

DISTRIBUTION COEFFICIENT CALCULATION IN TERNARY LIQUID-LIQUID SYSTEMS

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Abstract

A good description of liquid-liquid equilibrium is important to design extraction separation processes. Equilibrium data are normally needed as distribution coefficients for each individual component. In this paper we have combined activity coefficient models with Hand's equation for tie lines to calculate distribution coefficients in ternary systems. The proposed method gives better distribution coefficients than those calculated using only activity coefficient models. Besides, the proposed method could be employed to extrapolate experimental information when liquid-liquid equilibrium data are few.

1. Introduction

Prediction and/or correlation of ternary liquid-liquid equilibrium is of importance in chemical engineering applications such as extraction and, when combined with vapor-liquid equilibrium data, in heterogeneous azeotropic distillation. In the literature various methods have been used to correlate and to predict the compositions of equilibrium phases for ternary liquid-liquid systems. A series of recent articles (Sorensen *et al.* 1979a, 1979b; Magnussen *et al.* 1980) have presented an excellent review of experimental data sources, correlation models and prediction methods. Basically, there are two approaches to correlate data. One of them uses the equality of activities with a model for the activity coefficient, the other correlate data with equations such that of Hand (Treybal, 1963). Furthermore, for practical utilization of the equilibrium data in separation processes calculation it is convenient to describe the equilibrium in terms of the distribution coefficients for each component. As those distribution coefficients are system composition dependent, it is convenient to represent them as polynomials (Rod, 1976).

This paper presents a calculation scheme that combines the activity approach with the equation approach. The proposed method will improve coefficient distributions calculations in a way that is suitable for its correlation with polynomials.

2. Models and Method

2.1 Thermodynamics Models

A well-known empirical correlation for tie lines in liquid-liquid equilibrium is Hand's method (Treybal, 1963). Using molar fraction and natural logarithm, Hand's equation is given by:

$$\ln y_2/y_1 = k \ln x_2/x_3 + C \quad (1)$$

where component 2 is the solute, y_i is the composition of component i in the phase rich in component 1, x_i is the composition of component i in the phase rich in component 3, and k , C are ternary system dependent constants.

Other way to calculate liquid-liquid equilibrium is using the equality of chemical potential for each component in both phases. Normally the equality is rewritten in terms of activities. Using a model for the activity

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Table 1. Ternary Systems and Models Performance

System	Type	Temperature (K)	Reference	m_2 Calculation Performance ¹⁾
Toluene(1) 2-Propanone(2) Water(3)	I	283.15	Sorensen and Arlt,1980, Vol. 5/2,pág.497.	UNIQUAC spec.par.+Hand UNIQUAC spec.par. UNIFAC+Hand UNIFAC
Toluene(1) 2-Propanone(2) Water(3)	I	293.15	Sorensen and Arlt,1980, Vol. 5/2,pág.498.	UNIQUAC spec.par.+Hand UNIFAC+Hand UNIQUAC spec.par. UNIFAC
Toluene(1) 2-Propanone(2) Water(3)	I	303.15	Sorensen and Arlt,1980, Vol. 5/2,pág.499.	UNIQUAC spec.par.+Hand UNIQUAC spec.par. UNIFAC+Hand UNIFAC
1-Butanol(1) Succinic Acid(2) Water(3)	I	283.15	Sorensen and Arlt,1980, Vol. 5/3,pág.11.	UNIQUAC spec.par.+Hand UNIQUAC spec.par. UNIFAC+Hand UNIFAC
1-Butanol(1) Succinic Acid(2) Water(3)	I	303.15	Sorensen and Arlt,1980, Vol. 5/3,pág.14.	UNIQUAC spec.par.+Hand UNIQUAC spec.par. UNIFAC+Hand UNIFAC
Propanoic Acid,Ethyl Ester(1) 2-Propanone(2) Water(3)	I	303.15	Sorensen and Arlt,1980, Vol. 5/2,pág.474.	UNIQUAC spec.par. UNIQUAC spec.par.+Hand UNIFAC+Hand UNIFAC
Benzene(1) 1,4-Dioxane(2) Water(3)	I	298.15	Sorensen and Arlt,1980, Vol. 5/3,pág.72.	UNIQUAC spec.par.+Hand UNIQUAC spec.par. UNIQUAC com.par.+Hand UNIQUAC com.par.
Heptane(1) Cyclohexane(2) Aniline(3)	II	298.15	Sorensen and Arlt,1980, Vol. 5/3,pág.304.	UNIFAC+Hand UNIQUAC com.par.+Hand UNIFAC
Butane,2,2-Dimethyl(1) Cyclopentane(2) Aniline(3)	II	288.15	Sorensen and Arlt,1980, Vol. 5/3,pág.248.	UNIQUAC spec.par. UNIQUAC spec.par.+Hand UNIFAC+Hand UNIFAC
Acetic Acid,Ethyl Ester(1) 1-Propanol(2) Water(3)	I	293.15	Sorensen and Arlt,1980, Vol. 5/2,pág.550.	UNIQUAC spec.par.+Hand UNIQUAC spec.par. UNIFAC+Hand UNIFAC
Toluene(1) Acetaldehyde(2) Water(3)	I	290.15	Sorensen and Arlt,1980, Vol. 5/2,pág.215.	UNIFAC+Hand UNIFAC

