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## Property Calculation and Prediction for Selecting Solvent Systems in CCC

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### ABSTRACT

A theoretical method is presented for the property calculation and prediction in selecting solvent systems of countercurrent chromatography (CCC). A Universal Functional-group Activity Coefficients (UNIFAC) model is used as the solution model to describe the non-ideality of the liquid mixtures. The results are as follows.

1. Thermodynamic criterion is given to judge the possibility of phase split.
2. If the phase split takes place, calculation of phase composition is carried out.

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3. Calculate the volume ratio of the two immiscible phases in the system.
4. Densities are calculated without considering the volumetric non-ideality.
5. Viscosities are estimated by using the "cubic root summation."
6. Dielectric constants are obtained by using a semi-empirical mixing rule.
7. Interfacial tension is also estimated by another semi-empirical equation.

Compared with experimental data, the calculation results are satisfactory and accurate. A program is written for the computer calculation. Only the volume ratio of the solvents is needed for the input of the computation. A chosen system can be examined in a few minutes. If mobile phase (stationary as well) is wanted in the separation practice, there is no need to "equilibrate" the solvents, just "prepare" this phase of any desired quantity according to the result of calculation.

*Key Words:* Solvent selection; Countercurrent chromatography; Modified UNIFAC model.

## INTRODUCTION

Countercurrent chromatography (CCC) is a separation method based on the partition of solutes between two liquid phases as they flow in a countercurrent way within a thin tube, under a centrifugal force.

One advantage of this type of chromatography is that no solid packing is required to form a stationary phase, whereas, it is a chosen one of the two equilibrated liquid phases. Therefore, in using CCC, more attention must be paid to the selection of solvent systems, as well as, the apparatus and the operation parameters, so as to obtain the optimal settings of experimental factors for the satisfactory separation of the solutes. For the chemists engaged in CCC, a lot of time would be taken in searching for a suitable solvent system for a specific subject.

Our aim for the selection of solvent systems is to find a way that we can calculate the properties with, or without, a few experiments. The problem involved is whether there will be a phase split when two, three, or more solvents are put together, mixed thoroughly, and then allowed to settle. If there is, we want to know what is the volume ratio of the split two phases. This ratio is of importance for us in considering convenience and economy. We also want to know the properties of the two phases, which are, of course, very important for obtaining high retention of the stationary phase and good separation results. The





properties of interest are density, viscosity, interfacial tension, and polarity. If possible, we want to obtain the compositions of the two phases, which are difficult to obtain in usual circumstances. In most cases, we know only the initial total composition, i.e., the overall composition of the two phases.

For this purpose, we rely on thermodynamics. Solution non-ideality must be taken into consideration. Of course, we can use phase diagrams of solvent mixtures; but, when we attempt to use the diagrams, we find we need the details of tie-lines which, in general, are not given in the literature, except in the compilation by Sorensen and Arlt.<sup>[1]</sup>

Until now, many theoretical models have been established for the calculation of activity coefficients of the components in solution. For non-electrolyte solutions, Scatchard–Hildebrand theory,<sup>[2]</sup> Margules type equations,<sup>[3]</sup> and equations based on “local composition” are widely used. Each of them has its proper applicable area and its limit of usage.

The Wilson equation,<sup>[4]</sup> NRTL (Non-Random Two Liquids) equation,<sup>[5]</sup> UNIQUAC (Universal Quasi-lattice Activity Coefficients) equation,<sup>[6]</sup> UNIFAC (Universal Functional-group Activity Coefficients) equation,<sup>[7,8]</sup> and the Modified UNIFAC equation<sup>[9,10]</sup> are all “local composition” type equations. When we use them for calculations, we must know the interaction parameters between the solvents. These parameters are collected and extracted from data of vapor–liquid equilibria (VLE), liquid–liquid equilibria (LLE), and other experiments. Sometimes, the calculations are difficult to carry out for lack of interaction parameters of some solvent-pairs. One exception is the UNIFAC equation.

The UNIFAC equation is an algorithm based on “group contribution.” Conceptually, the properties of a solvent mixture are the integration of the interactions among the functional groups that construct the solvents in the mixture. Instead of “molecular” interaction parameters, here we use group interaction parameters for the calculation. Fortunately, we now have well-established tables for finding the parameters we need. The tables were built through years of efforts on giant data banks in which there are immense thermodynamic data collections. There are millions of compounds in the world, but merely scores of functional groups. The group interaction parameter number is limited to several thousands and this enables the tables to be established. Though the accuracy of UNIFAC equation is a little lower than the “molecular” equations, it can meet our needs in most cases. Commonly used solvents in CCC number several dozens. The group interaction parameters for them are easy to find. There appears to be no major problem to calculate and predict the properties of solvent mixtures in CCC by using the UNIFAC equation.

