041.05 + 52.446761T – 0.552085T^2 – 3.15\times10^{-4}T^3$ $+ 3.81368\times10^{-6}T^4 – 7.96395\times10^{-9}T^5 + 5.62597\times10^{-12}T^6$	This work
	Liquid	$119630.41 – 53.134383T + 7.07832T\ln(T) – 0.451575T^2 – 3.15\times10^{4}T^3$ $+ 5.9746500\times10^{-6}T^4 – 2.1968300\times10^{-8}T^5 + 3.4871\times10^{-11}$ $T^6 – 2.06836\times10^{-14}T^7$	This work
H_2O	Ice	$–305105.60 + 214.66\mathrm{T} – 39.88T\ln(T) + 0.00412T^2 – 5.60\times10^{-5}T^3$ $+ 1.75\times10^{5}/T$	[22]
	Water	$–332319.67 + 1078.60T – 186.87T\ln(T) + 0.2320948T^2 – 9.143\times10^{5}T^3$ $+ 978019/T$; $298.14 < T < 500$; $–62418.88 – 3288.19T$ $+ 495.13T\ln(T) – 0.505T^2 + 4.9210^{-5}T^3 – 18523425/T$; $500 < T < 540$; $–8528143.9 + 142414.45T – 22596.19T\ln(T)$ $+ 27.48508T^2 – 0.00631160667T^3 + 5.63356\times10^{8}/T$; $540 < T < 600$; $–331037.282 + 741.178606T – 117.41T\ln(T)$; $600 < T < 601$;	SGTE
SCN-H_2O	Liquid	${}^{0}L^{\mathrm{Liq}}_{\mathrm{SCN,H_2O}} = 19240 - 44.85T$ ${}^{1}L^{\mathrm{Liq}}_{\mathrm{SCN,H_2O}} = -9871 + 25.32T$ ${}^{2}L^{\mathrm{Liq}}_{\mathrm{SCN,H_2O}} = 9412 - 25.52T$ ${}^{3}L^{\mathrm{Liq}}_{\mathrm{SCN,H_2O}} = 19181 - 60.85T$	This work

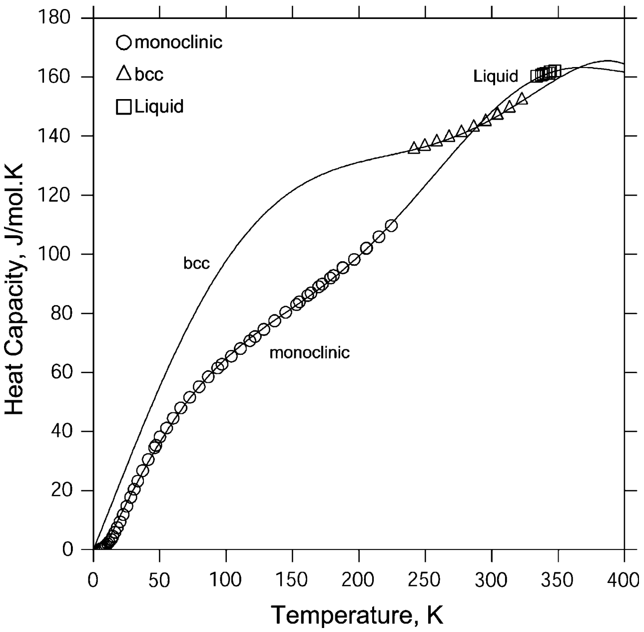

Fig. 1 Calculated heat capacity in the pure SCN system with experimental data ○ (monoclinic), △ (bcc), □ (liquid) by Wulff and Westrum[9] superimposed. (σ = 1.03%)