1) m_2 = distribution coefficient of component 2 = y_2/x_2

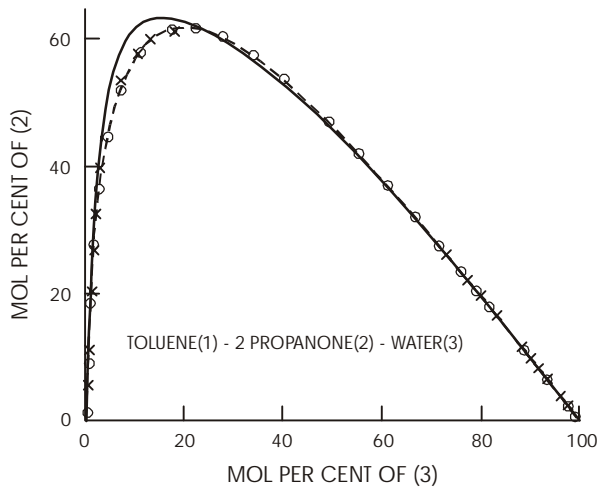


Fig.1a. Comparison of calculated binodal curve with experimental data: \times Experimental, — UNIFAC, - - - UNQUAC (“specific”), o o o UNQUAC (“common”).

coefficients one can carry out calculations to obtain liquid-liquid compositions (Sorensen *et al.*, 1979b). We used two models in our calculations: UNQUAC and UNIFAC. We took data, equations, parameters and programs from Sorensen and Arlt (1980) and Magnussen *et al.* (1981).

2.2 Proposed Method

We combined Hand’s equation and activity coefficient models in the following way: 1) We got k and C constants of Hand’s equation (Eqn. 1) using experimental liquid-liquid ternary equilibrium data, 2) we obtained the binodal curve of the ternary system under study using an activity coefficient model, 3) we got x_1 and x_3 from the binodal curve of step 2 after choosing a

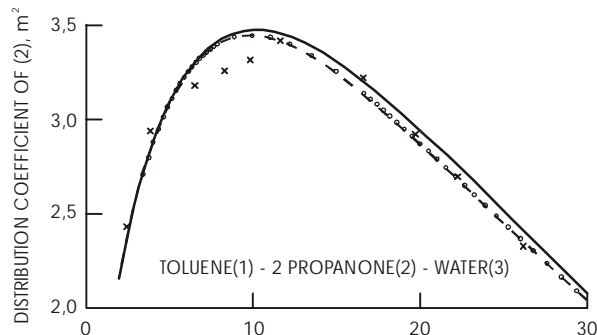


Fig.2a. Comparison of calculated distribution coefficient with experimental data: \times Experimental, — UNIFAC + Hand, o o o UNQUAC (“specific”) + Hand, - - - UNQUAC (“common”) + Hand.