Sometimes, people add some acids, bases, or salts into solvent systems to improve the separation, but their quantities are usually small. In most property





calculations, these small components can be disregarded. If their influence must be taken into account, we may use other types of equations, such as Pitzer's equation,<sup>[11,12]</sup> for more detailed treatment. Of course, that will make the calculation more complicated. Until now, we have not had the need to do this type of calculation.

## THEORY

### Phase Split: Criterion for the Stability of a Solvent System

When we put two, three, or more solvents together to make a mixture, will there be a phase split? In other words, will two phases will emerge? That is the problem of stability of a solvent system. When the system forms a single homogeneous phase, its Gibbs free energy is located at the minimum point, i.e.,  $\delta G > 0$ , the system is considered to be stable. Otherwise, it is unstable, and phase splitting will take place.

At the stable point of the system, the Taylor series expansion of  $\delta G$  is performed. Taking the second order term and performing reduction and some mathematical transformation, for a system of  $K$  components, we get a matrix

$$(\mu_{ij})_{K-1, K-1} = \begin{pmatrix} \mu_{11} & \mu_{12} & \cdots & \mu_{1, K-1} \\ \mu_{21} & \mu_{22} & \cdots & \mu_{2, K-1} \\ \vdots & \vdots & \vdots & \vdots \\ \mu_{K-1, 1} & \mu_{K-1, 2} & \cdots & \mu_{K-1, K-1} \end{pmatrix} \quad (1)$$

where  $\mu_i = \partial G / \partial n_i$ ,  $\mu_{ij} = \partial \mu_i / \partial n_j$ .

Thermodynamically, the criterion of the system's stability is that the sequential subdeterminants in the matrix are all positive. That is the sufficient and necessary condition of stability of the system.

For a binary system, there must be

$$\mu_{11} > 0$$

For a ternary system,

$$\mu_{11} > 0, \mu_{22} > 0$$

$$\begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} \geq 0$$





For a quaternary system,

$$\begin{aligned} &\mu_{11} > 0, \mu_{22} > 0, \mu_{33} > 0 \\ &\begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} \geq 0, \begin{vmatrix} \mu_{11} & \mu_{13} \\ \mu_{31} & \mu_{33} \end{vmatrix} \geq 0, \begin{vmatrix} \mu_{22} & \mu_{23} \\ \mu_{32} & \mu_{33} \end{vmatrix} \geq 0 \\ &\begin{vmatrix} \mu_{11} & \mu_{12} & \mu_{13} \\ \mu_{21} & \mu_{22} & \mu_{23} \\ \mu_{31} & \mu_{32} & \mu_{33} \end{vmatrix} \geq 0 \end{aligned}$$

and so forth.

To obtain the  $\mu_{ij}$ s, we use modified UNIFAC equation.

#### The Modified Universal Functional-Group Activity Coefficient Model

In modified UNIFAC model, the activity coefficient of a component  $i$  in the mixture is the sum of two parts: a combinatorial part  $\gamma_i^C$  and a residual one  $\gamma_i^R$ :

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

The combinatorial part is calculated in an empirical way to make it possible to deal with compounds which are very different in size:

$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - 5q_i \left[ 1 - \left( \frac{V_i}{F_i} \right) + \ln \left( \frac{V_i}{F_i} \right) \right] \quad (3)$$

Parameter  $V_i'$  can be calculated by using the relative van der Waals volumes  $R_k$  of the different groups:

$$V_i' = \frac{r_i^{3/4}}{\sum x_j r_j^{3/4}} \quad (4)$$

Other parameters are calculated as follows:

$$\begin{aligned} V_i &= \frac{r_i}{\sum x_j r_j} \\ r_j &= \sum v_k^{(j)} R_k \\ F_i &= \frac{q_i}{\sum_j x_j q_j} \\ q_i &= \sum v_k^{(i)} Q_k \end{aligned}$$



The residual part is obtained by

$$\ln \gamma_i^R = \sum v_k^{(i)} (\ln \Gamma_k + \ln \Gamma_k^{(i)}) \quad (5)$$

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \Theta_m \Psi_{mk} \right) - \sum_m \left( \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right) \right] \quad (6)$$

where  $\Gamma_k$  is group activity coefficient of group  $k$  in the mixture. The group area fraction  $\Theta_m$  and group mole fraction  $X_m$  are given by

$$\Theta_m = \frac{Q_m X_m}{\sum Q_n X_n}$$

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n (v_n^{(j)} x_j)}$$

Parameter  $\Psi_{nm}$  is temperature-dependent:

$$\Psi_{nm} = \exp \left[ \frac{-(a_{nm} + b_{nm} T + c_{nm} T^2)}{T} \right] \quad (7)$$

