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Computer Subroutines for Rapid Calculation of the Liquid Entropies of Ammonia/NaSCN and Ammonia/$LiNO_3$ Solutions

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Abstract

This paper proposes an alternative to the calculation of the liquid entropy of ammonia/NaSCN and ammonia $LiNO_3$ solutions in the form of correlation equations with higher computation speed. These correlation equations were obtained by using both the least squares method for the modelling of the reference liquid entropy and a classical matrix computer solving for modeling the liquid entropy. Goodness-of-fit parameters such as sum of squares of estimation errors (*SSE*), Pearson's factor (*R-squared*), root mean square error (*RMSE*) and relative error (ε) were computed and the different results were compared with those of the digitized data. The suggested correlations showed good accuracy in estimating the liquid entropy of ammonia/NaSCN and ammonia/$LiNO_3$ solutions, with an average *SSE* of $1.23.10^{-4}$, *R-squared* of 0.99, *RMSE* of $2.90.10^{-3}$ and ε of 0.59 % for ammonia/$LiNO_3$, and *SSE* of $1.57.10^{-4}$, *R-squared* of 0.99, *RMSE* of $3.2.10^{-3}$ and ε of 0.83 % for ammonia/NaSCN. These correlations are for the temperature range from 0 to 100 °C, and are decision support tools for combined systems for waste heat recovering at very low temperature and in which the couples ammonia/NaSCN and ammonia/$LiNO_3$ must be used.

Keywords*: Entropy; binary solutions; correlation equations; computer subroutines; thermodynamic*.

1. Introduction

The thermodynamic analysis of absorption systems using the Second Law of Thermodynamic can be directly carried out by the Carnot's theory. But when the energy improvement of components within the thermodynamic system is required, it is essential to calculate the entropy values. According to Farshi *et al*. [1], it is increasingly accepted that exergy analysis provides more meaningful information when assessing the performance of energy conversion systems and for this purpose, the entropy of solutions are needed as well. This task can be easy for the case of a simple pure solution but complicated for mixing solutions [2].

A widely used methodology in the entropy calculation of binary solutions as working fluids such as ammonia/NaSCN and ammonia/$LiNO_3$ solutions is based on the theories presented by Gupta *et al*. [3] and Koehler *et al*. [4]. In these theories, the reference entropy is calculated from Gibbs' free energy which the calculation needs some knowledge of the chemical potentials of the refrigerant and salt in the liquid solution. In the specific case of the salt chemical potential, the evaluation of the activity coefficient from a discretized integral relation [5] or based on the Meissner's method [6] is essential. With these procedures, many researches have theoretically obtained the entropies of ammonia/NaSCN and ammonia/$LiNO_3$ solutions [7, 8, 1], and more recently Saheli and Yari [9] used it in the exergoeconomic assessment of two novel absorption-ejection heat pump. Nevertheless, Aphornratana and Eames [6] as well as Farshi *et al*. [2] have indicated that such procedures for calculating the entropies of ammonia/$LiNO_3$ and ammonia/NaSCN solutions remain long and complicated. The field of using is thus restricted to specialists in chemical engineering and limited to some in energy engineering whose studies can be based on exergy analyses of systems using such mixtures.

In recent years, numerous research initiatives related to the dynamic simulation of organic Rankine cycles (ORC) combined with absorption cycles (Pourfarzad et al. [10]) for the conversion of energy at low temperatures ($T < 230$ °C [11]) have been carried out. More of these studies are those which use the water/LiBr couple as working fluid (CaO et al. [12], Morais et al. [13], Jafary et al. [14], Goigo and Hazarika [15], Cimşit [16]), and whose entropy models are easily implemented in simulation software as Engineering Equation Solver (EES). The use of ammonia/LiNO3 and ammonia/NaSCN in absorption machine systems appears as an alternative to resolve the efficiency and working fluid purification problems when using water/LiBr and ammonia/water solutions as working fluids. However,

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simulations of low temperature energy systems with ammonia/NaSCN or ammonia/$LiNO_3$ require entropy data when applying the Second Law. Such simulations require many thermodynamic property evaluations and therefore use very large amounts of computer process time if they use the methods proposed by Gupta *et al*. [3] or Koehler *et al*. [4]. Their implementation into computer simulation programs with low capabilities is, therefore, not always practical [17]. For this reason, simple correlations like those proposed by Gu and Gan [18] as well as Infante [19] using less process time would be helpful.

Farshi *et al*. [2], in order to overcome the weakness of Zhu's methodology in entropy calculation, provided a First and Second Law analysis of ammonia/salt absorption refrigeration systems. Over the entropy values of ammonia/NaSCN and ammonia/$LiNO_3$ generated using the method of Gupta *et al*. [3], a model in the form of a rational equation has been shown for these working fluids respectively. These equations presented a maximum error of 2 % and remain the only correlation equations indicated at the present time for the entropy calculation of ammonia/NaSCN and ammonia/$LiNO_3$ solutions. However, they have been defined for different temperature and ammonia concentration ranges; which does not already allow a comparative study of an absorption system because, as specified by Farshi *et al*. [2], the accuracy of the results will be lower and often unacceptable when the concentration values in ammonia and temperature will be taken outside the ranges for which these models were established. Apart these summary limitations, Cai *et al*. [5] also highlighted certain limitations of Farshi's [2] method in ammonia/salt solution entropy calculation. One of the limitations noted is the lack of enough accuracy in the exergy analysis of the absorption refrigeration cycle due to the neglect of the solution concentration variation from initial concentration to equilibrium concentration at corresponding surrounding temperature and pressure. Another noted limitation of Farshi's [2] method was related to the process adopted for obtaining the salt activity coefficient by integrating the Gibbs-Duhem equation from the solution concentration in liquid-solid equilibrium state to solution concentration in initial state at 0 °C. According to Cai *et al*. [5], such process did not firstly take into account the liquid-solid equilibrium state conditions for which ammonia/NaSCN and ammonia/$LiNO_3$ solutions can exhibit liquid ammonia mixtures with ammine sodium thiocyanate and liquid ammonia with ammine lithium nitrate, respectively, having different properties, and secondarily the maximum allowable generating temperature of the weak solution at the outlet of the generator according to the minimum mass concentration limit of ammonia linked to both the risk of crystallization and high viscosity of the solution.

