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Prediction of osmotic coefficients for ionic liquids in various solvents with artificial neural network

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Abstract: The relationship between the structural descriptions and osmotic coefficients of binary mixtures containing sixteen different ionic liquids and seven kinds of solvents has been investigated by back propagation artificial neural network (BP ANN). The influence of temperature on the osmotic coefficients was considered and the concentrations of ionic liquids were close to 1 mol kg^{-1}, except in acetonitrile. Multi linear regression (MLR) was used to choose the variables for the artificial neural network (ANN) model. A three layer BP ANN with seven variables containing structural descriptions of the ionic liquids and the character of the solvent as input variables was developed. Compared with experimental data, the osmotic coefficients calculated using the ANN model had a high squared correlation coefficient (R^2) and a low root mean squared error (*RMSE*).

Keywords: binary mixture; back propagation; artificial neural network; multi linear regression.

INTRODUCTION

Ionic liquids (ILs), as a type of widely applied green solvents, have aroused popular interest of academic community. Their excellent properties, such as chemical stability, thermal stability, low vapor pressure, high electronic conductivity, *etc*.[1] determine the extensive application of ionic liquids in different fields.[2] Currently, ILs have been successfully used in the extraction of bioactive components from natural products[3] and extraction of biological substances, such as proteins, amino acids, DNA, *etc*. The use of an extraction solvent demands an understanding of its physical chemistry. In these properties, the osmotic coefficient is thought to be very important for the selection of an extraction solvent.[5]

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1 **line 1, *etc.*, *etc*[4].**

Moreover, ionic liquids are thought to be designable solvents because their synthesis is relatively simple. A model that could predict the osmotic coefficients of ionic liquids would aid in the design of new and excellent ionic liquids as extraction solvents. A prediction model that could guide the chemical synthesis of ionic liquids is required by chemists.

Recently, the osmotic coefficients of ionic liquids in some ordinary solvents, such as water, alcohols, benzene, acetonitrile, *etc*., have been studied by experimental and theoretical methods.[6–8] However, compared with other physicochemical and related properties of ionic liquids (see Fig. 1[9–19]), theoretical models for estimating the osmotic coefficients of ionic liquids are relatively little researched at present.

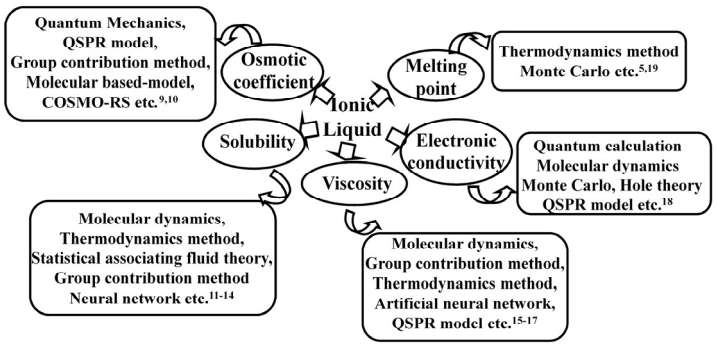

Fig. 1. Reported calculation methods in the study of some properties of ionic liquids.

For aqueous solutions, the osmotic coefficients could be calculated theoretically by the Pitzer equations or by the three-characteristic parameter correlation (TCPC) model.[20] In addition, the earlier and more popular Pitzer model was successfully used to correlate the osmotic coefficients of ionic liquid dissolved in water and acetonitrile.[5,21] Furthermore, Karimzadeh *et al.*[19] used Monte Carlo simulations to compute the osmotic coefficient of aqueous solutions of ionic liquids and reviewed computational models in the investigation of binary mixtures containing ionic liquids.

Within the methods concerning the investigation of ionic liquids, the quantitative structure–property relationship (QSPR) model has been widely used in the study of the properties of ILs and was proved to be an ideal method to fit and predict related data.[22] The artificial neural network (ANN) method that is good at predictions is a very important algorithm to develop a QSPR model and was successfully adopted to study the electronic conductivity of ionic liquids in a previous work.[18] In this context, a QSPR model based on the ANN method was set

up to correlate the structural characteristics and osmotic coefficients of seven solvents containing sixteen different ionic liquids.

