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The Applications of Quantum Mechanics Simulation for Solvent Selection in Chemicals Separation

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***Abstract*—**The quantum mechanics simulation was applied for calculating the interaction force between 2 molecules based on atomic level. For the simple extractive distillation system, it is ternary components consisting of 2 closed boiling point components (*A*, lower boiling point and *B*, higher boiling point) and solvent (*S*). The quantum mechanics simulation was used to calculate the intermolecular force (interaction force) between the closed boiling point components and solvents consisting of intermolecular between *A*-*S* and *B*-*S*.

The requirement of the promising solvent for extractive distillation is that solvent (*S*) has to form stronger intermolecular force with only one component than the other component (*A* or *B*). In this study, the systems of aromatic-aromatic, aromatic-cycloparaffin, and paraffin-diolefin systems were selected as the demonstration for solvent selection. This study defined new term using for screening the solvents called relative interaction force which is calculated from the quantum mechanics simulation. The results showed that relative interaction force gave the good agreement with the literature data (relative volatilities from the experiment). The reasons are discussed. Finally, this study suggests that quantum mechanics results can improve the relative volatility estimation for screening the solvents leading to reduce time and money consuming .

***Keywords*—**Extractive distillation, Interaction force, Quamtum mechanic, Relative volatility, Solvent extraction.

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I. Introduction

THE separation process is one of the important parts in chemicals industry. Normally, the chemicals in these industries mostly are the closed boiling point components which leads to difficulty in separation. One of techniques that employed to separate the closed boiling point components in commercial scale is extractive distillation. The key success factor for this technique is solvent design/selection. The general method to select the solvent is experimentally trial&error method (nonsystematic selection) which employed time consuming and chemical cost of the test. Some attempts on the model prediction of separation efficiency applying group contribution method (GC) was proposed to avoid nonsystematic method. The equation that uses to estimate the separation efficiency (called relative volatility) is shown in (1).

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Typically, in the GC, UNIFAC is one of the most famous methods which used to estimate the activity coefficient, γ_i.

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^0}{\gamma_i P_i^0} \quad (1)$$

The GC method calculates the interaction forces between the groups of the components in which the activity coefficient can be separated into 2 terms as shown in equation below.

$$ln\gamma_i = ln\gamma_i^C + ln\gamma_i^R \quad (2)$$

These 2 main terms are interactions dued to the molecular size and shape (γ_i^C) and intermolecular forces represented by (γ_i^R) the corresponding group interaction parameters. After calculation the activity coefficient of each component , these values were pluged into (2) in order to find the separation efficiency.

However, there is literature [1] showed that steric and molecular size of the solvent affect to the separation efficiency. M. L. Waters [2] proposed the effect of molecular shape on the interaction position and energy of benzene ring (aromatic) by using molecular mechanic. This research showed that aromatic with para-shape form strongly interaction with benzene ring. Therefore, in this study the quantum mechanics method was introduced as tool for calculating interaction forces of solvents and interested components and compare with the relative volatility of 3 systems using various solvents.

II. Theories

In extractive distillation or liquid-liquid extraction, an additional solvent (separating agent, entrainer) is used to change the relative volatility of the components to be separated. In this way, it is possible to obtain one pure component at the top of one column and the other, together with the solvent at the bottom, which may be separated easily in a secondary distillation column due to the high boiling point of the solvent. The solvent must be miscible with the separated components. The basic concept of miscibility is "Like dissolved Like" consisting of hydrogen bonding, polar, and dispersion interaction forces. In considering whether *A* component will dissolve in a liquid three possible interactions should be considered. In two-component system namely *A* and *B*, there are 3 interaction among these 2 components which are *A*-*A*, *B*-*B*, and *A*-*B*. If *A*-*B* interaction is strong or comparable to *A*-*A* or *B*-*B* associations then two liquid components are likely to be miscible and mixed with each other.

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According the deffinition of interaction forces between 2 molecules which is despripted in the previous paragraph. The first force which is the common for all component pairs is the instantaneous dipole - induced dipole interaction or dispersion force. When 2 components are attached together, the partial positive charge of one dipole will attract the partial negative in the neighboring molecule or vice versa.

