

Phase diagram of the ternary system urea—sodium thiocyanate—sodium nitrate

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Literature data on the binary systems $\text{CO}(\text{NH}_2)_2\text{—NaSCN}$, $\text{CO}(\text{NH}_2)_2\text{—NaNO}_3$, and NaSCN—NaNO_3 were verified and corrected. Using the DTA method, eight sections in the ternary system $\text{CO}(\text{NH}_2)_2\text{—NaSCN—NaNO}_3$ were investigated and the projection of the phase diagram of this system into the base was constructed. The experimental results are compared with the data calculated on the basis of knowledge of binary systems. The method of central projection and calculation based on application of the Haase model were used. Two new correlation methods based on the universal model for calculation of activities of components were proposed.

Были проверены и исправлены литературные данные по бинарным системам $\text{CO}(\text{NH}_2)_2\text{—NaSCN}$, $\text{CO}(\text{NH}_2)_2\text{—NaNO}_3$ и NaSCN—NaNO_3 . Используя метод ДТА были изучены 8 секций тройной системы $\text{CO}(\text{NH}_2)_2\text{—NaSCN—NaNO}_3$ и была построена проекция фазовой диаграммы этой системы на основание. Экспериментальные результаты были сравнены с данными, рассчитанными на основе результатов изучения бинарных систем. Были использованы метод центральной проекции и расчетный метод, основанный на применении модели Гаазе. Предложены две новые корреляционные методы, основанные на универсальной модели для расчета величин активностей.

The ternary system urea—sodium thiocyanate—sodium nitrate is interesting both from the practical and theoretical point of view. From the point of view of practical application it can be important that the system consists of relatively cheap substances which are available either from industrial wastes or are produced in large quantities for agriculture [1, 2]. All three substances have a low melting point [3] (Table 1). Combination of these properties predestinates this system as

Table 1
Thermochemical constants of the components

Component	$T_i(\text{fus})$ K	$\theta_i(\text{fus})$ °C	$\Delta H_i(\text{fus})$ J mol ⁻¹	$\Delta S_i(\text{fus})$ J K ⁻¹ mol ⁻¹
CO(NH ₂) ₂	406	133	15100	37.2
NaSCN	588	315	18400	31.3
NaNO ₃	581	308	15900	27.4

a promising medium for storage of thermal energy at the temperatures below 100 °C.

From the theoretical point of view it is interesting that the system consists of a nonelectrolyte with molecular structure and two electrolytes having ionic structure with different type of anions. This allows to verify correlation methods and physical models on the systems consisting of the substances of different nature.

The phase diagrams of all three binary systems have been already published in literature [4—6]. However, the binary systems containing urea have been studied only in limited concentration range with respect to the fast decomposition of urea over its melting point [7]. The systems CO(NH₂)₂—NaNO₃ and NaSCN—NaNO₃ are of simple eutectic character [4, 5]. In the system CO(NH₂)₂—NaSCN [6] the existence of incongruently melting compound 2CO(NH₂)₂·NaSCN has been claimed [6]. Incomplete phase diagram of the system does not give, however, a convinced evidence about the existence of that compound.

The ternary phase diagram of the system CO(NH₂)₂—NaSCN—NaNO₃ has not yet been studied neither the theoretical interpretation of the phase diagrams of the corresponding binary systems has been done. The problem of the character of crystallization and of undercooling has not been discussed in the cited papers either. This paper is a contribution to the solution of these topics.

Experimental

The chemicals used for investigation of the phase equilibria were of anal. grade (urea and sodium nitrate produced by Lachema, Brno, sodium thiocyanate by Reakhim, USSR). Their purity was tested by determination of their melting point on the apparatus PHMK 05 (VEB Analytik) with the precision ± 1 °C. Sodium nitrate and urea were further purified by double recrystallization from aqueous solutions. When the melting point of pure substances agreed with literature data better than 1 °C the substances were considered as pure.

