



Chapter Three

THEORETICAL FRAMEWORK

3.1 Intermolecular Forces

The thermodynamic properties of a given mixture are affected by the intermolecular forces acting on all of its components. In order to determine these forces, it is important to identify the nature of the individual components in the mixture, whether they are nonpolar, polar, or ions. For organic compounds, their polar or nonpolar nature can be identified based on the balance or imbalance in their electron density distribution, where the latter causes a given compound to have positive and negative ends that will allow them to be attracted to other components. On the other hand, ions can be identified from the salts present in the mixture because these salts dissociate when added into the mixture. The nature of the components causes them to associate and interact with specific type of intermolecular forces.

There are different intermolecular forces that can act among the components: dispersion forces, dipole-induced dipole forces, dipole-dipole forces where the strongest type are the hydrogen bonds, ion-dipole forces, and ion-ion forces. The weakest forces are the dispersion forces which are always present in any interaction of components, but is mainly present in the interaction of nonpolar components. The existence of this force between components is caused by the displacement of electrons on one side of the given component, hence making it instantaneously polar and allowing it to be attracted to other components. This is followed by dipole-induced dipole forces which are present in the interactions between nonpolar and polar components. The polar component induces the nonpolar component to have positive and negative ends, thus making it polar and allowing the attraction between them. Next is the dipole-dipole forces which allows the interaction of polar components. A special type of these forces are the hydrogen bonds, which are caused by the presence of H in one component and atoms N, O or F in the other component. This is the strongest type of dipole-dipole force since the highly electropositive H from one component is bonded to a highly electronegative N, O or F of another component. The



following intermolecular forces discussed so far are typically present in the interaction of water and organic solvents.

On the other hand, for interactions involving ions of salts, the attractive forces present are stronger than the previous intermolecular forces discussed. It is because ions are permanently charged, hence they are more capable of forming stronger attractions with other components. One of which is the ion-dipole force which exists in the interaction of ions with polar components. Another force is the ion-ion force which is present in the interaction of oppositely charged ions in solution, an example of which is the attraction of sodium and chloride ions in aqueous solution. Among the forces discussed, this is the strongest type of intermolecular force.

Table 3.1. Relative Strengths of Intermolecular Forces

Intermolecular Force	Relative Strength (kJ/mol)
Dispersion	0.05-40
Dipole-induced dipole	2-10
Dipole-dipole	5-25
Hydrogen bond	10-40
Ion-dipole	40-600
Ion-ion	400-4000

Since polar compounds with electronegative atoms (N and O) are present in the systems considered in this study, strong intermolecular forces in the form of hydrogen bonds will exist, as well as weak dispersion forces that are always present in any interaction involving polar compounds. For example, in ethanol + water + TRIS system, these intermolecular forces are present where the hydrogen bonds are caused by the interactions involving the OH group of ethanol and the OH and NH₂ groups of TRIS. For systems with salt, forces such as ion-dipole and ion-ion forces are additionally present. The existence of several groups with electronegative atoms in a given component is also important since it allows the component to form strong interaction with the other components. For example, since TRIS has multiple groups with electronegative N and O atoms, then it is capable of forming stronger interactions in a given system than the other components with few or no such groups.

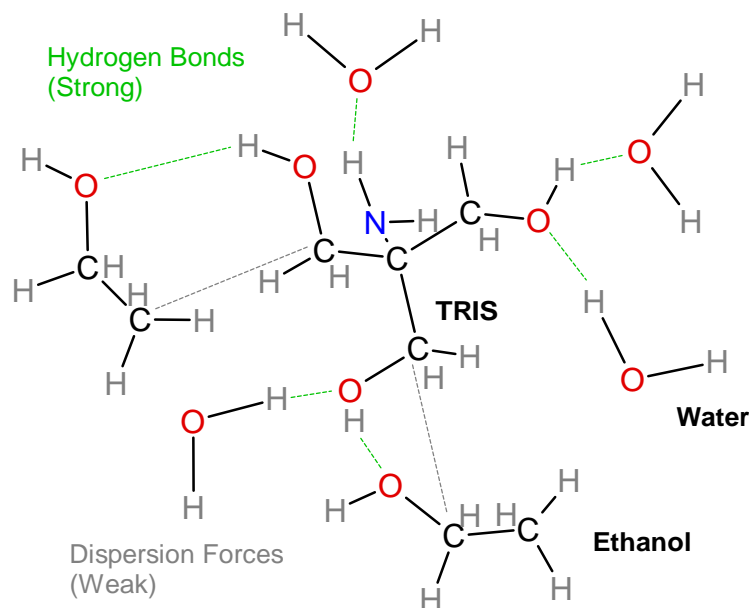


Figure 3.1. Intermolecular Forces in Ethanol + Water + TRIS System

The intermolecular forces have a consequence in the thermodynamic properties of different systems such as boiling points and liquid and vapor phase compositions. These forces explain why certain systems have higher boiling points or higher concentration of a certain component in the liquid or vapor phase over other systems. Thus, intermolecular forces are important in the understanding of the thermodynamic properties of a given system.