Cai *et al*. [5] overcame weakness of Farshi's [2] method in entropy calculation by proposing an exergy analysis of a novel air-cooled non-adiabatic absorption refrigeration cycle with ammonia/NaSCN and ammonia/$LiNO_3$ refrigerant solution. The solution concentration variation from initial concentration to equilibrium concentration at corresponding surrounding temperature and pressure has been taken into account; the Debye-Hückel limiting law [20] has been utilized to obtain the salt activity coefficient in the solution at a very low salt concentration and the mass concentration has been taken at $X_{NH_3} = 0.36$ for both ammonia/NaSCN and ammonia/$LiNO_3$ solution in order to specify the maximum allowable value of generating temperature to avoid crystallization as well as high viscosity of the solution. The entropy calculation results have been shown in the form of graphical curves. Although these graphical curves can be exploited, the entropy calculation in a computational process always remains long and complicated.

The aim of this paper is to propose an alternative solution for the liquid entropy calculation of ammonia/NaSCN and ammonia/$LiNO_3$ solutions from the simple correlations adapted to computer subroutines and giving both a fewer stages and greater computation speed. Cai's [5] graphical curves will be digitized and a database will be built. The least squares adjustment method will be applied.

2. Modelling

2.1. Mathematical Formulation

Neglecting the pressure effects and choosing the temperature of 0 °C (T_0 = 273.15 K) as the reference state for saturated liquid ammonia and pure solid NaSCN or $LiNO_3$, the liquid entropy $s(X_{NH_3}, T)$ at any temperature can be written as [5]:

$$s\left(X_{NH_3}, T\right) - s\left(X_{NH_3}, 0°C\right) = \int_{T_0}^{T} C_P\left(X_{salt}, T\right)\frac{dT}{T} \qquad (1)$$

Where $s(X_{NH_3}, 0\ °C)$ is the reference liquid entropy, and $C_p(X_{salt}, T)$ its heat capacity as a function of the salt concentration and temperature.

In Eq. (1), the integral calculation of the second member becomes easy when the correlation of $C_p(X_{salt}, T)$ is known. But the real difficulty lies in the calculation of the reference liquid entropy $s(X_{NH_3}, 0\ °C)$. As mentioned in the introduction, the current scientific approach is based on Koehler's [4] or Gupta's [3] method which remain however long and complex, which does not make it easy to use.

In the present study, the integral form of the right-hand side of Eq. (1) was transformed into an integral form defining the heat capacity according to the ammonia concentration and temperature. To make this, a function $\aleph(X_{NH_3}, T)$ was defined to take into account the errors related to the choice of $C_p(X_{NH_3}, T)$ model and the transformation of $C_p(X_{salt}, T)$ into $C_p(X_{NH_3}, T)$. Hence, Eq. (1) is rewritten as:

$$s\left(X_{NH_3}, T\right) = s\left(X_{NH_3}, 0°C\right) + \int_{T_0}^{T}\left[C_P\left(X_{NH_3}, T\right) + \aleph\left(X_{NH_3}, T\right)\right]\frac{dT}{T} \qquad (2)$$

The different correlations of the heat capacities of ammonia/NaSCN and ammonia/$LiNO_3$ solutions established by Infante [19] result from the experimental data obtained by Roberson *et al*. [21] for ammonia/$LiNO_3$ solution, and Blytas and Daniels [22] and Sargent and Beckman [23] for ammonia/NaSCN solution. In this present work, the correlation equation used for the heat capacity was defined as a function of ammonia concentration of the solution as [18, 19]:

$$C_p\left(X_{NH_3},T\right)=A_0+A_1\left(T-T_0\right)+A_2\left(T-T_0\right)^2 \quad (3)$$

Where,

$$A_0=2.4081-2.2814X_{NH_3}+7.9291X_{NH_3}^{2}-3.5137X_{NH_3}^{3} \quad (4)$$

$$A_1=10^{-1}\left(0.251-0.8X_{NH_3}^{2}+0.612X_{NH_3}^{3}\right) \quad (5)$$

$$A_2=10^{-3}\left(-0.1-0.3X_{NH_3}^{2}-0.1X_{NH_3}^{3}\right) \quad (6)$$

The coefficients of the equations for calculation of the constants A_0, A_1, and A_2 (Eq. 4, 5 and 6) have taken in the Refs. 18-19.

The function $\aleph\left(X_{NH_3},T\right)$ was defined under the non-nodal interpolation principle which consists to search the form of this function such as described in Eq. (7).

$$\aleph\left(X_{NH_3},T\right)=\sum_{i=0}^{n}K_i\left(T-T_0\right)^i \quad (7)$$

Where n, is the maximum number of parameters K_i, and defined according to the accuracy of the liquid entropy model sought.

The parameters K_i were defined as a function of the mass concentration of ammonia in the solution. The upper degree of the largest monomial was assumed to be 3, which corresponds to four parameters defined as follows:

$$\begin{cases} K_0=\sum_{j=0}^{3}a_jX_{NH_3}^{j} \\ K_1=\sum_{j=0}^{3}b_jX_{NH_3}^{j} \\ K_2=\sum_{j=0}^{3}c_jX_{NH_3}^{j} \\ K_3=\sum_{j=0}^{3}d_jX_{NH_3}^{j} \end{cases} \quad (8)$$

Where a_j, b_j, c_j and d_j, are the coefficients to determine. By integrating the form of the functions $C_p\left(X_{NH_3},T\right)$ and $\aleph\left(X_{NH_3},T\right)$, the liquid entropy described by Eq. (2) can therefore be written as

$$s\left(X_{NH_3},T\right)-s\left(X_{NH_3},0°C\right)=\pi_0\ln\left(\frac{T}{T_0}\right)+\sum_{i=1}^{n}\pi_i\left(T^i-T_0^i\right) \quad (9)$$

Where,

$$\begin{cases} \pi_0=\sum_{j=0}^{3}\eta_jX_{NH_3}^{j} \\ \pi_1=\sum_{j=0}^{3}\tau_jX_{NH_3}^{j} \\ \quad . \\ \quad . \\ \quad . \\ \pi_n=\sum_{j=0}^{3}\chi_jX_{NH_3}^{j} \end{cases} \quad (10)$$

The ultimate goal is therefore to determine with good precision the various coefficients $\eta_j, \tau_j, \ldots, \chi_j$ in the Eq. (10). Subsequently, the liquid entropy at any temperature is obtained by associating the reference liquid entropy with the two right-hand members of Eq. (9).

