

Original Article

# Extension of Hand Correlation Model to Obtain on Quaternary System (MTBE-hydroquinone-phenol-water)

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**Abstract** - The precise liquid-liquid equilibrium data are necessary to design extraction processes. The triangular diagram in which each apex represents a pure component illustrates the ternary system's mutual solubility curve and tie line. This requires that sufficient equilibrium data be available with difficulty that these data cannot be inserted in the computer; Several models have been devised for the correlation of equilibrium data. In general, there are two main approaches; one of them uses the activity with a model for the activity coefficient, such as the Non-Random Two liquid equation[NRTL]; the other correlates tie line data with equations such as that of Hand, Othmer-Tobias and Ishida correlations. In this study, Equilibrium data for the quaternary system (MTBE-hydroquinone-phenol-water) were obtained from the literature. Then an extension of hand was correlated for this quaternary system. And the results were good and gave a correlation coefficient near unity. It recommended that the same calculations have to be carried out by hand model obtained with the comparison of the results for the quaternary systems.

**Keywords** - Liquid-liquid equilibrium, Quaternary system correlation model, Tie-line data prediction.

## 1. Introduction

To determine equilibrium data for any mixtures, experimental methods are used; unfortunately, good experimental data are not easily obtained because they require appreciable experimental skill and experience<sup>[2]</sup>. Further, the possible number of fluid mixtures in technological processes is incredibly large, and it is unreasonable to expect that experimental equilibrium data will ever be available.<sup>[9]</sup>

As a result, The required data are often not at hand but must be estimated using suitable models whose parameters are obtained from the reduction and correlation of limited experimental data to make the best possible interpolation and extrapolation<sup>[23]</sup>. Also, an extraction calculation involving more than three components can't be made graphically but must be done by numerical solution equations representing the phase equilibrium and material balance<sup>[1]</sup>. These calculations are best conducted with computer aid methods. They may be advantageous for the design of ternary and quaternary, and multicomponent extraction systems, particularly when the number of stages is large<sup>[16],[18]</sup>

## 2. Literature Review

Unfortunately, good experimental data are not easily obtained because they require appreciable experimental skill, experience and patience. Further, the possible number of fluid mixtures in technological processes is huge, and it is unreasonable to expect that experimental equilibrium data

will ever be available for a significant fraction of this number. As a result, required data are often not at hand but must be estimated using suitable models whose parameters are obtained from the reduction and correlation of limited experimental data to make the best possible interpolation and extrapolation<sup>[10]</sup>.

Liquid-liquid equilibria are of interest in extraction operations. Unlike distillation processes which depend on the variation of vapor pressure with temperature, liquid-liquid extraction separations depend on the non-ideal behavior of the distribution of the component between the two liquid phases<sup>[22],[23]</sup>. The design of extraction equipment depends upon knowledge of the solubility of a solute between two solvents that are not completely miscible with each other<sup>[20]</sup>.

The simplest separation by extraction involves two substances and a solvent-ternary system<sup>[11],[25]</sup>. The graphical methods are still used to represent equilibrium data and perform extraction calculations for ternary systems; however, these methods are tedious and can't be used directly in cases requiring computer analysis<sup>[17],[19]</sup>. Further, quaternary higher multicomponent mixtures are often encountered in liquid-liquid extraction processes. But there is no compact graphical representation of their phase equilibrium<sup>[13]</sup>. Extraction calculation involving more than three components can't be made graphically but must be done by numerical solution of equations representing the phase equilibrium and material balance. These calculations are best conducted with



computer aid methods. Once such programs have been developed, they also may be advantageous for designing ternary extraction equipment, particularly when the number of stages is large<sup>[14],[15]</sup>.

Hence, methods for predicting and correlating liquid-liquid equilibrium have been developed. Basically, there are two approaches to correlation data. One of them uses equality of activity with a model for the activity coefficient; the other correlates data with empirical equations<sup>[21]</sup>.