3.2 Theories of Salt Effects

The interaction of the ions of salts with the other components in a given solution can be understood using theories of salt effect. Theories of salt effect can explain why a given salt, when added to a given solution, has a strong interaction with a certain component rather than with the other components. This has an effect on the volatility and solubility of the components in the solution. The interaction of salt with the other components of the solution can be explained by hydration, electrostatic, and van der Waals theories.



3.2.1 *Hydration Theory*

Hydration theory explains the interaction of the salt in a given mixture of water and nonelectrolytes such as alcohols. For a given alcohol-water mixture, when a salt is added into the mixture, the ions attract several water molecules around them, where the number of surrounding water molecules is known as the hydration number. The water molecules that are attracted to the ions become unavailable for the interaction with the alcohol molecules. As a result, the alcohols are left behind which can be readily separated from the solution either by extraction or vaporization. Thus, the application of this theory can be helpful in separating alcohols from water.

The number of water molecules surrounding a given ion depends on the nature of the ion. The nature of the ion determines the orientation of water molecules around it, where the right orientation causes it to attract several water molecules. Typically, the ions that are smaller in size can attract several water molecules because of greater charge density per unit volume and greater space around them. Hence, they are the most effective in separating the alcohols from water in the solution.

3.2.2 *Electrostatic Theory*

This theory shows why a solvent such as water are strongly attracted to the ions in a given mixture. According to the theory, the ions strongly attract water molecules because of their electrostatic fields and the high polarity of water. Hence, coulombic forces exist between them. As a result of this strong attraction, the other solvents present in the mixture can easily escape into the vapor phase. Thus, the application of this theory is useful for the separation of the less polar solvents from the significantly polar ones such as the mixture of alcohols and water.

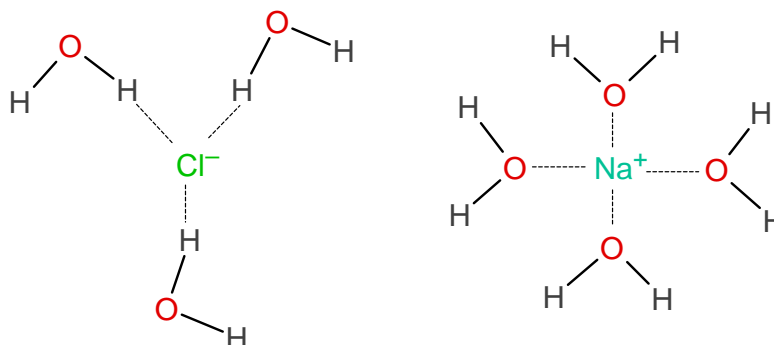


Figure 3.2. Interaction of Ions and Water by Electrostatic Forces

3.2.3 *Van de Waals Forces Theory*

This theory is helpful in explaining a few cases that are not consistent with the electrostatic theory. In these cases, it is the less polar nonelectrolytes such as alcohols that form stronger attraction with the ions instead of highly polar components such as water. According to this theory, aside from the coulombic or electrostatic forces, the dispersion forces between the ion and a given component such as alcohol must be considered since these forces may not be negligible. It is because it is possible that a given ion may have a large surface area or a weak electrostatic field, which causes a given alcohol, possibly with a large surface area, to have a strong attraction with it by dispersion forces. In this case, the dispersion forces are already significant, which should already be taken into account if the effects of the salt in the solution are being studied.

