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Development of a Simple Model for the Prediction of Tie-Lines for Ternary Systems

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Abstract: A novel, semi-analytic, and numerically convenient algorithm has been proposed for predicting the equilibrium tie-line composition with the given overall feed composition and binary interaction parameters of established models (UNIQUAC and modified UNIQUAC) for ternary liquid-liquid systems. The merit of the proposed model rests on the selection of the distribution coefficient of each component as unknown variables instead of the mole fraction. Moreover, the model relies on the analytical solution of the extract fraction instead of adopting any numerical schemes that are commonly practiced to solve the same. Its veracity has been successfully tested with the experimental results for standard ternary systems reported in literature. The calculation procedure renders a distinct advantage over the accepted existing methods from the utilitarian view point.

Keywords: Interaction parameters, liquid-liquid equilibria, model, ternary system, tie-line

INTRODUCTION

Liquid-liquid extraction, though compared to distillation, a fairly recent phenomenon as a means of separation, has found acceptance rather in

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electric rapidity. The primary reasons for which the extraction enjoys such a phenomenal growth may be attributed to the practical difficulties encountered in separating azeotropic or close-boiling liquid mixtures by conventional distillation. Excellent reviews on the industrial applications of extraction are discussed in literature (1–4). The calculation of isothermal ternary liquid-liquid equilibrium (LLE) compositions constitutes probably the most important prerequisite in the modelling and design of the stage-wise or agitated extractors. There is always a need for precise LLE data in order to design an efficient extractor. Detailed exposition of the experimental procedures and related theory on liquid-liquid extraction is delineated by Alders (5). For a ternary liquid-liquid system, the equilibrium tie-line composition can be calculated, for a given overall feed composition and interaction parameters of the model equation that determine the activity coefficients, in the same way as in the vapor-liquid equilibrium flash separation calculation solved by using the popular Rachford and Rice method (6). The pioneering procedure described by Prausnitz et al. (7) for calculating the LLE of the multi-component systems involves solving the equations that equate the activities (having advantages over the chemical potential that fugacities can be related to measurable properties) of the components at phase equilibria. The unknown variables of interest associated with this method are the mole fractions of the components in each phase. This method is widely accepted. Ammar and Renon (8) proposed a highly rigorous method, for isothermal phase split calculations based on the minimization of Gibbs free energy of mixing.

In this communication, we have developed a novel, albeit simple semi-analytic method for calculating LLE tie-line composition for ternary systems by solving the fugacities equations where the distribution coefficients (K_is) are unknown variables of interest instead of the mole fractions of the components. The selection of K_is as unknown variables has made the model novel and unique. Their rewarding influence on the proposed model as well as the additional computational edge in solving the extract fraction, will be discussed in the ensuing section. Since only ternary systems are considered here, the components are designated according to their function. The component 1 stands for the solvent that generally extracts the solute from the diluent, the component 2 denotes the diluent and the 3^{rd} component is designated as the solute that is initially dissolved in the diluent. A ternary system is called the Type I system, if the solute is completely soluble in both the diluent and the solvent, but the solvent and the diluent are either partially miscible or completely immiscible. The Type II system gets its name when the solute is partially soluble in either the solvent or the diluent.

THE MODEL

Material Balance and Phase Equilibria Equations

The overall material balance equation is given by,

$$F = E + R \tag{1}$$

where F is the molar feed, and E and R are the respective extract and the raffinate phases in moles.

The overall component mole balance yields,

$$Fz_i = Ex_i^E + Rx_i^R \tag{2}$$

where z_i is the mole fraction of i^{th}component in the feed with $\sum_{i=1}^{3} z_i = 1$, and x_i^E and x_i^R represent the equilibrium mole fractions of i^{th} component in extract (E) and raffinate (R) phases respectively.

The above two equations produce,

$$z_i = \alpha x_i^E + (1 - \alpha)x_i^R \tag{3}$$

where α ($=E/F$) and $(1 - \alpha)$ ($=R/F$) represent the fraction of feed in the extract and the raffinate phases respectively.

The phase equilibria equations are,

$$x_i^E \gamma_i^E = x_i^R \gamma_i^R \tag{4}$$

where γ_i^E and γ_i^R are the respective activity coefficients for i^{th} component in extract (E) and raffinate (R) phases.

