

Isobaric vapour–liquid equilibrium calculations of binary systems using a neural network

MEHMET BILGIN

Istanbul University, Engineering Faculty, Department of Chemical Engineering, 34320 Avcilar, Istanbul, Turkey (e-mail: mbilgin@istanbul.edu.tr)

(Received 13 November 2003, revised 3 March 2004)

Abstract: A model on a feed forward back propagation neural network was employed to calculate the isobaric vapour–liquid equilibrium (VLE) data at 40, 66.67, and 101.32 ± 0.02 kPa for the methylcyclohexane – toluene and isopropanol – methyl isobutyl ketone binary systems, which are composed of different chemical structures (cyclic, aromatic, alcohol and ketone) and do not show azeotrope behaviour. Half of the experimental VLE data only were assigned into the designed framework as training patterns in order to estimate the VLE data over the whole composition range at the mentioned pressures. The results were compared with the data calculated by the two classical models used in this field, the UNIFAC and Margules models. In all cases the deviations the experimental activity coefficients and those calculated by the neural network model (NNET) were lower than those obtained using the Margules and UNIFAC models.

Keywords: vapour–liquid, neural network, activity coefficients, UNIFAC, Margules model.

INTRODUCTION

The neural network model proposed in this work is an alternatively intensively used method for most prediction problems in engineering calculations and/or for different purposes. Many studies have claimed the potent applicability of neural networks for the analysis of some complex systems. Neural networks have succeeded in coping with a few biological and chemical problems, such as control of bio-reactors with unstable parameters,¹ prediction of the secondary dimensional structure of proteins,² analysis of overlapped spectra or chromatograms,³ property prediction of compounds,⁴ phase equilibrium prediction in aqueous two-phase extraction⁵ and the design of a combined mixing rule for the prediction of vapor–liquid equilibria.⁶ In the last work, where the prediction of VLE is handled, the design of an intelligent mixing rule formed by the combination of the Wong and Sandler mixing rule and the Huron and Vidal of order 1 mixing rule was performed using the basic principles of neural networks. In this work, the feed forward back propagation neural network

was employed for VLE-data prediction, assigning some experimental VLE-data direct (without using any mixing rule) into the designed framework as training patterns. It should be noticed that in this procedure the neural network is unable to offer any parameters such as the second virial coefficients in a thermodynamic meanings or any energy parameter in a detailed mechanism.

THERMODYNAMIC BASIS

At low pressures, the experimental activity coefficients can be obtained from vapor–liquid (VLE) measurements using the equation:

$$\gamma_i = \frac{y_i P}{x_i P_i^S} \quad (1)$$

where y_i is the mole fraction of component i in the vapour phase, x_i is the mole fraction in the liquid phase, P is the total pressure, γ_i is the activity coefficient of i in the fluid phase and P_i^S is the saturation (vapour) pressure.

NEURAL NETWORK MODEL

A neural network mimics the structure of human synapse connections to imitate the work of the brain. A typical structure of a neural net consist of multiple layers, each of them having a group of computing neurones. Every neurone in one layer is completely connected with others in the adjacent layers but not with ones in th same layer. The first layer merely stores and transports the values of the input features to the next layer, the last layer calculates the output values, and between them are the hidden layers.