The  $\mu_{ij}$ s can be deduced from

$$\mu_{ij} = \left( \frac{-RT}{n_t} \right) + RT \left( \frac{\partial \ln \gamma_i}{\partial n_j} \right) \quad (8)$$

When we have the molecular structure of the solvents, we know the values of  $r$ ,  $q$ ,  $R$ ,  $Q$ ,  $v$ , and  $V$ ,  $F$ ,  $x$ ,  $X$ ,  $\Theta$ ,  $\Psi$  can also be calculated. Parameters  $a$ ,  $b$ , and  $c$  are all listed in the parameter tables. Now, we can conduct the calculation of phase composition.

### Calculation of the Phase Composition

With two equilibrated phases for a system, the phase composition can be found by solving an equation set using optimization or analytical methods.

For a system of  $K$  components, if the total mole number and total composition of both phases are given, there are  $(4K+2)$  equations and equal variables.

For phase equilibrium of the components, based on the equality of activity between the upper and the lower phases, the  $K$  equations are:

$$x_i^u i^u = x_i^l i^l \quad i = 1, 2, \dots, K \quad (9)$$





Another set of  $(3K + 2)$  equations expresses mass balance:

$$x_i^u n_u + x_i^l n_l = x_i^t n_t \quad i = 1, 2, \dots, K \quad (10)$$

$$\gamma_i^u = f(x_1^u, x_2^u, \dots, x_K^u) \quad i = 1, 2, \dots, K \quad (11)$$

$$\gamma_i^l = f(x_1^l, x_2^l, \dots, x_K^l) \quad i = 1, 2, \dots, K \quad (12)$$

$$\sum x_i^u = 1, \quad \sum x_i^l = 1 \quad (13)$$

where  $x_i^t$  is total mole fraction of component  $i$  in both phases.  $n_t$  is total mole number of all the components in both phases.

Using an analytical solution method to avoid annoying multi-convergence, it becomes:

$p = n_u/n_l$  and  $w_i = x_i^u/x_i^l$ , that gives an equation of  $p$ :

$$\sum \left[ \frac{(w_i - 1)x_i^l}{(w_i - 1)p + 1} \right] = 0 \quad (14)$$

Now, using the Newtonian method in solving this equation, it further becomes

$$w_i = \frac{x_i^u}{x_i^l} = \frac{\gamma_i^l}{\gamma_i^u}$$

as the initial value of  $w_i$ . The initial value of  $p$  can be 0.5 in most cases.

The results will indicate whether there is a phase split, and what are the compositions of the phases.

Now that the phase compositions are known, the other properties of the phases are calculated.

### Calculation of Other Properties of the Phases

#### Density

Omitting the non-ideality of volume in mixing will give no major error in the estimation of phase volumes. So, the phase densities will be:

$$d_i^u = \frac{\sum_K x_i^u n_u M_i}{V_m^u} \quad d_i^l = \frac{\sum_K x_i^l n_l M_i}{V_m^l} \quad i = 1, 2, \dots, K \quad (15)$$

where  $V_m^u$  and  $V_m^l$  are volumes of the upper and the lower phase, respectively.  $n_u$  and  $n_l$  are the total numbers of the solvents in the two phases.  $M_i$  is molecular weight of component  $i$ .





Viscosity

The “cubic root summation” rule is used here. The cubic root of the viscosity of a mixture  $\eta_m$  will be the sum of the cubic roots of the viscosities of all the components in the phase:

$$\eta_m^{1/3} = \sum x_i \eta_i^{1/3} \tag{16}$$

Dielectric Constant

Dielectric constant of a liquid phase can be considered as an index of its polarity, though this index may be expressed in other ways.

In the calculation, we use the Oster mixing rule that is based on Kirkwood theory about dielectric constants. According to this theory, for a pure solvent, the polarization per unit volume is

$$p = \frac{(D - 1)(2D + 1)}{9D} \tag{17}$$

where  $D$  is dielectric constant.