**2.1. Tie Line Correlation for Ternary Systems**

In the case of many systems described in the literature, only a few tie lines have been experimentally determined. Direct interpolation of such data may lead to highly inaccurate results<sup>[3]</sup>. Several tie line correlations in equation form have been proposed<sup>[5]</sup> (identified with these subscripts):

- C → solute C in carrier phase A.
- AA → carrier A in carrier phase A.
- SA → solvent S in carrier phase A.
- CS → solute C in solvent phase S.
- AS → carrier A in solvent phase S.
- SS → solvent S in solvent phase S.

**2.2. Bachman's Correlation**

After the study of plots of Brancker, Hunter and Nash, Bachman<sup>[4]</sup> found that the equilibria in the type I system could be described by the expression:

$$X_{SS} = a + b \left( \frac{X_{SS}}{X_{AA}} \right)$$

Where a and b are constant, this indicates that plotting  $X_{SS}$  against  $\frac{X_{SS}}{X_{AA}}$  on arithmetic coordinates should provide a straight line.

**2.3. Othmer and Tobias' Correlation**

Othmer and Tobias<sup>[5]</sup> have found that a plot of conjugate values of  $\frac{1-X_{AA}}{X_{AA}}$  against  $\frac{1-X_{SS}}{X_{SS}}$  on logarithmic coordinates produced straight lines useful for interpolation and extrapolation:

$$\frac{1 - x_{SS}}{x_{SS}} = k \left( \frac{1 - x_{AA}}{x_{AA}} \right)^n$$

Where k, n are constants.

These methods suffer from the fact that the concentration of the distributed component (C) is not indicated in the coordinates.

**2.4. Ishida's Correlation**

Ishida's equation<sup>[5]</sup> for the correlation of tie-line data:

$$\frac{x_{CS} * x_{SA}}{x_{CA} * x_{SS}} = k \left( \frac{x_{AS} * x_{SA}}{x_{AA} * x_{SS}} \right)^n$$

Where k and n are constants, this equation should plot linearly on logarithmic coordinates.

**2.5. Hand's Correlation**

Hand showed that a logarithmic plot of  $x_{CA}/x_{AA}$  against  $x_{CS}/x_{SS}$  (which includes the concentration of the distributed component (C) in the coordinates) generally gives a rectilinear plot. Hand's equation for the correlation of tie line data is:

$$\frac{x_{CS}}{x_{SS}} = k \left( \frac{x_{CA}}{x_{AA}} \right)^n$$

Where k,n are constants.

The advantage of using these models is that they are comparatively easy and can be fed to the computer for the necessary design data, such as the number of theoretical stages and stage-to-stage calculations.<sup>[7],[8]</sup>

**3. Material and Methods**

**3.1. Selection of the Quaternary System**

The equilibrium data for the quaternary system (2-methoxy-2methylpropane-phenol-hydroquinone) obtained from PAPER(Yun Chen, Yong Lei, Xiuxi, measurement of liquid-liquid equilibrium for the system (2-Methoxy-2-methylpropane + Phenol+ Hydroquinone + water), Beijing,2013. Because of its industrial importance, this system was chosen; in cooling the crude gas in coal pressurized gasification, a large amount of wastewater was produced. It usually contains phenolic compounds, carbon dioxide, hydrogen sulfide, ammonia fatty acid, and so forth; these wastewaters are often characterized by a deep red color, foul odor, and pH 8-10<sup>[6]</sup>

For the design of industrial units for the phenol extraction process, reliable phase equilibrium data are essential. The LLE data indicate removing phenol and hydroquinone by extraction with MTBE from wastewater is feasible.

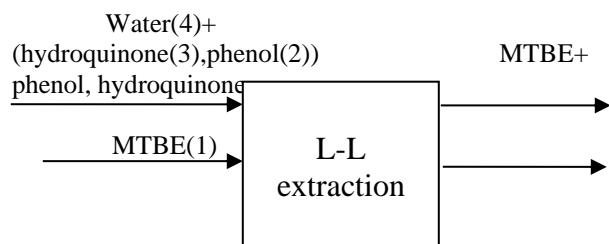


Fig. 1 The extraction process for the studying quaternary system

All correlation models are applicable in just ternary system, so the development of the hand model is done to make it applicable to quaternary systems as follow:

**3.2. Hand for the Ternary System**

$$\ln \left( \frac{w_2}{w_1} \right)^o = a_1 + b_1 \ln \left( \frac{w_2}{w_4} \right)^w$$