The distribution coefficient of the i^{th} component, K_i, between the E and R phases is given by,

$$K_i = \frac{\gamma_i^R}{\gamma_i^E} \left(= \frac{x_i^E}{x_i^R} \right) \tag{5}$$

and the material balance constraint for each component in each phase reads,

$$\sum_{i=1}^{3} x_i^E = \sum_{i=1}^{3} x_i^R = 1 \tag{6}$$

From Eqs. (3), (4), and (5), we obtain,

$$x_i^E = \frac{z_i K_i}{\alpha(K_i - 1) + 1} \tag{7}$$

$$x_i^R = \frac{z_i}{\alpha(K_i - 1) + 1} \tag{8}$$

and combining Eqs. (6), (7), and (8), yields,

$$f(\alpha) = \sum_{i=1}^{3} \frac{z_i(K_i - 1)}{\alpha(K_i - 1) + 1} = 0 \tag{9}$$

The central idea that led to this work is embedded into Eq. (9). For a given set of thermodynamic variables K_is ($0 < K_i < \infty$) and the material variables z_is ($0 < z_i < 1$), Eq. (9), a mathematically obedient equation, can be solved for α. If we examine carefully the Eq. (9), we observe that z_is are fixed as dictated by the feed concentration but K_is are to be determined from the Eq. (5). Needless to say, the Eq. (9) has a unique solution because

$$f'(\alpha) = -\sum_{i=1}^{3} \frac{z_i(K_i - 1)^2}{(\alpha(K_i - 1) + 1)^2} (< 0)$$

However, for estimating the physically admissible root ($0 < \alpha < 1$) from the Eq. (9), the following inequalities must be observed.

$$f(\alpha) > 0 \Longrightarrow \sum_{i=1}^{3} K_i z_i > 1 \tag{10}$$

and

$$f(\alpha) < 0 \Longrightarrow \sum_{i=1}^{3} \frac{z_i}{K_i} > 1 \tag{11}$$

Equation (9) demands a numerical procedure to solve. However, it can be expressed in the following ratio of functions

$$f(\alpha) = \frac{g(\alpha)}{h(\alpha)} = 0 \tag{12}$$

where $g(\alpha) = a\alpha^2 + b\alpha + c$ and $h(\alpha) = \prod_{i=1}^{3} [\alpha(K_i - 1) + 1]$ with

$$a = \prod_{i=1}^{3} (K_i - 1) \tag{13}$$

$$b = (K_1 - 1)(K_2 - 1)(z_1 + z_2) + (K_2 - 1)(K_3 - 1)(z_2 + z_3) + (K_3 - 1)(K_1 - 1)(z_3 + z_1) \tag{14}$$

$$c = \prod_{i=1}^{3} K_i z_i - 1 \tag{15}$$

The zeros of $f(\alpha)$ can now be evaluated analytically by solving

$$g(\alpha) = a\alpha^2 + b\alpha + c = 0 \tag{16}$$

This procedure possesses a perceptible numerical advantage. The two roots, α_1 and α_2, for Eq. (16) are given by,

$$\alpha_1 = \frac{q}{a} \tag{17}$$

$$\alpha_2 = \frac{c}{q} \tag{18}$$

where q is computed as

$$q = -\frac{1}{2}\left[b + \mathrm{sgn}(b)\sqrt{b^2 - 4ac}\right]$$

If we take care of the following constraints

$$g(0) = c > 0 (< 0) \tag{19}$$

and

$$g(1) = a + b + c < 0 \ (> 0) \tag{20}$$

one root would always lie between 0 and 1. The other root takes values either greater than unity ($\alpha > 1$) or less than zero ($\alpha < 0$). These values when construed physically, imply that the z_i refuses to split into phases. While examining the expression $h(\alpha)$, we find that the $h(\alpha)$ never becomes zero for $0 \leq \alpha \leq 1$, thus removing the possibility of the ratio as shown in Eq. (12) to become indeterminate. In fact, $h(0) = 1$ and $h(1) = K_1K_2K_3$ ensure that $h(\alpha)$ is always positive for K_is greater than zero. So, the procedure of solving $g(\alpha)$ establishes an additional beneficial characteristic of the model on numerical aspect.

In the widely used method, described by Prausnitz et al. (7), the algorithm starts with an initial guess, designated as old values, of composition of components, x_i^Es and x_i^Rs. These compositions are used to

obtain values of γ_i^Es, and γ_i^Rs using the model equation and these in turn are utilized to estimate K_is from Eq. (5). With these values of K_is, α is solved from Eq. (9) numerically where the rate of convergence depends upon the initial guess of α. Using the freshly calculated value of α and the K_is already computed, the new values of the x_i^Es and x_i^Rs are determined from Eqs. (7) and (8) respectively. If the deviation, $|x_i^{new} - x_i^{old}|$, in each phase is less than the prescribed tolerance, ε (say order of 10^{-3}), the *new* values of the compositions are the desired solutions, otherwise the entire loop of computation is repeated replacing the old values by the new values of the compositions until the prescribed tolerance is achieved. Indeed, the convergence rate depends upon the initial estimates of the compositions used.