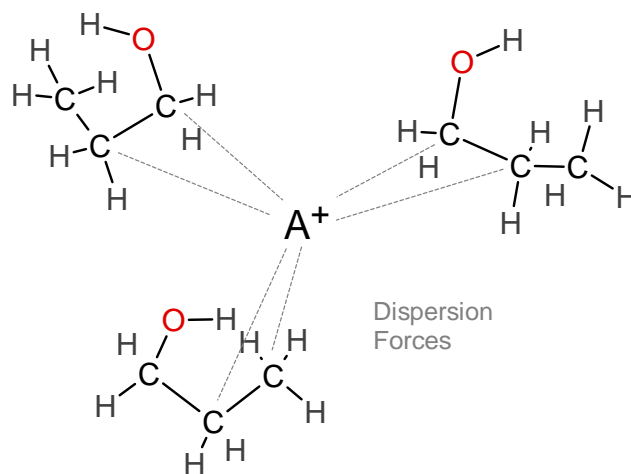


Figure 3.3. Interaction of Ion with Components by Dispersion Forces



3.3 Salting-Out and Salting-In Theories

It has been mentioned that the addition of salt into the mixture causes the attraction of certain components into the ions while leaving behind the other components in the solution. The attraction of certain components by the salt causes these components to increase their solubility into the solution, where the phenomenon is called salting-in effect. As a result, the other components become less soluble and more isolated, allowing them to readily escape out of the solution. This phenomenon is called the salting-out effect. These phenomena can be explained using the theories on the intermolecular forces and the salt effects previously mentioned. For mixtures of water and alcohols, upon the addition of salt, water is typically being salted-in into the solution while the alcohols are being salted-out. According to hydration and electrostatic theories, this is because of the attraction of water molecules through the strong electrostatic fields of ions, forming stronger ion-dipole interactions. As a result, water molecules, upon being salted-in, become unavailable for the alcohols, thus, alcohols are salted-out from the solution.

Since the size of a given ion usually determines the number of water molecules that surrounds it, then the ionic size also determines the significance of the salting-in and salting-out effects. As mentioned, the smaller the ionic size, the greater the water molecules that can be attracted, hence the greater is the salting-in effect for water and the salting-out effect for the alcohols.

In a few cases for large ions, the alcohols are being salted-in and water is being salted-out. This is because large ions have weak electrostatic fields and large surface area, thus, they can easily associate through dispersion forces with the less polar components such as alcohols, especially if the alcohols are long-chained.

The salting-in and salting-out phenomena have an effect on the thermodynamic properties of mixtures with salt. The addition of salt typically increases the bubble point of a given mixture, which is because of the formation of strong interactions between the salt and the components in the solution. Furthermore, it also results to the increase or decrease in the vapor composition of the components, where the former is because of the salting-out



effect while the latter is because of the salting-in effect. Since the salt affects the properties of a given mixture, they are widely used in the improvement of the distillation processes which requires the understanding of the vapor-liquid equilibrium (VLE).

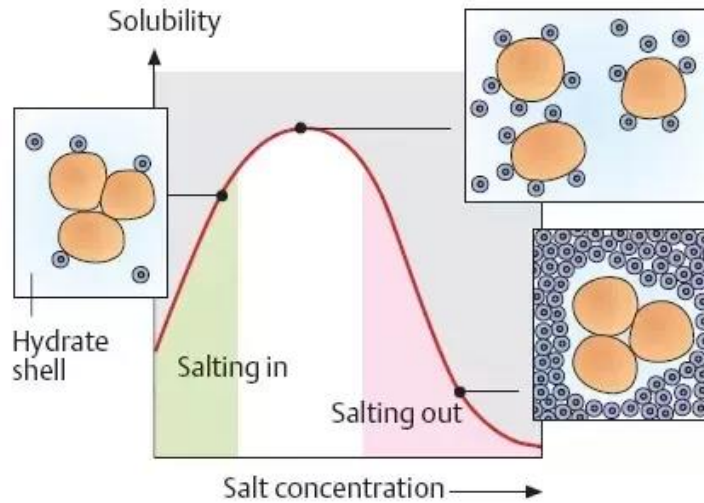


Figure 3.4. Salting-Out and Salting-In Effects in the Mixture
(Source: https://en.wikipedia.org/wiki/Salting_out)

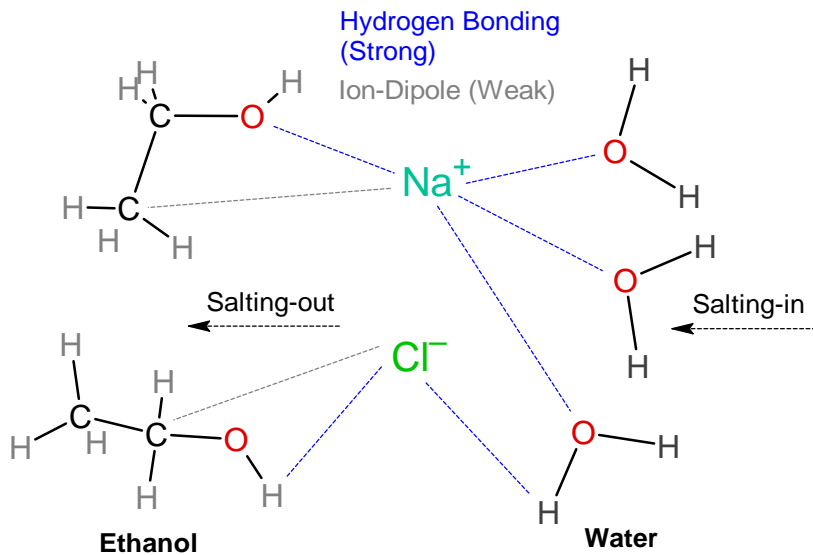


Figure 3.5. Salting-in and Salting-out Effects and Intermolecular Forces in Ethanol-Water Mixture with Salt