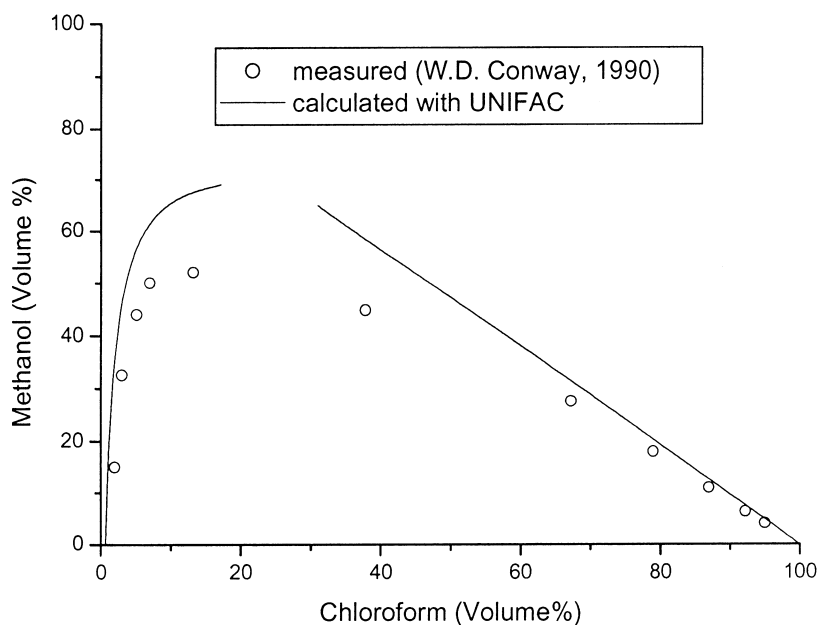


Figure 1. Calculated and experimental diagram for system CHCl<sub>3</sub>-CH<sub>3</sub>OH-H<sub>2</sub>O.





The Oster rule is, the polarization per unit volume of the solvent mixture is

$$p_m = \sum \varphi_i p_i \quad (18)$$

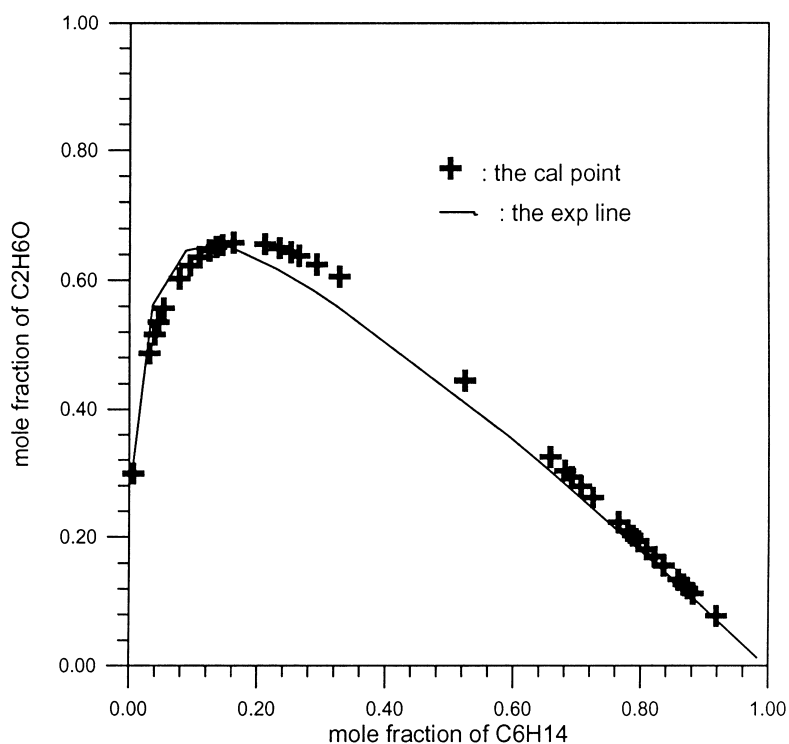
disregarding the mixing volume effect,  $\varphi_i$  is the volume fraction of component  $i$  in the mixture.

For the mixture, the expression of  $p$  remains valid:

$$p_m = \frac{(D_m - 1)(2D_m + 1)}{9D_m} \quad (19)$$

The dielectric constant of the mixture, then, is

$$D_m = \frac{(1 - 9p_m) + [(1 - 9p_m)^2 + 8]^{1/2}}{4} \quad (20)$$



**Figure 2.** Calculated and experimental phase diagram for system C<sub>6</sub>H<sub>14</sub>-C<sub>2</sub>H<sub>5</sub>OH-H<sub>2</sub>O.