2.2. Methodology

2.2.1. Curves digitizing

Cai's [5] graphical curves were digitized using the Getdata Graph Digitizer 2.26 software. This software allows you to digitize the original graphics, plots and maps, scanned in graphic formats of type TIFF or JPEG. It allows easy reorganization of points on a graph and export of data to Excel spreadsheet. Database obtained and exported to the Excel file were exported into Matlab 2015a. These database are reported in Table 1 and Table 2 for ammonia/NaSCN and ammonia/$LiNO_3$ respectively)

2.2.2. Modeling of reference liquid entropy

The least square method is a procedure which requires calculation and linear algebra to determine what the best fit line is to the data. The reference liquid entropy model can be reduced to a static model with a separable structure between spaces of descriptive quantities. In its linearized form, it is written as:

$$\hat{s}\left(X_{NH_3}(k),0°C\right)=k^T\left(X_{NH_3}(k)\right)\theta \quad (11)$$

The parameter θ is the vector of unknown parameters, k is the digitizing sequence and h^T is a vector function of the input quantity $X_{NH_3}(k)$.

Considering the sample of digitized values $\{X_{NH_3}(k), s(X_{NH_3}(k), 0\,°C)\}$ of the process described by Eq. (11) as being acquired, it is calculated at each sequence k the absolute error $\varepsilon(k,\theta)$ between the digitized and model values given by:

$$\varepsilon\left(k,\theta\right)=s\left(X_{NH_3}(k),0°C\right)-\left[h_1\left(X_{NH_3}(k)\right)\quad h_2\left(X_{NH_3}(k)\right)\quad \ldots \quad \ldots\quad h_N\left(X_{NH_3}(k)\right)\right]\begin{bmatrix}\theta_1\\ \theta_2\\ \\ \theta_3\end{bmatrix} \quad (12)$$

Table 1. Digitized data of the ammonia concentration and specific entropy obtained in this work for ammonia/NaSCN pair at the different temperatures from 0 to 100 °C.

X_{NH_3}	T_0	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}	T_{60}	T_{70}	T_{80}	T_{90}	T_{100}
0.3500	-0.792474	-0.706251	-0.626187	-0.539964	-0.459900	-0.373677	-0.293613	-0.219707	-0.143964	-0.073390	-0.010309
0.3994	-0.730886	-0.644663	-0.564599	-0.484535	-0.404471	-0.330565	-0.256660	-0.176596	-0.109849	-0.043110	0.025144
0.4501	-0.675457	-0.594109	-0.509685	-0.426788	-0.342883	-0.262819	-0.195072	-0.121167	-0.053420	0.017065	0.090439
0.4995	-0.620028	-0.527647	-0.445265	-0.359042	-0.268978	-0.195072	-0.115008	-0.041103	0.028644	0.101708	0.180614
0.5502	-0.564599	-0.472217	-0.376752	-0.282895	-0.188913	-0.105849	-0.023806	0.057438	0.131343	0.211408	0.297631
0.5996	-0.521488	-0.414471	-0.309977	-0.201231	-0.108849	-0.013567	0.072914	0.155979	0.248360	0.334583	0.420806
0.6490	-0.466059	-0.349042	-0.238503	-0.124247	-0.021426	0.082073	0.180614	0.279154	0.371536	0.463918	0.562458
0.6997	-0.416788	-0.287295	-0.163401	-0.041103	0.072914	0.180614	0.291472	0.402330	0.507029	0.605570	0.710269
0.7491	-0.361359	-0.219707	-0.084214	0.044821	0.168296	0.291472	0.408489	0.525506	0.642523	0.747222	0.864239
0.7998	-0.299771	-0.145802	-0.001181	0.134423	0.266837	0.396171	0.525506	0.648681	0.771857	0.895033	1.024370
0.8492	-0.232025	-0.066738	0.082733	0.223725	0.365377	0.500871	0.636364	0.771857	0.901192	1.036680	1.172180
0.8999	-0.158119	0.012165	0.168137	0.316107	0.457759	0.599411	0.741063	0.882715	1.024370	1.172180	1.313830
0.9506	-0.084214	0.090489	0.251836	0.402330	0.549982	0.685634	0.833445	0.981256	1.129070	1.283040	1.443160
1.0000	-0.004150	0.168296	0.334583	0.482394	0.630205	0.778016	0.919668	1.067480	1.227610	1.387740	1.560180

Table 2. Digitized data of the ammonia concentration and specific entropy obtained in this work for ammonia/$LiNO_3$ pair at the different temperatures from 0 to 100 °C.

X_{NH_3}	T_0	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}	T_{60}	T_{70}	T_{80}	T_{90}	T_{100}
0,3500	-0,741166	-0,666387	-0,591608	-0,510597	-0,429586	-0,348576	-0,267565	-0,186555	-0,107976	-0,033610	0,037782
0,3998	-0,753629	-0,672618	-0,585376	-0,498134	-0,410892	-0,323650	-0,236407	-0,149165	-0,061815	0,018856	0,100098
0,4496	-0,747397	-0,660155	-0,567081	-0,471321	-0,379734	-0,280028	-0,192786	-0,099313	-0,009570	0,078517	0,165241
0,4994	-0,747397	-0,641460	-0,535523	-0,435818	-0,336113	-0,236407	-0,136702	-0,041228	0,052703	0,149951	0,243425
0,5505	-0,710008	-0,604071	-0,498134	-0,385965	-0,273797	-0,167860	-0,063192	0,037782	0,137488	0,237193	0,343130
0,5990	-0,653923	-0,535523	-0,423355	-0,304955	-0,192786	-0,080618	0,027435	0,134088	0,243425	0,346556	0,461530
0,6501	-0,587376	-0,460744	-0,338113	-0,217713	-0,097313	0,021191	0,137488	0,249656	0,360806	0,480225	0,598625
0,6999	-0,516829	-0,385965	-0,255102	-0,124239	0,002085	0,125025	0,249656	0,368056	0,486456	0,611088	0,735720
0,7510	-0,435818	-0,298723	-0,161628	-0,027194	0,106330	0,237193	0,361825	0,486456	0,617320	0,748183	0,879046
0,8008	-0,354807	-0,211481	-0,068155	0,073217	0,212267	0,349362	0,480225	0,611088	0,748183	0,885278	1,022370
0,8493	-0,267565	-0,118007	0,031551	0,174877	0,318204	0,455298	0,598625	0,735720	0,879046	1,022370	1,171930
0,9004	-0,180323	-0,016786	0,139256	0,290981	0,438937	0,579930	0,723257	0,872815	1,016140	1,171930	1,333950
0,9502	-0,093081	0,075172	0,237961	0,394568	0,542541	0,692099	0,841657	0,997446	1,153240	1,315260	1,483510
1,0000	-0,005839	0,174877	0,343130	0,498920	0,660941	0,822962	0,978752	1,134540	1,296560	1,471050	1,651760

