Evolving a Least Square Support Vector Machine Using Real Coded Shuffled Complex Evolution for Property Estimation of Aqueous Ionic Liquids

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ABSTRACT: In this study, we demonstrate how least square support vector machine (LSSVM) evolution with the shuffled complex evolution (SCE) ameliorates the predictability and reliability of the support vector machine as an estimation tool for thermodynamic of ionic liquids solutions. This strategy is applied to forecast the osmotic-coefficient of the 26 different ionic liquids by utilizing the 1409 available archival literature data points. Our methodology is the development of a hybrid SCE-LSSVM algorithm. Shuffled complex evolution is used to decide the hyper parameters of support vector machines so that all the initial weights can be searched and obtained intelligently. The evolution operators and parameters are carefully designed and set to avoid premature convergence and permutation problems. The results demonstrate that carefully designed SCE-LSSVM outperforms the structural risk minimization of support vector machines, predicting the properties of aqueous solutions in a way, even better than the available models.

Key words: *Osmotic coefficient, LSSVM, SCE, Ionic liquids, Intelligent models*

1. Introduction

One of the most significant challenges of thermodynamic science is to develop an activity model for the solutions, thereby representing the non-ideal behavior of these solvents for matter of property estimation. The deviation of synthesized solvents from their ideal behavior is difficult to be determined, needing to estimate and considerations of too many interacting parameters. The key property for the representation of such non-ideality behavior of solvents is the osmotic coefficient [1]:

$$\varphi = \frac{\mu_A^* - \mu_A}{RT \ln x_A} \qquad 1$$

For calculation of osmotic coefficient, an accurate estimation of chemical potentials is essential which need the use of a robust thermodynamic models with taking too many fitting parameters into account of consideration. Theoretically, osmotic coefficient is calculated by the Pitzer equations [2] or three-characteristic-parameter correlation (TCPC) [3]. For majority of solvents, especially smart synthesized solvents such as ionic liquids the problem is rather complex needing to find the properties of usually unknown molecular structures. Another simple but equality efficient approach is to estimate the non-ideality behavior of synthesized solvents from their available datasets. The artificial intelligence models are now beginning to be applied in property estimation of rather complex molecular structures such as ionic liquids. One of the strongest advantages of these models is that they can provide a generalized numerical scheme over a considered dataset giving the property estimator this ability to interpolate and extrapolate among the data [4-6], a perquisite that thermodynamic models could rarely afford. In addition, the artificial intelligent approaches could identify almost any mal-defined system, especially when the number of influential parameters are many, successfully outclassing any conventional estimators and predictive tools in engineering problems.

Artificial intelligence are useful tools in the hands of process engineers to nearly characterize any ill-defined engineering problems. They have been increasingly applied to estimate the property of complex molecular structures of ionic liquids rather than the laboratory tests, which are usually difficult, expensive and time consuming. The capabilities of these synthesized solvents in separation processes of acid gases (H_2S, CO_2) from natural gases for instance have been successfully represented by intelligent approaches. The conventional use of the artificial intelligence is to use a network of neurons in several sublayers to establish a linear relationship among the sets of data. The use of such a network possess some limitations [7], such as determining the optimal values of the model parameters , arriving at local minima, having a low convergence speed, and exhibiting low generalization performance at some particular cases. The support vector machine (SVM) is a recently developed interesting smart intelligent model that is able to present any nonlinear, mathematically ill-defined, complicated, and stochastic problems of various engineering and science disciplines in a more efficient way than artificial neural network. SVM is a robust regression approach that can be used for pattern recognition, classification, and regression [8]. SVM does not only possess the advantages of artificial neural network in defining an every mal-defined system but also obviate the obstacles associated with the ANN models. The least square support vector machine (LSSVM) is a revamped version of the SVM which use simpler and more time-efficient way in the computations. One of the main drawbacks of support vector machines is that the global outcome is acquired in presence of many local optima, the fact that makes the support vector machine techniques complicated and time consuming. Conventional support vector machines are prone to getting into the local optimum and convergence is slow. To overcome these drawbacks, this study intends to combine the shuffled complex evolution to the LSSVM approach, hindering the local minima and attaining rapid global convergence by searching in several regions simultaneously the way natural selection happens on earth.

There are two main ways to apply SCE into LSSVM: one is to optimize the hyper parameters of the LSSVM approach, and the other is to optimize the outcome of the results. The former strategy will be applied in this study. The structural minimization of LSSVM approach is the dynamic process for continuous optimization of regression and functions. SCE is an optimization and search tool based on the principles of natural happenstances and selection. SCE has remarkable capabilities to solve non-smooth, non-continuous, non-differentiable fitness functions, thereby escaping from the local optima and maintaining a global optimization solution.

SCE is found to be quite effective when LSSVM receives an extensive domain of data for exploration. In spite of other optimization tools, SCE is a type of evolutionary computation that is rarely used in the architecture of support vector machines for purpose of optimization. This strategy is applied for the estimation of one of the ill-defined properties of ionic liquids. The applicability of least square support vector machines, as a modified version of SVM was tested, in conjunction of shuffled complex evolution is tested for estimation of osmotic coefficient of 24 different ionic liquids. The outline of this paper can be represented into three separate sections: First, in section 2, we identify the least square support vector machine model, the shuffled complex evolution, and the methodology to juxtapose real coded SCE with a SVM algorithm for finding the hyper parameters. The modelling results are given in the section 3 to demonstrate the efficacy and accuracy of the new proposed hybrid algorithm for osmotic coefficient of the ionic liquids compared with the conventional use of the LSSVM for the same observed data. The conclusions are discussed in the section 4. Finally, the proposed strategy was utilized for estimation of three main properties: vapor pressure drop, activity, and osmotic coefficient of the electrolyte solution with data point out of the considered dataset.

2. Methodology

In this part of the paper, the numerical algorithm of modelling is presented in four different parts. In the first section, an introduction to the support vector machines is given. The second part deals with the shuffled complex evolution. In the third part, the application of SCE to the LSSVM is discussed and fourth part shows the strategy used by SCE to optimize the performance of the LSSVM.

2.1 Least square support vector machine

The least square support vector machine methodology for the nonlinear regression are presented as follows [9-13]:

In least square support vector machine a classifier on a randomly selected train set -$\{y_k, x_k\}$, $k = 1, 2, 3, ..., N$ - should be constructed in the following form:

$$y(x) = \omega^T \varphi(x_k) + b\,, \;\; \alpha_k, b \in \mathbf{R}\,, \; \alpha_k > 0 \qquad 2$$

$\varphi(.)$ is a nonlinear function that maps the input space into a higher dimensional space. This function cannot be explicitly constructed. To discover the classifier, the following equality should be met:

$$y_k \left[w^T \varphi(x_k) + b \right] = 1 - e_k \qquad 3$$

To meet the above equality, new variables e_k are introduced, resulting into the least square classification as follows:

$$\min_{w,b,e} \mathcal{J}3(\mathrm{w,b,e}) = \frac{1}{2} w^T w + \gamma \frac{1}{2} \sum_{k=1}^{N} e_k^2 \qquad 4$$

To minimize the $\mathcal{J}3$, the Lagrangian expression can be formed:

$$\mathcal{L}3(\mathrm{w,b,e;\alpha}) = \mathcal{J}3(\mathrm{w,b,e}) - \sum_{k=1}^{N} \alpha_k \left\{ y_k \left[w^T \varphi(x_k) + b \right] - 1 + e_k \right\} \qquad 5$$

α_k indicates the Lagrange multiplier. The Lagrange multiplier can be either positive or negative depending on the following equality constraints (Kuhn-Tucker condition [14]).