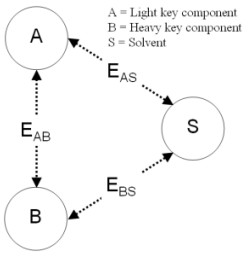


Fig. 1 The possible intermolecular forces

The second interaction force is permanent dipole and permanent dipole interactions (hydrogen bonding). If two atoms constituting a bond have significantly different electronegativities, the bond will be permanent polar and produce a permanent polar molecule. In generally, this type of interaction force occurs with hydrogen compound which attach with oxygen, nitrogen, and halide group. The last one is the interaction force that performs by permanent dipole and induced dipole interactions. This type of interaction force can be found between hydrocarbon and highly polar component such as HCl, alcohol component, and carboxylic acid component. The summations of these terms are applied in many applications. One of the most famous theories which is related to the interaction force is the solubility theory. Hansen et al. [3] mentioned that total solubility is related to 3 terms consisting of dispersion (δ_d), hydrogen bonding (δ_h), and polar (δ_p) solubility parameters as (3).

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{3}$$

The cohesive energy density (*CED*) is one calculation by appliying this concept. *CED* defined as the needed energy to evaporate one mole of liquid to be one mole of vapor which equals to internal energy called cohesive energy (E_{coh}).

$$CED = \frac{E_{coh}}{V_i^L} = \frac{\Delta U_i}{V_i^L} = \left(\frac{\Delta H_{vi} - RT}{V_i^L} \right) \tag{4}$$

Whereas V_i^L is liquid molar volumn, ΔU_i is internal energy of component i, ΔH_{Vi} is enthalpy of vaporization of component i, T is temperature, and R is gas constant. Hildebrand [4] defined the solubility parameter as:

$$\delta = CED^{1/2} = \left(\frac{\Delta U_i}{V_i^L} \right)^{1/2} = \left(\frac{\Delta H_{vi} - RT}{V_i^L} \right)^{1/2} \tag{5}$$

This equation is appropriated for the non-polar component because of no polar and hydrogen bonding effects. Therefore, the E_{coh} in polar component have to combine 3 forces together as shown in (6).

$$E_{coh} = \Delta U_i = E_d + E_p + E_h \tag{6}$$

When the 2 components are closed, the energy to attach these components together is E_{coh}. The E_{coh} in term of the solubility parameters are expressed the literature [4] as shown in (7).

$$E_{coh} = \Delta U_i = \Delta \delta_{ij} = \sqrt{(\delta_{d,i} - \delta_{d,j})^2 + (\delta_{p,i} - \delta_{p,j})^2 + (\delta_{h,i} - \delta_{h,j})^2} \tag{7}$$

Therefore, this value can be applied to calculate the interaction force between 2 components (i and j are 2 difference components). From Fig. 1, there are 3 components in the system. *A* and *B* are closed boiling point components while *S* represents solvent component. There are 3 cohesive energies to concern consisting of $E_{A\text{-}B}$, $E_{A\text{-}S}$, and $E_{B\text{-}S}$. The solvent (*S*) prefers to form with component that uses lowest cohesive energy when compared with the other rest 2 pairs. Therefore, it can be concluded that the lower of mixing energy, the easier of 2 components attach together.

In order to find the suitable solvent for given system, one of the interaction forces between the components in closed boiling point system and solvent have to be estimated. However, there are many solvents in the world. The hand calculation is not easy to perform. Therefore, the quantum mechanics simulation (one computer simulation for caculating the interaction force) can be use to estimate the interaction force between 2 components.

III. Methodology

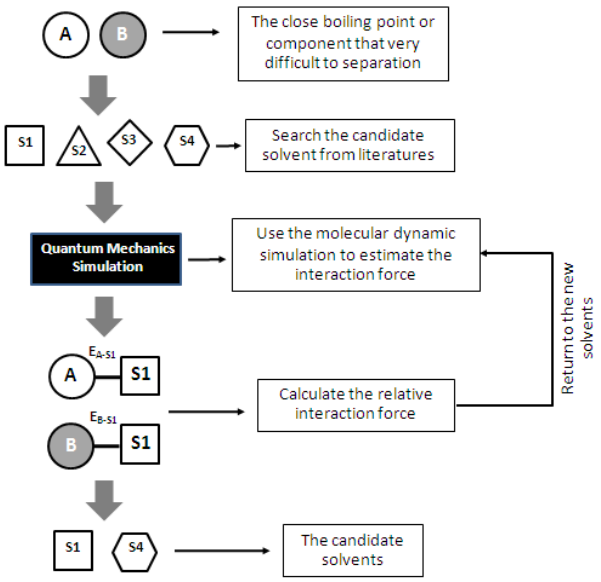


Fig 2 The methodology for screening the solvents

Fig. 2 shows the work methodology for this study. The study was started from 2 components which were very difficult to separate by using the conventional method. Afterwards, the candidate solvents were searched from the literatures or any methods leading to get the list of candidate solvents. The next step was deal with quantum mechanics simulation. All of the components including the candidate