COMPUTATIONAL DETAILS

Dataset and descriptors

84 sets of osmotic coefficient data for 16 types of ionic liquids in 7 kinds of solvents (chemical names and acronyms for the ILs are provided as Table I) at different temperatures were collected from the Ionic Liquid Database[23] and other references.[6,8,24,25]

TABLE I. Acronyms used for the studied ILs

Name	Acronym
1-Methyl-3-methylimidazolium methyl sulfate	[Mmim] [$MeSO_4$]
1-Butyl-3-methylimidazolium methyl sulfate	[Bmim][$MeSO_4$]
1-Ethyl-3-methylimidazolium ethyl sulfate	[Emim] [$EtSO_4$]
1-Ethyl-3-methylpyridinium ethyl sulfate	[Empy][$EtSO_4$]
1-Butyl-3-methylimidazolium octyl sulfate	[Bmim][$OctSO_4$]
1-Ethyl-3-methylimidazolium chloride	[Emim][Cl]
1-Butyl-3-methylimidazolium chloride	[Bmim][Cl]
1-Hexyl-3-methylimidazolium chloride	[Hmim][Cl]
1-Ethyl-3-methylimidazolium bromide	[Emim][Br]
1-Propyl-3-methylimidazolium bromide	[Pmim][Br]
1-*n*-Butyl-3-methylimidazolium bromide	[*n*Bmim][Br]
1-Pentyl-3-methylimidazolium bromide	[Pnmim][Br]
1-Hexyl-3-methylimidazolium bromide	[Hmim][Br]
1-Butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF_4]
1-Octyl-3-methylimidazolium tetrafluoroborate	[Omim][BF_4]
1-Butyl-3-methylimidazolium hexafluorophosphate	[Bmim][PF_6]

The 3D structural coordinates of ionic liquids were obtained from the Cambridge Structural Database (CSD).[26] To reflect the prediction capability of model, the data points of the same solvent containing the same ionic liquid were not divided into different datasets. The 84 sets of data were divided into three datasets, *i.e.*, a training set, a validation set and a test set containing 46, 24 and 30 % of the total data, respectively (Table II).

TABLE II. The solvents with ionic liquids and data sets; training set: entry 1–15, validation set: entry 16–24, test set: entry 25–36

Entry	Solvent	IL	Concentration, mol kg^{-1}	Temperature, K	Osmotic coefficient
1	1-Propanol	[Bmim][$MeSO_4$]	1.0071	323.15	0.629
2	1-Propanol	[Empy][$EtSO_4$]	0.9272	323.15	0.605
3	2-Propanol	[Mmim] [$MeSO_4$]	0.9721	323.15	0.461
4	Ethanol	[Bmim][Cl]	1.096	313.15	0.742
			1.096	333.15	0.63
5	Water	[Bmim][$MeSO_4$]	0.9552	298.15	0.698
			0.9552	308.15	0.716
			0.9552	318.15	0.732
			0.9552	328.15	0.76