In the present work, we rely on evaluating α analytically from Eq. (16) in the first step itself, with guessed values of K_is that are considered initially to be unknown parameters of interest for the theoretical determination of the tie-line composition. Such reliance stems from the utilitarian compromise.

It is a common practice in the engineering community not only to select a solvent (forming the extract phase (E)) that shows more affinity to the solute than the diluent (constituting the Raffinate phase (R)) but also to ensure that the solvent and the diluent should be scarcely soluble, though the mutual solubility increases with the addition of the solute till they become a single phase at the plait point. So, K_1 will always be greater than unity ($K_1 > 1$) and evidently, K_2 will always be less than unity ($K_2 < 1$). At the plait point, each K_i becomes equal to unity. So, the possible values of K_is that can be considered are given as

$$K_1 > 1, K_2 < 1 \,\&\, K_3 > 1 \tag{C1}$$

Choice of Initial Guess for K_1, K_2, and K_3

Since the initial guess of the K_is demands not only their numerical values to be in the range as described by (C1) but also fulfilling the conditions (19) and (20), we have resorted to the following choice,

$$K_1 = K_3 = \frac{1}{z_3} (> 1)$$

where z_3 is the given composition of the solute in the feed. With the above selection of K_1 and K_2, the condition (19) is satisfied and the maximum value of K_2 can be easily evaluated by solving $a + b + c = 0$, and is given by,

$$K_2^{\max} = \frac{1 - (z_1 + z_3)}{1 - z_3(z_1 + z_3)} \tag{21}$$

which is always positive and less than unity. So, the chosen value of K_2 must be less than the right hand side value of Eq. (21) respecting the condition (20). The other choices for the initial guess of K_1 and K_3, as furnished in (C1), are equally recommended, and K_2 can be determined from the condition (20). Indeed, the rate of convergence to the solution can be improved by judiciously guessing the initial values of K_is.

Once this initial guess is fixed, not only the inequality $a+b+c<0$ is maintained during the entire course of the computation of α but also the values of K_is that are guided by thermodynamical variables, γ_is, would also remain in the prescribed range displayed in (C1). The analytical determination of α, needless to say, alleviates the computational expenditure arising out while calculating the same numerically.

If the inequality constraints given in (C1) are reversed, the root α that lies between 0 and unity, will be replaced by $1-\alpha$. This intuitively certain result not only can be proved mathematically but also is the direct consequence of Eq. (1). This implies that the diluent will become the solvent and the solvent the diluent, and accordingly the solute distributes itself to the extract and raffinate phases. The identification of the problem is complete at this stage. The final values of the K_is would be the reciprocals of their counterparts that could have been obtained with the selected values of K_is complying the conditions displayed in (C1).

In order to predict the binary equilibrium data for the solvent (1) and diluent (2), the same procedure can be applied by assigning $K_3=1$ and $z_3=0$ with constraint $z_1+z_2=1$. These restrictions renders $a=0$, $b=(K_1-1)(K_2-1)$ and $c=K_1z_1+K_2z_2-1$. The relation for α can be solved directly from $b\alpha+c=0$ and the solution is given by $\alpha=-c/b$. The minus sign again demands that either of K_1 and K_2 must be less than unity. As regard to observing the condition $c>0$ and $b+c<0$ as in the case of the ternary equilibrium line prediction, the initial choice of K_2 is estimated by assigning $K_1=1/z_1$ (>1) as initial guess, as $K_2^{\max}=\frac{1}{1+z_1}$.

Model Equation for Activity Coefficients

The activity coefficients, γ_is, (the measure of non-ideality of the liquid mixtures) are related to the molar excess Gibbs energy which is a function of temperature, pressure, and composition of the components. Several models like UNIQUAC, modified UNIQUAC, NRTL etc. that account for the energy interaction between the liquid molecules are available in literature (9–11) which can be used for the theoretical estimation of γ_is. Since one of the key purposes of this work is to test our computational algorithm with the established systems (14–18), we have chosen the same

UNIQUAC and modified UNIQUAC model equations (10) for a multi-component mixture as used by Prausnitz et al. (7,13).