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solvents were drawn. Quantum mechanics simulation was used to calculate and optimize the size/shape and their individual energies. Then, each solvent was matched with both 2 close boiling point components. At that time, each pair will be calculated the interaction force and compared as relative interaction force as shown in (8).

$$E_{RIF} = \left|\frac{E_{A-S}}{E_{B-S}}\right| \quad (8)$$

Whereas;

E_{RIF} = Relative interaction force between solvent and component A/B

$E_{A\text{-}S}$ = Interaction force between component A and solvent

$E_{B\text{-}S}$ = Interaction force between component B and solvent

The E_{RIF}'s were calculated and compared with every solvent. The high E_{RIF} value means the high potential solvent to separate this system. Therefore, following this methodology the solvent can be screened.

IV. Case Studies

In the petrochemical industry, there are many hydrocarbon types which are difficult to separate because of closed boiling point or azeotrope components. Therefore, the solvent base separation is one alternative method which can separate these components apart. In this study, the quantum mechanics simulation is applied into 3 case studies consisting of aromatic-aromatic, aromatic-cycloparaffin, and paraffin-diolefin systems.

A. Aromatic-Aromatic Separation

The closed boiling point aromatic-aromatic separation is one of difficult technique because the similar structure and electron density. Therefore, the steric effect is play important role for selecting the solvent in this case. This case study is focus on the aromatic-aromatic separation from literature in order to compare the result between computer simulation and literature results. 10 solvents (Table I) were selected from the literatures [4] in order to prove the application of computer simulation. E_{RIF} is calculated by using (8). This equation consists of 2 important terms which are $E_{A\text{-}S}$ and $E_{B\text{-}S}$. The quantum mechanics simulation can estimate these interaction forces. The results from this simulation showed in Table I.

The second column is the relative interaction force which calculated from (8) while the forth column is the relative volatility which collected from literatures [4]. Even though, the values of these 2 parameters of the same solvent were not equal, the trends of these values were significant related. This showed that the relative volatility can be predicted by using this relation. Regarding to the significant relationship of these 2 parameters, the solvent screening can be used this parameter as well. In addition, the E_{RIF} and relative volatility (α_{ij}) were ranking as shown in the third and fifth columns. It was found that the ranking of the potential of solvent were good agreement.

From Fig. 3, it was found that the relationship of these 2 parameters fitted at 89.5% sum square error (R^2) which is good enough. The rest percentage, 10.5%, of sum square error can be explained by others uncontrollable factors such as molecular weight, density, and solvent to feed ratio.

TABLE I
SOLVENTS FOR SEPARATING AROMATIC-AROMATIC COMPOUNDS

Solvent Names	E_{RIF}	Ranking E_{RIF}	α_{ij}	Ranking α_{ij}
Pentachlorobutoxybenzene	1.347	1	1.260	1
2,4,5-trichlorophenol	1.150	2	1.147	2
2,4,6-trichlorophenol	1.100	3	1.136	3
P-dichlorobenzene	1.051	7	1.116	4
O-dichlorobenzene	1.069	5	1.095	5
O-chloronitrobenzene	1.071	4	1.094	6
P-chlorophenol	1.060	6	1.090	7
P-nitroanisole	1.014	8	1.085	8
P-chloroanisole	1.004	9	1.075	9

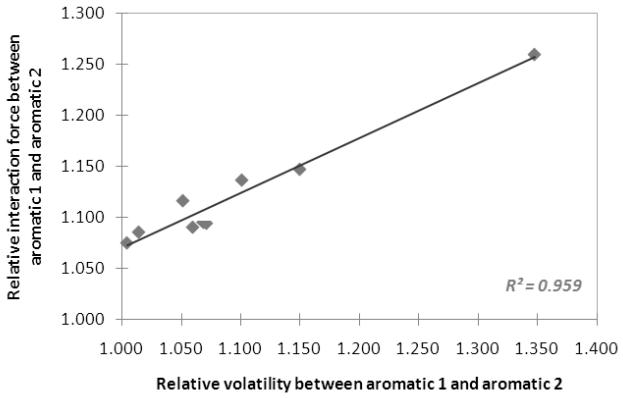


Fig. 3 The relationship between relative volatility from literatures and relative interaction forces (E_{RIF}) calculating from quantum mechanics simulation of aromatic 1 and aromatic 2 at various solvents

In addition, there were 10 solvents which collected from literatures showed that the high potential solvents for separating aromatic-aromatic system have to be aromatic components as well. M. L. Waters [5] showed that the aromatic-aromatic interaction force is the strongest interaction force when compared with the other hydrocarbons.