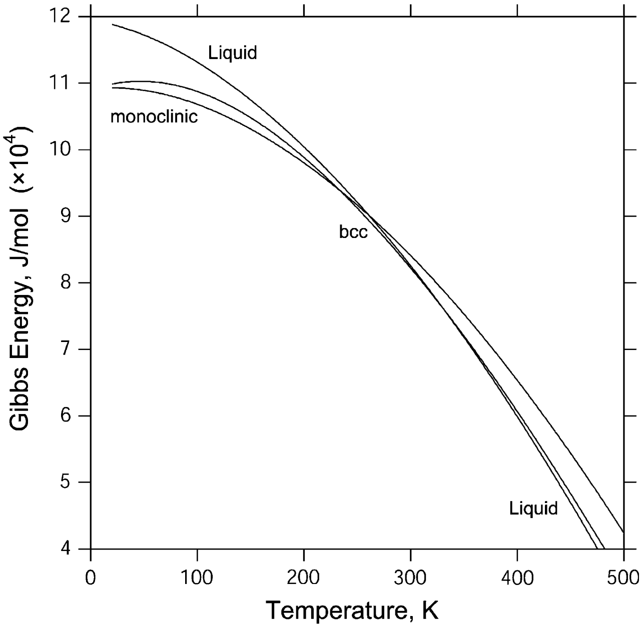

Fig. 2 Calculated Gibbs energy in the pure SCN system

The evaluation of model parameters in the SCN-H_2O system started with the liquid phase. Special attention was paid to the composition and temperature of the consolute point in the liquid miscibility gap to ensure the rational shape of the miscibility gap. The temperatures and compositions of monotectic and eutectic reactions were used to evaluate liquid parameters. Eight parameters had to be used to get a good agreement. The solubilities of SCN and H_2O in each other were not considered due to the lack of experimental information.

The thermodynamic description of the SCN-H_2O system obtained in the present work is listed in Table 3. The phase diagram calculated using these parameters is shown in Fig. 3 with the experimental data superimposed. It shows

Table 4 Invariant reactions and consolute point in the SCN-H_2O system

Reaction	Reference	Temperature, K	Concentration of H_2O, at.%		
Liquid1 = Bcc + Liquid2	Present work	291.94	31.61	0	97.47
	Experiment[6]	291.65	28	···	97.5
	Experiment[7]	291.97 ± 0.06	31.60 ± 0.05	···	···
Liquid2 = Bcc + Ice	Present work	272.11	98.94	0	100
	Experiment[6]	271.95	98.72	···	···
	Experiment[7]	271.89 ± 0.06	98.96	···	···
Consolute point	Present work	331.20	82.47		
	Experiment[7]	329.32 ± 0.06	82.70		
	Experiment[18]	329 ± 0.1	81 ± 5		

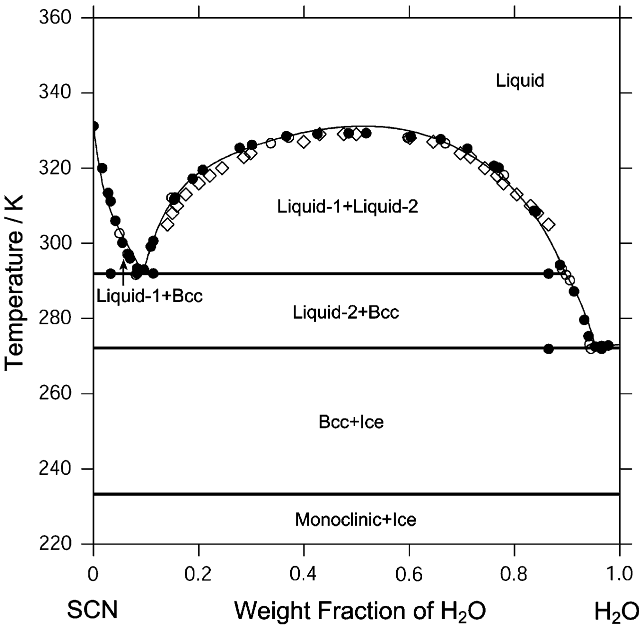

Fig. 3 Calculated SCN-H_2O phase diagram in comparison with experimental data ○ by Schreinemakers[6]; • by Smith et al.[7] and ◇ by Ashtari and Alizadeh[18] ($\sigma = 4.47\%$)

that most of the experimental data is well reproduced. The invariant equilibria and consolute point in the SCN-H_2O system are listed in Table 4 with the experimental data included. The present work agrees with experimental data very well.

5. Conclusions

A thermodynamic description of the SCN-H_2O system was developed based on experimental data. A set of self-consistent thermodynamic parameters describing Gibbs energies of individual phases in the SCN-H_2O binary system was obtained. All the calculated results compare favorably with the experimental data in the literature. The present work contributes to the development of a thermodynamic database of the SCN-H_2O system that can be incorporated into thermodynamic and kinetic codes for computational simulations.

Acknowledgments

This research was supported by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Industrial Technologies Program, Aluminum Industry of the Future, under the grant DE-FC36-02ID14403 and under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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