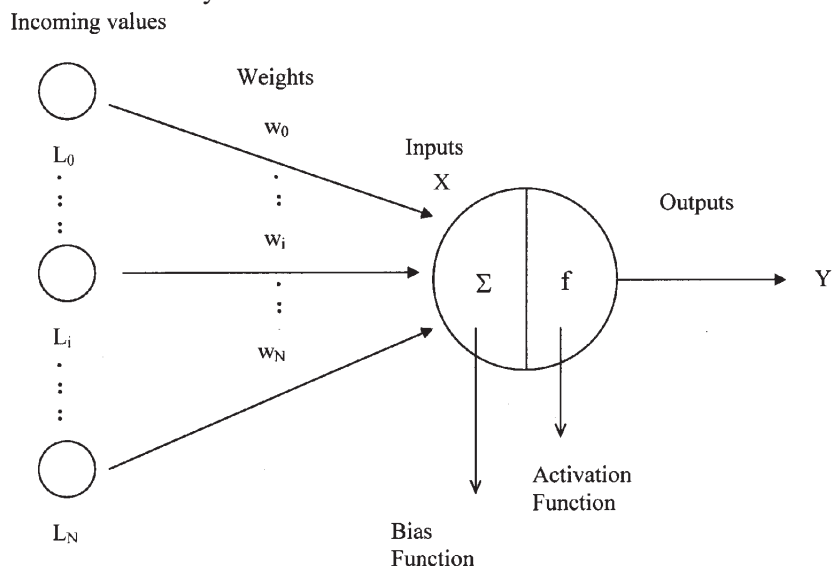


Fig. 1. A neurone model.

One typical neurone in such a neural net is shown in Fig. 1. The inputs X_i are the product of the incoming neurone values L_i and the synaptic weights w_i :

$$X_i = L_i w_i \quad (2)$$

The inputs are then summed and the activation function is applied to the obtained sum to reach the output value Y :

$$Y = f\left(\sum_{i=0}^N L_i w_i\right) = f(z) \quad (3)$$

where f is the activation function:

$$f(z) = \frac{1}{1 + e^{-z}} \quad (4)$$

Here, N is the number of incoming values from different neurones, and L is the vector of incoming neurones. There are a number of activation functions available to be adopted for a net. In this work, the log sigmoid function shown in Eq. (4) was preferred. As result of this preference, the input values can be any value in the range $-\infty$ to $+\infty$, but the output values are limited to between 0 and 1. In this sense, normalisation to the vapour-liquid equilibrium data was performed in order to obey the output ranges.

RESULTS AND DISCUSSION

In this work, the feature of the neural network has been adapted to deal with the prediction of the VLE data of the methylcyclohexane-toluene and isopropanol-methyl isobutyl ketone systems at (40, 66.67 and 101.32 \pm 0.02) kPa. The experimental data of the binary systems were taken from our preceeding studies and the systems are of significance as they present various chemical structures (cyclic, aromatic, alcohol and ketone).^{7,8}

TABLE I. Absolute mean deviations between the experimental and chalcuated activity coefficients

System/Pressure (kPa)	$\overline{\Delta Y}_i$, Margules		Lit.	$\overline{\Delta Y}_i$, UNIFAC		Lit.	$\overline{\Delta Y}_i$, NNET ^c	
	γ_1	γ_2		γ_1	γ_2		γ_1	γ_2
MCH-T ^a / 101.32	0.0099	0.0136	7	0.0106	0.0157	7	0.0102	0.0097
MCH-T / 66.67	0.0620	0.0300	7	0.0250	0.0369	7	0.0142	0.0113
MCH-T / 40.00	0.0817	0.1004	7	0.0499	0.0528	7	0.0200	0.0092
IP-MIBK ^b / 101.32	0.0388	0.0389	8	0.1243	0.1076	8	0.0224	0.0144
IP-MIBK / 66.67	0.1993	0.0740	8	0.0935	0.1439	8	0.0404	0.0132
IP-MIBK / 40.00	0.5767	0.1097	8	0.2020	0.1541	8	0.0728	0.0232

^aMethylcyclohexane – toluene; ^bIsopropanol – methyl isobutyl ketone; ^cNeural network

The application of the neural network model to the prediction of VLE data was performed using the MATLAB program (version 6.0), a widely used calculation and programming tool for engineering applications. For the purpose of gaining promising predictability, an approach based on the optimum neural network architecture was determined. The problem was handled as a generalization problem and the neural network calculations employed a feed-forward algorithm to calculate the output, along with back-propagation to recursively correlate the weights. The learning process, whereby the weights of the model are adjusted, is the most important part in the establishment of a predictable neural network. As the objective function in the learning process, the total squared error in each vector was taken as 0.001 (Eq. (5)).

$$\text{Total squared error} = \sum_{i=1}^n (Y_i^{\text{exp}} - Y_i^{\text{cal}})^2 \quad (5)$$

where Y_i^{exp} – experimental value; Y_i^{cal} – calculated value; n – number of experiments.