The Lagrange equation is optimized by the following conditions:

$$\left\{\begin{array}{l} \dfrac{\partial}{\partial w}(\\ \dfrac{\partial}{\partial b}(\\ \dfrac{\partial}{\partial e_k}(\\ \dfrac{\partial}{\partial \alpha_k}(\end{array}\right. \mathcal{J}3)=0 \rightarrow \begin{array}{c} w=\sum_{k=1}^{N}\alpha_k y_k \varphi(x_k) \\ \sum_{k=1}^{N}\alpha_k y_k = 0 \\ \alpha_k = \gamma e_k,\ k=1,2,3,\ldots,N \\ y_k\left[w^T\varphi(x_k)+b\right]-1+e_k=0,\ k=1,2,3,\ldots,N \end{array} \qquad 5$$

Here, satisfying above conditions lead to the set of linear equation.

$$\left[\begin{array}{c|c} 0 & -Y^T \\ \hline Y & ZZ^T+\gamma^{-1}I \end{array}\right]\left[\begin{array}{c} b \\ \hline \alpha \end{array}\right]=\left[\begin{array}{c} 0 \\ \text{f} \\ 1 \end{array}\right] \qquad 6$$

where $ZZ^T = y_k y_l \varphi(x_k)^T \varphi(x_l) = y_k y_l \psi(x_k, x_l)$ is the kernel function that can be obtained by implementing the Mercer's condition. For this test, the linear kernel function $K(x, x_k)$ is considered as follows:

$$K(x, x_k) = x_k^T x \qquad 7$$

And finally a linear function based on LSSVM model is obtained:

$$y(x) = \sum_{k=1}^{N} \alpha_k K(x, x_k) + b \qquad 8$$

2.2 Shuffled Complex Evolution

The shuffled complex evolution (SCE) is an effective, robust, efficient strategy for function optimization through concepts of probabilistic and deterministic, clustering, systematic evolution of the point spanning in the space, and competitive evolution. Two algorithms for the SCE optimization tool exists. The strategy of the SCE is to treat the global search similar to a process of natural evolution. In this algorithm, the dataset points are classified in a population with several complexes or communities. The communities can autonomously evolve and after several number of generations they are forced to mix and as a result form new communities through shuffling.

The members of the communities are potential parents with this ability to participate in the reproduction. To increase the competitiveness of the evolution, SCE conducts the better parents to contribute to the generation of offspring. The offspring are propagated at random locations of the feasible space under certain conditions to direct the evolution mellifluously without any deadlocks. This is imitation of mutation in biological evolution. The shuffled complex evolution algorithm allows each parents to participate in the reproduction at least once by replacing new offspring to the worst points of their complex rather than those in the entire population, thereby considering all information in the entire population. This numerical algorithm mimicked from natural evolution of species on earth was employed as an efficient optimization tool to acquire the hyper parameters of least square support vector machine.

2.3 Optimization with the Shuffled Complex Evolution

The shuffled complex evolution was utilized to estimate the hyper parameters of least square support vector machine using real coded programming in MATLAB®. The shuffled complex evolution executes the minimization of the mean square error (MSE) of the LSSVM model to attain the optimization goal. The size of complex (m) was considered 2n+1, where n is the dimension of problem or the numbers of input variables. The subcomplex with the size of n+1 is chosen for generation of an offspring (chosen based on [15]). The number of offspring β popping up from each independent evolving complex between consecutive shuffles equals with complex size (2n+1). For this analysis, only one step for evolution of complexes is allowed. After organizing the coded program, it was run for the defined data set points. The program was executed five times to eschew any premature convergence of the optimization and obtain the global optimal magnitude.

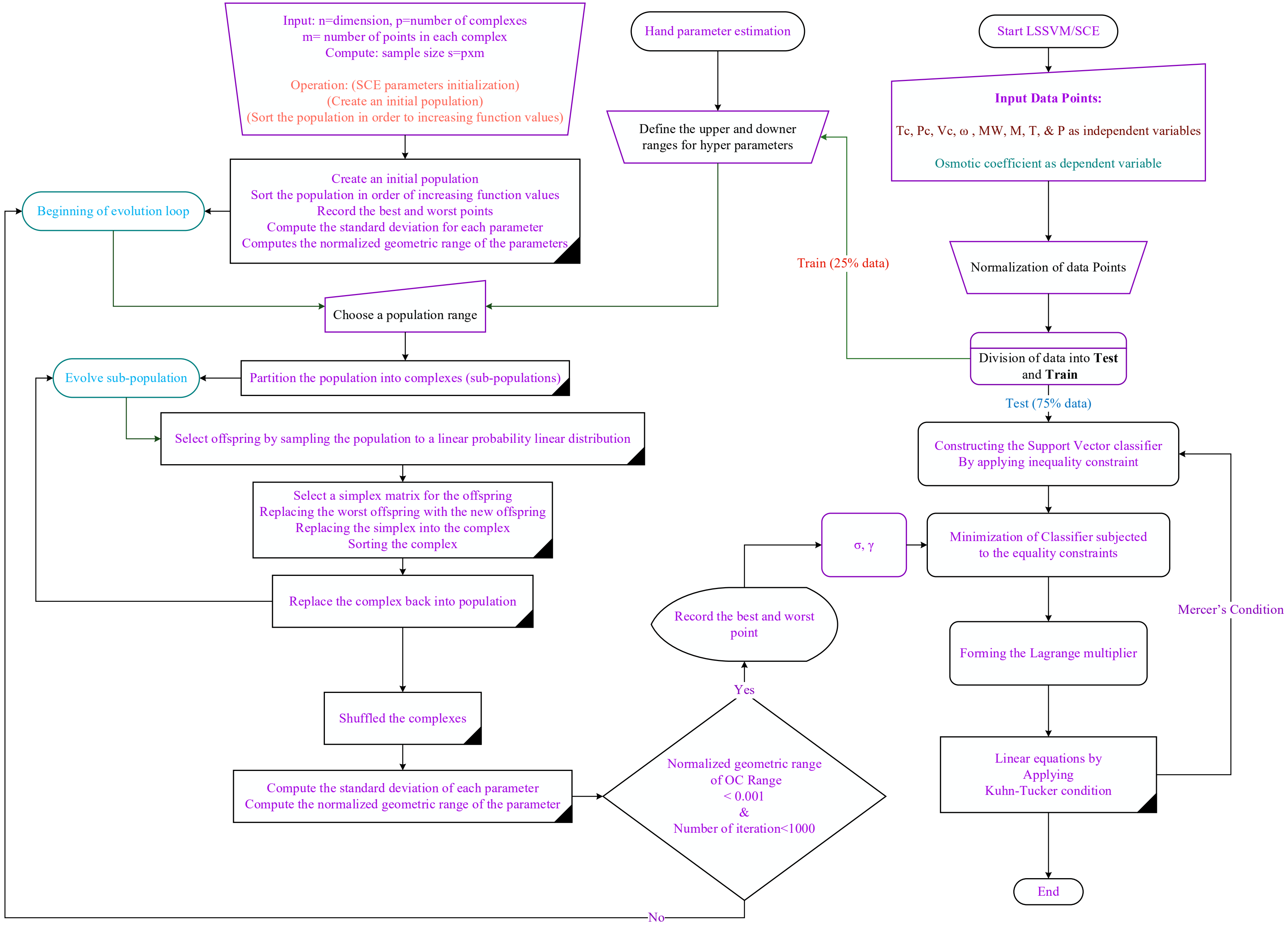
Input: n=dimension, p=number of complexes
m= number of points in each complex
Compute: sample size s=pxm
Operation: (SCE parameters initialization)
(Create an initial population)
(Sort the population in order to increasing function values)
Hand parameter estimation
Start LSSVM/SCE
Input Data Points:
Tc, Pc, Vc, ω , MW, M, T, & P as independent variables
Osmotic coefficient as dependent variable
Define the upper and downer ranges for hyper parameters
Create an initial population
Sort the population in order of increasing function values
Record the best and worst points
Compute the standard deviation for each parameter
Computes the normalized geometric range of the parameters
Beginning of evolution loop
Train (25% data)
Normalization of data Points
Choose a population range
Division of data into Test and Train
Evolve sub-population
Partition the population into complexes (sub-populations)
Test (75% data)
Select offspring by sampling the population to a linear probability linear distribution
Constructing the Support Vector classifier
By applying inequality constraint
Select a simplex matrix for the offspring
Replacing the worst offspring with the new offspring
Replacing the simplex into the complex
Sorting the complex
σ, γ
Minimization of Classifier subjected to the equality constraints
Replace the complex back into population
Record the best and worst point
Mercer's Condition
Forming the Lagrange multiplier
Yes
Shuffled the complexes
Linear equations by
Applying
Kuhn-Tucker condition
Normalized geometric range
of OC Range
< 0.001
&
Number of iteration<1000
Compute the standard deviation of each parameter
Compute the normalized geometric range of the parameter
End
No