TABLE II. Continued

Entry	Solvent	IL	Concentration, mol kg^{-1}	Temperature, K	Osmotic coefficient
6	Water	[Emim][Cl]	1.0472	313.15	0.861
			1.0472	333.15	0.812
7	Water	[Bmim][BF_4]	0.9322	298.15	0.523
7	Water	[Bmim][BF_4]	0.9322	308.15	0.545
			0.9322	318.15	0.564
			0.9322	328.15	0.589
8	Water	[Empy][$EtSO_4$]	1.0336	313.15	0.813
			1.0336	333.15	0.784
9	Water	[Pmim][Br]	1.0292	298.15	0.702
			1.0292	308.15	0.714
			1.0292	318.15	0.717
			1.0292	328.15	0.724
10	Benzene	[Bmim][$OctSO_4$]	1.1483	298.15	0.018
			1.1483	303.15	0.016
			1.1483	308.15	0.027
			1.1483	313.15	0.039
11	Methanol	[Bmim][$OctSO_4$]	1.1872	298.15	0.373
			1.1872	303.15	0.466
			1.1872	308.15	0.579
			1.1872	313.15	0.71
12	Propanol	[Omim][BF_4]	1.0008	298.15	0.045
			1.0008	303.15	0.097
			1.0008	308.15	0.165
			1.0008	313.15	0.201
13	Acetonitrile	[Bmim][PF_6]	0.1015	318.15	0.3139
14	Methanol	[Omim][BF_4]	1.2766	298.15	0.327
			1.2766	303.15	0.401
			1.2766	308.15	0.481
			1.2766	313.15	0.543
15	Water	[Emim][Br]	0.4422	298.15	0.85881
16	Propanol	[Bmim][$OctSO_4$]	1.0548	298.15	0.057
			1.0548	303.15	0.202
			1.0548	308.15	0.319
			1.0548	313.15	0.417
17	2-Propanol	[Emim] [$EtSO_4$]	0.9702	323.15	0.575
18	Ethanol	[Bmim][$MeSO_4$]	0.9851	323.15	0.496
19	Ethanol	[Empy][$EtSO_4$]	0.982	323.15	0.498
20	Water	[nBmim][Br]	0.9713	318.15	0.7125
21	Water	[Mmim] [$MeSO_4$]	0.9792	313.15	0.896
			0.9792	333.15	0.87
22	Benzene	[Omim][BF_4]	1.4487	298.15	0.026
			1.4487	303.15	0.036
			1.4487	308.15	0.075
			1.4487	313.15	0.173

line 1 Propanol, 1-Propanol.

line 2 Propanol, 1-Propanol.

Comment [N1]: Isomer?

Answer: According to reference (J. Chem. Eng. Data 2006, 51, 518-525, which reference the data from), the propanol should be 1-propanol.

Comment [N2]: Isomer?

Answer: According to reference (J. Chem. Eng. Data 2006, 51, 518-525, which reference the data from), the propanol should be 1-propanol.

TABLE II. Continued

Entry	Solvent	IL	Concentration, mol kg^{-1}	Temperature, K	Osmotic coefficient
23	Water	[Hmim][Cl]	1.0049	313.15	0.765
			1.0049	333.15	0.732
24	Water	[Hmim][Br]	1.1189	298.15	0.384
			1.1189	308.15	0.397
24	Water	[Hmim][Br]	1.1189	318.15	0.413
			1.1189	328.15	0.429
25	1-Propanol	[Emim] [$EtSO_4$]	0.9772	323.15	0.596
26	2-Propanol	[Bmim][$MeSO_4$]	0.9823	323.15	0.523
27	2-Propanol	[Empy][$EtSO_4$]	0.9707	323.15	0.594
28	Ethanol	[Emim] [$EtSO_4$]	0.9888	323.15	0.504
29	Ethanol	[Mmim] [$MeSO_4$]	0.9868	323.15	0.449
30	Ethanol	[Hmim][Cl]	1.0138	313.15	0.677
			1.0138	333.15	0.5679
31	Water	[Pnmim][Br]	1.0258	298.15	0.618
			1.0258	308.15	0.637
			1.0258	318.15	0.632
			1.0258	328.15	0.649
32	Water	[Emim] [$EtSO_4$]	0.8919	298.15	0.706
			0.8919	308.15	0.721
			0.8919	318.15	0.73
			0.8919	328.15	0.747
33	Ethanol	[Omim][BF_4]	1.0646	298.15	0.107
			1.0646	303.15	0.197
			1.0646	308.15	0.255
			1.0646	313.15	0.33
34	1-Propanol	[Mmim] [$MeSO_4$]	0.9815	323.15	0.454
35	Acetonitrile	[Bmim][BF_4]	0.1043	318.15	0.3139
36	Ethanol	[Bmim][$OctSO_4$]	0.7636	298.15	0.036
			0.7636	303.15	0.061
			0.7636	308.15	0.106
			0.7636	313.15	0.137

The cations and anions of the ionic liquids were optimized using the B3LYP method[27,28] with the 6-31G(d) basis set, respectively. The optimization calculations were performed with the Gaussian03 program[29] and quantum mechanics descriptors, such as energy (E), volume (V), the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}) of the cations and anions, were considered. The molecular connectivity index, which is thought to be helpful in the investigation of the physical properties,[30] was considered and chi index of zero order (^0X), first order (^1X) and second order (^2X) of the ions were also calculated. All descriptors of the ions are listed in Table III.

