

ANALYSIS OF PARTITION COEFFICIENTS OF TERNARY LIQUID-LIQUID EQUILIBRIUM SYSTEMS AND FINDING CONSISTENCY USING UNIQUAC MODEL

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The objective of this study is to investigate the change in partition coefficient with a change in the concentration of the solute in a liquid system consisting of two relatively immiscible solvents. To investigate the changes in the partition coefficients, the data of the partition coefficients at infinite dilution and the ternary Liquid-Liquid Equilibrium (LLE) data at finite concentrations of the solute should be consistent. In this study, 29 ternary systems that are found in literature and for which the partition coefficients at infinite dilution and the ternary LLE data cannot be predicted accurately by the universal quasi-chemical (UNIQUAC) model are identified. On the basis of this model, some consistent and inconsistent ternary systems are introduced. Three inconsistent systems, namely hexane-butanol-water, CCl_4 (carbon tetrachloride)-PA (propanoic acid)-water, and hexane-PA-water, are chosen for detailed analysis in this study. The UNIQUAC activity coefficient model is used to represent these data over a range of concentrations. The results show large errors, exhibiting the inability of this model to correlate the data. Furthermore, some ternary systems in which cross behavior of solutes between two phases observed are identified.

Keywords: partition coefficients, UNIQUAC model, consistent systems, inconsistent systems, cross behavior

1. INTRODUCTION

The concept of partition coefficient is used in various areas of applied science such as environmental science, separations, and pharmaceuticals. Partition coefficients are used for various purposes. They are used for measuring equilibria, concurrent distributions, dissolution and partitioning rate of drugs, hydrophobic bonding ability and structure and activity parameters, aquatic toxicity, and biomagnifications. They are also used to estimate water solubility, adsorption and mobility in the soil, adsorption coefficient of soils and sediments, bioaccumulation in fish, and melting and boiling points. Further, partition coefficients play an important role in the study of hydrophile-lipophile balance (HLB), liquid ion-exchange media and ion-selective electrodes, risk assessment, transmembrane transport; they are also used in the modeling of the fate transport of pollutants. The partition coefficient (K_{sw}) of a solute is defined as the ratio of the concentration of the solute in a water-saturated solvent (organic) phase to the concentration of the solute in a solvent-saturated aqueous phase. Environmental scientists usually prefer using octanol/water partition coefficient (K_{ow}) to study the distribution of chemicals between water and lipids. However, in chemical thermodynamics, researchers usually refer to distribution coefficient (D_{sw}), which is the ratio of the mole fraction of a solute in an organic phase to

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its mole fraction in an aqueous phase. Both K_{sw} and K_{ow} are determined at a negligibly small concentration of the solute or alternatively at infinite dilution.

Partition coefficient is usually defined at the infinite dilution. It can also be predicted using ternary systems provided the two solvents are immiscible. It is expected that if a liquid state model can represent the ternary data well then it should also be able to predict the correct partition coefficient. The goal of this study is to check for such consistency in ternary systems (water–solute–solvent) by using the UNIQUAC model (Abrams and Prausnitz, 1975).

For a solute partitioned between a solvent and water,

$$X_i^s \gamma_i^s = X_i^w \gamma_i^w \quad (1)$$

At very dilute concentrations, the solute mole fraction can be expressed as the product of the solute molar concentration and the molar volume of the respective phase.

$$C_i^s \hat{V}_i^s \gamma_i^s = C_i^w \hat{V}_i^w \gamma_i^w \quad (2)$$

The distribution coefficient is expressed as follows:

$$D_{sw} = \frac{X_i^s}{X_i^w} = \frac{\gamma_i^w}{\gamma_i^s} \quad (3)$$

From Equations 2 and 3, the partition coefficient

$$K_{sw} = \frac{C_i^s}{C_i^w} = \frac{\hat{V}_i^w \gamma_i^w}{\hat{V}_i^s \gamma_i^s} = \frac{\hat{V}_i^w}{\hat{V}_i^s} D_{sw} \quad (4)$$

Equation 4 can be used to relate K_{sw} and D_{sw} .