**Table I.** Equilibrated phase volumetric compositions for quaternary system  $C_6H_{14}-EtOAc-CH_3OH-H_2O$ .

Total volumetric composition (relative) $C_6H_{14}-EtOAc-CH_3OH-H_2O$		Data source <sup>a</sup>	Composition, $x_i$ (upper phase) $C_6H_{14}-EtOAc-CH_3OH-H_2O$		Composition, $x_i$ (lower phase) $C_6H_{14}-EtOAc-CH_3OH-H_2O$	
5	5		5	Cal	0.5286–0.3874–0.0804–0.0036	0.0063–0.0594–0.2791–0.6553
			Exp	0.4932–0.4130–0.0714–0.0225	0.0006–0.0530–0.2876–0.6588	
6	4	5	Cal	0.6096–0.3116–0.0721–0.0067	0.0053–0.0447–0.2843–0.6656	
			Exp	0.6232–0.3244–0.0408–0.0116	0.0005–0.0445–0.2984–0.6565	
7	3	5	Cal	0.7019–0.2277–0.0703–0.0000	0.0045–0.0339–0.2875–0.6742	
			Exp	0.7334–0.2458–0.0156–0.0052	0.0005–0.0334–0.3020–0.6555	
8	2	5	Cal	0.7927–0.1416–0.0656–0.0000	0.0037–0.0241–0.2910–0.6811	
			Exp	0.8203–0.1716–0.0069–0.0012	0.0004–0.0220–0.3028–0.6748	
9	1	5	Cal	0.8998–0.0502–0.0500–0.0000	0.0032–0.0160–0.2957–0.6852	
			Exp	0.9210–0.0730–0.0055–0.0004	0.0002–0.0102–0.3088–0.6808	
4	5	4	Cal	0.4146–0.4903–0.0929–0.0022	0.0024–0.0417–0.2384–0.7174	
			Exp	0.4038–0.4713–0.0872–0.0377	0.0005–0.0464–0.2517–0.7014	
3	5	3	Cal	0.2832–0.4977–0.1185–0.1006	0.0011–0.0334–0.1868–0.7787	
			Exp	0.3032–0.5229–0.0935–0.0672	0.0002–0.0328–0.1913–0.7757	
2	5	2	Cal	0.2124–0.5871–0.0902–0.1103	0.0004–0.0288–0.1334–0.8374	
			Exp	0.2181–0.5873–0.0748–0.1198	0.0004–0.0288–0.1499–0.8209	
1	5	1	Cal	0.1093–0.6775–0.0730–0.1402	0.0001–0.0130–0.0674–0.9195	
			Exp	0.1113–0.6764–0.0482–0.1641	0.0001–0.0194–0.0741–0.9063	

<sup>a</sup>Experiment data are taken and converted from Oka et al., 1991.<sup>[17]</sup>

**Table 2.** Calculated and experimental volume ratio of the two phases in equilibrium for system C<sub>6</sub>H<sub>14</sub>-EtOAc-CH<sub>3</sub>OH-H<sub>2</sub>O.

No.	Total volumetric composition (relative)				Volume ratio (exp) <sup>a</sup>	Volume ratio (cal) <sup>b</sup>	Relative deviation (%)
	C <sub>6</sub> H <sub>14</sub>	EtOAc	CH <sub>3</sub> OH	H <sub>2</sub> O			
1	10	1	5	5	1.05	1.004	-4.38
2	9	2	5	5	0.96	0.892	-7.08
3	8	3	5	5	0.88	0.871	-1.02
4	7	4	5	5	0.82	0.845	+3.05
5	6	5	5	5	0.77	0.808	+4.94
6	5	5	5	5	0.74	0.750	+1.35
7	4	5	4	5	0.80	0.802	+0.25
8	3	5	3	5	0.86	0.860	+0.00
9	2	5	2	5	0.85	0.889	-4.41
10	1	5	1	5	0.92	0.890	-3.26

<sup>a</sup>Data from Oka et al., 1991.<sup>[17]</sup><sup>b</sup>This work.

### Interfacial Tension

A semi-empirical model<sup>[13,14]</sup> is used to estimate the interfacial tension. For a ternary system, for example, if there is a phase split the interfacial tension  $\sigma$  is expressed as

$$\sigma = \frac{(CRTS)}{[A_{\omega\omega} \exp(S)(x_1''q_1 + x_2''q_2 + x_{3r}q_3)]} \quad (21)$$

where R is the gas constant, 8.3143 J/mole/K; C, constant, regressed value, equals to 0.9414; T, absolute temperature, K;  $A_{\omega\omega}$ , van der Waals facial area,  $2.5 \times 10^9$ /mole;  $S = -\ln(x_1'' + x_2'' + x_{3r})$ ;  $x_1''$ ,  $x_2''$  are mole fractions of component 1 and 2 in the two phases;  $x_1'' < x_1'$ ;  $x_2'' < x_2'$ ;  $x_{3r}$  is the mole fraction of component 3 in the rich phase.

The equation is proven by the data of 54 binary systems and 23 ternary systems. The deviation is less than 20% when checked with the experiments.