The solvents were described by their dielectric constant. The osmotic coefficients of ionic liquids are influenced by temperature and their concentration in solvents. In this context, the concentration of ionic liquids was kept close to 1 mol kg^{-1}, except for acetonitrile, because the osmotic coefficient is much larger in this solvent than in the other solvents and related experimental data are lacking. To predict the osmotic coefficients of ionic liquids at different

temperatures, temperature must be considered as a variable in the related models. To decrease the redundancy existing in the descriptor data matrix, the correlation among related descriptors and their correlation with the osmotic coefficient of the ILs were examined and collinear descriptors (*i.e.*, $|r| > 0.9$) were detected.[31] Among the collinear descriptors, those showing high correlation with the osmotic coefficient were retained and the others were removed from the data matrix.

TABLE III. Data on the calculated descriptors of cations and anions

Ion	E / Ha	V $cm^3\ mol^{-1}$	E_{HOMO} eV	E_{LUMO} eV	${}^0X$	${}^1X$	${}^2X$
$[Mmim]^+$	–305.2307599	79.190	–0.43626	–0.18467	4.587512694	2.176597520	1.663519480
$[Bmim]^+$	–423.1786802	131.637	–0.42798	–0.17697	6.110675649	3.752718471	2.226796000
$[Emim]^+$	–344.5497093	91.159	–0.43158	–0.1805	5.294619475	2.752718471	1.828497838
$[Empy]^+$	–366.6178078	106.616	–0.44336	–0.23357	5.924756000	3.211203000	1.979076000
$[Hmim]^+$	–501.8072113	176.128	–0.40700	–0.17572	7.524889200	4.752718000	2.933903000
$[Pmim]^+$	–383.8648154	98.590	–0.42903	–0.17839	5.403569000	3.252718000	1.873243000
$[nBmim]^+$	–423.1828425	122.342	–0.42344	–0.17091	7.087513000	3.452991000	3.427070000
$[Pnmim]^+$	–462.4932894	101.983	–0.42303	–0.17662	6.817782430	4.252718471	2.580349390
$[Omim]^+$	–580.4349008	166.481	–0.37963	–0.17545	8.939102800	5.752718000	3.641010000
$[MeSO_4]^-$	–738.9948944	72.761	–0.06002	0.25643	3.080207000	1.090822000	0.495772000
$[EtSO_4]^-$	–778.3139770	102.525	–0.06373	0.23851	3.787313539	1.678356102	0.834257000
$[OctSO_4]^-$	–1014.197168	149.131	–0.06399	0.14990	8.029954230	4.678356102	3.549402980
$[Cl]^-$	–460.2522333	22.518	0.01479	0.64337	0.00	0.00	0.00
$[Br]^-$	–2571.7613390	35.840	0.21400	0.50035	0.00	0.00	0.00
$[BF_4]^-$	–424.4990828	39.883	–0.11504	0.45846	2.218964673	1.069044968	0.606092000
$[PF_6]^-$	–940.6433857	60.874	–0.15668	0.28100	2.767786838	1.133893419	1.071429000

Prediction models

The retained descriptors, temperature and concentration were selected as input variables of the multilinear regression model (MLR) model. To decrease the number of input variables for an ANN model, the descriptors usually need to be selected. The MLR model was thought to be a simple selection method that was successfully used in other studies.[18,32] All the 84 sets of data were used to study the MLR relationship between the descriptors and osmotic coefficients by statistical products and service solutions (SPSS) software. The descriptors contributing the most were selected according to the squared correlation coefficient (R^2) of MLR model. The descriptors selected by MLR model were collected as input variables for the back propagation (BP) ANN model. A brief description of the ANN has already been given:[33] "A computational neural network consists of simple processing units called neurons. The strength of the neurons is determined by the weights (adjusted) that are first summed (combined) and then passed through a transfer function to produce the output for that neuron." The BP algorithm means that the determination of the weight change is based on the error of the output unit. The fundamental theory and formulas of BP ANN and transfer functions can be found elsewhere.[33,34] The experimental data of the osmotic coefficients were the output variable. A three-layer BP ANN model usually used to deal with data was set up. All parameters were first normalized to a scale of 0 to 1 before training, validation or testing to avoid numerical overflows during the ANN processing. The initial weights of the training network and momentum factor were random. Then different transfer functions, learning rates and num-

ber of neurons were inputted to calculate the osmotic coefficient of the ILs in the training sets by the BP ANN method. The ANN algorithms were implemented in MATLAB programming language.

