Vapor Pressure Prediction Using Group Contribution Method

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ABSTRACT

A group contribution method was developed for prediction of pure hydrocarbon vapor pressure in the reduced temperature range from 0.45 up to near critical point (0.95 T_c). Experimental vapor pressure data of totally 456 hydrocarbon compounds were collected and used to obtain model parameters. The developed model employs the combinatorial and the residual UNIFAC terms and fugacity of pure hydrocarbons. The proposed modified model is incomparable accuracy to existing similar models that shows an excellent agreement between estimated and experimental data.

INTRODUCTION

Thermodynamic properties of substances are vital in process and design calculations. One of the most important pure component properties needed in design calculations is the vapor pressure of pure substances, which is not available experimentally for a wide range of materials. A number of correlations are available in literature to estimate vapor pressure among which those that are based on group contribution methods can be used as predictive tools[1-3].

Nowadays, the DIPPR, DDB, PPDS[4] data banks provide a large amount of experimental data and correlations for estimating vapor pressure of pure compounds.

Even though, these data banks contains thermodynamics properties, such as vapor pressure for more than 6000 compounds, many substances are not stable at high temperatures and decompose due to temperature rise; it is not possible to obtain their vapor pressure experimentally and as a result, it is impossible to obtain a correlation for predicting their properties like vapor pressure based on experimental data. This is the reason why group contribution methods based on UNIFAC groups have found great interest in the recent decades. Without having all detailed knowledge of component physical properties, the methods can be capable to predict properties. Among these methods is the method proposed by Fredenslund et al. in 1975 [3]. They developed a procedure to estimate the excess Gibbs free energy of the solution by decomposing the component into a set of its characteristic groups (group contribution technique); and then, the non-ideality of the component due to the differences in

the sizes and shapes of component groups, as compared to the other components in the mixture is estimated. The residual contribution also is calculated.

In group contribution method based on UNIFAC groups, the compound is broken down into constituent groups which follows the assumption that vapor pressure is determined by group–group interaction parameters, then interaction parameters is used for prediction of vapor pressure of interest compound.

However, some researchers have proposed correlations for estimation of pure compound vapor pressure. In this work, a correlation based on UNIFAC groups using group contribution method is developed in which, the focus is on the estimation of vapor pressures in wide – pressure region.

Theory

Fredenslund and Rasmussen[4] have introduced a group contribution method based on UNIFAC groups for the prediction of vapor pressure of pure organic compounds by relating UNIFAC molar Gibbs free energy differences to the vapor pressure. In their proposed method the vapor pressure of component i (P_i^s) is obtained from Eq. 1.

$$RT \ln\left(\varphi_i^s P_i^s\right) = \sum_k v_k^{(i)} \Delta g_k + RT \sum_k v_k^{(i)} \ln\Gamma_k^{(i)} \quad ...(1)$$

where R is the universal gas constant, T is the temperature, $v_k^{(i)}$ is the number of groups of type k in molecule i, φ_i^s is the fugacity coefficient of molecule i at vapor liquid equilibrium and N is the total number of groups. Δg_k is the contribution of gibbs energy due to group k and $\Gamma_k^{(i)}$ is the activity coefficient of group k in molecule i. Based on the method of Fredenslund Δg_k is obtained from Eq. 2. The first term on the right hand side of Eq. 2 is related to temperature and the second term is related to the configuration.

$$\sum_k v_k^{(i)} \Delta g_k = \sum_k v_k^{(i)} \Delta g_k' + \Delta G_i'' \quad ...(2)$$

The best temperature dependency for is obtained by Fredenslund is introduced by Eq. 3.

$$\Delta g_k' = \frac{A_{k,1}}{T} + A_{k,2} + A_{k,3}T + A_{k,4}\ln T \quad ...(3)$$

$\Delta G_i'$ is a week function of temperature [4] and is a function of the structure of the molecule from the view point of the presence of different groups, the number of carbon atoms in the largest ring and the location of the branches in a molecule. Fredenslund and Rasmussen have proposed a different correlation for each group. The correlations are linear functions of temperature for some groups. In this work, a new procedure for obtaining the dependence of is introduced.