Figure 1 The flowchart showing how SCE operates alone and in conjunction to the LSSVM

Figure 1 presents how the flow chart of the SCE adjusts the hyper parameters of the leas square support vector machine, and how the overall algorithm of least square support vector machine evolves with shuffled complex evolution.

2.4 Parameter optimization using hybrid SCE-LSSVM

For parameter optimization, an objective function is defined to minimize the experimental and predicted quantities of OC. The objective function represents the proximity of the predicted values to experimental values:

$$OF = abs\left|\frac{\varphi^{cal} - \varphi^{\exp}}{\varphi^{\exp}}\right| \qquad 9$$

where φ denotes the OC and superscripts cal and exp represent the calculated and experimental quantities respectively.

The shuffled complex evolution tries to minimize the output of the above-defined OF. The SCE steps towards this end by finding the hyper parameters of the LSSVM in a specific range. For [δ σ^2], the upper and downer ranges [1 0.001] and [1000 0.5] were defined for SCE for localizing the optimum hyper parameters. To reduce the statistical errors, this optimization approach was iterated twice.

3. Case study

The estimation of properties of ionic liquids are desirable in many industrial applications due to their high versatility and applicability. The molecular structures of ionic liquids could be extremely complex accommodating many elements according to what they were designed for. This have made any developed model and property estimator specialized for specific type of ionic liquid only under certain pressure and temperature. Osmotic coefficient is one of the desirable properties of ionic liquids, highly matter of interest to represent the behavior of these complex structures in the presence of impurities or as the main part of a solution. In the systems with several interacting components, osmotic coefficient represents the nonideality of the mixture of ionic liquid, thereby forming a key parameter for phase behavior identification of the system.

Our primary objective was to develop a robust model that can successfully predict the osmotic coefficient based on the property of the system rather than complex molecular interactions and forces. Variables employed for the model development include: Tc, Pc, Vc, acentric factor, molecular weight, and molality and of ionic liquids, temperature and pressure of the system. To strengthen the model and increase its universality, a comprehensive repository including 1409 osmotic coefficient data points for 26 different ionic liquids were built. Table 1 lists the detailed information about the constructed repository of data involving the name of ionic liquids, ranges of pressure, temperature, molality, osmotic coefficient and the reference from which these data have collected.

Table 1 The range input data used for the model development

Ref.	**Ionic liquid**	**No.**	**Osmotic Coeff. range**	**Molality range**	**Pressure**	**Temperature**
[16]	$C_6H_{12}N_2SO_4$	30	[0.864 0.994]	[0.0323 3.2928]	101 kPa	313, 333 K
[17]	$C_{11}H_{20}N_4$	33	[0.424 1.0519]	[0.024 1.4962]	101 kPa	313, 323, 328 K
[17]	$C_9H_{20}IN$	27	[0.392 0.789]	[0.0656 1.6508]	101 kPa	313, 323, 328 K
[16]	$C_8H_{15}N_2Cl$	28	[0.8 0.993]	[0.0566 3.15]	101 kPa	313, 333 K
[18]	$C_8H_{15}N_2Cl$	80	[0.686 1.004]	[0.0105 2.9617]	101 kPa	298, 308, 318, & 328 K
[18]	$C_8H_{15}N_2I$	72	[0.362 0.91]	[0.0133 2.5889]	101 kPa	298, 308, 318, & 328 K
[16]	$C_9H_{18}N_2SO_4$	30	[0.695 0.995]	[0.0519 4.091]	101 kPa	313, 333 K
[19]	$C_9H_{18}N_2SO_4$	64	[0.743 0.923]	[0.0132 2.177]	101 kPa	298, 308, 318, & 328 K
[19]	$C_9H_{18}N_2SO_5$	72	[0.392 1.023]	[0.012 2.0659]	101 kPa	298, 308, 318, & 328 K
[20]	$C_6H_{11}N_2Cl$	27	[0.1847 4.1131]	[0.855 0.97]	101 kPa	313, 333 K
[19]	$C_8H_{16}N_2SO_4$	80	[0.694 1.019]	[0.0086 2.7627]	101 kPa	298, 308, 318, & 328 K
[20]	$C_{10}H_{17}NO_4S$	26	[0.815 0.956]	[0.1419 3.3025]	101 kPa	313, 333 K
[16]	$C_{10}H_{19}N_2Cl$	34	[0.588 0.985]	[0.0932 3.9846]	101 kPa	313, 333 K
[21]	$C_{10}H_{19}N_2Cl$	34	[0.1399 3.0984]	[0.672 0.9842]	101 kPa	298 K

[17]	$C_{12}H_{23}N_2Cl$	48	[0.479 1.046]	[0.0346 1.7738]	101 kPa	313, 323, 328 K
[22]	$C_9H_{17}ClN_2$	76	[0.771 0.949]	[0.014 1.7972]	101 kPa	298, 308, 318, & 328 K
[23]	$C_7H_{13}N_2Br$	80	[0.671 0.961]	[0.0071 2.7049]	101 kPa	298, 308, 318, & 328 K
[23]	$C_9H_{17}N_2Br$	80	[0.561 1.008]	[0.0079 2.0049]	101 kPa	298, 308, 318, & 328 K
[24]	$C_8H_{16}N_2SO_5$	39	[0.836 0.914]	[0.0122 1.3471]	101 kPa	308, 318, & 328 K
[23]	$C_{10}H_{19}BrN_2$	76	[0.271 0.768]	[0.0155 2.3976]	101 kPa	298, 308, 318, & 328 K
[25]	$C_{15}H_{34}ClN$	42	[0.14 0.9431]	[0.009991 0.8645]	101 kPa	298 & 310 K
[25]	$C_{15}H_{34}BrN$	44	[0.107 0.9655]	[0.009006 0.7876]	101 kPa	298 & 310 K
[26]	$C_{10}H_{24}IN$	34	[0.242 0.8694]	[0.0575 3]	101 kPa	298 K
[26]	$C_9H_{22}IN$	36	[0.322 0.9221]	[0.0542 2.344]	101 kPa	298 K
[27]	$C_{13}H_{30}BrN$	46	[0.524 0.873]	[0.8404 1.0045]	101 kPa	283, 288, 293, 298 K
[25]	$C_{18}H_{40}ClN$	36	[0.154 0.9441]	[0.01011 0.8026]	101 kPa	298 & 310 K
[27]	$C_{11}H_{26}BrN$	46	[0.524 0.873]	[0.8404 1.0045]	101 kPa	283, 288, 293, 298 K
[26]	$C_7H_{18}IN$	35	[0.447 0.9283]	[0.0539 1.6875]	101 kPa	298 K

The thermodynamic properties for some ionic liquids which was not reported in the archival literature was estimated based on the Valderrama [28] group contribution method. Table 2 give the structure, IUPAC name, and properties of ionic liquids. It is notable that the average percentage of experimental errors for osmotic coefficient was about 5% based on their reports and method of analysis.