RESULTS AND DISCUSSION

Descriptor selected by MLR method

The collected descriptors were the independent variables and the osmotic coefficient was the dependent variable. The good correlations with the experimental osmotic coefficient were selected based on the squared correlation coefficient (R^2). After discarding the descriptors without effective influence on the squared correlation coefficient, the model with the least number of descriptors and a high R^2 was developed. The correlation obtained for 84 data points of the osmotic coefficient of the ILs was presented by a seven-parameter equation as follows:

$$\begin{aligned} Y = {} & 0.496 + 0.00459X_1 + 0.00148X_2 - 0.0440X_3 + \\ & + 0.00376X_4 + 0.202X_5 - 0.268X_6 + 0.212X_7 \\ & R^2 = 0.774,\ F = 37.199,\ \text{adjusted } R^2 = 0.753 \\ & \text{Standard error} = 0.129 \end{aligned} \tag{1}$$

where Y is the predicted osmotic coefficient of the ionic liquids and X_1 to X_7 represent the descriptors of ionic liquids and solvents. The MLR model was developed to predict the osmotic coefficient of the ILs as follows: X_1 is the dielectric constant of the solvents; X_2 is the energy of the cations; X_3 is the anion chi index of second order; X_4 is the temperature; X_5 is the concentration of the ILs in solution; X_6 and X_7 are the energies of the HOMO and LUMO of the anion, respectively.

The root mean squared error (*RMSE*), which is calculated as below, was used to measure the difference between the actual and the estimated values.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}\left(y_i^{\exp} - y_i^{\text{calc}}\right)^2}{n}} \tag{2}$$

where i represents the i-th sample, $y_i^{\exp}$ is an experimental value, y_i^{calc} is the corresponding value predicted by the model and n is the number of samples in the dataset.[35] The *RMSE* of the above MLR model was 1.0014, which showed that the calculated osmotic coefficient of the ionic liquids had large deviations from the experimental data. The MLR model to predict the osmotic coefficient of the ionic liquids did not have enough precision to guide in the design of new ionic liquids. However, the descriptors that enabled the MLR model to have high R^2 values in Eq. (1) may be major factors influencing the osmotic coefficient.

To avoid chance correlations, the *y*-randomization test was applied to the MLR model. The calculation procedure was repeated twenty-five times after shuffling the *y* vector randomly. The *y*-randomization results were that the highest R^2 within 25 time-calculations was 0.151, and the average R^2 of 25 time--calculations was 0.077. The low R^2 values suggest minor risks of chance correlations.

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BP ANN model

The descriptors selected by the MLR model were used as input variables for the BP ANN model, and the osmotic coefficient was the output variable. A three-layer ANN, which was usually used in QSPR models because of the good prediction capability, was chosen in this study. After optimization for the model several times, the number of neurons in the hidden layers was 7 and the learning rate was 0.06. A tan-sigmoid transfer function within the hidden layer and a linear transfer function within the output layer were selected for the ANN model. Multiple calculations were performed in order to obtain the global best results. Finally, the developed ANN model that achieved the goal of the training set and had good performance for the validation set was selected as the prediction model for the osmotic coefficient of ILs. The test set without contribution in model development steps was calculated to test the prediction capability of the ANN model. The osmotic coefficients calculated by the ANN model are displayed in Fig. 2.

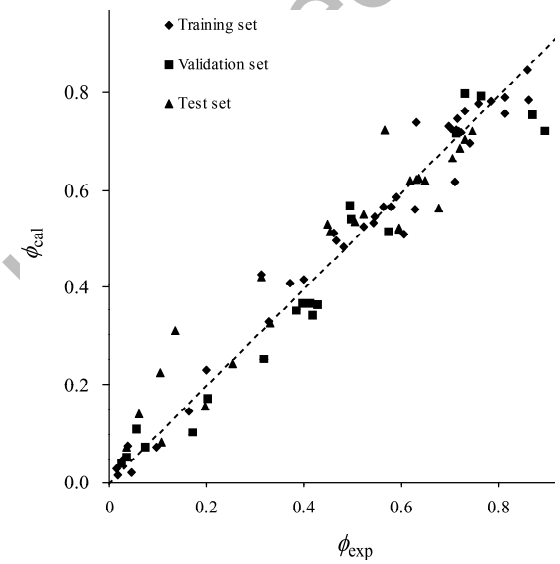

Fig. 2. The plots of the osmotic coefficient calculated by the ANN model *versus* the experimental values. The dotted line presents $y = x$.