Table 3.2. Solubility of NaCl and KCl in Various Solvents

Component Number	Component	NaCl Solubility (per 100 g solvent)	Reference Temperature (°C)	KCl Solubility (per 100 g solvent)	Reference Temperature (°C)
1	Ethanol	0.065	18.5	0.051	20
2	Water	35.9	20	34.4	20
3	Glycerol	8.2	25	6.7	25
4	Ethylene Glycol	7.1	30	5.4	30
5	1-Butanol	0.005	20	0.005	25
6	1-Propanol	0.012	25	0.004	25
7	2-Propanol	0.0027	25	0.0023	25

3.4 Vapor-Liquid Equilibrium (VLE)

Fundamentally, two phases α and β are in equilibrium if all of their components i have equal fugacity in both phases (Lewis, 1901), hence:

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \quad (3.1)$$

For vapor-liquid equilibrium, which involves the coexistence of both the liquid and vapor phases at equilibrium, the equation can be rewritten by setting $\alpha = V$ and $\beta = L$:

$$\hat{f}_i^V = \hat{f}_i^L \quad (3.2)$$

For the vapor phase, the fugacity of component i in the vapor mixture, \hat{f}_i^V , can be determined using the equation:

$$\hat{f}_i^V = \hat{\phi}_i y_i P \quad (3.3)$$

where $\hat{\phi}_i$ is the fugacity coefficient of component i in the vapor mixture, y_i is the vapor mole fraction of component i , and P is the total pressure.



For the liquid phase, the fugacity of component i in the liquid mixture, \hat{f}_i^L can be expressed in terms of the fugacity of pure component i , f_i^L , the activity coefficient, γ_i and the liquid mole fraction of component i in the liquid mixture, x_i :

$$\hat{f}_i^L = \gamma_i x_i f_i^L \quad (3.4)$$

Activity coefficient is defined as the measure of deviation of the characteristics of the components in mixture to their characteristics when present in an ideal solution. A solution is ideal if the total intermolecular forces from the interactions of the same components is equal to that of the interactions of the different components.

Combining equations 3.3 and 3.4 yields the following equation:

$$\hat{\phi}_i y_i P = \gamma_i x_i f_i^L \quad (3.5)$$

For low to moderate pressures, f_i^L can be expressed as:

$$f_i^L = \varphi_i^{sat} P_i^{sat} \quad (3.6)$$

where φ_i^{sat} is the fugacity coefficient of pure component i at the saturated state and P_i^{sat} is the vapor pressure of component i , also at the saturated state.

Combining equations 3.5 and 3.6 yields the gamma/phi formulation for the VLE:

$$\hat{\phi}_i y_i P = \gamma_i x_i \varphi_i^{sat} P_i^{sat} \quad (3.7)$$

3.5 Modified Raoult's Law

Modified Raoult's Law is applied for mixtures with pressures of at most 1 atm. It assumes that the vapor phase of the mixture behaves like an ideal gas. When this assumption is applied, the values of $\hat{\phi}_i$ and φ_i^{sat} are unity, therefore, equation 3.7 becomes:

$$y_i P = \gamma_i x_i P_i^{sat} \quad (3.8)$$



The variable P_i^{sat} is defined by equilibrium temperature T provided by the Antoine equation.

$$\ln P_i^{sat}(\text{bar}) = A - \frac{B}{T(K) + C} \quad (3.9)$$

where variables A , B and C are constants.

The activity coefficient γ_i is an important thermodynamic property because it describes the strength of the interaction of the components in a given mixture. For a given component i , if $\gamma_i < 1$, then component i has a stronger interaction with the other components than with its fellow component i . If $\gamma_i > 1$, then component i has a stronger interaction with its fellow component i than with other components. For example, for a given mixture of ethanol and water, if all components have activity coefficients that are greater than 1, then the interactions of the same component, which are ethanol-ethanol and water-water interactions, are stronger than ethanol-water interactions. On the contrary, the ethanol-water interactions will be the strongest if the activity coefficients of all components are less than 1.