Table 2 The name, chemical formula, abbreviations, and properties of the ILs

Abbreviation	Formula	IUPAC Name	Mw [gr/mol]	Tc [k]	Pc [bar]	Vc [cm^3/mol]	ω
[dmim] [MSO4]	$C_6H_{12}N_2SO_4$	1,3-dimethylimidazolium methylsulfate	208.2	1040	52.9	545.6	0.3086
[BMPYR][DCA]	$C_{11}H_{20}N_4$	1-butyl-1-methylpyrrolidinium dicyanamide	208.3	993.03	25.0767	705.13	0.79868
[BMPYR][I]	$C_9H_{20}IN$	1-butyl-1-methylpyrrolidinium iodide	269.17	826.005	29.3243	600.58	0.4381
[bmim] [Cl]	$C_8H_{15}N_2Cl$	1-butyl-3-methylimidazolium chloride	174.7	789	27.8	568.8	0.4914
[bmim] [I]	$C_8H_{15}N_2I$	1-butyl-3-methylimidazolium iodide	266.1	871.2	28.6	607.5	0.4835
[bmim] [MSO4]	$C_9H_{18}N_2SO_4$	1-butyl-3-methylimidazolium methyl sulfate	250.3	1081.6	36.1	716.9	0.4111
[bmim] [BF4]	$C_9H_{18}N_2SO_5$	1-butyl-3-methylimidazolium tetrafluoroborate	226	643.2	20.4	655	0.8877
[emim] [Cl]	$C_6H_{11}N_2Cl$	1-ethyl-3-methylimidazolium chloride	146.6	748.6	34.2	454.5	0.4165
[emim] [ESO4]	$C_8H_{16}N_2SO_4$	1-ethyl-3-methylimidazolium ethyl sulfate	236.3	1067.5	40.5	659.8	0.3744
[empyr][ESO4]	$C_{10}H_{17}NO_4S$	1-ethyl-3-methylpyridinium ethylsulfate	247.31	1023.78	42.9967	652.9	0.34118
[hmim] [Cl]	$C_{10}H_{19}N_2Cl$	1-hexyl-3-methylimidazolium chloride	202.7	829.2	23.5	683	0.5725
[moim] [Cl]	$C_{12}H_{23}N_2Cl$	1-methyl-3-octylimidazolium chloride	230.8	869.4	20.3	797.2	0.6566

[mpim] [Cl]	$C_9H_{17}ClN_2$	1-methyl-3-pentylimidazolium chloride	188.7	763.605	25.835	618.98	0.48214
[mpim] [Br]	$C_7H_{13}N_2Br$	1-methyl-3-propylimidazolium bromide	205.1	769.363	33.4634	519.28	0.40054
[pmim] [Br]	$C_9H_{17}N_2Br$	1-pentyl-3-methylimidazolium bromide	233.2	854.2	27.2	640.4	0.5292
[prmim] [MSO4]	$C_8H_{16}N_2SO_5$	1-propyl-3-methylimidazolium methylsulfate	236.3	1067.49	40.4626	659.78	0.37442
[hmim] [Br]	$C_{10}H_{19}BrN_2$	3-hexyl-1-methyl-1H-imidazolium bromide	247.175	873.47	25.0137	697.49	0.57054
-	$C_{15}H_{34}ClN$	dodecyldimethylammonium chloride	263.894	757.452	14.573	990.98	0.82138
-	$C_{15}H_{34}BrN$	dodecyltrimethylammonium bromide	294.321	796.793	14.7863	1005.5	0.80143
-	$C_{10}H_{24}IN$	heptyltriethylammonium iodide	285.231	720.5	20.6504	744.14	0.63148
-	$C_9H_{22}IN$	hexyltriethylammonium iodide	271.231	698.575	22.1413	687.03	0.58812
-	$C_7H_{18}IN$	N-methyltriethylammonium iodide	243.13	654.38	25.8651	572.81	0.5028
-	$C_{13}H_{30}BrN$	N,N,N-trimethyl-1-decanaminium bromide	280.288	752.17	17.271	891.28	0.7527
-	$C_{18}H_{40}ClN$	N,N,N-trimethyl-1-dodecanaminium chloride	305.97	826.738	12.718	1162.31	0.92178
-	$C_{11}H_{26}BrN$	octyl trimethyl ammonium bromide	252.24	707.733	19.5117	777.06	0.66824
-	$C_7H_{18}IN$	pentyltriethylammonium iodide	299.24	742.373	19.3451	801.25	0.67485

4. Results and discussion

To evaluate the optimization of the shuffled complex evolution within least square support vector machine, the LSSVM was applied for the same dataset points of the SCE-LSSVM. Fig. 2 gives the comparison between predicted and measured OC values at the training and validation phase for both LSSVM and hybrid SCE-LSSVM models using the experimental repository gathered from the literature for 24 different ionic liquids The SCE-LSSVM was constructed with a number of complex of 2, a number of subcomplex of 1, and a number of offspring twice the data numbers plus one. Only one step for evolution of complexes was allowed. The SCE-LSSVM was trained by 2 generations, followed by a hyper parameter optimization approach.