3.2.1. Improved hand for the quaternary system

$$\ln\left(\frac{w_2 + w_3}{w_1}\right)^o = a_1 + b_1 \ln\left(\frac{w_2 + w_3}{w_4}\right)^w$$

O----- organic phase

w-----aqueous phase

Or it can be written as follow:

$$\left(\frac{w_2 + w_3}{w_1}\right)^o = k \left(\left(\frac{w_2 + w_3}{w_4}\right)^w\right)^n$$

w<sub>1</sub>-----mass fraction for MTBE

w<sub>2</sub>-----mass fraction for hydroquinone

w<sub>3</sub>-----mass fraction for phenol

w<sub>4</sub>-----mass fraction for water

So We can said Y=K\*X<sup>n</sup> which is a straight-line equation.

Where:

$$Y = \frac{w_2 + w_3}{w_1}, X = \frac{w_2 + w_3}{w_4}$$

4. Result

Table 1. Equilibrium data for the quaternary system( 2-methoxy-2methylpropane(1)-phenol(2)-hydroquinone(3)-water(4))

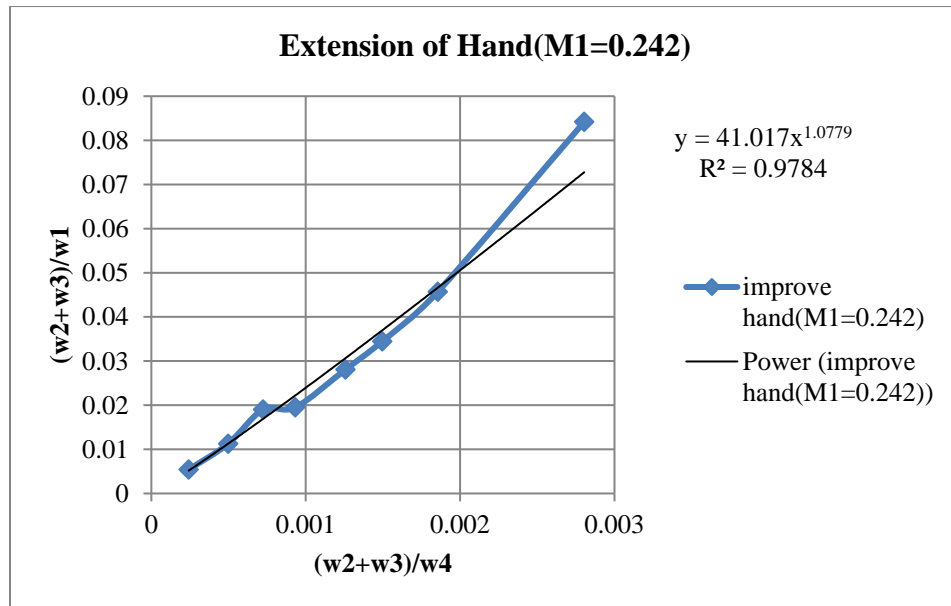
Organic phase				Aqueous phase			
w1	w2	w3	w4	w1	w2	w3	w4
			<b>M1=0.242</b>				
0.896335	0.066504	0.008936	0.028225	0.016447	0.001196	0.001554	0.980803
0.93067	0.03665	0.005857	0.026823	0.017502	0.000665	0.001154	0.980679
0.942965	0.028057	0.004436	0.024542	0.018101	0.000517	0.000949	0.980433
0.949529	0.022904	0.003765	0.023802	0.018365	0.000472	0.000761	0.980402
0.96143	0.016237	0.002527	0.019806	0.019389	0.000316	0.000597	0.979698
0.96309	0.016036	0.002279	0.018595	0.020318	0.000275	0.000433	0.978974
0.972862	0.009473	0.001489	0.016176	0.022066	0.000182	0.000304	0.977448
0.979512	0.004577	0.000724	0.015187	0.024031	0.000097	0.000139	0.975733
			<b>M2=0.495</b>				
0.91956	0.03451	0.016678	0.029216	0.017002	0.000653	0.003908	0.978437
0.952676	0.014731	0.007312	0.02528	0.019826	0.00026	0.001742	0.977817
0.960384	0.0119	0.005946	0.02177	0.021955	0.000206	0.00133	0.976509
0.966989	0.008178	0.004635	0.020198	0.022895	0.000168	0.001041	0.975896
0.97418	0.005757	0.002716	0.017348	0.023552	0.000103	0.000569	0.975775
0.977744	0.004501	0.001166	0.016589	0.025289	0.000073	0.000246	0.974393
			<b>M2=0.495</b>				
0.91956	0.03451	0.016678	0.029216	0.017002	0.000653	0.003908	0.978437
0.952676	0.014731	0.007312	0.02528	0.019826	0.00026	0.001742	0.977817
0.960384	0.0119	0.005946	0.02177	0.021955	0.000206	0.00133	0.976509
0.966989	0.008178	0.004635	0.020198	0.022895	0.000168	0.001041	0.975896
			<b>M3=0.748</b>				
0.935374	0.01451	0.023207	0.026909	0.016111	0.000292	0.005776	0.977821
0.953069	0.009445	0.016327	0.021159	0.017799	0.000196	0.004202	0.977803
0.964609	0.005508	0.009055	0.021159	0.019911	0.000117	0.002372	0.977601
0.969247	0.004062	0.007183	0.019509	0.020992	0.000092	0.001915	0.977002
0.973896	0.002899	0.005989	0.017216	0.021673	0.000065	0.001369	0.976892
0.978482	0.001915	0.003622	0.015981	0.023108	0.00005	0.00104	0.975802
0.980452	0.001475	0.003011	0.015062	0.02396	0.000045	0.000651	0.975344