The activity coefficient can be calculated using various thermodynamic models, where one of the best thermodynamic models is the UNIFAC Dortmund model as will be discussed in the next section.

Table 3.3. Normal Boiling Points and Antoine Constants for Various Solvents

Component Number	Component	Normal Boiling Point (°C)	Antoine Constants		
			A	B	C
1	Ethanol	78.3	12.2917	3803.98	-41.68
2	Water	100.0	11.6834	3816.44	-46.13
3	Glycerol	290.1	10.6190	4487.04	-140.2
4	Ethylene Glycol	197.3	13.6299	6022.18	-28.25
5	1-Butanol	117.7	10.5958	3137.02	-94.43
6	1-Propanol	97.2	10.9237	3166.38	-80.15
7	2-Propanol	82.5	12.0727	3640.20	-53.54



3.6 UNIFAC Dortmund Model

The UNIFAC models are one of the most widely used group contribution models. These models assume that the interactions in the mixture are not defined by the components as a whole but by their functional or structural group constituents called subgroups. Thus, through the determination of subgroups present in a given mixture, the thermodynamic properties can already be predicted even without an available experimental data. The first of the UNIFAC models, which is the original UNIFAC model, was developed by Fredenslund et al. (1975), and is widely applicable for nonelectrolyte systems that have positive or negative deviations from Raoult's Law. The model can be applied to systems containing hydrocarbons, alcohols, esters, ketones and other organic compounds. From the application of this model to various systems, some limitations and weaknesses can also be observed. One of which are the limited conditions where the model can be used, which are only for moderate pressures and with temperatures of about 300-400 K. Furthermore, poor prediction results are obtained for systems with asymmetric components and for systems whose components have totally different sizes as the components from the first development of the model. Thus, the modification of the model to address the weaknesses mentioned has been necessary.

This led to the development of two modified UNIFAC models in the same year through the collaboration of Larsen et al. (1987) and Weidlich and Gmehling (1987). The group of Larsen et al. (1987) developed the UNIFAC Lyngby model by revising the combinatorial term of the original UNIFAC model to improve the prediction of the thermodynamic properties of asymmetric mixtures. More importantly, new temperature-dependent parameters were introduced which are different from the original UNIFAC model. The application of the resulting model showed that the prediction of thermodynamic properties at VLE has slightly improved as compared to the prediction results of the original UNIFAC. Hence, the new model can be used for a much wider range of temperatures and pressures as compared to the original UNIFAC. On the other hand, Weidlich and Gmehling (1987) developed the UNIFAC Dortmund model also by modifying the combinatorial term and by introducing new temperature-dependent parameters. However, the following



revisions performed are based on the assumptions that are different from the UNIFAC Lyngby model. Using the resulting model, it was observed that the predictions are significantly better, where the relative deviations for the activity coefficients were reduced by a factor of 2 as compared to those of the original UNIFAC (Gmehling et al., 2015). Hence, the model is currently one of the most widely-used group contribution models, which are being applied to a wide range of compounds such as alcohols, hydrocarbons, aromatics, esters and especially ionic liquids based from the recent developments.

The UNIFAC Dortmund model, similar with the other UNIFAC models, accounts for both the size and the interactions of the components in the system in the calculation of activity coefficient which can be defined as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (3.10)$$

where γ_i is the activity coefficient of component i in the system, $\ln \gamma_i^C$ accounts for the size of the components and is called the combinatorial term as previously mentioned, and $\ln \gamma_i^R$ accounts for the interaction of the components and is called the residual term.

The combinatorial and residual terms of the UNIFAC Dortmund model are defined as follows:

$$\ln \gamma_i^C = 1 - J_i' + \ln J_i' - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right) \quad (3.11)$$

$$\ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k} \right) \right] \quad (3.12)$$

where k is the corresponding number for subgroups. As mentioned, the combinatorial term was revised from the original UNIFAC model. This was performed, as shown in equation 3.11, by the introduction of parameter J_i' , where the formula for this parameter is shown:



$$J_i' = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j} \quad (3.13)$$

where j is the corresponding variable of component i . This equation is the modified form of the equation for parameter J_i from the original UNIFAC model, where the exponent $3/4$ was introduced to provide good correlation for mixtures of alkanes and alcohols (Weidlich and Gmehling, 1987).