The temperatures of primary crystallization in the binary systems CO(NH₂)₂—NaNO₃ and NaSCN—NaNO₃ were verified using the method of visual observation of samples in the melting point apparatus PHMK 05. Accuracy of the measurement was ± 1 °C. The

temperatures of primary crystallization in the system $\text{CO}(\text{NH}_2)_2\text{—NaSCN}$ were determined visually by the synthetic polythermal method [8] in a closed Simax cell containing 20—30 g of the sample. The temperature could be read with the accuracy $\pm 1^\circ\text{C}$ and the composition was adjusted with the precision 0.3 mole %. When the sample was cooled spontaneously an appreciable undercooling was observed. For that reason the maximum temperature after beginning of solidification of the system was read as the temperature of phase transition. Reproducibility of all experimental values of temperatures of phase transition was several times checked.

In the study of the ternary system $\text{CO}(\text{NH}_2)_2\text{—NaSCN—NaNO}_3$ it was necessary to determine not only the temperature of primary but also the temperatures of the secondary and ternary crystallization. The following method was used. Two samples having the same mass (ca. 0.5 g) were placed in small glass cells. The third cell contained silicon oil which was used as a standard. Nickel—nickelchromium thermocouples were immersed directly into the measured and standard samples. Both temperature of the sample and the difference in temperatures of the sample and of the standard were measured and recorded. The cells with samples were placed in the heated bronze block. The thermocouples were calibrated on the phase transitions of ammonium nitrate (85, 125.2, and 169.6°C), naphthalene (80.2°C), resorcin (111°C), and water (0°C) [9]. The temperature and the DTA curves were plotted on two recorders EZ 2 (Laboratorní přístroje, Prague) with the precision of reading $\pm 1^\circ\text{C}$.

X-Ray diffraction records of polycrystalline substances were obtained using three methods: a) The Debye—Scherrer method (apparatus Mikrometa 2, Chirana with Siemens—Halsky chamber, diameter 57.3 mm; copper anode and nickel filter as monochromator ($\lambda(\text{CuK}_\alpha) = 154.184\text{ pm}$). b) The same method as in the former case with Weissenberg chamber equipped with electrical furnace, which allowed to take the X-ray records at elevated temperatures. c) Diffractographic method with monochromatic radiation ($\lambda(\text{CuK}_\alpha) = 154.184\text{ pm}$, monochromator $\alpha\text{-SiO}_2$) which was registered by the Geiger—Müller tube and recorded by a linear recorder.

All calculations (including calculation of the curves of liquidus) could be carried out with a programmable calculator TI-57.

Results and discussion

An attempt to prepare compound $2\text{CO}(\text{NH}_2)_2 \cdot \text{NaSCN}$ by crystallization from the melt

The mixture of dried sodium thiocyanate and urea in mole ratio 1:2 (8.1 g NaSCN plus 12 g $\text{CO}(\text{NH}_2)_2$) was melted under mixing in a glass cell in air bath at the temperature of 130°C and kept at this temperature for 30 min. Approximately 10 % of sodium thiocyanate remains unsolved. Then the hot melt is poured into a teflon dish and cooled in a desiccator. Frozen sample was investigated by X-ray methods. It was found that the diffraction record was identical with the record of mechanical mixture of urea and thiocyanate (mole ratio = 1:2). The

next X-ray records were taken with the samples containing 25 mole % NaSCN + 75 mole % $\text{CO}(\text{NH}_2)_2$. In this case the frozen melt was investigated at the ambient temperature or at the temperature of 80 °C when the mixture just solidified in capillary. Again the X-ray records were identical with the records of single components. Thus it can be excluded that the compound decomposes at a laboratory ambient temperature into its components.

Phase diagrams of the binary systems

In the systems containing urea the region accessible to measurement is limited by the decomposition of urea at higher temperatures. At 130 °C the decomposition is so fast that it is impossible to obtain reproducible results. This temperature limit makes it possible to investigate phase equilibria in the system $\text{CO}(\text{NH}_2)_2$ —NaSCN only up to 27.2 mole % of NaSCN and in the system $\text{CO}(\text{NH}_2)_2$ — NaNO_3 to 26.2 mole % of NaNO_3 . The systems containing urea have the tendency to form a glassy state, especially at the concentrations close to the composition of eutectic mixtures. In the system $\text{CO}(\text{NH}_2)_2$ —NaSCN the undercooling reaches at these conditions as much as 10 °C.

