Applying Pareto Design of GMDH-Type Neural Network for Solid-Liquid Equilibrium of Binary Systems (Isotactic Poly 1-Butene (1)-Organic Solvents (2))

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ABSTRACT: *Isotactic poly (1-butene), ipbu-1, was synthesized by using a metallocene catalyst. The thermodynamic phase behavior of polymer–organic solvents systems is very important in every polymer application. In this paper, the solid–liquid equilibrium of ipbu-1 with different organic solvents (1-heptyne, cyclo octane) was studied by a mathematical model. By considering the experiments temperature-mole fraction results, phase diagram of the polymer solvent systems could be constructed. The temperature and activity coefficient based on mole fraction phase diagrams were predicted by using Pareto genetic design of GMDH-type neural network. The results were very encouraging and congruent with the experimental data.*

KEY WORDS: *Solid-liquid equilibrium, Isotactic poly (1-butene), GMDH type-neural network, Organic solvents.*

INTRODUCTION

The thermodynamic phase behavior of a polymer–organic solvent system is very important in every polymer application. The main focus of this work was to obtain the (solid-liquid) phase diagrams of the SLE of iPBu-1 with different hydrocarbons at normal pressure by using mathematical model. The organic solvents that have been studied are important components of gasoline and motor oils. Isotactic poly-1-butene (ipbu-1) is one of the most used commercial polyolefin which was discovered by *Natta et al*, [1].

Group contribution activity coefficient models have been used to describe the non ideal behavior of the liquid phase of semi crystalline polymers with different degrees of crystalline and molecular weight in different solvents [2] . *Kang & Sandler* studied polymer-polymer aqueous solution using the UNIQUAC model [3]. *Wu et al.* modified the NRTL model and studied the liquid-liquid equilibrium phase behavior of polymer-polymer and polymer-salt aqueous binary systems [4]. A neural network model used for prediction of phase equilibrium in polymer solutions [5]. *Ghanadzadeh H. et al.* studied phase behavior binary systems and multi systems of LLE by using GMDH type-neural network [6]. *N. Narimanzadeh & A. Jamali* proposed a new model of GMDH neural network and this model can solve nonlinear systems with high accuracy [7]. *Domaska et al. & Koslowska et al*. have produced sets of equilibrium data for the SLE of ipbu-1 in different organic solvent

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in recent year [8]. In this work the temperature-mole fraction phase diagrams were predicted by using Pareto genetic design of GMDH-type neural network. Finally, the polymer activity coefficients are discussed.

THEORITICAL SECTION

Experimental data for the SLE of ipbu-1 in different organic solvents were produced by *Domanska et al.* [1].

GMDH Type-Neural Network (Group method of data handling)

Using the GMDH algorithm, a model can be represented as a set of neurons in which different pairs of them in each layer are connected through anquadritic polynomial and, therefore, produce new neurons in the next layer. Such representation can be used in modeling to map inputs to outputs. The formal definition of the identification problem is to find a function, $\hat{f}$, that can be approximately used instead of the actual one, f ,. In order to predict output $\hat{y}$ for a given input vector X=(x_1, x_2, x_3 , ..., x_n) as close as possible to its actual output y. Therefore, given number of observations (M) of multi-input, single output data pairs so that:

$$y_i = f\left(x_{i1}, x_{i2}, x_{i3}, ..., x_{in}\right), \left(i = 1, 2, ..., M\right) \quad (1)$$

It is now possible to train a GMDH-type-NN to predict the output values $\hat{y}_i$ for any given input vector =(x_{i1}, x_{i2}, x_{i3} , ..., x_{in}), that is,

$$\hat{y}_i = \hat{f}\left(x_{i1}, x_{i2}, x_{i3}, ..., x_{in}\right), \left(i = 1, 2, ..., M\right) \quad (2)$$

In order to determine a GMDH type-NN, the square of the differences between the actual output and the predicted one is minimized, that is,

$$\sum_{i=1}^{M}\left[\hat{f}\left(x_{i1}, x_{i2}, ..., x_{in}\right) - y_i\right] \rightarrow \min \quad (3)$$

The general connection between the inputs and the output variables can be expressed by a complicated discrete form of the Volterra functional series in the form of:

$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n}\sum_{j=1}^{n} a_{ij} x_i x_j + \quad (4)$$

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} a_{ijk} x_i x_j x_k + ...$$

Where is known as the Kolmogorov-Gabor polynomial [9]. The general form of mathematical description can be represented by a system of partial quadratic polynomials consisting of only two variables (neurons) in the form of:

$$\hat{y} = G\left(x_i, x_j\right) = a_0 + a_1 x_i + a_2 x_j + a_3 x_i^2 + \quad (5)$$

$$a_4 x_j^2 + a_5 x_i x_j$$

In this way, such partial quadratic description is recursively used in a network of connected neurons to build the general mathematical relation of the inputs and output variables given in Eq.(4). The coefficients a_i in Eq.(5) is calculated using regression techniques. It can be seen that a tree of polynomials is constructed using the quadratic form given in Eq.(5). In this way, the coefficients of each quadratic function G_i are obtained to fit optimally the output in the whole set of input–output data pairs, that is,

$$E = \frac{\sum_{i=1}^{M}\left(y_i - G_i(\ )\right)^2}{M} \text{Min} \quad (6)$$

In the basic form of the GMDH algorithm, all the possibilities of two independent variables out of the total n input variables are taken in order to construct the regression polynomial in the form of Eq. (5) that best fits the dependent observations (y_i, i = 1,2,3 …, M) in a least squares sense. Using the quadratic sub-expression in the form of Eq. (5) for each row of M data triples, the following matrix equation can be readily obtained as:

$$Aa = Y \quad (7)$$

where a is the vector of unknown coefficients of the quadratic polynomial in Eq. (5),

$$a = \left\{a_0, a_1, a_2, a_3, a_4, a_5\right\} \quad (8)$$

And,

$$Y = \left\{y_1, y_2, y_3, ..., yM\right\}^T \quad (9)$$

Here Y is the vector of the output's value from observation. It can be readily seen that:

$$A = \begin{bmatrix} 1 & x_{1p} & x_{1q} & x_{1p}x_{1q} & x_{1p}^2 & x_{1q}^2 \\ 1 & x_{2p} & x_{2q} & x_{2p}x_{2q} & x_{2p}^2 & x_{2q}^2 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & x_{Mp} & x_{Mq} & x_{Mp}x_{Mq} & x_{Mp}^2 & x_{Mq}^2 \end{bmatrix} \quad (10)$$

The least squares technique from multiple regression analysis leads to the solution of the normal equations in the form of:

$$a = \left(A^T A\right)^{-1} A^T Y \tag{11}$$

RESULTS AND DISCUSSION

Dynamic experiments were performed over a large concentration range at 280-376.8 K in order to construct phase diagram for the ipbu-1(1)-hydrocarbons (2) systems. The experimental data correspond to the crystalline form (form 1) of ipbu-1. The equilibrium temperature, T at specific mole fraction of the crystallographic modification of ipbu-1 (form 1) x, are presented in [1]. Respectively, The SLE data for solutions with high concentrations of polymer are very difficult to measure experimentally [10]. Thus the results of the correlations may be used to estimate the solubility of such solutions. In fact, this is one of the easiest ways to estimate the solubility of the polymer at higher concentrations. The feed-forward GMDH-type neural network for the binary systems of (ipbu-1(1), organic solvents (2)) was constructed using an experimental data set which has previously been reported [1]. The results obtained with the GMDH-type neural network are presented in Tables and figures. These statistical values are based on R^2 as absolute fraction of variance and RMSE as root-mean squared error which are defined as fallows

$$R^2 = 1 - \left[\frac{\sum_{i=1}^{n}\left(Y_{i,exp} - Y_{i,model}\right)^2}{\sum_{i=1}^{n}\left(Y_{i,exp}\right)^2}\right] \tag{12}$$

$$RMSE = 1 - \left[\frac{\sum_{i=1}^{n}\left(Y_{i,exp} - Y_{i,model}\right)^2}{n}\right]^{\frac{1}{2}} \tag{13}$$