Only half of the experimentally determined VLE data points were assigned into the designed framework as training patterns in order to estimate the whole systems. The results were verified by examining the distribution of the output errors and the dynamic response of the learning process. In the application, concentrations of the low boiling component in the liquid phase (x_1) were given as input val-

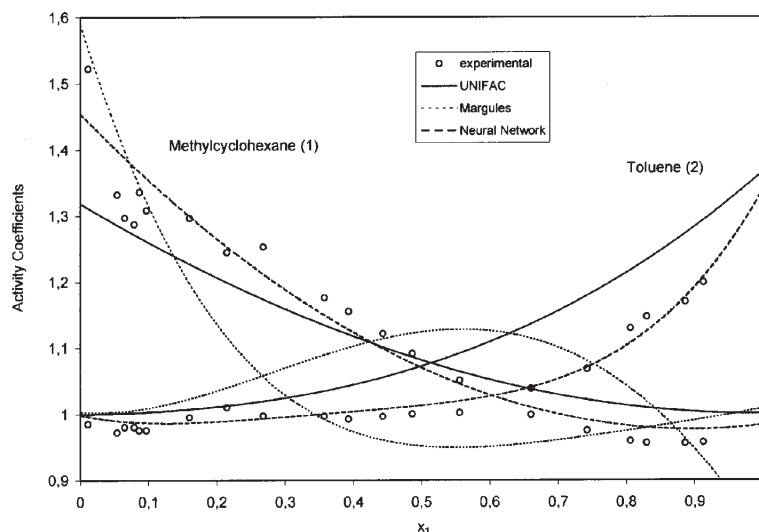


Fig. 2. Comparison of the calculated and experimental activity coefficients at 40.00 kPa, for the methylcyclohexane + toluene system.

ues to the net and, as result, the concentrations of the low boiling component in the vapour phase (y_1) and the liquid phase activity coefficients (γ_1, γ_2) were taken as output values.

The experimental activity coefficients, γ_1 and γ_2 , were calculated applying the experimental T - x_1 - y_1 values to Eq. (1). The experimentally observed activity coefficients were compared with the values estimated from the neural network, the UNIFAC-original⁹ model and the two-parameter Margules equation.¹⁰ The UNIFAC model is presented in detail in mentioned reference, from where the group-volume and surface-area parameters of the considered chemicals were taken as well. Table I presents a quantitative assessment of the calculations achieved by each model with respect to the absolute mean deviation of the activity coefficients. This deviation, taken as described elsewhere,¹¹ is shown in Eq. (6).

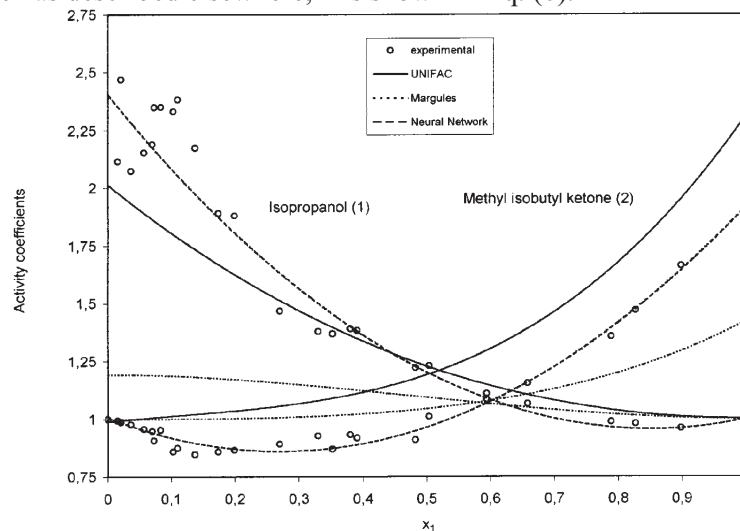


Fig. 3. Comparison of the calculated and experimental activity coefficients at 40.00 kPa, for the isopropanol + methyl isobutyl ketone system.