B. Aromatic-Cycloparaffin Separation

In this case study, it is difference from the first case because, this case, the shapes of these 2 components are quite the same except the polarity. The aromatic compound will have the high electron density at the middle leading to be negative charge at the cavity. On the other hand, the cycloparaffin will have the positive charge because of the hydrogen atom arrangement. Therefore, the solvents which can be separated the aromatic and cycloparaffin have to be either strong positive charge interacting with aromatic or strong negative charge interacting with cycloparaffin. In this case, there were 10 solvents which were collected from the

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literatures [6, 7]. The results from the simulations were followed this hypothesis which showed in Table II.

TABLE II
SOLVENTS FOR SEPARATING AROMATIC-CYCLOPARAFFIN COMPOUNDS

Solvent Names	E_{RIF}	Ranking E_{RIF}	α_{ij}	Ranking α_{ij}
Adiponitrile	3.195	2	3.270	1
Morpholine	3.222	1	2.210	2
Phenol	2.909	3	1.800	3
Ethyl acetoacetate	1.617	5	1.700	4
1-methoxy-2-propanol	1.604	6	1.650	5
Cresol	1.427	7	1.600	6
Ethyl acetate	1.215	10	1.600	6
Dimethylsulfoxide	1.363	8	1.370	8
Sulfolane	1.747	4	1.350	9
N-methyl-2-pyrolidone	1.263	9	1.300	10

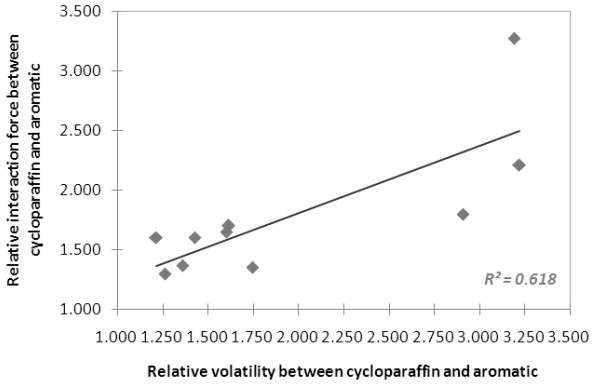


Fig. 4 The relationship between relative volatility from literatures and relative interaction forces (E_{RIF}) calculating from quantum mechanics simulation of cycloparaffin and aromatic at various solvents

However, from Fig. 4, it was shown that the plot between these 2 parameters was fair acceptation (61.8%) because the sum square error (R^2) is larger than 60% but lower than 70%. From the quantum mechanics simulation result, it was found that this system was one of the most difficult cases in separation because these 2 components (aromatic and cycloparaffin) are matching in polar (i), their boiling points are much closed (ii), and most of these systems are azeotrope systems which are very strong interaction forces (iii). Moreover, the ranking of these 2 parameters were compared in Table II. It was found that the ranking of E_{RIF} was shown the fair agreement with the ranking of relative volatility. Namely, the first five solvents which were selected by these 2 parameters were almost the same.

The solvents in Table II were strong positive charge and large positive area such as morpholine, and adiponitrile (from the simulation). These solvents prefer to form the interaction force with aromatic than the paraffin leading to high E_{RIF} which can be confirmed by the high relative volatility of aromatic and olefin using these 2 solvents. However, the other factors, such as molecular weight and solubility were required to fulfill the solvent screening result.

C. Paraffin-Diolefin Separation

Normally, the paraffin and diolefin in chemicals are the light hydrocarbons (*C1-C5*) which are very low boiling point. The separation by using solvent is very difficult to test in laboratory (high pressure and low temperature) because of expensive laboratory equipment. Furthermore, these 2 components are difficult to separate as well because these 2 components are closed boiling point. Therefore, the computer simulation is one alternative that can be applied to reduce the expense from laboratory.

There were 14 solvents which collected from literatures [8]. In these solvents, there were only 5 solvents that have the data from literature (relative volatility) while the rest solvents are the co-solvents to separate the paraffin and diolefin. Therefore, they will not be compared the E_{RIF} with relative volatility. However, these solvents can improve the relative volatility.

In this case study, generally, paraffin is not polar component while the diolefin/olefin is slightly negative charge component at double bond position(s). Therefore, the appropriate solvents have to be positive charge. From the literature, it was found that the most of the solvent for separating paraffin and diolefin is cyclic organic compounds such as sulfolane, aniline, morpholine, and dioxane which were positive charge solvents.