The other variables are calculated similar to the original UNIFAC as shown:

$$J_i = \frac{r_i}{\sum_j r_j x_j} \quad (3.14)$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \quad (3.15)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (3.16)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (3.17)$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \quad (3.18)$$

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk} \quad (3.19)$$

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \quad (3.20)$$

$$s_k = \sum_m \theta_m \tau_{mk} \quad (3.21)$$



where m the corresponding variable of the subgroup k . The constants R_k and Q_k corresponds to the van der Waals volume and surface area parameters of the subgroups.

As mentioned, new temperature-dependent binary interaction parameters were introduced from the original UNIFAC model, where the modified equation is shown below:

$$\tau_{mk} = \exp\left(-\frac{a_{mk} + b_{mk}T + c_{mk}T^2}{T}\right) \quad (3.22)$$

The UNIFAC Dortmund binary interaction parameters a_{mk} , b_{mk} , and c_{mk} are the important constants in the model. The binary interaction parameters correspond to a given interaction of two subgroups in the mixture. It is assumed that the binary interaction parameters do not change regardless of the mixture or system considered. For example, the interactions of CH_3 and primary OH should have fixed binary interaction parameters whether they are present in ethanol, water and 1-butanol system, or present in ethanol, water and 1-propanol system. Hence, the UNIFAC Dortmund binary interaction parameters are universal values and should applicable to any mixture. Moreover, the values of the binary interaction parameters are determined from the general classification of subgroups involved in the interaction, which is called the main group. Thus, the values of binary interaction parameters for CH_3 and primary OH is based on the values provided for CH_2 -OH main group pairs since CH_3 belongs to the CH_2 main group while primary OH is classified under the OH main group.

The UNIFAC Dortmund binary interaction parameters have an important role in the modelling using the UNIFAC Dortmund model. These parameters are the constants that are adjusted so that the model can predict VLE with a minimum possible deviation from the experimental VLE. Therefore, it is important that the parameters correspond to an acceptable value so that these can be used in the prediction of VLE of specific systems that will be separated through distillation.



The physical significance of the τ_{mk} is also important in the model. If $\tau_{mk} > 1$, then subgroup k has a stronger interaction with the other subgroups than with its fellow subgroup k. If $\tau_{mk} < 1$, then subgroup k has a stronger interaction with its fellow subgroups than with the other subgroups. Hence, the higher the τ_{mk} , the stronger is the interaction between subgroups. For example, water forms strong interactions with the OH group of ethanol ($\tau_{mk} = 3, \tau_{mk} > 1$), and weak interactions with its alkyl chain ($\tau_{mk} = 0.48, \tau_{mk} < 1$) as shown:

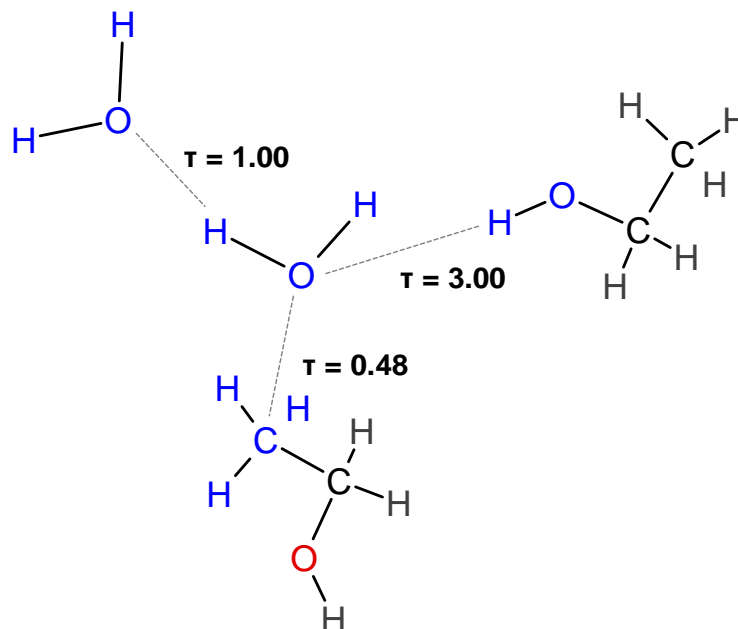


Figure 3.6. Interactions and Corresponding τ_{mk} Values



The UNIFAC Dortmund model also has weaknesses, where improvements are necessary to provide good predictions for mixtures containing alcohols of different types (primary, secondary and tertiary), isomers, or components with multiple groups and highly electronegative atoms. For primary, secondary and tertiary alcohols, the model is still being developed to adequately account for the differences in their OH groups. For isomers, the model is also being adjusted to provide distinctions among them. It is because although isomers have the same composition of functional groups, they have different properties which should be accounted. For components with multiple groups and highly electronegative atoms, the model is being developed to account for the effects experienced by a given group from its neighboring groups within the same component, especially if the neighboring atoms are too electronegative. This is known as the proximity effect. An example of which is glycerol, where the interaction of each of its OH group might be affected by the other neighboring OH groups. Another example is 1-butanol where the interaction to its OH group might be sterically hindered by its nonpolar alkyl chain. Since the UNIFAC Dortmund model does not account for these proximity effects, different prediction results are sometimes obtained by the model such as the prediction of strong interactions between components instead of weak interactions or vice versa.