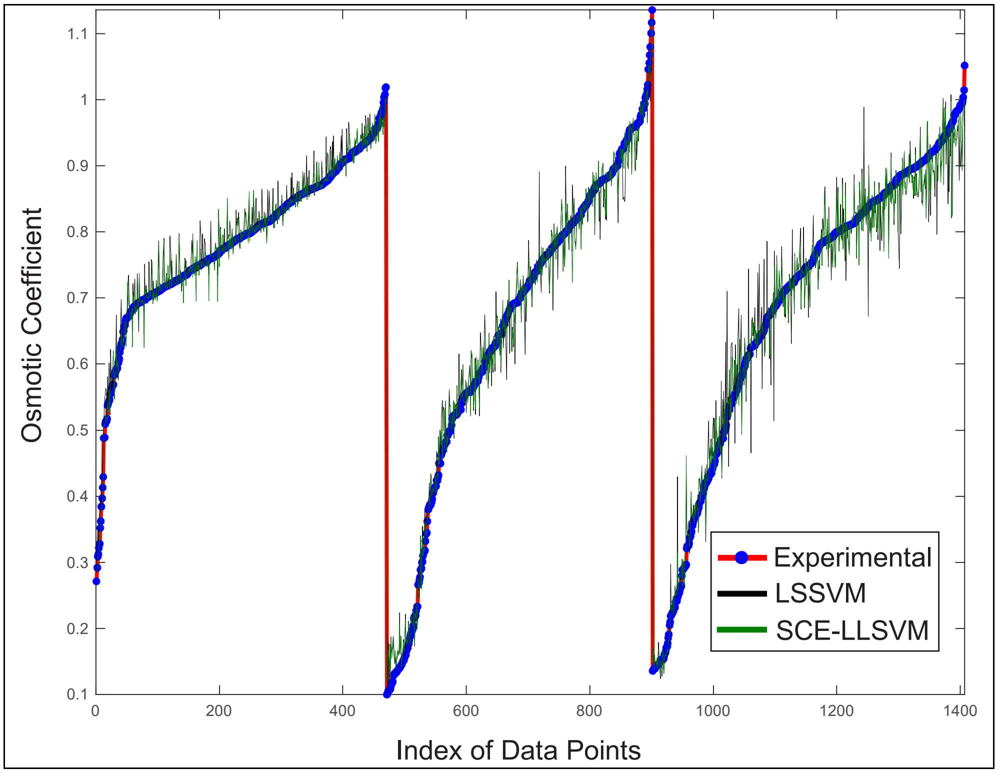

Figure 2 Comparison between the measured and predicted osmotic coefficient

The output of the model representing in Fig. 2, reveal a great match of simulated data with the target data for both LSSVM and SCE-LSSVM approaches. Apparently, the SCE-LSSVM outclasses the predictions of LSSVM by lowering the oscillation in the predicted data. The simulation performance for the two investigated algorithms was more comprehensively evaluated on the basis of the mean square error (RMSE) and efficiency coefficient R^2, average absolute relative deviation %AARD. The parameters RMSE =0.0319, R^2 = 0.97619, %AARD = 4.4335, STD = 0.2067 in contrast to RMSE = 0.0465, R^2 = 0.94931, %AARD = 5.8524, and STD = 0.2012 for validation phase attest to remarkable improvements in the performance of LSSVM in conjunction with SCE. However, the performance of both models are great in prediction of OC. In general, a R^2 more than 0.9 demonstrates a great model prediction, in the range 0.8-0.9 indicates a good performance, and less than 0.8 signifies mal predictions [29].

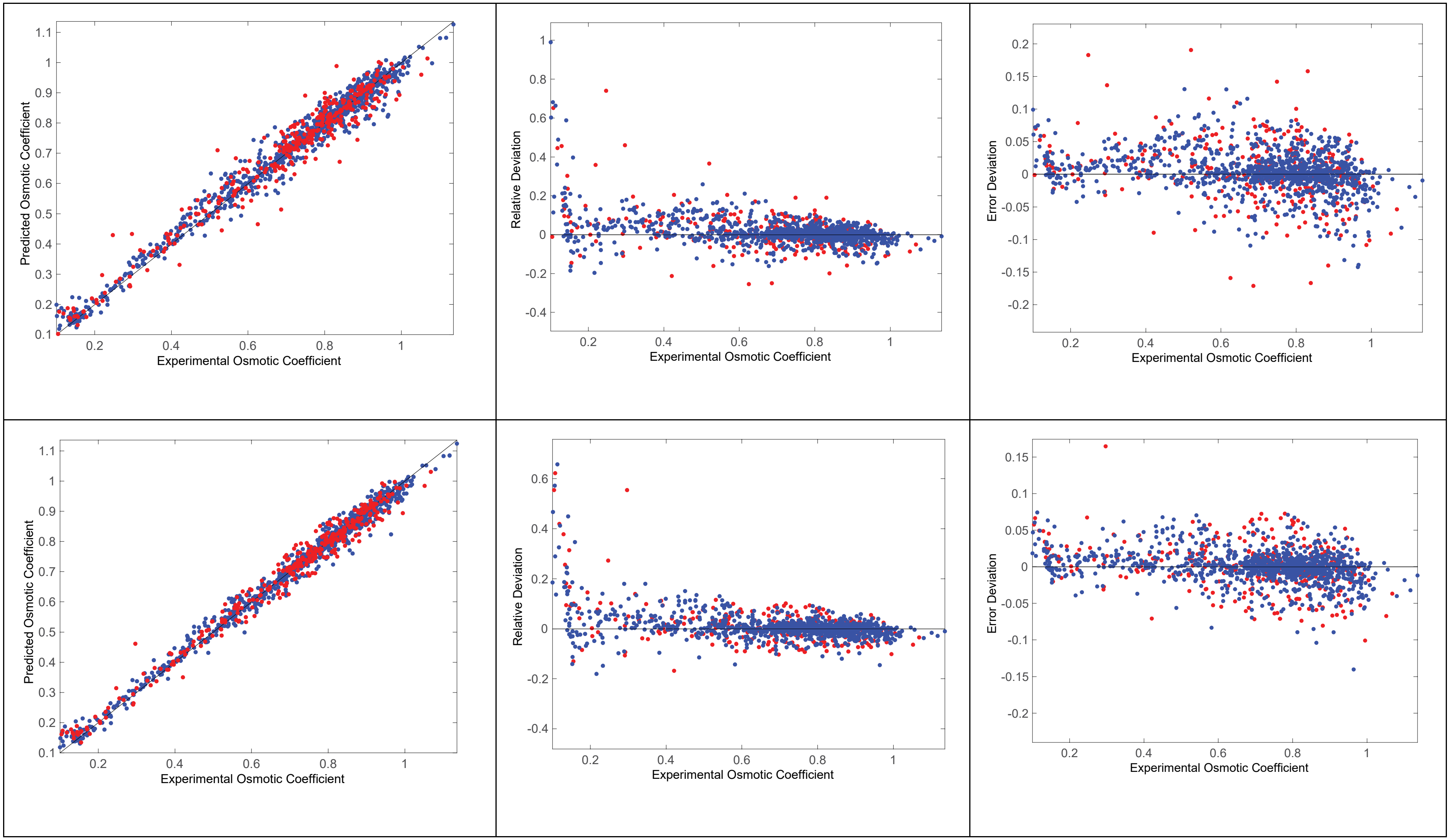

Figure 3. The statistical parameters of LSSVM (upper subplots) and SCE-LSSVM (downer subplots)-blue dots: test set, red dots: train sets

Fig. 3 shows the accordance between the measured and predicted OC values by SCE-LSSVM and LSSVM in terms of scatter plots. It shows the predicted experimental data in relation to the measure data over y=x line, the relative deviation and error deviation (for definition see [30]). These graphs show that the SCE-LSSVM is capable of escaping from the traps of local optima which is likely due to the combination of global search ability of SCE and local search ability of LSSVM.