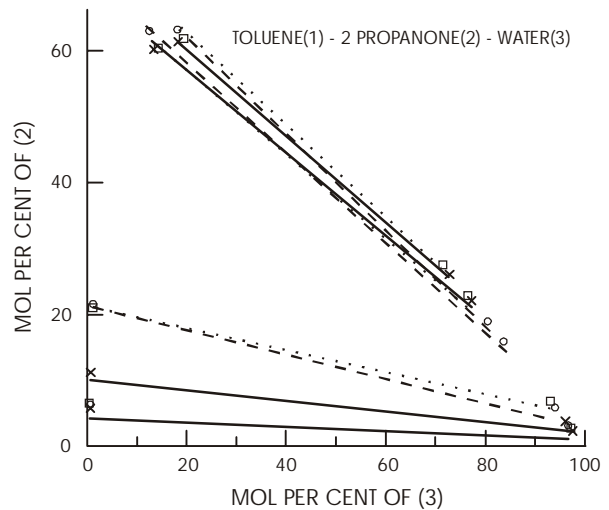


Fig.1b. Comparison of calculated tie lines with experimental data: \times — \times Experimental, o - - - o UNIFAC, \square \square UNQUAC (“specific”).

value for x_2 , 4) with x_2/x_3 , k and C from previous steps and using Eqn.1 we got y_2/y_1 , 5) from the binodal curve and y_2/y_1 we calculated y_1, y_2 and y_3 , 6) we computed m_i , where $m_i = y_i / x_i$.

3. Results and Discussions

Table 1 contains the systems we did in this study. Experimental reference, temperature, and type of mixture are written down in the table. The sample of systems under study encompasses ternary mixtures with and without water, with one and two immiscible binaries, and some mixtures at different

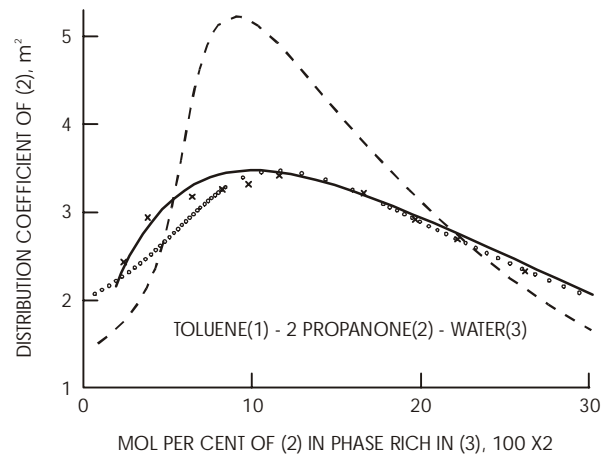


Fig.2b. Comparison of calculated distribution coefficient with experimental data: \times Experimental, — UNIFAC + Hand, - - - UNIFAC, o o o UNQUAC (“specific”).

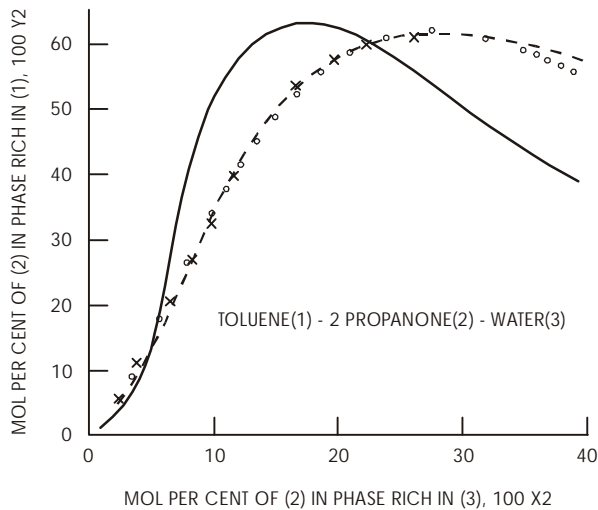


Fig.3. Comparison of calculated solute distribution with experimental data: \times Experimental, — UNIFAC, - - - UNIQUAC (“specific”), o o o UNIQUAC (“specific”) + Hand.