The UNIFAC Dortmund subgroups used in this study, the van der Waals volume and surface area parameters R_k and Q_k , and the binary interaction parameters a_{mk} , b_{mk} , and c_{mk} parameters are provided as follows:



Table 3.4. Corresponding UNIFAC Dortmund Subgroups of the Components Used in This Study

Component Number	Component	Structure	Subgroups
1	Ethanol		1 CH ₃ , 1 CH ₂ , 1 OH
2	Water		1 H ₂ O
3	Glycerol		2 CH ₂ , 1 CH, 2 OH (p)*, 1 OH (s)*
4	Ethylene Glycol		2 CH ₂ , 2 OH
5	1-Butanol		1 CH ₃ , 3 CH ₂ , 1 OH
6	1-Propanol		1 CH ₃ , 2 CH ₂ , 1 OH
7	2-Propanol		2 CH ₃ , 1 CH, 1 OH (s)*
8	Sodium Chloride	Na ⁺ Cl ⁻	1 Na ⁺ , 1 Cl ⁻
9	Potassium Chloride	K ⁺ Cl ⁻	1 K ⁺ , 1 Cl ⁻
10	TRIS		3 CH ₂ , 3 OH, 1 CNH ₂

*p – primary group, s – secondary group



Table 3.5. R_k and Q_k Values of the Subgroups Used in This Study

Main Group	Subgroup	R_k	Q_k
CH ₂	CH ₃	0.6325	1.0608
	CH ₂	0.6325	0.7081
	CH	0.6325	0.3554
OH	OH (p)*	1.2302	0.8927
	OH (s)*	1.0630	0.8663
H ₂ O	H ₂ O	1.7334	2.4561
CH ₂ NH ₂	CNH ₂	1.6607	0.9850
Cl ⁻	Cl ⁻	0.9861	0.9917
K ⁺	K ⁺	3.0000	3.0000
Na ⁺	Na ⁺	3.0000	3.0000

*p – primary group, s – secondary group

Table 3.6. Existing UNIFAC Dortmund Binary Interaction Parameters Involving CH₂, OH and H₂O Groups (DDBST, 2022)

Main Group 1	Main Group 2	Binary Interaction Parameters					
		a_{12}	a_{21}	b_{12}	b_{21}	c_{12}	c_{21}
CH ₂	OH	2,777	1,606	-4.674	-4.746	0.001551	0.000918
	H ₂ O	1,391.3	-17.253	-3.6156	0.8389	0.001144	0.000902
OH	H ₂ O	-801.9	1,460	3.824	-8.673	-0.00751	0.01641

NA – not available, subject to estimation

Table 3.7. Existing UNIFAC Dortmund Binary Interaction Parameters Involving CH₂NH₂ Group (DDBST, 2022)

Main Group 1	Main Group 2	Binary Interaction Parameters					
		a_{12}	a_{21}	b_{12}	b_{21}	c_{12}	c_{21}
CH ₂ NH ₂	CH ₂	326.04	6,731.4	-2.6348	4.9683	0.00336	-0.01025
CH ₂ NH ₂	OH	-75.63	4,286.2	-0.1511	2.468	NA	NA
CH ₂ NH ₂	H ₂ O	-980.6	5.3069	3.671	-5.869	-0.00591	0.01032



Table 3.8. Existing UNIFAC Dortmund Binary Interaction Parameters Involving Salts from the Literature (Aznar & Telles, 2001)

Main Group 1	Main Group 2	Binary Interaction Parameters			
		a_{12}	a_{21}	b_{12}	b_{21}
Cl ⁻	CH ₂	-7,424.5	6,731.4	20.728	46.963
	OH	4,950.2	4,286.2	-15.522	-62.547
	H ₂ O	-144.82	5.3069	-0.0174	0.4377
	Na ⁺	-2,425.8	23,275	0.0221	2.224
	K ⁺	-6,110.8	18.581	0	0
Na ⁺	CH ₂	-1,899	6,767.4	72.291	49.151
	OH	-2,974.7	-7,007.6	8.1759	14.053
	H ₂ O	-552.42	-1,970.2	-0.0097	1.2864
K ⁺	CH ₂	12,803	-2,071.6	5.1318	0.228
	OH	399.74	-5,941.1	0.0053	0.0032
	H ₂ O	-481.55	-5,616.8	-0.0051	0.4801