$$\text{Mean deviation} = \overline{\Delta Y}_1 = \sum_{k=1}^n |Y_{i,k}^{\text{exp}} - Y_{i,k}^{\text{cal}}| / n \quad (6)$$

In all cases the deviations between the experimental activity coefficients and those calculated by the neural network (NNET) were lower than the deviations obtained using the Margules and the UNIFAC models for the calculations (see also Figs. 2 and 3). From this point of view, although the experimental database was restricted in this study, a neural network can be treated as an efficient tool for estimating the VLE data over a wide range of pressure and for different multiple mixtures which will be considered in the future.

NOMENCLATURE

L – Vector of incoming neurones

n – Number of experiments

N – Number of incoming values in a neural net

P – Pressure (kPa)
 P_i^S – Saturation (vapour) pressure of pure liquid i
 T – Temperature (K)
 w – Synaptic weights
 x_i – Mole fraction of component i in the liquid phase
 y_i – Mole fraction of component i in the vapour phase
 ΔY_i – Absolute mean deviation
 γ_i – Activity coefficient of i in the fluid phase

ИЗВОД

ИЗРАЧУНАВАЊЕ ИЗОБАРСКИХ ПАРА – ТЕЧНОСТ РАВНОТЕЖНИХ ПОДАТАКА ЗА БИНАРНЕ СИСТЕМЕ КОРИШЋЕЊЕМ НЕУРОНСКЕ МРЕЖЕ

МЕHMET BILGIN

Istanbul University, Engineering Faculty, Department of Chemical Engineering, 34320 Avcilar, Istanbul, Turkey

Модел заснован на feed forward back propagation neural network коришћен је за израчунавање изобарних података за равнотеже пара – течност (VLE) за 40, 66, 67 и 101,32 ± 0.02 kPa бинарне системе метилциклохексантолуен и изопропанол – метил изобутил кетон, који су сачињени од различитих хемијских структура (цикличне, ароматске, алкохолне и кетонске), а немају азеотропско понашање. Половина експерименталних података унета је у пројектовани оквир у оквиру припремне фазе како би се проценили одговарајући подаци за цео опсег концентрације при поменутиим притисцима. Добијени резултати су упоређени са подацима израчунатим помоћу два класична модела који се у овој области користе, UNIFAC и Margules. У свим случајевима разлике између експериментално одређених коефицијената активности и израчунатих помоћу модела неуронске мреже (NNET) су мање него при примени модела Margules или UNIFAC.

(Примљено 13. новембра, ревидирано 3. марта 2004)

REFERENCE

1. M. J. Syu, G. Tsao, *Biotechnol. Bioeng.* **42** (1993) 376
2. S. R. Holbrook, I. Dubchak, S. H. Kim, *Biotechniques* **14** (1993) 984
3. J. Gesteiger, J. Zupan, *Angew. Chem. Int. Ed. Engl.* **32** (1993) 503
4. D. Cheraoui, D. Villemin, *J. Chem. Soc. Faraday Trans.* **90** (1994) 97
5. P. Kan, C. J. Lee, *Ind. Eng. Chem. Res.* **35** (1996) 2015
6. E. Alvarez, C. Riverol, J. M. Correa, J. M. Navaza, *Ind. Eng. Chem. Res.* **38** (1999) 1706
7. M. Bilgin, *Chemica Acta Turcica* **28** (2000) 33
8. M. Bilgin, P. U., *J. of Engin. Sci.* **8** (2002) 103
9. A. Fredenslund, R. L. Jones, J. M. Prausnitz, *AIChE Jorunal* **21** (1975) 1086
10. J. M. Smith, H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, Singapore, 1988, p. 351
11. A. Fredenslund, J. Gmehling, M. Michelsen, P. Rasmussen, J. M. Prausnitz, *Ind. Eng. Chem., Process Des. Dev.* **16** (1977) 450.