For the i^{th}component, the activity coefficient given by modified UNIQUAC model equation (10) is,

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{22}$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2}\right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j^N x_j l_j \tag{23}$$

$$\ln \gamma_i^R = -q_i' \ln \left(\sum_j^N \theta_j' \tau_{ji} \right) + q_i' - q_i' \sum_j^N \frac{\theta_j' \tau_{ij}}{\sum_k^N \theta_k' \tau_{kj}} \tag{24}$$

where

$$\phi_i = \frac{r_i x_i}{\sum_j^N r_j x_j} \tag{25}$$

$$\theta_i = \frac{q_i x_i}{\sum_j^N q_j x_j} \tag{26}$$

$$\theta_i' = \frac{q_i' x_i}{\sum_j^N q_j' x_j} \tag{27}$$

$$l_j = \frac{Z}{2}(r_j - q_j) - (r_j - 1) \tag{28}$$

where γ_i^C is the combinatorial part, γ_i^R is the residual part, Z is the lattice coordination number which is set equal to 10, ϕ is the segment fraction, θ and θ' are the area fractions, r_i or r_j is the relative van der Waals volume per molecule, and q_i or q_j and q_i' or q_j' are the relative surface areas per molecule. For the simple UNIQUAC model equation, q_i and q_i' are equal.

Computational Algorithm

1. Specifying feed composition: Assign the feed composition z_is as input ensuring that $\sum_1^3 z_i = 1$.
2. Initialization: Select the initial guess for K_1^{old}, K_2^{old} and K_3^{old}. Set $K_1^{old} = K_3^{old} = \frac{1}{z_3}$, and choose $K_2^{old} < K_2^{\max}$, given by Eq. (21).
3. Solving Eq. (16) analytically: Solve for α from Eq. (16) and accept the root that lies between 0 and unity.
4. Estimation of component compositions in E and R phases: Calculate x_i^E and x_i^R from Eq. (7) and (8) respectively.

Table 1. UNIQUAC and Modified UNIQUAC binary interaction parameters for components (12,17,18)

System	T (°C)	a_{12} (K)	a_{21} (K)	a_{13} (K)	a_{31} (K)	a_{23} (K)	a_{32} (K)
Modified UNIQUAC Parameters							
n-Heptane (1)	45	545.71	23.71	245.42	−135.93	60.28	89.57
Acetonitrile (2)							
Benzene (3)							
Acrylonitrile (1)	60	471.21	155.78	183.65	−142.35	122.02	122.07
Water (2)							
Acetonitrile (3)							
2,2,4-Trimethylpentane (1)	25	410.08	−4.98	80.91	−27.13	71.00	12.00
Furfural (2)							
Benzene (3)							
UNIQUAC Parameters							
Water (1)	25	91.88	404.83	353.18	−171.90	357.47	−201.58
Methyl Isobutyl Ketone (2)							
Propanoic acid (3)							
Water (1)	25	220.86	228.75	−42.38	384.16	152.13	−46.41
2-Ethyl-1-Hexanol (2)							
Acetone (3)							

5. Calculation of activity coefficients: Compute γ_i^Es and γ_i^Rs from UNIQUAC model Eq. (22).
6. Updating distribution coefficients: Evaluate K_i^{new}s from Eq. (5).

Table 2. UNIQUAC structural parameters for components (7,10)

Component	r	q	q'
n-Heptane	5.170	4.400	4.400
Benzene	3.190	2.400	2.400
Acetonitrile	1.870	1.720	1.720
Acrylonitrile	2.310	2.050	2.050
Water	0.920	1.400	1.000
2,2,4-Trimethyl Pentane	5.850	4.940	4.940
Furfural	3.168	2.484	2.484
Propanoic acid	2.877	2.612	2.612
Methyl Isobutyl Ketone	4.596	3.952	3.952
Acetone	2.570	2.340	2.340
2-Ethyl-1-Hexanol	6.151	5.208	

Table 3. Experimental data (14–18) and the predicted values computed from the model