M denotes the content(mass fraction) of hydroquinone in hydroquinone mixtures.

Obtained from the literature [DECHEMA-Chemistry Data series; V5 liquid-liquid equilibrium data collection].

**Table 2. Comparison between  $y_{calculated}$  and  $y_{experimental}$  for the quaternary system by Hand**

$Y_{cal}$	$X_{cal}$	$y_{exp}$	Error
0.08416496	0.00280383	0.07313369	0.01103127
0.04567355	0.00185484	0.0468657	-0.0011922
0.03445833	0.00149526	0.03715857	-0.0027002
0.02808656	0.00125765	0.03084002	-0.0027535
0.01951676	0.00093192	0.02233112	-0.0028144
0.01901691	0.00072321	0.01699476	0.00202215
0.01126779	0.00049721	0.01135184	-8.405E-05
0.00541188	0.00024187	0.00522404	0.00018784
	<b>M1=0.495</b>		
0.05566575	0.00466152	0.40737444	-0.4073744
0.02313798	0.00204742	0.19197811	-0.1919781
0.01858215	0.00157295	0.15908896	-0.159089
0.01325041	0.00123886	0.11906258	-0.1190626
0.00869757	0.00068868	0.08300206	-0.0830021
0.005796	0.00032738	0.05861726	-0.0586173
	<b>M3=0.748</b>		
0.04032291	0.00620563	0.03698199	0.00334092
0.02704106	0.00449784	0.02694291	9.8157E-05
0.01509731	0.00254603	0.01539069	-0.0002934
0.01160179	0.00205424	0.01246058	-0.0008588
0.00912623	0.00146792	0.00895208	0.00017415
0.00565877	0.00111703	0.00684202	-0.0011833
0.00457544	0.00071359	0.00440235	0.00017309
0.00264807	0.00038863	0.00242096	0.00022711