temperatures. Table 1 and Figs. 1 to 9 compare and display results from the calculations described in item 2: Models and Method. Table 1 shows in its last column calculated distribution coefficient for the solute, component 2, in a qualitative way. In that last column an order is written reflecting the agreement of the model/method with the experimental information.

The model named first in the list is the one that presents the best agreement. The picture of the agreement results of three representative systems could be appreciated from Fig.1 to 9. As expected, correlation of data (UNIQUAC) is better than prediction (UNIFAC) for phase envelope and tie

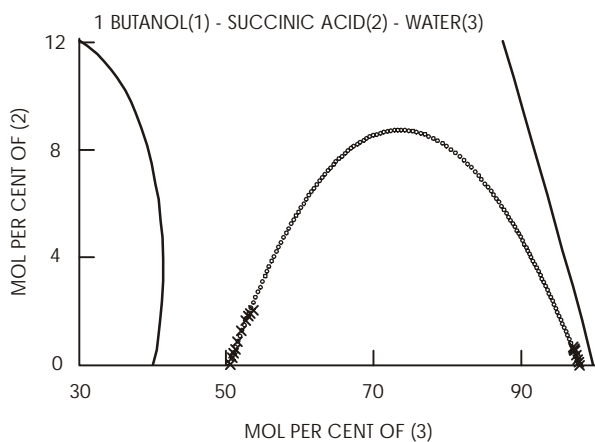


Fig.4a. Comparison of calculated binodal curve with experimental data: \times Experimental, — UNIFAC, o o o UNIQUAC (“specific”).

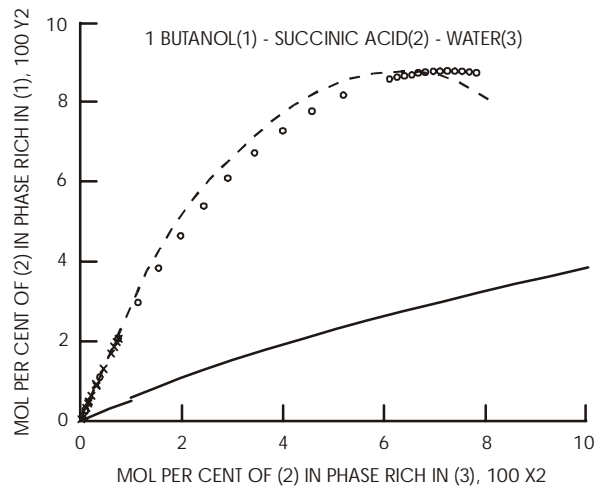


Fig.6. Comparison of calculated solute distribution with experimental data: \times Experimental, — UNIFAC, - - - UNIQUAC (“specific”), o o o UNIQUAC (“specific”) + Hand.

lines determination. Those facts that are not written in Table 1 could be seen in Figs.1, 4 and 7. In Table 1 it is also possible to see under its last heading that the calculation methods that combine a thermodynamics model (UNIQUAC or UNIFAC) with the Hand correlation give better coefficient distribution than the one calculated using the thermodynamics model itself. In some cases the combination UNIFAC plus Hand is even better than correlation of data using UNIQUAC. Figure 1 presents phase envelope (Fig.1a) and tie lines (Fig.1b) for Toluene(1)-2 Propanone(2)-Water(3). Figure 1a shows experimental, UNIQUAC, and UNIFAC results. Results from UNIQUAC belong to two different sets of parameters (Sorensen and Arlt, 1980). The parameters