All the investigated systems have a simple eutectic character. The experimental results for binary systems are summarized in Figs. 1—3 and in Table 2 where they are compared with literature data.

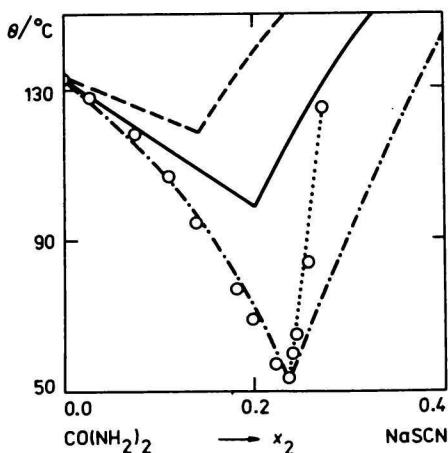


Fig. 1. Phase diagram of the binary system $\text{CO}(\text{NH}_2)_2$ —NaSCN.

Dashed line — the ideal model; full line — the Haase model; dot-and-dashed line — the liquidus curve of $\text{CO}(\text{NH}_2)_2$ and of NaSCN calculated according to the universal model; $k_{st}(1/2)=1.000$; dotted line — the liquidus curve of NaSCN calculated according to the universal model; $k_{st}(1/2)=0.177$.

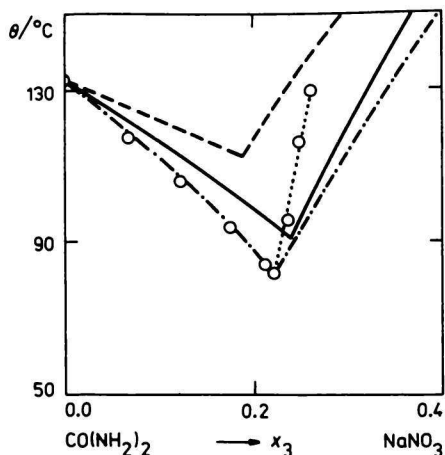


Fig. 2. Phase diagram of the binary system $\text{CO}(\text{NH}_2)_2\text{—NaNO}_3$.

Dashed line — the ideal model; full line — the Haase model; dot-and-dashed line — the liquidus curve of $\text{CO}(\text{NH}_2)_2$ and of NaNO_3 calculated according to the universal model; $k_{\text{Si}}(1/3)=1.000$; dotted line — the liquidus curve of NaNO_3 calculated according to the universal model; $k_{\text{Si}}(1/3)=0.155$.

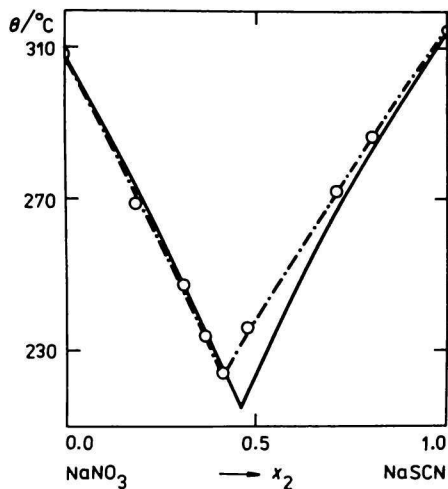


Fig. 3. Phase diagram of the binary system NaSCN—NaNO_3 .

Full line — the liquidus curve calculated according to the ideal or the Haase model; dot-and-dashed line — the universal model.