## RESULTS AND DISCUSSION

According to the above theoretical discussion, a calculation program for practical use was elaborated. Now, the calculated results can be compared with



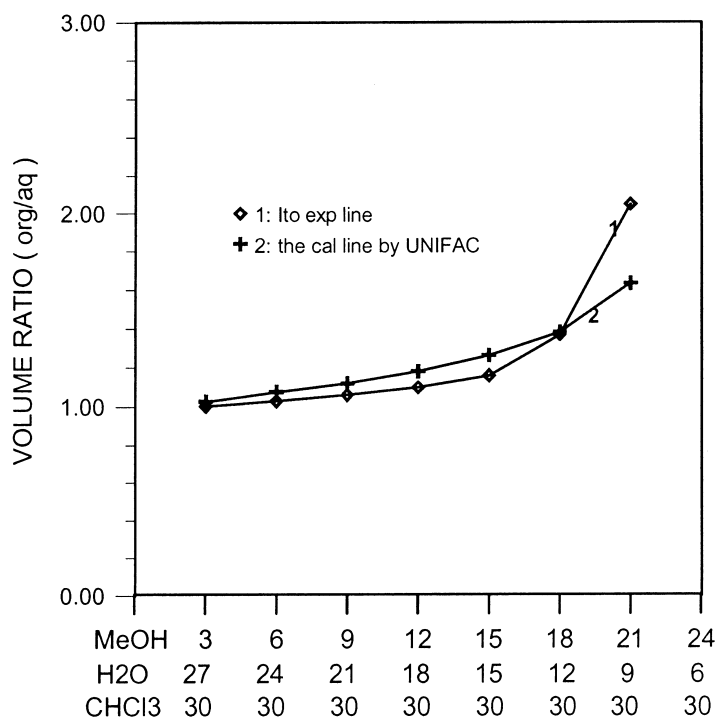


Figure 3. Volume ratios for the system  $\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$ .

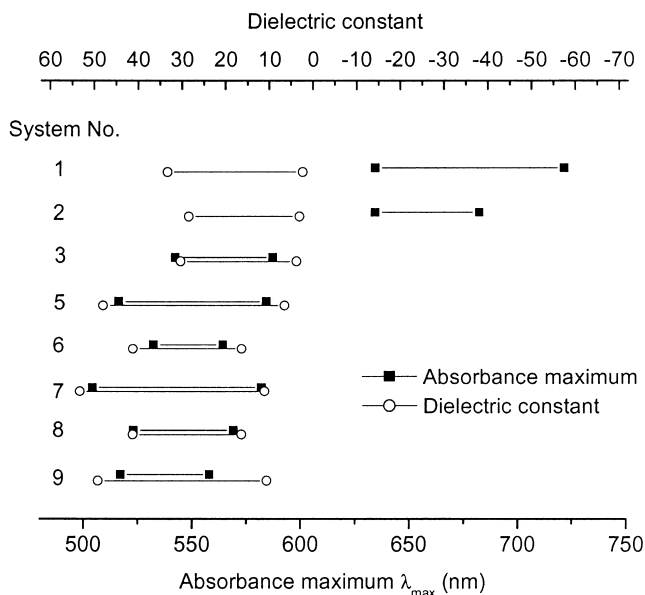
that of experiments or data in the literature. We have published part of the results previously.<sup>[15]</sup>

### Phase Split and Phase Composition

Taking system  $\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$  as an example, Fig. 1 is its phase diagram. The calibration is in volume percentage. Experimentally, the lower part (area surrounded by the circles) is the two-phase area. For a suitable system, the initial total composition must be located in this area and the compositions of the split phases must be at the intersection of the boundary line and the "tie-line." The circles (○) are the measured boundary of the two-phase area.<sup>[16]</sup> The solid line is the calculated boundary. We can see that, if the total composition we give is not located very close to the boundary, we would usually have a correct judgment for phase split.

Another example is given in Fig. 2. For the system  $\text{C}_6\text{H}_{14}\text{-C}_2\text{H}_5\text{OH-H}_2\text{O}$ , the calculated and experimental results are much better than for the system





**Figure 4.** Dielectric constants of the two phases and the maximum absorbance of Reichardt's dye in eight systems.

$\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$ . Empirically, systems containing chlorine are more difficult to treat in thermodynamics. That is to say, that the predicted results for chlorine-containing systems are usually less accurate than in other systems. A quaternary system, system  $\text{C}_6\text{H}_{14}\text{-EtOAc-CH}_3\text{OH-H}_2\text{O}$ , is also treated. The result is given in Table 1.

### Volume Ratio of the Two Phases in Equilibrium

For the quaternary system  $\text{C}_6\text{H}_{14}\text{-EtOAc-CH}_3\text{OH-H}_2\text{O}$ , for example, the accuracy of volume ratio estimation is fairly good, as shown in Table 2. If more mobile (or stationary) phase is wanted in the experiment, any desired quantity can be obtained by "preparation," according to the calculated mole fraction or volumetric composition. We used this kind of "prepared" solvent to replace the "equilibrated" solvents; the obtained chromatograms were almost the same in both cases.