For $k = 1,2,\cdots,N$ an error vector is obtained having N components $\varepsilon(1,\theta),\varepsilon(2,\theta),\cdots,\varepsilon(N,\theta)$ whose mean square $J(k,\theta)$ is equal to:

$$J(N,\theta) = \frac{1}{N}\sum_{k=1}^{N}\left\|\varepsilon(k,\theta)\right\|^2 = \frac{1}{N}\sum_{k=1}^{N}\left[s\left(X_{NH_3}(k),0°C\right) - \hat{s}\left(X_{NH_3}(k),0°C\right)\right]^2 \quad (13)$$

The principle of the least square's method consists in solving the problem of static optimization without constraint, the functional criterion of which is given by the Eq. (14).

$$\underset{\theta}{Min}\left(J(N,\theta) = \frac{1}{N}\sum_{k=1}^{N}\left\|\varepsilon(k,\theta)\right\|^2\right) \quad (14)$$

The best estimated parameter $\theta^*(N)$ in the sense of the least squares is then defined by:

$$\theta^*(N) = \left[\sum_{k=1}^{N} h\left(X_{NH_3}(k)\right)h^T\left(X_{NH_3}(k)\right)\right]^{-1} \times \left[\sum_{k=1}^{N} h\left(X_{NH_3}(k)\right)s\left(X_{NH_3}(k)\right)\right] \quad (15)$$

Table 3. Selected data of the ammonia concentration and specific entropy after calculation for modeling of the liquid entropy difference for ammonia/NaSCN.

X_{NH_3}	T_0	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}	T_{60}	T_{70}	T_{80}	T_{90}	T_{100}
0.3500	0	0.086223	0.166287	0.252510	0.332574	0.418797	0.498861	0.572767	0.648510	0.719084	0.782165
0.3994	0	0.086223	0.166287	0.246351	0.326415	0.400321	0.474226	0.554290	0.621037	0.687776	0.756030
0.4501	0	0.081348	0.165772	0.248669	0.332574	0.412638	0.480385	0.554290	0.622037	0.692522	0.765896
0.4995	0	0.092381	0.174763	0.260986	0.351050	0.424956	0.505020	0.578926	0.648672	0.721736	0.800642
0.5502	0	0.092382	0.187847	0.281704	0.375686	0.458750	0.540793	0.622037	0.695942	0.776007	0.862230
0.5996	0	0.107017	0.211511	0.320257	0.412639	0.507921	0.594402	0.677467	0.769848	0.856071	0.942294
0.6490	0	0.117017	0.227557	0.341813	0.444633	0.548132	0.646673	0.745213	0.837595	0.929977	1.028517
0.6997	0	0.129493	0.253387	0.375686	0.489702	0.597402	0.708260	0.819118	0.923817	1.022358	1.127057
0.7491	0	0.141652	0.277145	0.406180	0.529655	0.652831	0.769848	0.886865	1.003882	1.108581	1.225598
0.7998	0	0.153969	0.298590	0.434194	0.566608	0.695942	0.825277	0.948452	1.071628	1.194804	1.324141
0.8492	0	0.165287	0.314758	0.455750	0.597402	0.732896	0.868389	1.003882	1.133217	1.268705	1.404205
0.8999	0	0.170284	0.326256	0.474226	0.615878	0.757530	0.899182	1.040834	1.182489	1.330299	1.471949
0.9506	0	0.174703	0.336050	0.486544	0.634196	0.769848	0.917659	1.065470	1.213284	1.367254	1.527374
1.0000	0	0.172446	0.338733	0.486544	0.634355	0.782166	0.923818	1.071630	1.231760	1.391890	1.564330

From the database imported into Matlab 2015a, a script was first generated and next the reference liquid entropy model as a function of the mass concentration of ammonia was obtained using a subroutine of least square method. The polynomial correlation function was chosen with regard to the shape of the point cloud of the reference liquid entropy and the degree of polynomial was fixed with respect to the good fit parameters obtained after several iterations as the sum of squared estimate errors (*SSE*), Pearson's factor (*R-squared*), root mean square error (*RMSE*) and the relative error (ε). These parameters show how close each model is to the fitted values.

2.2.3. Modelling of the liquid entropy $s(X_{NH_3}, T)$

A calculation of the liquid entropy difference was performed for each temperature relative to the reference temperature at 0 °C as shown in the attached Excel file (see third and fourth tabs for ammonia/NaSCN and ammonia/$LiNO_3$ respectively).

The model of Eq. (8) indicates four unknown variables depending on the concentration of X_{NH_3} which justify the choice of four curves to generalize the fit (shaded X_{NH_3} values in Tables 3 and 4, respectively).

Table 4. Selected data of the ammonia concentration and specific entropy after calculation for modeling of the liquid entropy difference for ammonia/$LiNO_3$.