Calculation of liquidus curves in binary systems

The liquidus curves in binary systems were calculated according to the Le Chatelier—Shreder equation

$$T_i = \frac{\Delta H_i(\text{fus})}{\Delta S_i(\text{fus}) - R \ln a_i} \quad (1)$$

where T_i is the temperature of solidus—liquidus equilibrium of the i -th component, a_i is the activity of this component and $\Delta H_i(\text{fus})$, $\Delta S_i(\text{fus})$ are the changes in molar enthalpy and entropy of fusion of the pure i -th component at its temperature of fusion $T_i(\text{fus})$. R is the gas constant [10]. The following relationships between the activity a_i and the mole fraction x_i were used:

a) The relationship valid in ideal systems, viz.

$$a_i = x_i \quad (2)$$

Table 2

Eutectic points of the binary systems

System	This paper					Literature						
	T_E/K	$\theta_E/^\circ C$	$x_{E,1}$	$x_{E,2}$	$x_{E,3}$	T_E/K	$\theta_E/^\circ C$	$x_{E,1}$	$x_{E,2}$	$x_{E,3}$	Ref.	Comments
$CO(NH_2)_2-NaSCN$	327	54	0.764	0.236	—	337	64	0.78	0.22	—	[6]	Formation of a compound
$CO(NH_2)_2-NaNO_3$	355	82	0.768	—	0.232	357	84	0.77	—	0.23	[4]	—
$NaSCN-NaNO_3$	497	224	—	0.410	0.590	499	226	—	0.43	0.57	[5]	—

Table 3

Constants of the universal relationship for binary systems

System	$k_{s_i}(j/1)$	$k_{s_i}(j/2)$	$k_{s_i}(j/3)$	$b(j/1)$	$b(j/2)$	$b(j/3)$
$CO(NH_2)_2-NaSCN$	2.000	0.177	—	-2.126	-1.198	—
$CO(NH_2)_2-NaNO_3$	2.000	—	0.155	-0.769	—	-1.161
$NaSCN-NaNO_3$	—	1.000	1.000	—	+0.498	-0.126

b) The Haase relationship [11] which was formally extended also for the mixtures of electrolytes with nonelectrolytes [12]. According to this model the activity of fully dissociated component is proportional to the product of ionic fractions of cations and anions and the activity of nondissociated component equals its mole fraction in the mixture. The proportionality constants follow from the boundary condition

$$\lim_{x_i \rightarrow 1} a_i = 1$$

In the system consisting from one fully dissociated and one nondissociated compound (e.g. the system $\text{CO}(\text{NH}_2)_2\text{—NaNO}_3$) we obtain for the activities of components the following relationships

$$a_1 = \frac{x_1}{2 - x_1} \quad (3)$$

$$a_3 = \left(\frac{2x_3}{1 + x_3} \right)^2 \quad (4)$$

In these equations, 1, 2, and 3 denote the components $\text{CO}(\text{NH}_2)_2$, NaSCN , and NaNO_3 , respectively. (These abbreviations symbols hold throughout this paper.) Similar expressions as (3) and (4) hold also in the system $\text{CO}(\text{NH}_2)_2\text{—NaSCN}$. In the case of fully dissociated component with common ion, e.g. in the system NaSCN—NaNO_3 , the Haase relationship is identical with the ideal relationship, i.e. $a_2 = x_2$ and $a_3 = x_3$.

c) The universal relationship [13, 14]

$$\ln a_i = \frac{k_{\text{St}}(j/i)}{1 + b(j/i) \cdot (1 - x_i)} \cdot \ln x_i \quad (5)$$

where $k_{\text{St}}(j/i)$ is the Stortenbecker factor which denotes the number of new (foreign) particles brought into the substance i by one molecule of the component j . $b(j/i)$ is an empirical constant which is to be determined from the liquidus curve of the component i in the system $j\text{—}i$. In this paper the numerical values of this constant were determined from coordinates of the eutectic points. The values of the Stortenbecker factors and of the constants $b(j/i)$ for the components of binary systems are summarized in Table 3.