Thus, much solvent can be saved if ratio estimation is fairly good, as shown in Table 2.



**Table 3.** Examples of polarities for eight systems.<sup>a</sup>

No.	System	Absorbance maxima <sup>a</sup> $\lambda_{\max}$ of the two phases, nm			Dielectric constants <sup>b</sup> $D_m$ of the two phases		
		High	Low	Mean <sup>c</sup>	High	Low	Mean
1	<i>n</i> -Hexane–acetonitrile (1 : 1)	721	634	677	33.20	2.30	17.75
2	<i>n</i> -Hexane–acetonitrile– chloroform (5 : 5 : 1)	682	634	659	28.27	2.95	16.11
3	<i>n</i> -Hexane–ethanol–water (6 : 5 : 1)	587	542	670	30.12	3.60	16.86
5	<i>n</i> -Hexane–ethyl acetate–methanol– water (1 : 1 : 1 : 1)	584	516	550	47.72	6.27	27.00
6	Chloroform–methanol– water (13 : 7 : 2)	564	532	548	40.86	16.08	28.47
7	Chloroform–methanol– water (1 : 1 : 1)	582	504	543	52.97	10.81	31.89
8	Chloroform–methanol– water (7 : 13 : 8)	569	523	546	40.85	16.11	28.48
9	Toluene–acetonitrile– water–ethanol (3 : 4 : 3 : 2)	558	517	537	48.79	10.31	29.55

<sup>a</sup>From Ref.<sup>[18]</sup><sup>b</sup>This work.<sup>c</sup>Mean = (high + low)/2.

Volume ratios for the ternary system  $\text{CHCl}_3\text{--CH}_3\text{OH--H}_2\text{O}$  are given in Fig. 3. Line 1 is experimental data,<sup>[17]</sup> whereas, line 2 is the predicted result of this work.

### Polarity Estimation

Using dielectric constants to describe solvent polarity has the advantage of being able to carry out the calculation easily. Some authors use the Reichardt's dye to estimate the polarity of the solvent. Figure 4 shows an example of the comparison of the above two methods. The eight systems are chosen from published data of Abbott et al.<sup>[18]</sup> All systems in the original paper (Table 3) were studied. We overlapped Abbott's results (absorbance maxima) onto our calculated dielectric constant values in the chart. There are



**Table 4.** Sequence of polarity of the system  $\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$ .

No.	Volumetric composition of the system $\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$	Distribution coeff. $K^a$		Dielectric constants <sup>d</sup>		$D_m$ of the two phases	
		1 <sup>b</sup>	2 <sup>c</sup>	High	Low	Mean	Span <sup>e</sup>
A	13:7:8	0.1	0.06	57.44	9.42	33.43	48.02
B	4:4:3	0.29	0.14	48.30	12.55	30.43	35.75
C	5:9:7	0.32	0.16	46.28	13.41	29.85	32.87
D	13:7:4	0.34	0.18	49.04	12.25	30.65	36.79
E	5:6:4	0.39	0.23	45.10	13.94	29.52	31.16
F	5:5:3	0.44	0.25	44.35	14.29	29.32	30.06
G	43:37:20	0.47	0.29	43.75	14.58	28.62	29.17
H	10:12:7	0.50	0.32	42.41	15.25	28.83	27.16
I	7:13:8	0.54	0.34	40.85	16.11	28.48	24.47
J	50:57:30	0.54	0.35	40.64	16.20	28.42	24.44
K	5:10:6	0.57	0.36	39.73	16.72	28.23	23.01

<sup>a</sup>From Ref.<sup>[19]</sup><sup>b</sup>Using *D*(+)-Glucosamine as standard solute.<sup>c</sup>Using PNP- $\alpha$ -*D*-Glucopyranoside as standard solute.<sup>d</sup>This work.<sup>e</sup>Span = high – low.

obvious similarities between the two sets of data, except for the first two systems.

It is not wise to speak about system polarity in a general way. The polarity of a particular phase should, instead, be given as the “polarity of the system.” If a polarity position (such as mean of the values in the two phases) and a span (such as the difference of the values in the two phases) are indicated, the “polarity of the system” is then clearly certified.

Another example of comparison of experimental and calculated polarity sequence is shown in Table 4. Experimental data are taken from Conway,<sup>[16,19]</sup> who used partition coefficients of some “standard materials” as an index of polarity of a system.

### Density and Viscosity

Density and viscosity are important factors that influence much of the mass transfer and phase split for which investigators use “settling time” to indicate the degree of difficulty of phase splitting. Table 5 is an example of the calculated and experimental results.