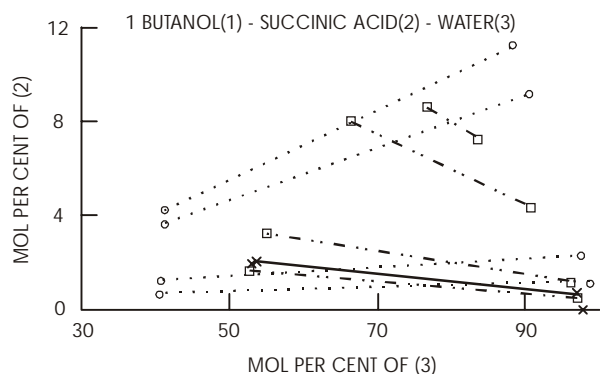


Fig.4b. Comparison of calculated tie lines with experimental data: \times — \times Experimental, o.....o UNIFAC, \square -...- \square UNIQUAC (“specific”).

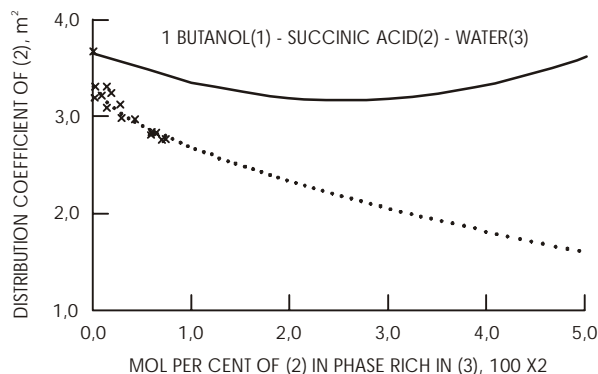


Fig.5a. Comparison of calculated distribution coefficient with experimental data: \times Experimental, —UNIFAC + Hand, $\cdots\cdots$ UNIQUAC (“specific”) + Hand.

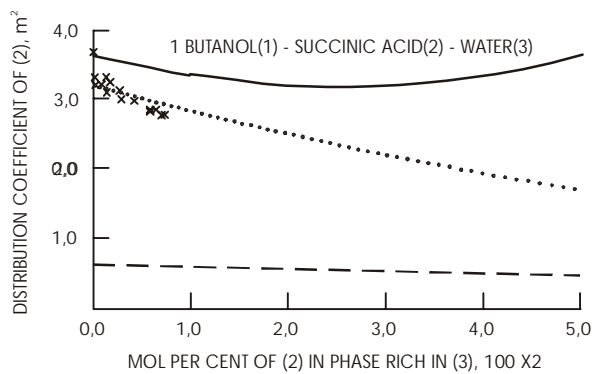


Fig.5b. Comparison of calculated distribution coefficient with experimental data: \times Experimental, —UNIFAC + Hand, - - -UNIFAC, $\cdots\cdots$ UNIQUAC (“specific”).

are “specific” when they are fitted to one particular system. The parameters are “common” when they are determined by simultaneous correlation of experimental data from different systems. Figure 1b shows a few tie lines near plait point and another few at low concentration of the distributed component. The tie lines are from experimental data, UNIQUAC with specific parameters and UNIFAC. The objective of Fig.1 is to show the fact that UNIQUAC/UNIFAC represent better the binodal curve of liquid-liquid equilibrium in ternary mixtures than their corresponding tie lines. The association of Hand with UNIQUAC/UNIFAC proposed in this paper is built in that fact. Figure 2 presents the distribution coefficient of 2-Propanone. The coefficient is calculated dividing the concentration of

2-Propanone in the Toluene rich phase by the concentration of 2-Propanone in the Water rich phase. Figure 2 is split in Fig.2a and 2b to facilitate the visualization of results. The distribution coefficient belonging to the combination Hand with UNIFAC was drawn in both figures (Fig.2a and Fig.2b) as a reference for comparison. Examination of Fig.2 indicates that the use of Hand correlation improves the description of distribution coefficient. Any model in combination with Hand’s equation (UNIQUAC with specific or common parameters, or UNIFAC) gives a better distribution coefficient than the use of any model alone. Figure 3 displaying 2-Propanone concentration in both phases shows the same result than Fig.2: combination of model with Hand gives better results.