In Figs. 1—3 the experimental data are compared with the liquidus curves calculated according to the models a , b , and c . Validity of the relationship for regular solutions [15] was tested as well. For the regular solutions it holds

$$\ln a_i = \ln x_i + \frac{w(1 - x_i)^2}{RT_i} \quad (6)$$

It was found that the model of regular solutions does not suit well for the studied systems. In the system NaSCN—NaNO₃ the deviations were almost the same as in the case of ideal model and for the binary systems containing urea as one component this approach is not applicable at all.

From Figs. 1—3 it may be seen that the ideal relationship gives the largest deviations from experimental data. Closer to experiment are the liquidus curves calculated on the basis of the Haase model. In the case of the system NaSCN—NaNO₃ this model gives identical results as the ideal model. Very good fit with experiment in the system NaSCN—NaNO₃ is achieved when the universal relationship is used ($k_{st}(2/3) = k_{st}(3/2) = 1$). Similarly in the systems with urea the universal relationship gives good results for the liquidus curves of urea ($k_{st}(2/1) = k_{st}(3/1) = 2$). This may be explained by the fact that the universal relationship contains one adjustable parameter which is calculated from coordinates of the eutectic point.

When the liquidus curves of salts are calculated under the assumption that urea is in the melt molecularly dispersed, *i.e.* $k_{st}(1/2) = k_{st}(1/3) = 1$, the calculated liquidus curve is in the vicinity of the eutectic point less steep than the experimental data. This phenomenon, *viz.* the steepness of the liquidus curves of salts in their mixtures with urea, is not exceptional and it appears also in other binary systems containing urea as one component [4]. If the calculated liquidus curves of NaSCN and NaNO₃ in binary systems with urea should fit with experimental data then the value of the Stortenbecker factor in the universal relationship had to be much smaller than 1. These values $k_{st}(1/i)$ were found by solving two equations (5). The unknown parameters $k_{st}(1/i)$ and $b(1/i)$ were obtained. The values of a_i required in eqn (5) were calculated from the Le Chatelier—Shreder equation (1) for two sufficiently remote points. The eutectic point and the point corresponding to the highest measured temperature were chosen (Figs. 1 and 2). It follows that the values of $k_{st}(1/i)$ ($i = \text{NaSCN, NaNO}_3$, Table 3) are close to $1/6 = 0.1\bar{6}$ and their mean equals exactly this value. This corresponds to the assumption that 1 mole of urea brings into the melt of relevant sodium salt $1/6$ mole of new particles, *i.e.* six molecules of urea form associates. We may assume that the oxygen atoms of six urea molecules are coordinated around the sodium cation. In any case the interactions in the systems with urea are too complex to be explainable by a simple model.

Phase diagram of the ternary system

The eutectic curves in the ternary system and the coordinates of the ternary eutectic point were determined both experimentally and by correlation calculations from the known liquidus curves of binary systems. From each of the three groups of correlation methods [16] we chose the most suitable one. From the geometrical

methods the method of central projection was chosen because it is especially suitable for the system consisting of two binary systems with similar phase diagrams (urea—sodium salt) and a third system (two sodium salts in our case) with comparable melting points of pure components and the eutectic mole fractions of components close to 0.5. This means that the ternary system is approximately symmetrical according to the plane going through the urea vertex and dividing the binary system NaSCN—NaNO₃ approximately into halves. Composition coordinates of the ternary eutectic point E₁ found by the method of the central projection (Table 4 and Fig. 4) are in agreement with this reality. The temperature of the ternary point is, however, higher (56 °C) than the eutectic temperature of the binary system CO(NH₂)₂—NaSCN (54 °C). This is caused by formal averaging of

Table 4
Ternary eutectic points

Method	Point	T _E /K	θ _E /°C	y _{E,1}	y _{E,2}	y _{E,3}
Experiment	E ₀	322.1	49.0	0.767	0.181	0.052
Central projection	E ₁	329	56	0.78	0.11	0.11
Haase model	E ₂	357	84	0.70	0.12	0.18
Universal model (linear)	E ₃	323.6	50.5	0.702	0.109	0.189
Universal model (corrected)	E ₄	318.5	45.4	0.738	0.118	0.144

the temperatures of liquidus curves in the binary systems containing urea at the construction of the phase diagram.