**Table 5.** Densities and viscosities (room temperature).

C <sub>6</sub> H <sub>14</sub> -EtOAc-CH <sub>3</sub> OH-H <sub>2</sub> O	Total volumetric composition (relative)		Data source <sup>a</sup>	Density <i>d</i> , g/cm <sup>3</sup>		Viscosity $\eta_m$ , cP		Settling time, sec
	5	5		UP <sup>b</sup>	LP <sup>c</sup>	UP	LP	
5	5	5	Cal	0.7450	0.8905	0.378	0.816	
			Exp	0.7444	0.9260			26
6	4	5	Cal	0.7267	0.8910	0.367	0.823	
			Exp	0.7193	0.9251			22
7	3	5	Cal	0.7071	0.8917	0.351	0.829	
			Exp	0.6985	0.9252			20
8	2	5	Cal	0.6886	0.8922	0.339	0.834	
			Exp	0.6797	0.9267			14
9	1	5	Cal	0.6695	0.8924	0.323	0.837	
			Exp	0.6660	0.9255			8
4	5	4	Cal	0.7721	0.9048	0.395	0.850	
			Exp	0.7641	0.9349			28
3	5	3	Cal	0.7990	0.9204	0.457	0.881	
			Exp	0.7894	0.9504			30
2	5	2	Cal	0.8236	0.9374	0.470	0.912	
			Exp	0.8282	0.9615			30
1	5	1	Cal	0.8546	0.9615	0.438	0.952	
			Exp	0.8452	0.9777			30

<sup>a</sup>Experimental data from Ref.<sup>[17]</sup> Predicted values, this work.

<sup>b</sup>Upper phase.

<sup>c</sup>Lower phase.


**Table 6.** Calculated and experimental interfacial tension at room temperature for system  $\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$ .

Volumetric composition (relative) $\text{CHCl}_3\text{-CH}_3\text{OH-H}_2\text{O}$			Experimental interfacial tension <sup>a</sup> $\sigma_{\text{exp}}$ (dyne/cm)	Calculated interfacial tension <sup>b</sup> $\sigma_{\text{cal}}$ (dyne/cm)	Relative deviation (%)
42.1	6.52	6.66	8.8	8.01	-8.98
41.2	8.58	5.93	6.7	6.17	-7.91
40.7	10.1	5.37	5.3	5.06	-2.69
40.8	12.3	4.35	3.7	3.55	-4.05
39.9	13.4	4.04	2.7	3.02	11.8
39.1	14.2	3.84	2.2	2.65	20.5
38.4	17.4	2.58	1.0	1.16	16.0

<sup>a</sup>Data from Ref.<sup>[17]</sup><sup>b</sup>This work.

### Interfacial Tension

Interfacial tension has great influence on the stability of immiscible dispersed systems. Although the equation for viscosity is a semi-empirical one, it gives rather good results for the system (Table 6).

### NOMENCLATURE

$\alpha_{nm}$	UNIFAC group interaction parameter between groups $n$ and $m$ (K)
$b_{nm}$	UNIFAC group interaction parameter between groups $n$ and $m$
$c_{nm}$	UNIFAC group interaction parameter between groups $n$ and $m$ ( $\text{K}^{-1}$ )
$d$	density of a phase ( $\text{g}/\text{cm}^3$ )
$D$	dielectric constant
$D_m$	dielectric constant of a liquid mixture
$F_i$	auxiliary property for component $i$ (surface fraction/mole fraction)
$q_i$	relative van der Waals surface area of subgroup $k$
$Q_k$	relative van der Waals surface area of subgroup $k$
$r_i$	relative van der Waals volume of component $i$
$R$	gas constant, 8.3143 J mole/K.
$R_k$	relative van der Waals volume of subgroup $k$
$T$	absolute temperature (K)
$V_i$	auxiliary property for component $i$ (volume fraction/mole fraction)
$V_t$	empirically modified $V_t$ -value

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$x_i$	mole fraction of component $i$
$X_m$	group mole fraction of group $m$
$\Gamma_k$	group activity coefficient of group $k$ in the mixture
$\Gamma_k^{(i)}$	group activity coefficient of group $k$ in the pure substance
$\gamma_i$	activity coefficient of component $i$
$\eta$	viscosity of solvent (c.p.)
$\eta_m$	viscosity of a liquid mixture (c.p.)
$\sigma$	interfacial tension (dyne/cm)
$\Theta_m$	surface fraction of group $m$
$v_k^{(i)}$	number of structural groups of type $k$ in molecule $i$
$\Psi_{nm}$	UNIFAC group interaction parameter between groups $n$ and $m$

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