$$\Delta G_i'' = \sum_k \sum_j v_{kj}^{(i)} \Delta g_{kj}'' \quad ...(4)$$

The second term of Eq. 1 is the residual contribution, which is calculated by UNIFAC method as below:

$$\ln\Gamma_k^{(i)} = Q_k \left[1 - \ln\left(\sum_m^m \theta_m^{(i)} \psi_{mk} \right) - \sum_m^m \frac{\theta_m^{(i)} \psi_{km}}{\sum_n^n \theta_n^{(i)} \psi_{nm}} \right] \quad ...(5)$$

$$\theta_m^{(i)} = \frac{Q_m v_m^{(i)}}{\sum_n^n Q_n v_n^{(i)}} \quad ...(6)$$

$$\psi_{nm} = \exp\left(\frac{-a_{nm}}{T} \right) \quad ...(7)$$

In Eqs. 5-7 Q is the constant representing the group surface, is the summation of the area fraction of group m in molecule i, is the group interaction parameter and is a measure of the interaction energy between groups and is energetic interaction between group m and n.

Table 1: Parameters for Δg_k (J/mol), Average, Root Mean Square Deviation.

Our No.	$A_{k,1}$	$A_{k,2}$	$A_{k,3}$	$A_{k,4}$	AAD %	RMSD	R^2
1	-1.127957E+04	-2.514455E+04	1.423447E+01	4.352953E+03	6.035604	0.082216	0.988943
2	-2.505042E+05	-1.318758E+04	-8.354845E-01	1.993524E+03	6.035604	0.082216	0.988943
3	-4.781359E+05	1.451928E+04	-9.203898E+00	-3.396957E+03	7.878507	0.101211	0.986871
4	6.561573E+06	-1.851088E+05	-6.330330E+01	2.951178E+04	15.752890	0.193023	0.965818
5	6.220684E+06	-2.013580E+05	-3.155745E+01	3.308874E+04	55.772273	0.613053	0.442643
6	-1.631648E+07	4.943819E+05	9.835866E+01	-8.328138E+04	45.547180	0.500336	0.616662
7	-1.186104E+07	3.227619E+05	3.861353E+01	-5.305674E+04	31.237050	0.322232	0.797367
8	-1.068807E+05	-7.701109E+03	3.918814E+00	1.271866E+03	8.242045	0.107101	0.986720
9	3.372766E+04	-9.579847E+03	4.845912E-01	1.366798E+03	17.148776	0.201954	0.959271
10	-2.736007E+04	-7.006887E+03	7.164323E-01	9.715681E+02	11.997182	0.155530	0.976572
11	6.575525E+05	-2.966663E+04	-9.208088E+00	4.748907E+03	14.532157	0.171835	0.985276
12*	8.504856E+05	-3.347936E+04	-1.297019E+01	5.207861E+03	14.532157	0.171835	0.985276
13	7.526280E+06	-2.371378E+05	-4.283566E+01	3.930046E+04	60.406764	0.651243	0.524303
14	2.894187E+06	-8.868985E+04	-1.665888E+01	1.441115E+04	37.021069	0.468200	0.483693
15	-	-	-	-	-	-	-
16*	-5.155850E+06	1.462680E+05	3.114366E+01	-2.438186E+04	0.048299	0.000554	0.999999
17	-	-	-	-	-	-	-
18*	-3.633669E+06	9.786927E+04	1.675100E+01	-1.667247E+04	0.048299	0.000554	0.999999
19	-8.844901E+05	1.601227E+04	1.005501E+01	-2.817918E+03	10.768506	0.142003	0.979231
20	3.456509E+04	-1.080543E+04	1.383821E+00	1.439093E+03	9.529110	0.124530	0.984414
21	-5.423793E+04	-4.585528E+03	1.082175E+00	7.426856E+02	21.738593	0.382814	0.908310
22	2.411664E+06	-5.154640E+04	-7.042193E+00	7.760181E+03	21.738593	0.382814	0.908310
23	-4.381115E+07	1.143939E+06	1.868607E+02	-1.858234E+05	83.789066	0.891470	0.266973
24	1.012842E+05	-1.161636E+03	-3.349938E+00	-2.291968E+01	27.264122	0.331223	0.892594
25	3.657540E+06	-2.291589E+05	1.703115E+01	3.519349E+04	27.346419	0.308353	0.864532
26	-4.681999E+07	1.318770E+04	2.370210E+02	-2.174846E+05	95.813364	0.969128	0.058643
27	1.314185E+06	-2.702740E+04	-8.128309E+00	3.687168E+03	27.484676	0.413632	0.961816
28	1.963555E+05	-6.513485E+03	2.477658E+00	6.661400E+02	54.211133	0.606619	0.602351
29*	-1.825893E+06	5.285610E+04	7.215419E+00	-9.151695E+03	0.263359	0.003139	0.999967
30	1.084027E+07	-2.697217E+05	-4.595489E+01	4.300021E+04	64.642235	0.756185	0.146713