Structural parameters of Pareto genetic design of GMDH-type neural network are presented at Table 1. The developed GMDH neural network was successfully used to obtain four models for calculation of the SLE. The optimal structures of the developed neural network with 2-hidden layers are shown in Fig. 1 For instance, ‘‘aabcacbc’’ and‘‘bccccccc’’ are corresponding genome representations for the Temperature and Activity coefficient in the binary systems of ipbu-1(1) - n-hexadecane (2), and in Fig. 4 For instance, ‘‘aaaaacbb’’ and ‘‘bbccbccc’’ are corresponding genome representations for the Temperature and Activity coefficient in the binary systems of ipbu-1(1) -1-heptane (2) respectively. In which, a, b and c stand for mole fraction, standard temperature and Activity coefficient for calculation of equilibrium temperature and a, b and c stand for mole fraction, equilibrium temperature and standard temperature for calculation of activity coefficient respectively. All input variables were accepted by the models. In other words, the Pareto genetic design of GMDH-type neural network provides an automated selection of essential input variables, and builds polynomial equations for the SLE modeling. These polynomial equations show the quantitative relationship between input and output variables. Z is index of neurons.

Table 1: The techniques common to GMDH

Population size	200
Number of iteration	100
Mutation	0.01
Crossover	0.95
Number of objective function	2.00
Number of hidden layer	2.00

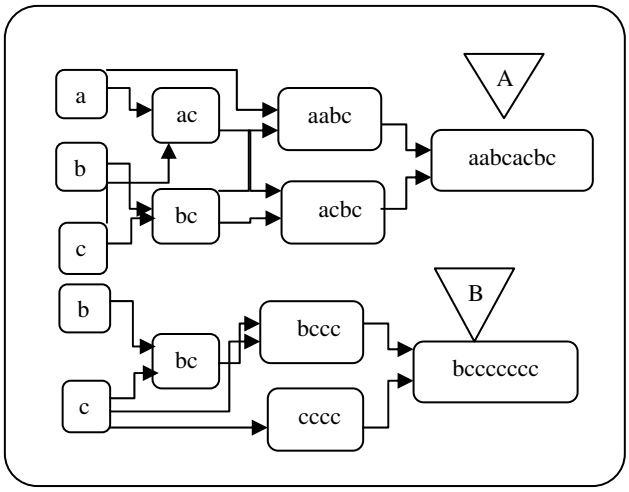

Fig. 1: Developed structure of GMDH-type-NN model for the systems (ipbu-1 (1) - 1-heptyne (2)). A: Temperature , B: Activity coefficient.

Table 2: Polynomial equation of the GMDH model for the systems (ipbu-1 (1) - 1-heptyne (2))

$Z_1 = 368.77 + 79T_0 - 75\left(-\ln\gamma_1^{exp}\right)0015T_0^2 + 000536\left(-\ln\gamma_1^{exp}\right)^2 + 6.187T_0\left(-\ln\gamma_1^{exp}\right)$
$Z_2 = 4.67e-8+1.4e-5X+8.335e-6\left(-\ln\gamma_1^{exp}\right)+4.15e-3X^2+4.754e-4\left(-\ln\gamma_1^{exp}\right)^2-2.485e-3X\left(-\ln\gamma_1^{exp}\right)$
$Z_3 = 368.77 + 79T_0 - 754\left(-\ln\gamma_1^{exp}\right)+0015T_0^2+000563\left(-\ln\gamma_1^{exp}\right)^2+6.187\times T_0\left(-\ln\gamma_1^{exp}\right)$
$Z_4 = -1.54e-11-4.61e-9X+1.126e-5Z_1-1.37e-6X^2-1.365e-6Z_1^2+3.3567e-3XZ_1$
$Z_5 = 00333+5Z_2+5Z_3-00083Z_2^2+00082Z_3^2+6.27e-6Z_2Z_3$
$T = 00244+5Z_3+5Z_4-055Z_3^2+055Z_4^2+2.57e-5Z_3Z_4$

Table 3: Polynomial equation of the GMDH model for the systems (ipbu-1 (1) - 1-heptyne (2)).