X_{NH_3}	T_0	T_{10}	T_{20}	T_{30}	T_{40}	T_{50}	T_{60}	T_{70}	T_{80}	T_{90}	T_{100}
0,3500	0	0,074779	0,149558	0,230569	0,311580	0,392590	0,473601	0,554611	0,633190	0,707556	0,778948
0,3998	0	0,081011	0,168253	0,255495	0,342737	0,429979	0,517222	0,604464	0,691814	0,772485	0,853727
0,4496	0	0,087242	0,180316	0,276076	0,367663	0,467369	0,554611	0,648085	0,737827	0,825914	0,912638
0,4994	0	0,105937	0,211874	0,311579	0,411284	0,510990	0,610695	0,706169	0,800100	0,897348	0,990822
0,5505	0	0,105937	0,211874	0,324043	0,436211	0,542148	0,646816	0,747790	0,847496	0,947201	1,053138
0,5990	0	0,118400	0,230568	0,348968	0,461137	0,573305	0,681358	0,788011	0,897348	1,000479	1,115453
0,6501	0	0,126632	0,249263	0,369663	0,490064	0,608567	0,724864	0,837032	0,948182	1,067601	1,186001
0,6999	0	0,130864	0,261727	0,392590	0,518914	0,641854	0,766485	0,884885	1,003285	1,127917	1,252549
0,7510	0	0,137095	0,274190	0,408625	0,542148	0,673011	0,797643	0,922274	1,053138	1,184001	1,314864
0,8008	0	0,143326	0,286652	0,428024	0,567074	0,704169	0,835032	0,965895	1,102990	1,240085	1,377177
0,8493	0	0,149558	0,299116	0,442442	0,585769	0,722863	0,866190	1,003285	1,146611	1,289935	1,439495
0,9004	0	0,163537	0,319579	0,471304	0,619260	0,760253	0,903580	1,053138	1,196463	1,352253	1,514273
0,9502	0	0,168253	0,331042	0,487648	0,635622	0,785180	0,934738	1,090527	1,246321	1,408341	1,576591
1,0000	0	0,180716	0,348969	0,504759	0,666780	0,828801	0,984591	1,140379	1,302399	1,476889	1,657599

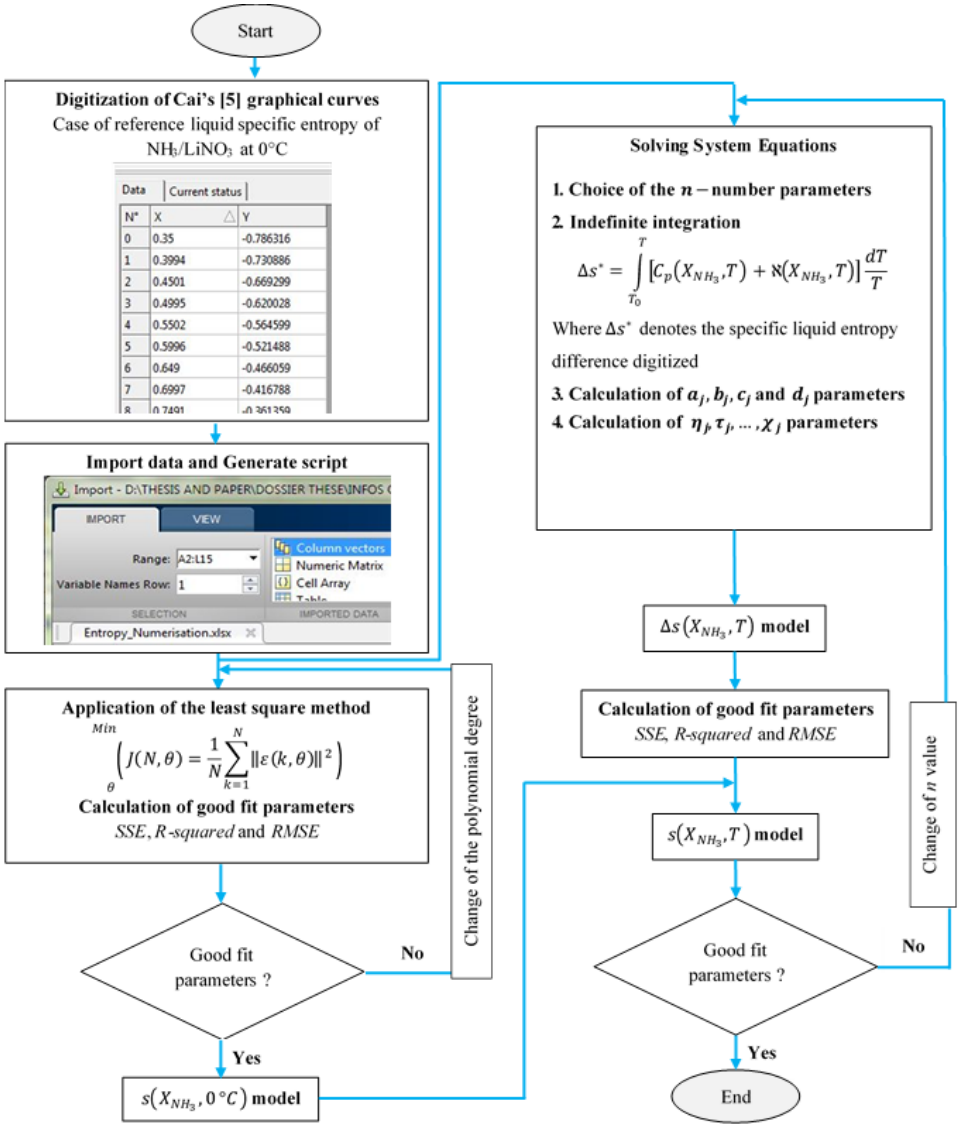


Figure 1. Flow chart of the methodology used in calculation of specific liquid entropies of NH_3/NaSCN and NH_3/$LiNO_3$ solutions at any temperature.

Subsequently, each Cai's [5] selected curve was considered to be a one-dimensional cubic element defined in 2D in a (X_{NH_3}, s) plane (four nodes in temperature) whose fitting node coordinates for each binary pairs are shaded in Tables 3 and 4, respectively. Thus, for any (X_{NH_3}, T) pair, the explicit approach leading to the formulation of the liquid entropy difference of each binary pair is such that:

- Choice of the parameter n from the Eq. (7);
- Indefinite integration of equation Eq. (2);
- Calculation of the coefficients a_j, b_j, c_j and d_j from the Eq. (8);
- Calculation of the coefficients $\eta_j, \tau_j, \ldots, \chi_j$ from the Eq. (10);
- Calculation of the liquid entropy $s(X_{NH_3}, T)$ from the Eq. (9);
- Check of the goodness-of-fit parameters and proceeding to the following iteration $(n+1)$ if necessary.

A computer subroutine of resolution was developed in Matlab 2015a for the rapid calculation of the parameters sought. Fig. 1 is a simplified illustration of the methodology used in the modeling of the liquid entropies of ammonia/NaSCN and ammonia/$LiNO_3$ solutions.