Another method of calculation of the ternary phase diagram is based on the Haase model in similar way as it has been done in the case of binary systems. In this case the activities of components are as follows

$$a_1 = \frac{y_1}{2 - y_1} \quad (7)$$

$$a_2 = \frac{4y_2(y_2 + y_3)}{(1 + y_2 + y_3)^2} \quad (8)$$

$$a_3 = \frac{4y_3(y_3 + y_2)}{(1 + y_3 + y_2)^2} \quad (9)$$

y₁, y₂, and y₃ are the mole fractions of components in the ternary system. The temperature of the ternary eutectic point E₂ (84 °C) determined on the basis of the Haase model is also too high in comparison to the experimental eutectic points of

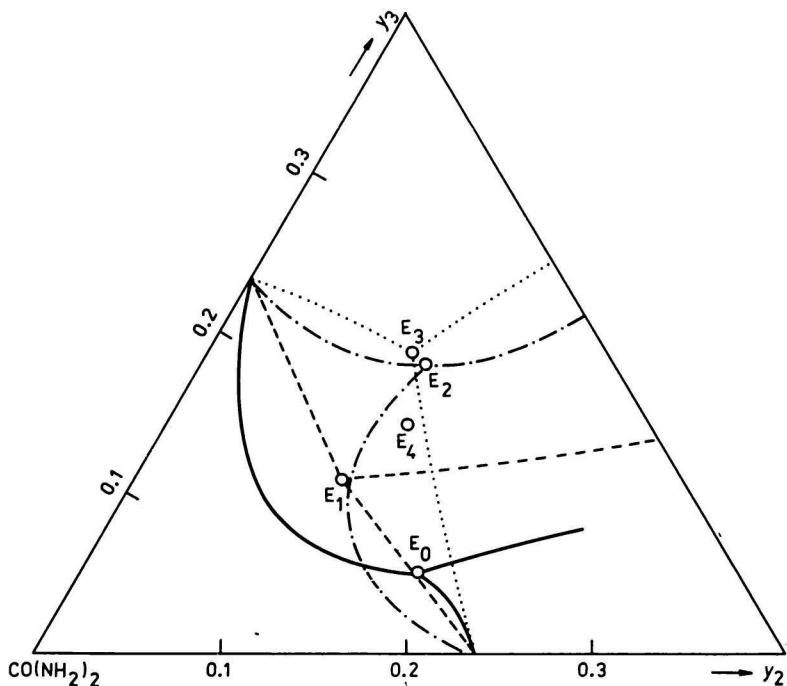


Fig. 4. The section of the phase diagram of the ternary system



y_2 — the mole fraction of NaSCN, y_3 — the mole fraction of NaNO₃. E_0 and full lines — the experimental data; E_1 and dashed lines — the central projection; E_2 and dot-and-dashed lines — the Haase model; E_3 and dotted lines — the universal model with linear combination of constants; E_4 — the universal model corrected with respect to the eutectic temperatures.

the binary systems. However, it is adequately lower than the binary eutectic temperatures calculated on the basis of the Haase model (Figs. 1—3).

For experimental study of the ternary system firstly a quasi-binary section with constant ratio $y_1 : y_2$ (going through the vertex of the component NaNO₃) close to the calculated composition of the ternary eutectic points was chosen. The next quasi-binary sections were chosen on the basis of positions of the cross-sections of the curves of primary crystallization obtained in the foregoing experimental series. Two quasi-binary sections had the constant mole fraction of sodium nitrate, $y_3 = 3$ and $y_3 = 6$, respectively. Five sections had the constant ratio $y_1 : y_2$ ranging from 5.0 to 2.7. These sections allowed to map the part of the ternary system having the temperatures of primary crystallizations lower than 140 °C. The course of the

eutectic curves and the composition and temperature of the ternary eutectic point E_0 are presented in Fig. 4 and Table 4.