$Z_1 = 10e-7-3.466e-5T^{exp}+3e-5T_0+0.00256T^{exp2}+0.0089T_0^2-0.01T_0\times T^{exp}$
$Z_2 = -3.38e-12+1.12e-5Z_1-10e-9T_0+3.09e-6Z_1^2-3e-7T_0^2+0.003356T_0Z_1$
$\gamma_1 = \dfrac{1}{\exp\left(\left(1\times10^{-15}\right)+1.125e-5Z_2+2.73e-12T_0+8.36e-9Z_2^2+8.14e-9T_0^2+0.00335Z_2T_0\right)}$

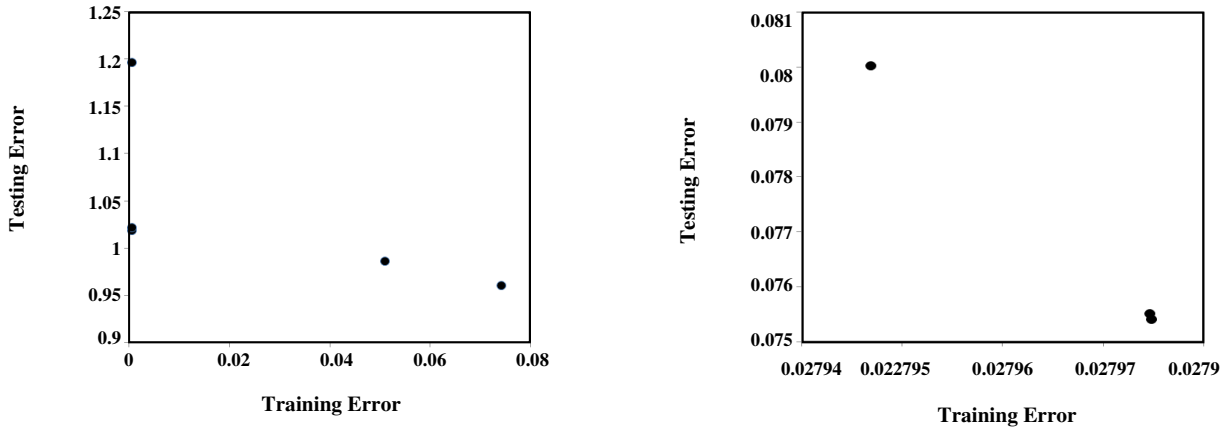

Fig. 2: Prediction error variation with training error in multi objective optimization for binary systems (ipbu-1 (1) - 1-heptyne (2)).

Ipbu-1 (1) - 1-heptyne (2)

Polynomial equation of the GMDH model for this binary systems presents at Table 2 and 3 .Prediction of testing error with training error in 2-objective optimization show at Fig. 2. Fig. 3 shows plot of the experimental data and GMDH neural network model. This diagram demonstrates that the predicted values are close to the experimental values, as many of the data points fall very close to the diagonal line. The results of the developed models give a close agreement between observed and predicted values of the SLE.

Ipbu-1(1) - cyclo octane (2)

Polynomial equation of the GMDH model for this binary systems presents at Tables 4 and 5 .Prediction of testing error with training error in 2-objective

Table 4: Polynomial equation of the GMDH model for the systems (ipbu-1 (1) – cyclooctane (2)).

$Z_1 = 368.34 + 5.4338X - 714\left(-\ln \gamma_1^{exp}\right)07834X^2 + 0001834\left(-\ln \gamma_1^{exp}\right)^2 + 4.6X\left(-\ln \gamma_1^{exp}\right)$
$Z_2 = 1.1e-10 + 1.2e-5Z_1 + 3.2e-8T_0 + 8.1e-6Z_1^2 + 9.52e-6T_0^2 + 003336T_0Z_1$
$T = 0064 + 1.9e-5X + Z_2 + 1.9e-6X^2 - 2.24e-6Z_2^2 + 00899XZ_3$

Table 5: Polynomial equation of the GMDH model for the systems (ipbu-1 (1) – cyclooctane (2)).