3. Results and Discussions

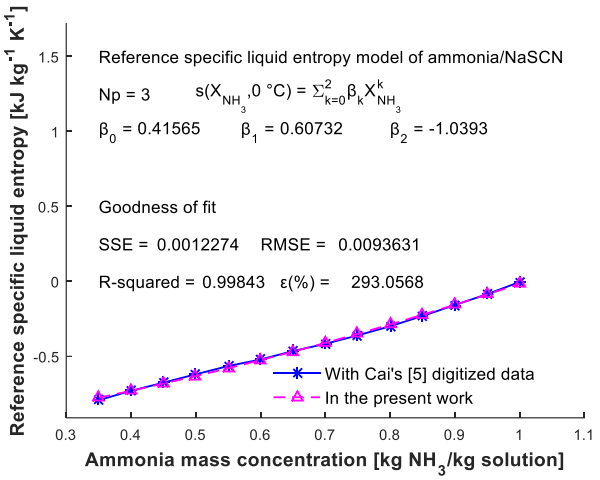
3.1. Reference Liquid Entropy Model

Fig. 2 shows the comparison between the reference liquid entropy curves of ammonia/NaSCN from this study with that corresponding to the digitized data from Cai *et al.* [5], for different values of the number of parameters Np into the model. As shown in Fig. 2.a, some points of the liquid entropy curve obtained in the present study remain slightly shifted from the digitized ones, despite the quality of the fitting parameters obtained.

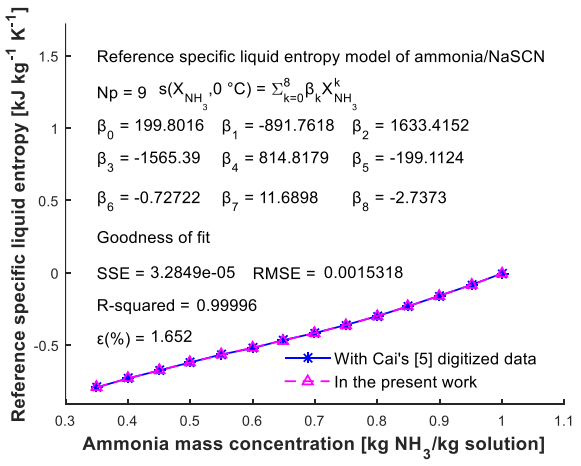
This shift is observed when the number of parameters Np = 3 for ammonia mass concentrations between 0.35 and 0.6, and between 0.75 and 0.9. Figure 2.b shows that by increasing the number of parameters Np in the reference liquid entropy model, the fitting parameters are improved and the points of the entropy curve obtained in the present study are considerably closer to the digitized ones. However, the final choice of the number of parameters Np was conditioned by the accuracy of the final ammonia/NaSCN liquid entropy model. The best model obtained for the reference liquid entropy for ammonia/NaSCN solution is an eighth-degree polynomial function written as:

$$s\left(X_{NH_3},0°C\right)=\sum_{k=0}^{N}\beta_k X_{NH_3}^{k} \quad (16)$$

Where β_k denotes the different coefficients found of reference liquid entropy model of ammonia/NaSCN and reported in Fig. 2.b and Table 5. A value of *SSE* of $3.28.10^{-5}$, *R-squared* of 0.99, and *RMSE* of $1.53.10^{-3}$ were observed for Np = 9. The maximum relative error ε of 1.65 % was observed for the mass concentration of X_{NH_3} = 1.00.



(a)



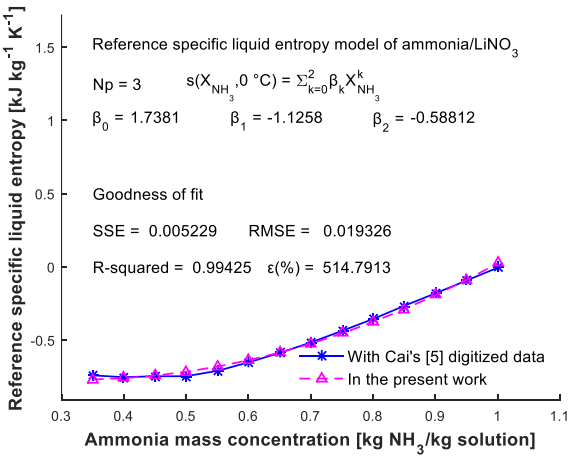
(b)

Figure 2. Comparison of the reference specific liquid entropy of ammonia/NaSCN solution in the present work with that of the digitized data of Cai's [5] at 0 °C, for the optimal parameters Np in the model (a): Np = 3 and (b): Np = 9.

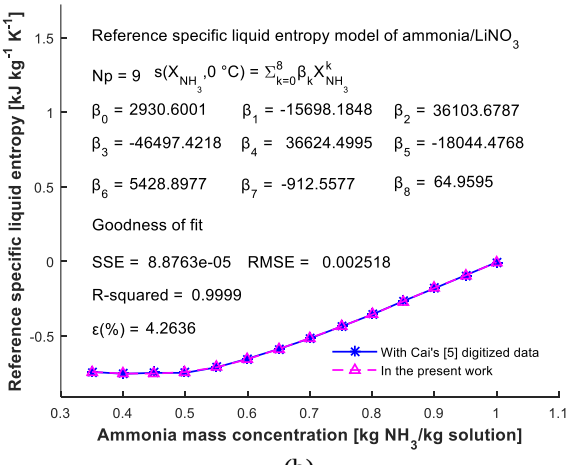
Fig. 3 shows the comparison between the reference liquid entropy curves of ammonia/$LiNO_3$ from this study with that corresponding to the digitized data from Cai [5], for different values of the number of parameters Np into the model. As shown in Figure 3.a, some points of the liquid entropy curve obtained in the present study for ammonia/$LiNO_3$ are slightly shifted with respect to the points of the digitized curve. This shift is also observed when Np = 3 for the whole range of ammonia mass concentrations except for the concentrations of 0.40, 0.65 and 0.95. Figure 3.b shows that by increasing the number of parameters Np in the reference liquid entropy model, the fitting parameters also are improved and the entropy curve of ammonia/$LiNO_3$ obtained in the present study are considerably closer to the digitized curve. As in the case of ammonia/NaSCN, the final choice of the number of parameters Np was conditioned by the accuracy of the final ammonia/$LiNO_3$ liquid entropy model. Therefore, the best model obtained for the reference liquid entropy for the ammonia/$LiNO_3$ solution is also an eighth-degree polynomial function as defined in equation (16).