3.7 Constrained Optimization Theory

An optimization is the process of finding a set of parameters $x = \{x_1, x_2, x_3 \dots x_p\}$ that will optimize an objective function under certain constraints. The general formulation of an optimization problem is shown as follows:

$$\begin{aligned}
 & \min_x f(x) \\
 & g_i(x) = 0; [i = 1, 2, \dots, m] \\
 & g_j(x) \leq 0; [j = 1, 2, \dots, n] \\
 & x_l \leq x \leq x_u
 \end{aligned}
 \tag{3.23}$$

where $f(x)$ is the objective function, $g_i(x) = 0$ are the equality constraints, $g_j(x) \leq 0$ are the inequality constraints, m is the number of equality constraints, n is the number of inequality constraints, and x_l and x_u are the allowable bounds for the parameters. The problem should converge to a solution $x = x^*$, where $x^* = \{x_1^*, x_2^*, x_3^*, \dots x_p^*\}$ and the elements of the set are real numbers. Optimization can be useful for the modelling of various engineering and industrial systems whose aim is to fit a certain model into the given data with the least difference as possible with respect to the variable of interest as defined in the objective function $f(x)$.



There are specific types of optimization problems depending on the nature of the objective function and constraints. If both the objective functions and the constraints are linear, then the problem is a linear programming (LP) problem. If the objective function is quadratic, then it is a quadratic programming (QP) problem. There are also known as the nonlinear programming (NLP) problems, where both the objective functions and constraints are nonlinear. This kind of problem is difficult to solve analytically, hence numerical or iterative methods are used. Numerical methods that are applied to solve NLP problems usually involve the formulation of optimization subproblems for every iteration, which are typically linear or quadratic subproblems. Among the most commonly known efficient numerical methods is the sequential quadratic programming, which generates quadratic subproblems as will be discussed in the next section.

3.8 Sequential Quadratic Programming (SQP)

The sequential quadratic programming, or SQP, is one of the fastest methods used for constrained optimization that was developed by Powell (1978). This method is applied for optimization problems with continuous objective and constraint functions, with their derivatives that are also continuous for a given range of parameters (Schittkowski, 1986). This method formulates a quadratic subproblem for every iteration and solves the subproblem in order to calculate a new set of parameters \mathbf{x}^{k+1} from the previous set \mathbf{x}^k in the iteration process, until a convergence to a parameter solution set \mathbf{x}^* is achieved. In order to create quadratic subproblems, the method linearizes the nonlinear constraint functions $g_i(\mathbf{x})$ and minimizes the quadratic approximation of Lagrangian function whose equation is in the form:

$$L(\mathbf{x}, \boldsymbol{\lambda}) = f(\mathbf{x}) + \sum_{i=1}^m \lambda_i g_i(\mathbf{x}) + \sum_{j=1}^n \lambda_j g_j(\mathbf{x}) \quad (3.24)$$

where $\boldsymbol{\lambda}$ are Lagrange multipliers that are being approximated to obtain the parameter solution \mathbf{x}^* at the optimum value of objective function $f(\mathbf{x})$.



Furthermore, at every iteration, the Karush-Kuhn-Tucker (KKT) equations must be satisfied to ensure that the convergence at x^* is obtained, which are provided as follows:

$$\nabla f(x^*) + \sum_{i=1}^m \lambda_i \nabla g_i(x^*) + \sum_{j=1}^n \lambda_j \nabla g_j(x^*) = 0 \quad (3.25)$$

$$\lambda_i g_i(x^*) = 0 \quad (3.26)$$

$$\lambda_j \geq 0 \quad (3.27)$$

There are several advantages of using the SQP method. First, the method is known to be suitable for calculating the parameters at the optimum regardless of the nonlinearity of the functions considered (Boggs & Tolle, 2000). It is because this method capitalizes well on good initial guesses (Gill & Wong, 2012) and that the constraints need not to be satisfied in every iteration. The only requirement for this method is to satisfy the KKT equations in every iteration, hence the constraints may be satisfied even only at the last iterations. Furthermore, the method is always applicable even for optimization problems with large number of constraints and variables (Boggs & Tolle, 2000), although the efficiency of the method may decrease and errors may sometimes be observed. In general, this method has been shown to be efficient in solving various optimization problems in engineering.