$Z_1 = 9.3e-8-3e-5T^{exp} + 2.77e-5T_0 + 0.00191T^{exp\,2} + 0.00827T_0^2 - 0.009T_0T^{exp}$
$Z_2 = 9.3e-8-3e-5T^{exp} + 2.77e-5T_0 + 0.00191T^{exp\,2} + 0.00827T_0^2 - 0.009T_0T^{exp}$
$Z_3 = 3.4e-12 + 1.12e-5Z_1 + 1e-9T_0 + 2.85e-6Z_1^2 + 3e-7T_0^2 + 0.00335T_0Z_1$
$\gamma_1 = \frac{1}{\exp\left(0.021 + 05Z_2 + 0.5Z_3 - 0.0282Z_2^2 + 0.0282Z_3^2 + 6.2e-7Z_2Z_3\right)}$

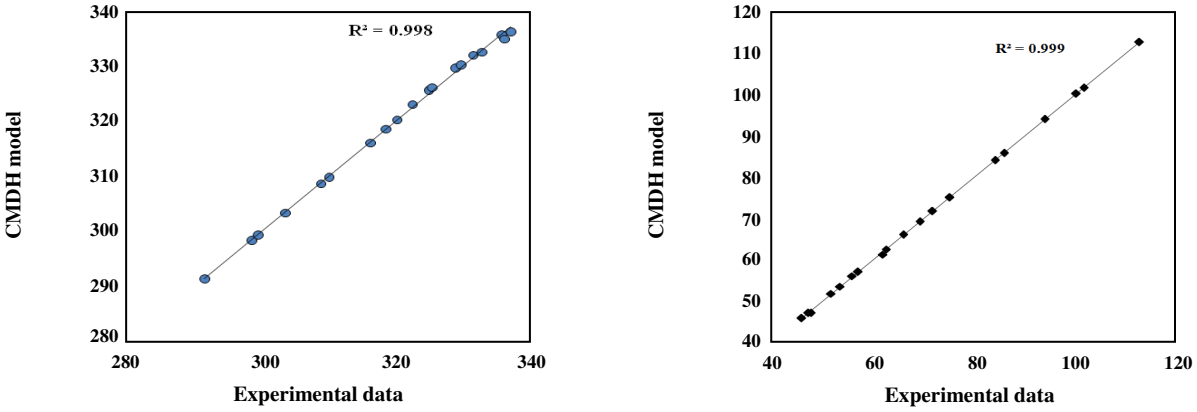

Fig. 3: Comparison between experimental data and GMDH-type neural network modeling in (ipbu-1 (1) - 1-heptyne (2)) A: Temperature, B: Activity coefficient.

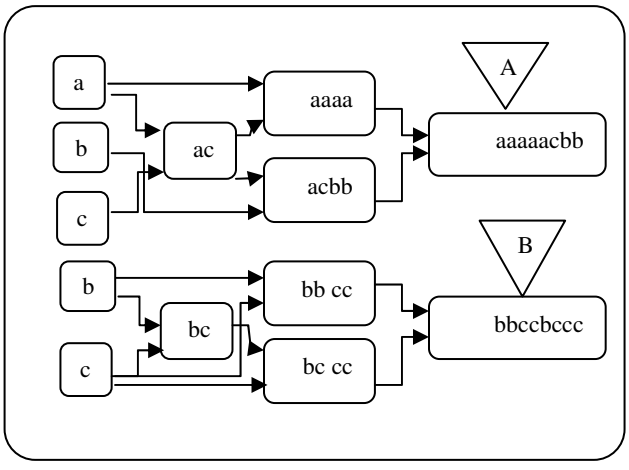

Fig. 4: Developed structure of GMDH-type-NN model for the systems (ipbu-1 (1) – cyclooctane (2)). A: Temperature , B: Activity coefficient

optimization show at Fig. 5. Fig. 6 shows plot of the experimental data and GMDH neural network model. This diagram demonstrates that the predicted values are close to the experimental values, as many of the data points fall very close to the diagonal line. . The results of the developed models give a close agreement between observed and predicted values of the SLE.

The experiment data and predict data show at figures. In order to determine the accuracy of the models some statistical measures are given in Table 6.