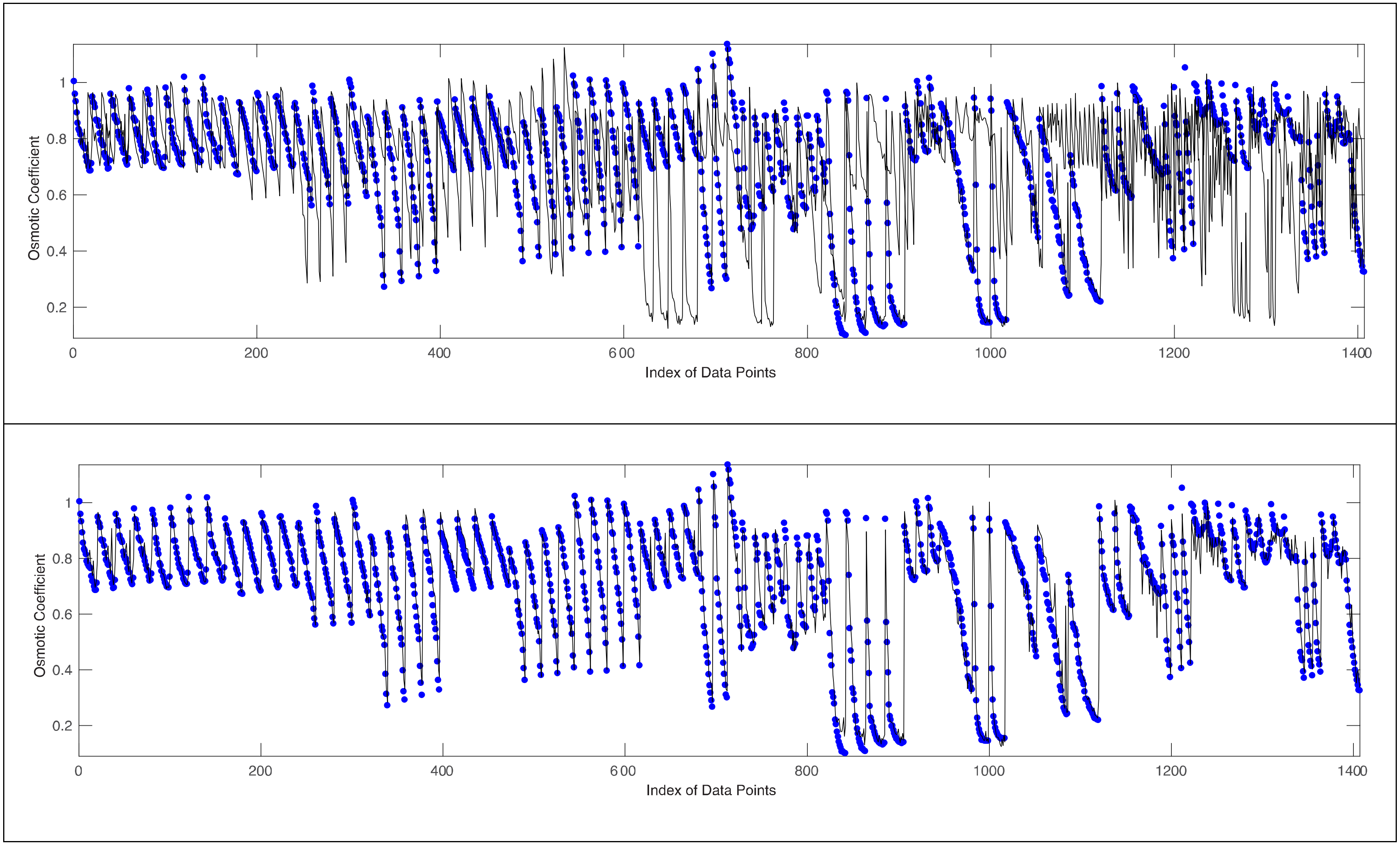

Figure 4. predicted (blue dots) and measurements (solid line) (Above: LSSVM and below: SCE-LSSVM)

Fig. 4 shows the prediction and experimental sets of data in the same graph for showing the accuracy of the models in giving the OC at higher and lower values. The below subplot in the figure 4 corresponds to the SCE-LSSVM showing the predicted values-blue dots are more closely in the measured values-solid black lines compared to the above subplots for LSSVM.

For a better comparison, the overall capability of models with statistical data are presented Table 3 represents the RMSE = 0.0226, R^2 = 0.98868, %AARD = 2.9319, STD = 0.2045 for the two different models of the validation phases and their hyper parameters. It can be readily observed from these data that the performance of SCE-LSSVM is better than the sole LSSVM model.

Table 3 The statistical errors of the models

Model	**Model's Parameters**		**Train**				**Test**			
	γ	σ^2	R^2	%AARD	RMSE	STD	R^2	%AARD	RMSE	STD
LSSVM	160.23	0.0301	0.97703	3.9694	0.0320	0.2068	0.94931	5.8524	0.0465	0.2012
SCE-LSSVM	34.55	0.0063	0.98868	2.9319	0.0226	0.2045	0.97619	4.4335	0.0319	0.2067

The most important question of about this approach is to what extent the model is well predictable in extrapolation and interpolation for a dataset out of that utilized in the article. To answer this question, a set of 15 OC experimental data for the $[EMIM]H_2SO_4$ was extracted from the Rafiee and Frouzesh [31] which is new in terms of material-ionic liquid: Mw=208.2 $gr.mol^{-1}$, Tc= 1073.8 K, P_c= 57.6 atm, V_c= 550.7 $cm^3.kg^{-1}$, ω=0.6411 (obtained from Valderama [32] Group Contribution approach)-and operating conditions (pressure=87 kPa, temperature=298.15 K). Fig. 5 authenticates that the application of SCE-LSSVM and LSSVM models are both just for prediction of OC, while the SCE-LSSVM ability in extrapolation of OC through a system of data out of the initially considered values is comparatively stronger than the sole LSSVM. The calculated RMSE% for SCE-LSSVM and LSSVM are 0.0003728 and 0.001182, respectively showing that the SCE-LSSVM model outclasses the LSSVM in OC estimation.

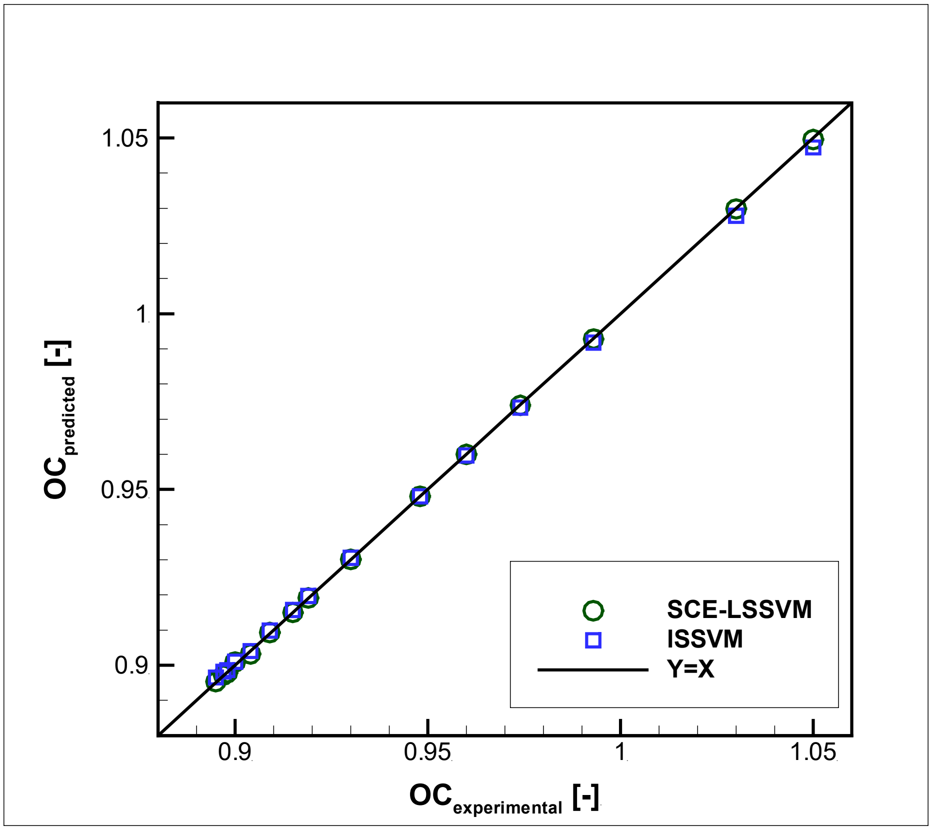

Figure 5 Showing extrapolation ability of models in OC prediction (measurements from [31])

The SCE-LSSVM as an estimation tool is further analyzed by depicting its accuracy. The capability of our strategy over molality is shown in the Fig. 6. Fig. 6 represent the predictability ranges of the SCE-LSSVM by giving the scatter plots of model and experimental data in relation to each considered input variables. This graphs depicts the high accuracy of the SCE-LSSVM in prediction of the diluted ionic liquid solutions. This is the basis of the activity calculations for the ionic liquid solutions.

