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PREDICTIONS OF VAPOR PRESSURES OF TEN IONIC LIQUIDS USING PATEL TEJA EQUATIONS OF STATE

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ABSTRACT

Ionic liquids are considered as green solvents. They are useful in many aspects. Thermodyanmic data are required for proper simulation of the processes. Prediction of properties using Cubic Equations of State (CEOS) is an attractive option as it requires only pure component data. Ionic liquids have very low vapor pressure and hence estimating vapor pressure is very challenging. Zero pressure fugacity approach was used in the present work. For ten ionic liquids vapor pressure predictions were carried out using Patel-Teja equation of state. This CEOS was used with six different cohesion factor models. Optimized parameters were generated for all the IL's for six cohesion factors and are provided in the paper. Generalization was also done using acentric factor and mass connectivity index for all the models and the comparison was done. It was found that exponential form of cohesion factor gave the highest accuracy for generalized model.

KEYWORDS: Ionic Liquid, Vapor Pressure, Cohesion Factor, Mass Connectivity Index, PT EOS

INTRODUCTION

Ionic liquids (ILs) are referred to as room-temperature molten salts. They can replace organic solvents, reduce the chemical wastage and improve the safety of processes and products (Barcelo 2011), due to their attractive properties like, negligible volatility, good thermal and chemical stability, high ionic conductivity (Roshan *et. al.*, 2003). Ionic liquids are useful in number of different applications like, heat storage media, electrochemical applications, organic synthesis, absorption of gases, reaction solvents and many others. Vapor pressure is important for many reasons; some of them are listed below (Rebleo *et. al.*, 2005),

- Important in several applications of ionic liquids like Potential solvents,
- For understanding of phase transition
- For the development of models for other thermodynamic properties

Experimental vapor pressure data for ionic liquids are very less. Thus, the development of models for correlating and predicting the vapor pressure of ionic liquids has been slow. Recently Valderrama et.al, 2012 proposed an analytical expression for vapor pressure prediction of ionic liquids based on PR (Peng and Robnison, 1976) equation of state using low pressure fugacity. In present study same concept is used for prediction of vapor pressure using Patel Teja (PT) (Patel and Teja, 1982) Equations of state. Six cohesion factors available in the literature were compared for prediction of vapour pressure using PT EOS.

DATABASE & MODELLING

Experimental vapor pressure data for ten (10) ionic liquids belonging to two different families were considered for the study. The details are given in Table 1. Temperature, pressure and experimental vapor pressure data ranges are shown in Table 2. Critical properties for all the ILs were calculated by the model proposed by Valderrama *et. al.*, 2008.

Table 1: Details of Vapor Pressure Data Used

Sr.No	Ionic Liquid Family	No. of Ionic Liquids	Data Points	Reference
1	[NTf2]	9	128	7
2	[dca]	1	5	8

Table 2: Range of Temperature, and Experimental Vapor Pressure

Parameter	Minimum	Maximum
Temperature (K)	445.30	538.2
Pressure (bar)	0.69×10^{-7}	9.27×10^{-5}

Vapour pressure prediction using CEOS requires a proper cohesion factor expression. In present study six cohesion functions were studied. The model equations of all the cohesion factors are presented in Table 3. Vapor pressure data were fitted to obtain the values of compound specific parameters for all cohesion functions. For the purpose of optimizing parameters of cohesion functions ten ionic liquids, 9 from [NTf2] and 1 from [dca] family were used. An algorithm for optimizing cohesion factor parameter(s) using low pressure fugacity approach is shown in Fig. 1. Optimized parameters for the six cohesion factors are listed in Table 4. These parameters were generalized using acentric factor and mass connectivity index. Generalization of single parameter models and SV model were done by minimizing the sum of the square of the difference of optimized parameters and calculated parameters. For Hyene-2 and GL model perturbation approach suggested by Figueria *et. al.* 2007 was adopted. Generalized expressions are given in Table 5 for all the models. For Hyene-2 and GL models one needs to solve the two expressions to get the values of m and n parameters.

RESULTS AND DISCUSSIONS

In present study vapor pressures were estimated and compared in terms of %AAD using low pressure fugacity approach. %AAD is defined follows,

$$\%AAD = (100 * \mathrm{Abs}\left(P^{sat}{}_{Cal} - \frac{P^{sat}{}_{Exp}}{P^{sat}{}_{Exp}}\right))/N \quad (1)$$

The %AAD values for optimized and generalised parameters are listed in Table 6. SV model was found to be better compared to all.