CONCLUSIONS

In this study, a feed-forward GMDH-type neural network model was developed using experimental SLE data for the (ipbu-1(1), hydrocarbons (2)) binary systems

Table 6: Model statistics and information for the GMDH-type neural network model for predicting SLE data

Binary systems		Error	
		RMSE	R^2
1-heptyne (2)-ipbu-1 (1)	Temperature	0.4056	1.0000
	Activity coefficient	0.4640	0.9999
ipbu-1 (1) – cyclo octane (2)	Temperature	1.0814	1.0000
	Activity coefficient	0.6142	0.9999

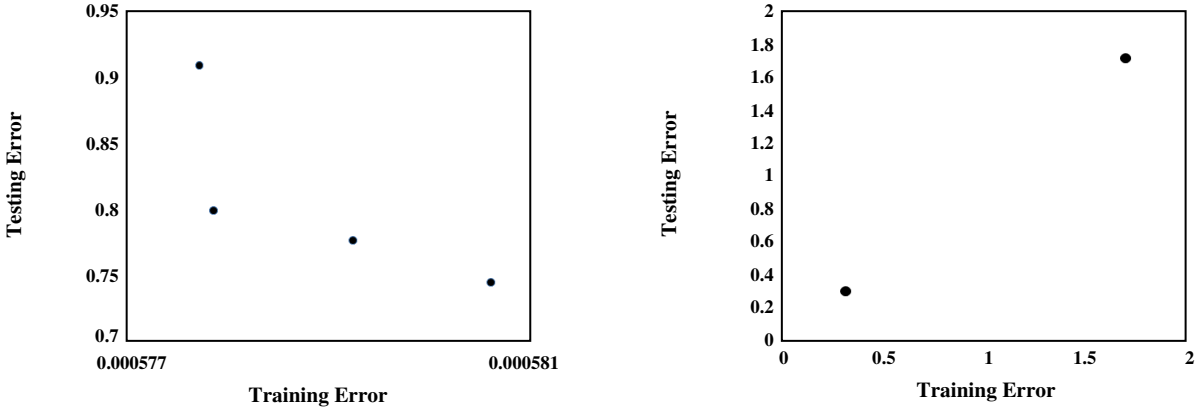

Fig. 5: Prediction error variation with training error in multi objective optimization for binary systems(ipbu-1(1) – cyclooctane(2)) A: Temperature, B: Activity coefficient.

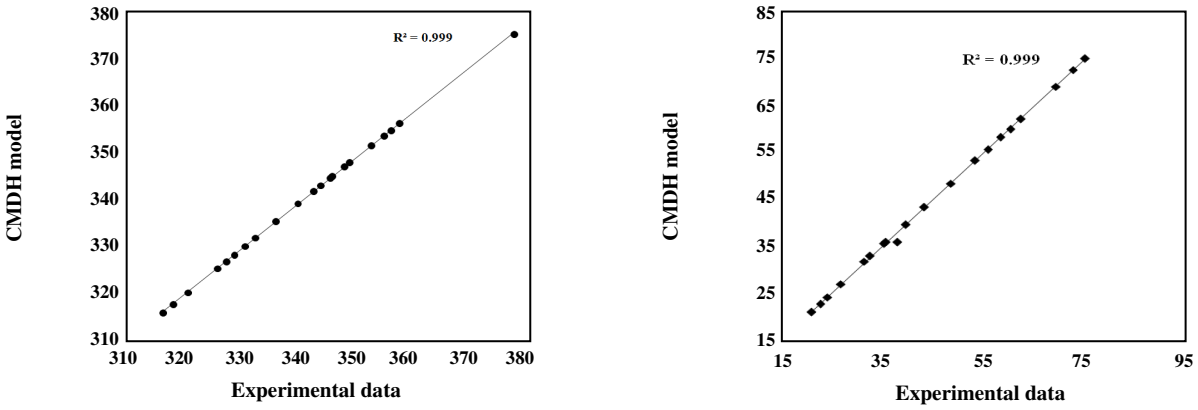

Fig. 6: Comparison between experimental data and GMDH-type neural network modeling in (ipbu-1 (1) – cyclooctane (2)) A: Temperature, B: Activity coefficient.

over the temperature range of 280.5–376.8 K. The SLE data were predicted by the GMDH model and the results compared with the experimental data. Despite the complexity of the system studied, the GMDH model permits a good prediction of the phase equilibrium. Thus, the GMDH model is suitable for predicting the SLE data. The agreements between the experimental and calculated data were found to be excellent. For the investigated system, the average R^2 values between the observed and calculated mole fractions using the GMDH models were 1 respectively. As it can be seen, the level of deviations indicates the superiority of genetic design of GMDH-type neural network as the preferred predicting model for the system considered.

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