Optimization of the parameters of the model

To optimize the parameters of the model the Root Mean Square Deviation (RMSD) of the relative error in predicting the vapor pressure of 456 number of pure compounds have been minimized. The RMSD is defined by Eq.15. Subscripts *i* and *j* stand for the number of pure compounds and number of experimental data points for each compound, respectively.

$$RMSD = \sqrt{\frac{1}{\sum_{i}^{N_C} N_T(i)} \sum_{i}^{N_C} \sum_{j}^{N_T(i)} \left(1 - \frac{P_i^{sat,p}(T_j)}{P_i^{sat,e}(T_j)}\right)^2} \quad ...(8)$$

The range of reduced temperature has been chosen to be 0.45-0.95 with 0.1 intervals. The maximum pressure for the correlation is 35 atm, which is higher than the maximum pressure of which is 3 atm.

The minimum value produced by optimization depends on the initial guess. For other groups, initial guess is chosen randomly. In order to provide confidence that obtained minimum value is the true global minimum of the optimization, all groups is again optimized by initial random guesses. The fitting function was minimized using "*Nedler-Mead simplex direct search*" algorithm. This is a direct search method that does not use numerical or analytic gradients. On the other hands, the algorithm find minimum of unconstrained multivariable function using derivative-free method.

RESULTS AND DISCUSSION

Based on the criteria proposed by Marrero, a comprehensive set of first-order groups based on UNIFAC groups has been defined. The most important issue in determining first-order groups is that atom of the molecule should not be included in more than one group groups. On the other hands, no group should not be overlapped to any other first-order group. The contributions from first-order groups that construct a wide variety of hydrocarbon compounds including aliphatic, aromatic, heterocyclic, cycloaliphatic and many other different classes of hydrocarbon compounds are introduced in Table 1.

First, the Gibbs free energy without considering the molecular structure is obtained. In this one, the Gibbs free energy is only function of temperature. After that, besides to the temperature consequence, effect of molecular structure is considered.

As it is observed, the error is reduced which is attributed to using PR EOS, the combinatorial term for the groups and fugacity coefficient. Optimization is performed respectively based on our No. in Table 1.

CONCLUSIONS

In this study, group contribution method based on UNIFAC groups has been developed for prediction of pure hydrocarbon vapor pressure as function of temperature and molecular structure. The method requires knowledge of only the molecular structure.

According to the result presented, the proposed method yielded results that compared to existing similar models, is more accurate in predicting the vapor pressure of pure hydrocarbon compound when the effect of material structure to be considered. The method finds most useful application in the wide-pressure region. Equations related to the gas - liquid equilibrium with regard to molecular structure of compounds was developed. Considering molecular structure of compound was increased model accuracy and decreased error less than 15 percent. It is worth noting that in previous similar models due to withdraw from these parameters, vapor pressure prediction error significantly is higher than the present model.

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