Table 5. Coefficients of the Eq. (eq.16).

	Ammonia/NaSCN	Ammonia/$LiNO_3$
k	β_k	β_k
0	199.8016	2930.6001
1	−891.7618	−15698.1848
2	1633.4152	36103.6787
3	−1565.39	−46497.4218
4	814.8179	36624.4995
5	−199.1124	−18044.4768
6	−0.72722	5428.8977
7	11.6898	−912.5577
8	−2.7373	64.9595
Goodness-of-fit parameters		
SSE	3.28×10^{-5}	8.88×10^{-5}
RMSE	1.53×10^{-3}	2.52×10^{-3}
R-squared	0.99	0.99
Maximum relative error	1.65	4.26



(a)



(b)

Figure.3. Comparison of the reference specific liquid entropy of ammonia/$LiNO_3$ solution in the present work with that of the digitized data of Cai's [5] at 0 °C, for the optimal parameters Np in the model (a): Np = 3 and (b): Np = 9.

The β_k coefficients for the liquid entropy reference of ammonia/$LiNO_3$ are also reported in Fig. 3.b and Table 5. A value of *SSE* of $8.88.10^{-5}$, *R-squared* of 0.99 and *RMSE* of $2.52.10^{-3}$ were observed for Np = 9. The maximum relative error ε of 4.65 % was observed for the mass concentration of $X_{NH_3} = 1.00$.

The reference liquid entropy models obtained is valid for the mass concentration range of ammonia of $0.35 \leq X_{NH_3} \leq 1$. These models can be applied to interpolate the intermediate values of reference liquid entropy in the considered range of mass concentration of ammonia.

For example, at 0 °C, the reference liquid entropy of mass concentration of ammonia at 0.56 is $-0.5572\ kJ.kg^{-1}.K^{-1}$ for ammonia/NaSCN, whereas it is $-0.7009\ kJ.kg^{-1}.K^{-1}$ for ammonia/$LiNO_3$.

3.2. Liquid Entropy Model

The best fitting parameters for the liquid entropy are obtained for $n = 3$. Their maximum values are observed at the temperature T = 90 °C respectively, where for the ammonia/NaSCN solution, a *SSE* of $0.32.10^{-3}$, *R-squared* of 0.99 and *RMSE* of $4.7.10^{-3}$ were observed, whereas for the ammonia/$LiNO_3$ solution a *SSE* of $0.22.10^{-3}$, *R-squared* of 0.99 and *RMSE* of $2.6.10^{-3}$ were observed. The maximum relative errors are respectively observed at concentration $X_{NH_3} = 0.39$ such as for the ammonia/NaSCN solution it is 1.84 %, while for the ammonia/$LiNO_3$ solution it is 1.45 %.

The value $n = 3$ corresponds to 4 parameters $(\eta, \lambda, \tau, \chi)$ which are listed in the Table 6 for both binary fluids studied. From these coefficients, the parameters $\pi_i; i \in \{0, \ldots, 3\}$ in the liquid entropy can be calculated.

Finally, the liquid entropy model at any temperature was obtained by combining the reference liquid entropy with the liquid entropy difference models.

Table 6: Coefficients obtained in the present work for the calculation of specific liquid entropy parameters in Eq. (10)

Ammonia/NaSCN				
j	η_j	λ_j	τ_j	χ_j
0	4.1608×10^3	-39.4125	0.0621	-4.3257×10^{-5}
1	-2.0869×10^4	197.5409	-0.3108	2.1642×10^{-4}
2	3.1729×10^4	-300.2053	0.4723	-3.2889×10^{-4}
3	-1.5032×10^4	142.3542	-0.2242	1.5634×10^{-4}
Ammonia/$LiNO_3$				
j	η_j	λ_j	τ_j	χ_j
0	564.2332	-5.5382	0.0090	-6.4399×10^{-6}
1	-1.8383×10^3	18.1902	-0.0297	2.1346×10^{-5}
2	533.5661	-6.2264	0.0115	-9.1956×10^{-6}
3	828.4942	-7.1147	0.0101	-6.2051×10^{-6}

The average goodness-of-fit obtained are like, an *SSE* of $1.23.10^{-4}$, *R-squared* of 0.99, *RMSE* of $2.90.10^{-3}$ and ε of 0.59 % for ammonia/$LiNO_3$, and *SSE* of $1.57.10^{-4}$, *R-squared* of 0.99, *RMSE* of $3.2.10^{-3}$ and ε of 0.83 % for ammonia/NaSCN.

Fig. 4 and 5 show the comparison of the entropy curves of ammonia/NaSCN and ammonia/$LiNO_3$ solutions obtained in the present work with those of the digitized data of Cai's [5], respectively. For the optimal parameters Np = 9 and n = 3, a good corroboration between the curves of this study and those obtained from the digitized Cai's [5] data is observed. This is justified with the goodness-of-fit parameters listed in Table 7 and 8, respectively for ammonia/NaSCN and ammonia/LiNO3, and related to each curve for a given temperature. These parameters show indeed that the obtained entropy models allow computing with a good approximation the values of the liquid entropies of the ammonia/NaSCN and ammonia/$LiNO_3$ solutions, respectively.

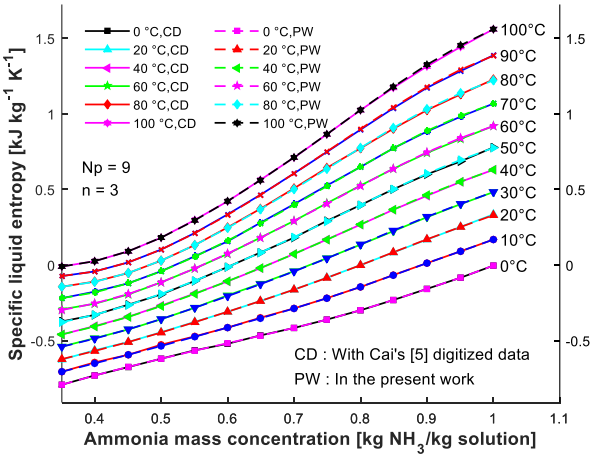


Figure. 4. Comparison of entropy curves of ammonia / NaSCN solution obtained in the present work with those of the digitized data of Cai's [5].