Recalling the E_{RIF}, this equation refers to the comparative interaction force between 2 components (*A* and *B*) with given solvent. If this value is larger than 1, it means that the solvent forms stronger interaction force with *A* than *B*. On the others hand, if this value is smaller than 1, it means that the solvent forms weaker interaction force with *A* than *B*.

TABLE III
SOLVENTS FOR SEPARATING PARAFFIN-DIOLEFIN COMPOUNDS

Solvent Names	E_{RIF}	Ranking E_{RIF}	α_{ij}	Ranking α_{ij}
Aniline	3.159	1	2.245	1
3-methoxypropionitrile	2.253	7	1.475	2
Acetonitrile	2.076	8	1.450	3
Morpholine	1.774	10	1.344	4
Dimethyl-sulfoxide	1.708	11	1.295	5
N-hydroxy-ethylpyrrolidone	3.025	2	-	-
Sulfolane	2.771	3	-	-
Phenol	2.541	4	-	-
Dioxane	2.280	5	-	-
Butylolacetone	2.254	6	-	-
N-hydroxy-ethylphthalimide	1.804	9	-	-
3-formyl-morpholine	1.449	12	-	-
Acetylacetone	1.266	13	-	-
N-acetonyl-morpholine	1.220	14	-	-

From Table III, the E_{RIF} for paraffin and diolefin separation using these solvents, the simulation showed that these solvents are approporiate sovents because E_{RIF} which calculated from

quantum mechanics simulation give high value (larger than 1.2).

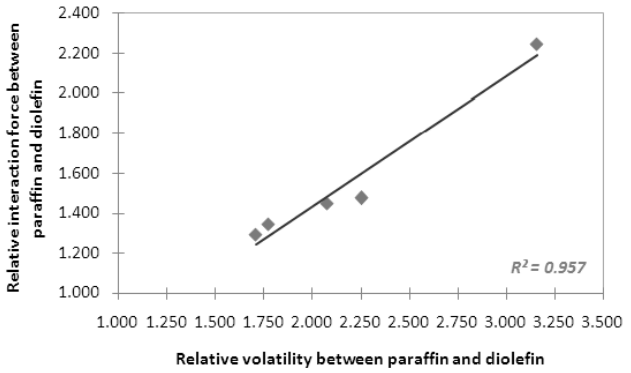


Fig. 5 The relationship between relative volatility from literatures and relative interaction forces (E_{RIF}) calculating from quantum mechanics simulation of paraffin and diolefin at various solvents

Moreover, the existing relative volatility of 5 solvens (acetonetrile, dimethyl sulfoxide, anilline, 3-methoxy propionitrile, and morpholine) were significant related to the E_{RIF} because, from Fig. 5, it was found that the sum squuare error (R^2) of this relation was 95.7% including their rankings.

V. Conclusion

There are many components in chemicals industry which are very difficult to separate such as close boiling point and azeotrope components. If these components have to be separated, the solvent based separation techniques such as extractive distillation and liquid-liquid extraction are potential one. In addition, the key success factor for this technique is using appropriate solvent which can be obtained from solvent selection method. Generally, there are few solvent selection concepts such as UNIFAC equation using to predict relative volatility and experiment that using to find predicted or real relative volatility of system respectively. These techniques seem likely to consume too much time and chemicals especially experiment. Quantum mechanics simulation is one solution that can reduce these consumptions. The concerned parameter from this simulation is interaction force between solvent and given close boiling point components. After that, the relative interaction force can be calculated from this parameter and compared with relative volatility from literatures. The simualtion results show that the relative volatilities of each system at vaious solvents were the same trend with the E_{RIF} parameters. The sum square error of the trend between relative volatility and E_{RIF} for aromatic-aromatic, aromatic-cycloparaffin, and paraffin-diolefin case studies were 89.5%, 61.8%, and 95.7%, respectively. According to the simulation results, it can be concluded that the appripropiate solvents for separating aromatic-aromatic systems were the aromatic oganic compound with strong positive charge and high steric effect. The recommended solvents for separating aromatic-cycloparaffin were less negative charge and greater positive charge area. In order to separate paraffin and diolefin, the cyclic solvents such as aniline, sulfolane, and dioxane were recommended because their character (small positive charge area) was matched with diolefin component. However, the other factors/properties of solvents such as boiling point, molecular weight, and solubility should be taking account into solvent screening in order to fulfill the screening results. However, the laboratory is still required for proving the high potential solvents obtaining from simulation result. In addition, the appropriate solvent to feed ratio, which is one of the important factor for selecting the solvent and for operating conditions design, are required to set up laboratory as well.

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