**Fig. 2 Hand extension for quaternary system At  $M_1= 0.242$**

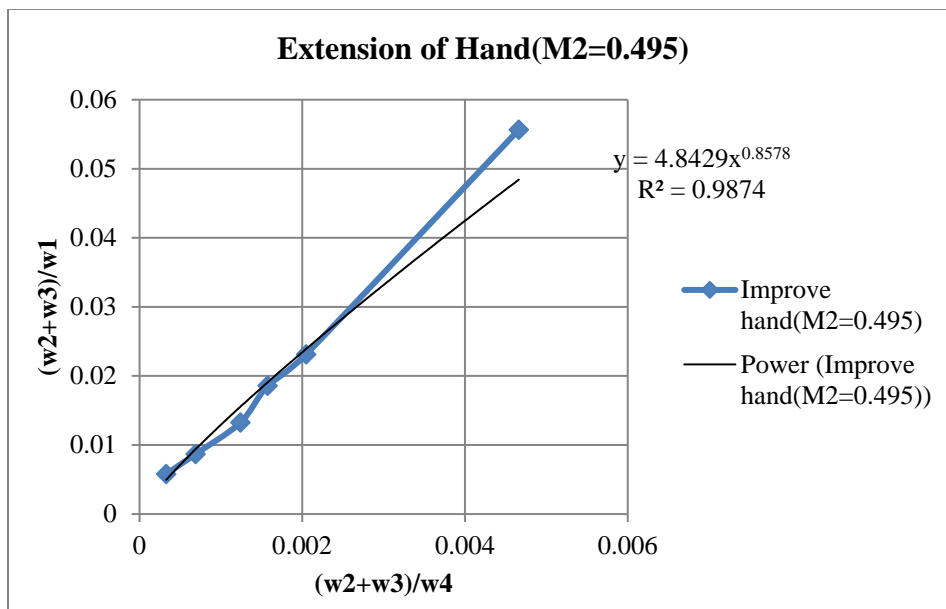


Fig. 3 Extension of hand for quaternary system At  $M_1=0.495$

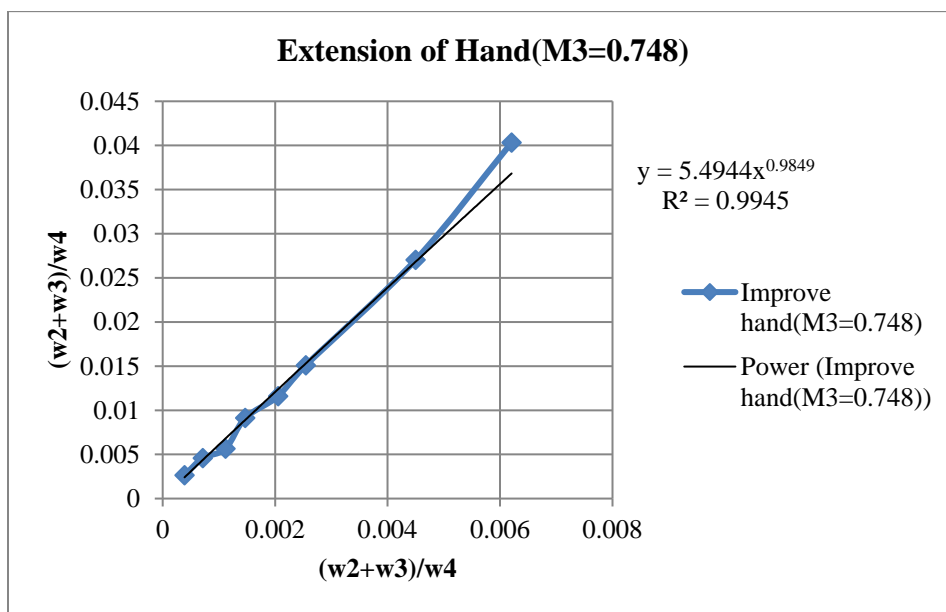


Fig. 4 Extension of Hand for quaternary system At  $M_1=0.748$

Table 3. Summary of Hand correlation and Regression factor for the quaternary systems

M	Equation	Regression factor $R^2$
$M_1$	$Y=41.01X^{1.077}$	0.986
$M_2$	$Y=4.84X^{0.975}$	0.975
$M_3$	$Y=5.49X^{0.984}$	0.989

### 5. Discussions

A suitable extension of Hand correlation models was made for the quaternary system( 2-methoxy-2methylpropane(1)-phenol(2)-hydroquinone(3)-water(4)), and it is seen that the values of the obtained correlation coefficient were all close to unity.

### 6. Conclusion

The improved hand model done here is applicable for quaternary systems and was given good results when it was applied to the system(MTBE-hydroquinone-phenol-water).

## 7. Recommendations

- The development hand's equation is helpful in the correlation of the quaternary system, which was not available in the past.
- The other model can be developed in the same way of hand.
- The developed hand's correlation models can be more developed to applicable for multicomponent systems.

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