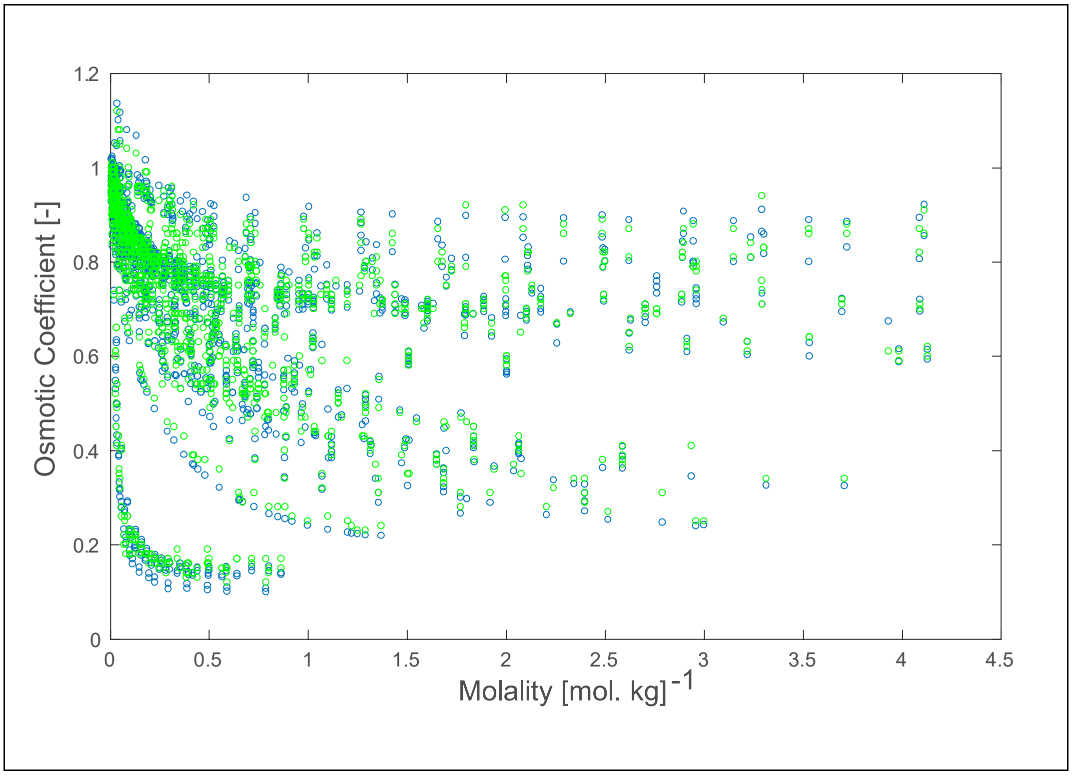

Figure 6. The SCE-LSSVM prediction of OC for different ionic liquids molality

The results of SCE-LSSVM is now employed to calculated the mean molal activity coefficient and for comparison with available most accurate thermodynamic models. The models widely used for analyzing this coefficient are Pitzer:

$$\ln\gamma\pm = -A_\phi\left[\frac{I^{1/2}}{1+bI^{1/2}}\right]+\frac{2}{b}\ln\left(1+bI^{1/2}\right)+m\left[2\beta^0_{MX}+2\beta^1_{MX}\frac{1-\exp(-\alpha I^{1/2})(1+\alpha I^{1/2}-1/2\alpha^2 I)}{\alpha^2 I}\right]+\frac{m^2}{2}\left(3C^\phi_{MX}\right) \tag{10}$$

Pitzer-Archer:

$$\begin{aligned}\ln\gamma\pm =& -\left|Z_M Z_X\right| A_\phi\left[\frac{I^{1/2}}{1+bI^{1/2}}+\frac{2}{b}\ln\left(1+bI^{1/2}\right)\right]+\\ & m\left(2v_M v_X\right)\left\{2\beta_{MX}^0+2\beta_{MX}^1\frac{1-\exp(-\alpha I^{1/2})(1+\alpha I^{1/2}-1/2\alpha^2 I)}{\alpha^2 I}\right\}+\\ & m^2\left(2v_M^2 v_X/v\right)Z_M\left\{3C_{MX}^0+4C_{MX}^1\left[6-\left(6+6\alpha I^{1/2}+3\alpha^2 I+\alpha^3 I^{3/2}-\alpha^4 I^2/2\right)\frac{\exp(-\alpha I^{1/2})}{\alpha^4 I^2}\right]\right\}\\ & +\frac{m^2}{2}\left(3C_{MX}^\phi\right)\end{aligned} \tag{11}$$

The modified Pitzer model:

$$\begin{aligned}\ln\gamma\pm =& -A_\phi\left[\frac{I^{1/2}}{1+b_{MX}I^{1/2}}\right]+\frac{2}{b_{MX}}\ln\left(1+b_{MX}I^{1/2}\right)\left|Z_M Z_X\right|+4\left(v_M v_X/v\right)mB_{MX}+\\ & \left[6\left(v_M v_X\right)^{3/2}/v\right]\left|Z_M Z_X\right|^{1/2}m^2 C_{MX}\end{aligned} \tag{12}$$

And the Scatchard's model:

$$\begin{aligned}&\ln\left\{\gamma\pm\left(IL\right)\right\}=\ln\left\{\gamma_\pm^*\left(IL\right)\right\}+Z_1\left\{\phi(y-1)+\left[(1-y)/2\right]A-[(1-y)^2/2]B\right\}\\ &A=b_{01}I+b_{02}I^2+b_{03}I^3\\ &B=(1/2)b_{02}I^2+(2/3)b_{03}I^3\end{aligned}$$

where model constants are given in table 4. Other unidentified parameters not included in table 4 are at T=298.15 K Debye-Hückel osmotic coefficient $A^\phi=0.39145$ [33], adjustable parameters $\alpha=2.0\ (kg/mol)^{1/2}$ and $b=1.2\ (kg/mol)^{1/2}$ [34], $\alpha_2=2.0\ (kg/mol)^{1/2}$, $\gamma_\pm^*(IL)$ is the activity coefficient of the pure ionic liquids, y is the ionic strength fraction of electrolytes, $Z_i=\left|Z_{iM}Z_{iX}\right|$, Z_{iM} is the charge of the cation and Z_{iX} is the charge of the anion for the solute i. $v_i=v_{iM}+v_{iX}$ is the total number of ions in the solute i.

Now the results of the SCE-LSSVM model has been used to analyze osmotic coefficient, activity and vapor pressure depression of the ionic liquids solutions. The standard deviations or RMSE% of the models are also given for the activity models in prediction of the OC for [BMIM]H_2SO_4. Even the best estimation of available thermodynamic models which is 0.002 by modified Pitzer model is around 40% more than the LSSVM alone. The shuffled complex evolution significantly improves the estimation ability of LSSVM approach leading to the lowest RMSE% 0.000373 among the considered models.