Figures 4 and 5 display identical results than Figs.1 and 2 for 1-Butanol(1)- Succinic

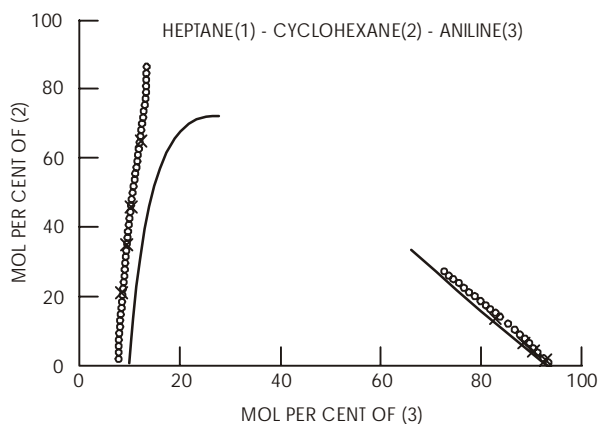


Fig.7a. Comparison of calculated binodal curve with experimental data: \times Experimental, —UNIFAC, $\circ\circ\circ$ UNIQUAC (“common”).

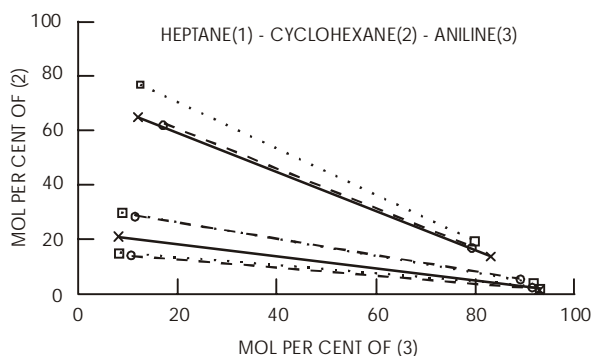


Fig.7b. Comparison of calculated tie lines with experimental data: \times — \times Experimental, \circ — \circ UNIFAC, \square — \cdots — \square UNIQUAC (“common”).

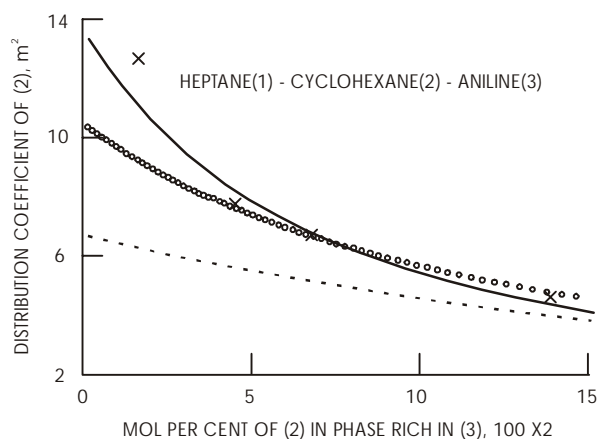


Fig.8a. Comparison of calculated distribution coefficient with experimental data: \times Experimental, —UNIFAC + Hand, - - -UNIFAC, o o o UNIQUAC (“common”).