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The R^2 of the training set, the validation set and the test set were 0.9733, 0.9478 and 0.9102, respectively. The *RMSE* of the training set, the validation set and the test set were 0.0428, 0.0658 and 0.0726, respectively. The results in Fig. 2 suggest that the osmotic coefficient calculated by the ANN model were similar to the experiment data. The training set was used to construct the ANN model, the high R^2 and small *RMSE* suggested that the ANN model was able to fit the osmotic coefficient of ionic liquids. The validation set was used to determine the parameters of the ANN model. The data of test set did not appear in training and validation sets and did not participate in the construction of the ANN model. Thus, the test set could examine the prediction ability of the ANN model. The small *RMSE* of the test set suggested that the ANN model could be used to predict the osmotic coefficient of ionic liquids.

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Variable analysis

The value of the variation inflation factor (*VIF*), which is thought to reflect the statistic significance of a model,[35] was calculated using the following equation:

$$VIF = \frac{1}{1 - r^2} \tag{3}$$

where, r is the correlation coefficient of the multiple regression equation between one descriptor and the others. The *VIF* value of the seven variables employed in the MLR and ANN models were 2.025, 2.532, 3.257, 1.453, 1.748, 4.000 and 1.261, respectively. For each descriptor, its *VIF* value was less than five, which indicated the model had obvious statistical significance. In the seven variables, except temperature and concentration, the other five variables were dielectric constant of solvents, the energy of cations, the anion chi index of second order, and the energy of the HOMO and LUMO of the anion, respectively. There were three descriptors related with the anion: the chi index belonging to molecular topology information, which affects the combination of atoms in a molecule, and the energies of the HOMO and LUMO, which is related to the reaction activity of molecule. There was only one descriptor of the cation, which affects the stability of ions in the model.

CONCLUSIONS

In this study, an ANN model was established based on MLR analysis to fit and predict the osmotic coefficient of seven solvents containing various ILs at different temperatures. The ANN model with R^2 = 0.9733 and *RMSE* = 0.0428 for the training set showed its good fitting capability. The predictive capability of the ANN model was proven by R^2 = 0.9102 and *RMSE* = 0.0726. The selection of the descriptors by the MLR method were investigated and proved by good results. The analysis of the descriptors reflected the model had obvious statistical significance.

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ИЗВОД

ПРЕДВИЂАЊЕ ОСМОТСКИХ КОЕФИЦИЈЕНАТА ЗА ЈОНСКЕ ТЕЧНОСТИ У РАЗЛИЧНИМ РАСТВАРАЧИМА ПОМОЋУ ВЕШТАКИХ НЕУРОНСКИХ МРЕЖА

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Релација између структурних описника и осмотских коефицијената бинарних смеша које садрже шеснаест различитих јонских течности и седам врста растварача истраживана је са унатраг напредујућим вештачким неуронским мрежама (BP ANN). Узет је у обзир утицај температуре на осмотске коефицијенте а концентрација јонских течности је била близу 1 mol kg^{-1} изузев у ацетонитрилу. Мултилинеарна регресија (MLR) коришћена је за избор варијабли за модел вештачке неуронске мреже (ANN). Развијен је трослојни BP ANN са седам варијабли које садрже структурне описнике јонских течности и карактера растварача као улазне варијабле. Поређењем са експерименталним подацима, осмотски коефицијенти израчунати са ANN моделом имају висок корелациони коефицијент (R^2) и малу просечну квадратну грешку (*RMSE*).

(Примљено 17. септембра, ревидирано 23. децембра 2016, прихваћено 9. јануара 2017)

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Answer: According to the original reference, the page number should be 162.

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