System	T (°C)	z_i	x_i^E Expt.	x_i^E Pred.	RD%*	x_i^R Expt.	x_i^R Pred.	RD%	α Pred.
n-Heptane (1)	45	0.4587	0.8492	0.8360	1.55	0.0683	0.0683	0.00	0.5085
Acetonitrile (2)		0.5148	0.1167	0.1310	10.92	0.9129	0.9119	0.11	
Benzene (3)		0.0265	0.0341	0.0330	3.23	0.0188	0.0198	5.05	
n-Heptane (1)		0.3563	0.5506	0.5629	2.19	0.1619	0.1305	19.40	0.5222
Acetonitrile (2)		0.4873	0.2723	0.2562	5.91	0.7025	0.7399	5.06	
Benzene (3)		0.1564	0.1771	0.1809	2.10	0.1356	0.1296	4.43	
Acrylonitrile (1)	60	0.350	0.688	0.6964	1.21	0.036	0.0341	5.28	0.4769
Water (2)		0.600	0.196	0.2140	8.41	0.950	0.9520	0.21	
Acetonitrile (3)		0.050	0.116	0.0896	22.76	0.014	0.0139	0.71	
Acrylonitrile (1)		0.150	0.210	0.2092	0.38	0.053	0.0431	18.68	0.6437
Water (2)		0.600	0.482	0.4689	2.72	0.831	0.8368	0.69	
Acetonitrile (3)		0.250	0.308	0.3219	4.32	0.116	0.1201	3.41	
2,2,4-Trimethyl Pentane (1)	25	0.400	0.6734	0.6721	0.19	0.0766	0.0797	3.89	0.5407
Furfural (2)		0.400	0.1003	0.1114	9.96	0.7366	0.7397	0.42	
Benzene (3)		0.200	0.2263	0.2165	4.33	0.1868	0.1806	3.32	
2,2,4-Trimethyl Pentane (1)		0.270	0.4879	0.4577	6.19	0.1267	0.1442	12.14	0.4013
Furfural (2)		0.400	0.1715	0.1963	12.63	0.5708	0.5365	6.01	
Benzene (3)		0.330	0.3406	0.3460	1.56	0.3025	0.3193	5.26	

Water (1)	25	0.6255	0.976	0.9780	0.21	0.275	0.2676	2.69	0.5038
Methyl Isobutyl Ketone (2)		0.2920	0.007	0.0045	35.71†	0.577	0.5839	1.18	
Propanoic acid (3)		0.0825	0.017	0.0175	2.86	0.148	0.1485	0.34	
Water (1)		0.7360	0.931	0.9285	0.27	0.541	0.5396	0.26	0.5049
Methyl Isobutyl Ketone (2)		0.1005	0.009	0.0083	7.78	0.192	0.1945	1.29	
Propanoic acid (3)		0.1635	0.060	0.0632	5.06	0.267	0.2659	0.41	
Water (1)	25	0.6032	0.9795	0.9759	0.37	0.2270	0.2239	1.37	0.5044
2-Ethyl-1-Hexanol (2)		0.3077	0.0001	0.0003	66.67†	0.6152	0.6205	0.85	
Acetone (3)		0.0891	0.0204	0.0238	14.29	0.1578	0.1556	1.39	
Water (1)		0.7484	0.9389	0.9429	0.42	0.3040	0.2465	18.92	0.7207
2-Ethyl-1-Hexanol (2)		0.1179	0.0004	0.0005	20.00	0.3920	0.4208	6.84	
Acetone (3)		0.1337	0.0607	0.0566	6.76	0.3040	0.3327	8.63	

*Relative Deviation Percent $= \frac{\left|x_i^{\exp t} - x_i^{pred}\right|}{\max\left(x_i^{\exp t}, x_i^{pred}\right)}$.

†Because of tiny experimental values (appear to be in the measurement noise range), the RD% is high.

7. Deviation test: Compare K_i^{old}s and K_i^{new}s. If $\left|\frac{K_i^{old}-K_i^{new}}{K_i^{old}}\right| < \varepsilon(10^{-3})$ for all the three components, the output is the final result and the program is terminated otherwise execute step 8.
8. Iteration: Replace K_i^{old}s by K_i^{new}s and repeat from step 3.

ILLUSTRATIVE EXAMPLES

Several reported Type I systems (14–18), that are considered to be the benchmark systems, were used in the present work for estimating the tie-line compositions to check the efficiency of the present algorithm. The values of UNIQUAC and modified UNIQUAC binary interaction parameters between the components, and their structural parameters are given in Tables 1 and 2 respectively. The set of values that contain the extract fraction (α) and tie-line compositions (x_is) which have been predicted by the present method, is listed in Table 3 along with the experimental data. The results clearly demonstrate that the present algorithm reproduces the experimental data very well for a given set of binary interaction parameters.

CONCLUSION

A simple generalized method for predicting tie-line composition has been developed with given overall feed composition and binary interaction parameters. The algorithm uses distribution coefficients, K_is, as the unknown variables of interest. The analytical determination of α lends a perceptible advantage over the current accepted methods in terms of plausible algorithm stability and computational cost. The veracity of the model has been tested for UNIQUAC and modified UNIQUAC model equations against the reported Type I systems. The model is applicable with the same capacity to predict the ternary equilibrium composition for the Type II systems. We are hopeful that the new algorithm for predicting the tie-line composition of ternary systems would be useful in the design of extractors.

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