For computational correlation based on an empirical relationship the universal model was used. This model agrees well with experiment in the case of binary systems. Firstly an attempt to derive a correlation method based on a linear combination of the Stortenbeckers factors $k_{St}(j/i)$ and the constants $b(j/i)$ from binary systems data (eqn (5)) has been done. It follows

$$K_{St,1} = \frac{y_3}{y_3 + y_2} \cdot k_{St}(3/1) + \frac{y_2}{y_2 + y_3} \cdot k_{St}(2/1) \quad (10)$$

$$B_1 = \frac{y_3}{y_3 + y_2} \cdot b(3/1) + \frac{y_2}{y_2 + y_3} \cdot b(2/1) \quad (11)$$

Expressions for the other two components can be derived cyclicly in similar way. In eqns (10) and (11) $K_{St,1}$, $k_{St}(2/1)$, $k_{St}(3/1)$ represent the Stortenbecker factors for urea in the ternary system and in the binary systems, respectively. B_1 , $b(2/1)$, $b(3/1)$ are the analogical constants in the denominator of eqn (5). Eqns (10) and (11) fulfil the limiting conditions for transformation of the ternary to binary systems

$$\lim_{y_3 \rightarrow 0} K_{St,1} = k_{St}(2/1), \quad \lim_{y_2 \rightarrow 0} K_{St,1} = k_{St}(3/1) \quad (12)$$

$$\lim_{y_3 \rightarrow 0} B_1 = b(2/1), \quad \lim_{y_2 \rightarrow 0} B_1 = b(3/1) \quad (13)$$

The coordinates of the ternary eutectic point E_3 and the course of binary eutectic curves constructed according to this correlation are presented in Table 4 and Fig. 4. It follows that the composition coordinates of the eutectic point E_3 are almost identical with those obtained from the Haase model (denoted as E_2). In contradistinction to the Haase model also the calculated temperature of the eutectic point E_3 (50.5 °C) agrees very well with experimental value of this parameter, viz. 49 °C (E_0). As a serious drawback of this procedure one may consider the fact that the binary eutectic curve in the system $\text{CO}(\text{NH}_2)_2\text{—NaSCN}$ does not fall monotonously from the binary eutectic point of this system (54 °C) to the ternary eutectic point E_3 but it goes through a mild maximum at 55 °C. This can be explained by that the constants $K_{St,1}$ and B_1 characterize the course of liquidus curves of single binary systems but they do not reflect the mutual position of these binary systems in the temperature scale. An attempt to improve this defect was done so that a correction on the eutectic temperatures of binary systems was introduced into eqn (11). The resulting equation must fulfil the same limiting conditions (13) at transformation from the ternary system to the binary systems as eqn (11). This condition is fulfilled by a relatively simple expression

$$B_1 = \frac{y_3}{y_3 + y_2} \cdot b(3/1) \cdot \left(1 + \frac{y_2}{y_2 + y_3} \cdot \ln \frac{T_1^2}{T_2 \cdot T_3} \right) + \frac{y_2}{y_2 + y_3} \cdot b(2/1) \cdot \left(1 + \frac{y_3}{y_3 + y_2} \cdot \ln \frac{T_1^2}{T_2 \cdot T_3} \right) \quad (14)$$

Similar expressions for B_2 and B_3 can be readily cyclicly derived. T_1 , T_2 , T_3 denote the eutectic temperatures in the binary systems NaSCN—NaNO₃, CO(NH₂)₂—NaNO₃, and CO(NH₂)₂—NaSCN, respectively. The coordinates of the ternary eutectic point E_4 calculated according to the relations (10) and (14) are presented in Table 4 and in Fig. 4. Calculation of the binary eutectic curves has not been done because it would require a more advanced computing technique than that used in this work. In comparison with E_3 the concentration coordinates of the eutectic point E_4 are closer to the experimentally determined coordinates of E_0 . The calculated temperature corresponding to E_4 , i.e. 45.4 °C, is again in good agreement with experiment.

Study of general validity of the newly proposed correlation methods and of alternative temperature corrections and comparison of these methods with those based on the concept of activity coefficients is in progress.

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