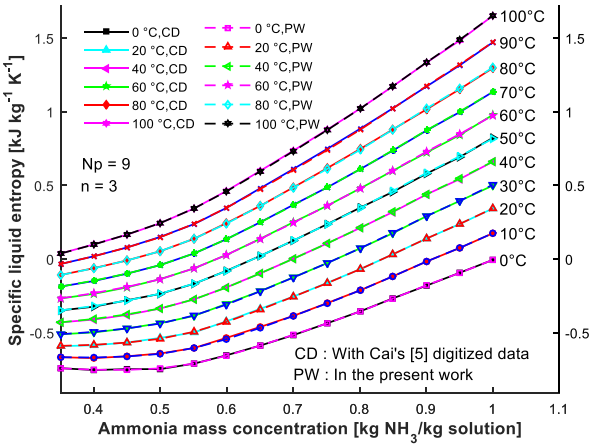


Figure 5. Comparison of entropy curves of ammonia/$LiNO_3$ solution obtained in the present work with those of the digitized data of Cai's [5].

In summary, the implementation of the algorithm realized of each model proposed uses 03 steps with 18 lines of code, in particular: (i) the declaration of the coefficients or constants of the different models, (ii) the declaration of the variables of temperature and ammonia concentration, and (iii) the development of the iterative loop for the calculation of specific entropy. The classical approach used in the literature [4, 5], would require more than 03 steps and

more than 18 lines of code for the calculation of specific entropy. This supplementary steps and lines of code would lead to more computation time compared to the approach proposed which in addition of its simplicity will allow relative gains of time.

Table 7. Goodness-of-fit parameters of the specific liquid entropy of ammonia/NaSCN.

Temperature (°C)	Ammonia/NaSCN			
	$SSE \times 10^{-3}$	$R - squared$	$RMSE \times 10^{-2}$	$\varepsilon(\%)$
0	0.03	0.99	0.15	0.36
10	0.14	0.99	0.31	0.59
20	0.07	0.99	0.22	0.86
30	0.08	0.99	0.24	1.32
40	0.06	0.99	0.21	0.88
50	0.21	0.99	0.39	1.01
60	0.12	0.99	0.30	0.95
70	0.19	0.99	0.37	1.37
80	0.32	0.99	0.47	0.88
90	0.21	0.99	0.39	0.45
100	0.29	0.99	0.45	0.44
Average	0.16	0.99	0.32	0.83

Table 8. Goodness-of-fit parameters of the specific liquid entropy of ammonia/$LiNO_3$ solutions in the present work.

Temperature (°C)	Ammonia/$LiNO_3$			
	$SSE \times 10^{-3}$	$R - squared$	$RMSE \times 10^{-2}$	$\varepsilon(\%)$
0	0.09	0.99	0.25	0.80
10	0.15	0.99	0.33	0.47
20	0.11	0.99	0.28	0.50
30	0.09	0.99	0.26	0.62
40	0.07	0.99	0.22	0.49
50	0.17	0.99	0.35	0.77
60	0.15	0.99	0.33	0.68
70	0.04	0.99	0.17	0.47
80	0.16	0.99	0.33	0.68
90	0.22	0.99	0.40	0.64
100	0.10	0.99	0.26	0.44
Average	0.12	0.99	0.29	0.59

4. Conclusion

A widely used methodology for calculating the liquid entropy of binary solutions as working fluids, such as ammonia/NaSCN and ammonia/$LiNO_3$ solutions, is based on the theories presented by Gupta and Koehler. These procedures for calculating the entropies of ammonia/$LiNO_3$ and ammonia/NaSCN solutions remain long and complicated, as some researchers have indicated. For this reason, simple correlations using less processing time would be helpful. In this paper, an alternative in the form of correlated equations with greater computation speed was proposed. The least square method was used to model the reference liquid entropy and a subroutine was used to calculate the entropy difference. The fitting parameters were calculated. The results obtained were compared with those of Cai. The correlations suggested for an optimal number of parameters Np equal to 9, showed good accuracy in estimating the entropy of ammonia/NaSCN and ammonia/$LiNO_3$ solutions with, in general, an average *SSE* of $1.23.10^{-4}$, an *R-squared* of 0.99, an *RMSE* of $2.90.10^{-3}$ and a relative error ε of 0.59 % for ammonia/$LiNO_3$, and a *SSE* of $1.57.10^{-4}$, an *R-squared* of 0.99, an *RMSE* of $3.2.10^{-3}$ and an ε of 0.83 % for ammonia/NaSCN.

The suggested correlations may be suitable for many practical situations in the simulation of thermodynamic systems using ammonia/NaSCN and ammonia/$LiNO_3$ binary solutions. Moreover, these correlations appear to be simple mathematical tools for engineers and researchers.

An additional advantage of this work is its approach that can be well applied to real background data without going through digitized data. In summary, the proposed models use 03 steps with 18 lines of code which in addition of its simplicity will allow relative gains of time compared to the classical approaches used in the literature.

Nomenclature

Ancronyms

CD	Cai's digitized data
JPEG	Joint photographic experts group
NH_3	Ammonia refrigerant
NaSCN	Sodium thiocyanate
$LiBr$	Lithium bromide
$LiNO_3$	Lithium nitrate
PW	In the present work
RMSE	Root mean square error
$R - squared$	Coefficient of determination or Pearson's factor
SSE	Sum of squares of estimation errors
TIFF	Tagged image file format

Symbols

A_0, A_1 and A_2	Coefficients in the calculation of the heat capacity model
a, *b*, *c* and *d*	Coefficients used to calculate the parameters of the function ψ
C_p	heat capacity ($kJ.kg^{-1}.K^{-1}$)
h	Vector function of the input quantity
J	Mean square
k	Digitization sequence
Min	Minimal function
s	Liquid entropy ($kJ.kg^{-1}.K^{-1}$)
T	Temperature (°*C or K*) or Transpose of *h*-vector
X	Mass concentration of ammonia (kg ammonia/kg solution)

Greek Symbols

Δ	For the liquid entropy difference
β	Coefficients in the calculation of the reference entropy model
ε	Relative error (%)
θ	Vector of unknown parameters
π	Coefficients in the calculation of the liquid entropy model
τ, η and χ	Coefficients in the calculation of the parameters π_i

Subscripts

i, j	Iteration values
N	End iteration value

N_p	Number of parameters in the reference liquid entropy model
n	Number of parameters in the function א
$salt$	Salt

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