Table 3: Six Cohesion Functions Used in the Present Study

Cohesion Function	Model Equation	Reference
Soave	$\alpha(T) = \left[1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2$	10
Joshipura	$\alpha(T) = \exp\left[m_1\left\{1 - \frac{T}{T_c}\right\}\right]$	11
Heyen-2	$\alpha(T) = \exp\left[m_2\left\{1 - \left(\frac{T}{T_c}\right)^n\right\}\right]$	4
SV	$\alpha(T) = \left\{1 + \left[m + n\left(1 + \sqrt{T_r}\right)(0.7 - T_r)\left(1 - \sqrt{T_r}\right)\right]\right\}^2$	12
GL	$\alpha(T) = 1 + m(T_r - 1) + n\left(\sqrt{T_r - 1}\right)$	12
Polishuk	$\alpha(T) = \frac{1}{1 + m\left(T_r{}^{2/3} - 1\right)}$	13

Table 4: Optimized Parameters for Six Cohesion Factors

Optimized Cohesion Parameters for PT EOS										
Cohesion Function		Soave	Joshipura	Heyen-2		SV		GL		Polishuk
Sr.No	Ionic Liquid Abbreviation	m	m	n	m	m	n	m	n	m
1	[C2C1im][NtF2]	1.3902	1.3798	1.0238	1.8913	1.9194	-1.0041	-3.0943	1.4502	0.7488
2	[C3C1im][NtF2]	1.3390	1.3375	1.0153	1.7565	1.7835	-0.8563	-2.6835	0.9652	0.7344
3	[C4C1im][NtF2]	1.3053	1.3104	1.0551	1.5277	1.6459	-0.6483	-1.4805	-0.8865	0.7257
4	[C5C1im][NtF2]	1.2652	1.2775	1.1677	1.1741	1.4440	-0.3397	-0.0541	-3.0660	0.7136
5	[C6C1im][NtF2]	1.2277	1.2468	1.1975	1.0730	1.3518	-0.2335	0.3040	-3.5360	0.7022
6	[C7C1im][NtF2]	1.2015	1.2250	1.2405	0.9787	1.2109	-0.0178	1.3589	-5.1538	0.6938
7	[C8C1im][NtF2]	1.1843	1.2105	1.2457	0.9521	1.2032	-0.0355	1.2340	-4.9030	0.6882
8	[C10C1im][NtF2]	1.1597	1.1910	1.5723	0.6493	1.0117	0.2728	2.6245	-7.0578	0.6803
9	[C12C1im][NtF2]	1.0845	1.1276	1.5197	0.6279	0.9092	0.3160	2.9254	-7.3108	0.6553
10	[bmim][dca]	1.5101	1.4675	2.6688	0.4499	1.2215	0.6791	6.6173	-14.8085	0.7928

However, all the models fitted the data with less than 5% AAD. For generalized models however, single parameter models were better. Joshipura *et. al.*, 2010 was showing the least deviation.

Table 5: Generalized Cohesion Factors Expressions

Cohesion Function	Correlation Based on Low Pressure Fugacity for PT EOS
Soave	$m = 0.639\lambda^2 - 0.5781\lambda - 0.0854\omega + 0.4160$
Joshipura	$m = 0.0556\lambda^2 - 0.4871\lambda + 0.1203\omega + 2.1749$
Heyen-2	$1 + mn = 0.4235\lambda^2 - 2.6734\lambda - 2.001\omega + 7.3275$ $mn(n - (1 + mn)) = -0.1239\lambda^2 + 1.1693\lambda - 0.2155\omega - 3.8984$
SV	$m = 0.3338\lambda^2 - 2.1892\lambda - 1.8460\omega + 5.6364$ $n = -0.6892\lambda^2 + 4.0103\lambda + 3.7304\omega - 7.4507$
GL	$1 - m\,{}^{n}/_{2} = 0.4942\lambda^2 - 3.1057\lambda - 3.4818\omega + 8.7115$ ${}^{n}/_{4} = 0.0210\lambda^2 - 0.2449\lambda - 6.5158\omega + 2.2388$
Polishuk	$m = 0.0160\lambda^2 - 0.1598\lambda - 0.0146\omega + 1.0410$

Table 6: %AAD for Generalized and Optimized Cohesion Factors

Sr.No.	Cohesion Function	%AAD(Global)	
		Generalized Cohesion Parameters	Optimized Cohesion Factors
1	Soave	11.0755	4.1784
2	Joshipura	10.7851	3.8767
3	Heyen-2	12.3596	0.9592
4	SV	21.6180	0.7538
5	GL	25.8195	0.7804
6	Polyshuk	11.1882	4.4805

CONCLUSIONS

Low pressure fugacity approach was applied to predict the vapor pressures of ten ionic liquids. Effect of cohesion factor was observed during the study. It was found that most of the mathematical form of cohesion factor works well for compound specific models but the exponential form (Joshipura *et. al.*, 2010) and two parameter polynomial[12] works better for generalized ones. However, Joshipura *et. al.*, 2010 type functions can be considered as superior as the model uses only single adjustable parameters. This will be useful when predicting properties of the mixtures. It was also observed that PR EOS is predicting vapor pressure accurately compared to PT EOS. The study was limited to vapor pressure and that too for a limited number of compounds. The future work will concentrate on predicting other properties using various cohesion factor models and comparing them.

NOMENCLATURE

P Pressure

T Temperature

EOS Equation of state

PR Peng-Robinson

PT Patel-Teja

Greek Symbols

ω acentric factor

ϕ^v vapour phase fugacity coefficient

ϕ^L liquid phase fugacity coefficient

f^v vapour phase fugacity

f^L liquid phase fugacity

Subscripts

r Reduced

sat Saturated

c Critical

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