Acid(2)-Water(3). Figure 6 shows solute (Succinic Acid) distribution in both phases. Figures 7, 8 and 9 displays the same form of behavior for the Heptane(1)-Cyclohexane(2)-Aniline(3) system than the other two earlier systems. This last ternary system is a type II mixture, meaning that two binaries are immiscible: Heptane-Aniline, and Cyclohexane -Aniline. The previous two systems are type I mixtures with only one binary showing immiscibility. In Figs.7 and 8 the numbers for the UNIQUAC with specific parameters are missing because the parameters were not available from the data source (Sorensen and Arlt, 1980). Distribution coefficients for the other two components of the ternary systems show the same behavior than distribution

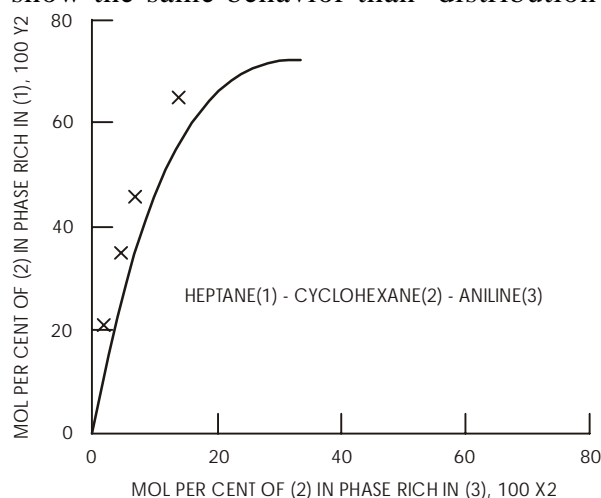


Fig.9. Comparison of calculated solute distribution with experimental data: \times Experimental, —UNIFAC + Hand.

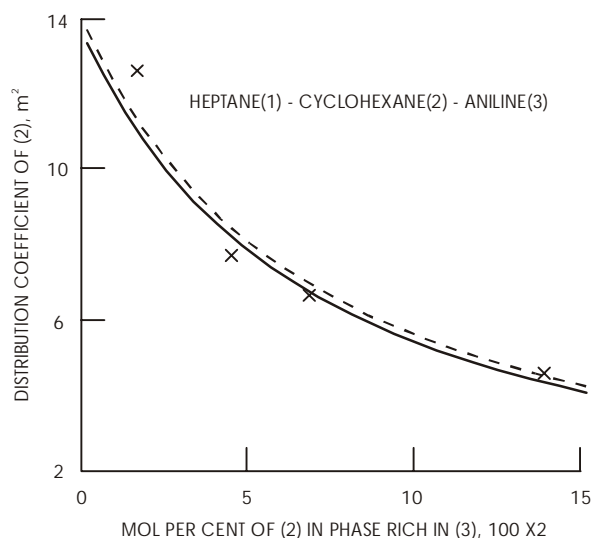


Fig.8b. Comparison of calculated distribution coefficient with experimental data: \times Experimental, — UNIFAC + Hand, - - -UNIQUAC (“common”) + Hand.

coefficient for component 2 in all the ternary mixtures under study.

The proposed combination seems to work because it uses the best of each of the approaches cited earlier in this work. The orientation of the tie lines is set by Hand's equation and the binodal curve is set by UNIQUAC/UNIFAC. We could guess that the proposed method is going to work better in cases where tie line's differences between UNIQUAC and experiments are larger. The combination works even when the available experimental information is little allowing for extrapolation of data. The minimum experimental information required for the combination to work is two tie lines that are needed to obtain Hand's parameter k and C of Eqn. 1. Then, it is possible to use the proposed combination to get a table of extrapolated distribution coefficients that are fitted with polynomials as recommended in the literature (Rod, 1976). Additional undertaking is necessary to evaluate completely the proposed calculation method. Two things will be done: a) a systematic study of many more systems; b) an analysis of how to assemble Hand's equation with UNIQUAC/UNIFAC at the very low composition of the distributed component and at the plait point.

4. Conclusions

This paper presents a method to calculate coefficient distributions for liquid - liquid ternary systems. The proposed method combines Hand's equation with UNIQUAC or UNIFAC model. The combination gives distribution coefficients that agree with experimental ones better than the coefficients calculated using the models alone. In addition, the proposed method could be used to extrapolate scarce experimental information.

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