Table 4 The parameters of the Archer expansion of the Pitzer correlation

Model	**Model parameter**	**Standard deviation (σ)**
Pitzer	$\beta^{(0)}=0.0337$, $\beta^{(1)}=0.3227$, $C^{\varphi}_{MX}=0.0010$	0.003
Pitzer-Archer	$\beta^{(0)}_{MX}=0.1111$, $\beta^{(1)}_{MX}=0.0125$, $C^{(0)}_{MX}=-0.0011$ $C^{(1)}_{MX}=-0.0546$	0.003
Modified Pitzer	$b_{MX}=2.224$, $B_{MX}=0.1148$, $C_{MX}=-0.0021$	0.002
Scatchard		
Binary Solution		
Pitzer	$b_{01}=-1.508$, $b_{02}=1.172$, $b_{03}=-0.152$	0.03
Pitzer-Archer	$b_{01}=-1.399$, $b_{02}=1.116$, $b_{03}=-0.145$	0.03
Modified Pitzer	$b_{01}=-1.463$, $b_{02}=1.150$, $b_{03}=-0.1497$	0.03

The activity of the aqueous ionic liquid solution was also successfully predicted. Figure 7 gives the activity obtained from the experimentations and SCE-LSSVM. The RMSE% of SCE-LSSVM was estimated 0.0000362123 which is acceptably low, making the SCE-LSSVM a reliable tool for the activity analysis of ionic liquids solutions.

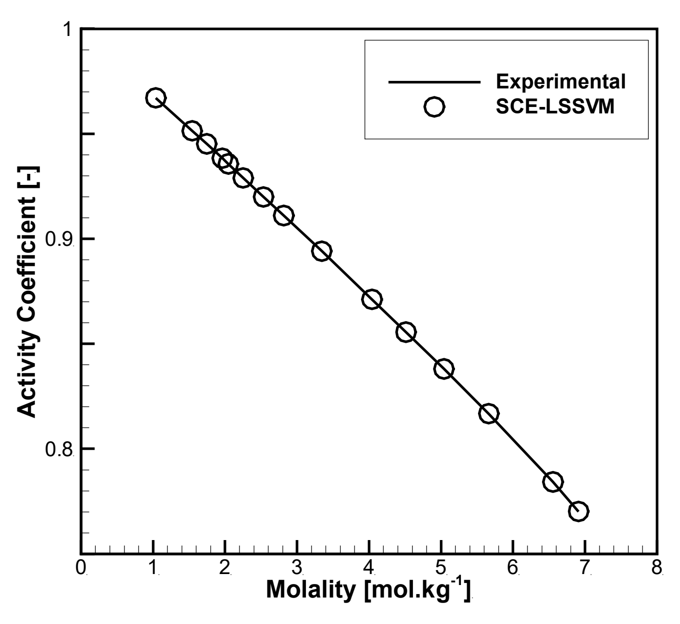

Figure 7 Activity coefficient of ionic liquid solution versus molality

The vapor pressure reduction is an incident happening during the formation of solutions because of the interactions among the solvent and solute. This is a very crucial solvent property which help counteracting the solvent loss during the separation processes. This event is more prevalent in electrolyte solutions where the interactions of solute-solvent are strong. To show the superiority of SCE-LSSVM in thermodynamic analysis, the vapor pressure depression of LiCl-[BMIM]H_2SO_4 solution was calculated by this intelligent approach and was compared with the experimental data. To calculate the vapor pressure drop, the following relationship between the OC and activity of the solvent is formed:

$$\phi = -\ln a_w / v m_s M_w$$

The calculated activity of the water is now used for the determination of the vapor pressure of the water in these solutions:

$$\ln a_w = \ln\left(p / p^*\right) + \left(B - V_w^*\right)\left(p - p^*\right) / RT$$

In these two latter equations, m_s denotes molality of the solution, M_w indicates the molar mass of the solvent and v is the stoichiometric number of the solute, B indicates the second virial coefficient of water vapor, V_w^* is the molar volume calculated from the density and p^* is the vapor pressure of the pure water. To calculate the second virial coefficient of the water *B* at different temperatures,

The electrolyte variables ($b = 3.2$, $\alpha_1 = 2$ kg$^{1/2}$.mol$^{-1/2}$, $\alpha_2 = 7$ kg$^{1/2}$. mol$^{-1/2}$, $\alpha_3 = 1$ kg$^{1/2}$.mol$^{-1/2}$) reported to have the best fit for electrolytes solutions, were utilized in calculation of the activity coefficient.

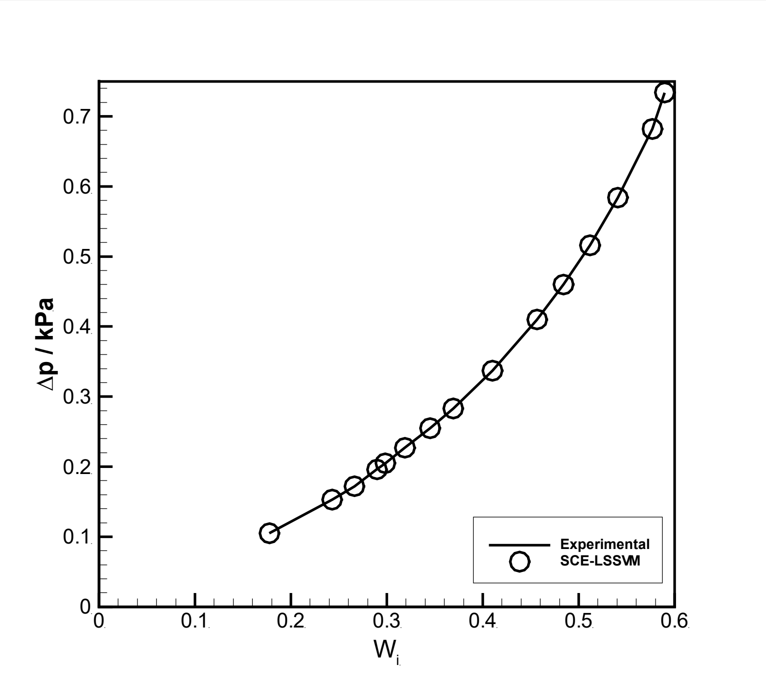

Figure 8 Vapor pressure depression of aqueous ionic liquid solution versus molality

The activity of the mean molal activity coefficient calculation in the above equations strongly depends on the capacity of the models to describe the osmotic coefficient in the diluted regions. Fig. 8 also confirms that the SCE-LSSVM is a reliable tool for estimation of vapor pressure depression of the aqueous ionic liquids solutions. The RMSE for the fig. 8 is 0.000115 which is desirably low for estimation of vapor depression.

6. Conclusion

In this paper, we introduced a shuffled complex evolution evolved least square support vector machine. Our strategy professes a shuffled complex based least square support vector machine (SCE-LSSVM), which effectively commingle the local searching ability of the shuffled complex evolution with the global searching ability of the least square support vector machine. The methodology of this work is that each initial point of LSSVM is chosen by a standard shuffled complex evolution, and the fitness of shuffled complex evolution is determined by the LSSVM. The shuffled complexes are carefully designed to optimize the LSSVM, to avoid premature convergence and permutation problems. The experiments of OC data have shown that the oracular performance of the implemented strategy is superior to the traditional least square support vector machine. This can be achieved by the changes of the hyper parameters γ and σ^2 of the least square support vector machines. One significant problem associated with the combination of the least square support vector machines with the shuffled complex evolution is the estimation of a ranges within the hyper parameters were optimized. This range of parameters for SCE-LSSVM in this analysis was determined manually. A surrogate strategy is to implement the SCE for optimization of data ranges, which will be a part of our future work. After the development of SCE-LSSVM, it was used for estimation of the properties of aqueous ionic liquid solutions (activity, vapor pressure depression, and osmotic coefficient) with characteristics out of the considered dataset for the model development.

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