Different models are available for correlating liquid–liquid equilibria. Some of the simplest and most effective models are the Margules, Van Laar, Redlich–Kister, and Black equations (Prausnitz et al., 1999). These models often yield good results; however extrapolation to concentrations beyond the range of data or the prediction of ternary phase diagrams from only binary information should not be carried out using these models because the results are often not qualitatively correct. Local composition models such as NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) have been proven to be superior to the above mentioned models for correlating binary and ternary liquid–liquid equilibria as well as for predicting ternary phase diagrams from binary data. The UNIQUAC model has two adjustable parameters per binary. Abrams and Prausnitz (1975) showed that the UNIQUAC model performs reasonably well in predicting ternary diagrams from binary information as well as correlating ternary diagrams. Anderson and Prausnitz (1978) showed that the UNIQUAC model predicts ternary diagrams from binary information very well when binary vapor–liquid and liquid–liquid equilibrium data are correlated simultaneously. Essentially, the UNIQUAC model is a two–parameter model and is of considerable use because of its wide applicability to various liquid solutions. In order to obtain better results for systems containing water and alcohols, Anderson and Prausnitz (1978) have empirically modified the UNIQUAC equation by using different values for the pure component area parameter, q , for water and alcohols in combinatorial and residual parts. In the UNIQUAC equation q represents pure-component molecular structure constants depending on molecular size and external surface area, combinatorial parts account for size and shape differences and residual parts account for energy differences among the molecules (Prausnitz et al., 1999). Nagata and Katoh (1981) have proposed another modified UNIQUAC equation for a variety of systems containing alcohols and water. However, there are some problems involved in the extension of systems with more than three components.

2. LITERATURE STUDIES AND COMPUTATIONAL WORK

Extensive collections of binary, ternary, and quaternary data are available in DECHEMA Chemistry Data Series by Macedo and Rasmussen (1987) and Sorensen and Arlt (1979, 1980a, 1980b). Volume I of this series deal with binary systems and volumes II, III, and IV deal with ternary and quaternary systems. In the DECHEMA series, the common UNIQUAC parameters for almost all binary systems are mentioned. The common parameters for a binary system, A–B, are the UNIQUAC parameters that may be used in liquid–liquid equilibrium calculations for any system containing the components A and B. These parameters are regressed from mutual solubility data if the two components are partially miscible. When the two components are completely miscible, the parameters are regressed by considering a number of systems containing the binary pair of interest. In some cases, the UNIQUAC parameters regressed from vapor–liquid equilibrium data can be used as common parameters.

A large collection of $\log K_{sw}$ is available in literature (Mackay et al., 1991). On the basis of the availability of UNIQUAC parameters and $\log K_{sw}$, a number of ternary systems are selected for this study. For these systems, the calculated D_{sw} values and the values obtained from literature (Hansch and Leo, 1979) are compared. In the case of some systems, the calculated values are in agreement with those obtained from literature, while in the case of some other systems, the values obtained by calculation and those obtained from literature differ by an order-of-magnitude. The former systems are referred to as consistent systems and the latter systems are called inconsistent systems. All computational work has been carried out using FORTRAN 77 and Absoft 10.1 as the compiler. The algorithm shown in Figure 1 was used for LLE calculation. Literature D_{sw} values were calculated from $\log K_{sw}$ (Hansch and Leo, 1979) by using Eq. (4). Lists of \hat{V}^s and \hat{V}^w used are shown in Table 1.

Table 1. Lists of \hat{V}^s and \hat{V}^w

System	Solubility (Sorensen and Arlt, 1980a, 1980b)		V^s [cm ³ /mol] (Mackay et al., 1991a, 1991b)	\hat{V}^s [cm ³ /mol]	\hat{V}^w [cm ³ /mol]
	M_s^w	M_w^s			
benzene – water	0.04	0.30	89.90	89.68*	18.04*
butanol – water	1.92	51.20	92.90	54.55	19.45
2-butanone – water	7.63	34.20	90.20	65.51	23.52
diethyl ether – water	1.55	5.22	103.89	99.41	19.34
toluene – water	0.011	0.237	106.90	106.68	18.02
tetrachloro methane – water	0.0092	0.081	97.10	97.03	18.02
ethyl acetate – water	1.6	13.80	98.50	87.40	19.30
cyclohexane – water	0.0467	0.167	108.03	107.87	18.05
hexanol – water	20.0	0.1045	125.57	125.45	39.52
dipropyl ether – water	0.0675	2.52	142.30	139.17	18.09
hexane – water	0.000278	0.0606	131.60	131.53	18.016
octanol – water	0.000703	20.70	158.40	129.34	18.016
butyl acetate – water	0.096	0.00	133.50	133.50	18.020
heptane – water	0.00005	0.0703	146.50	146.41	18.016

* sample calculation:

$$\hat{V}^s = V^s \cdot (1 - M_w^s / 100) + 18.016 \cdot M_w^s / 100 = 89.9 \cdot (1 - 0.003) + 18.016 \cdot 0.003 = 89.68$$

$$\hat{V}^w = V^s \cdot M_s^w / 100 + 18.016 \cdot (1 - M_s^w / 100) = 89.9 \cdot 0.004 + 18.016 \cdot (1 - 0.004) = 18.04$$

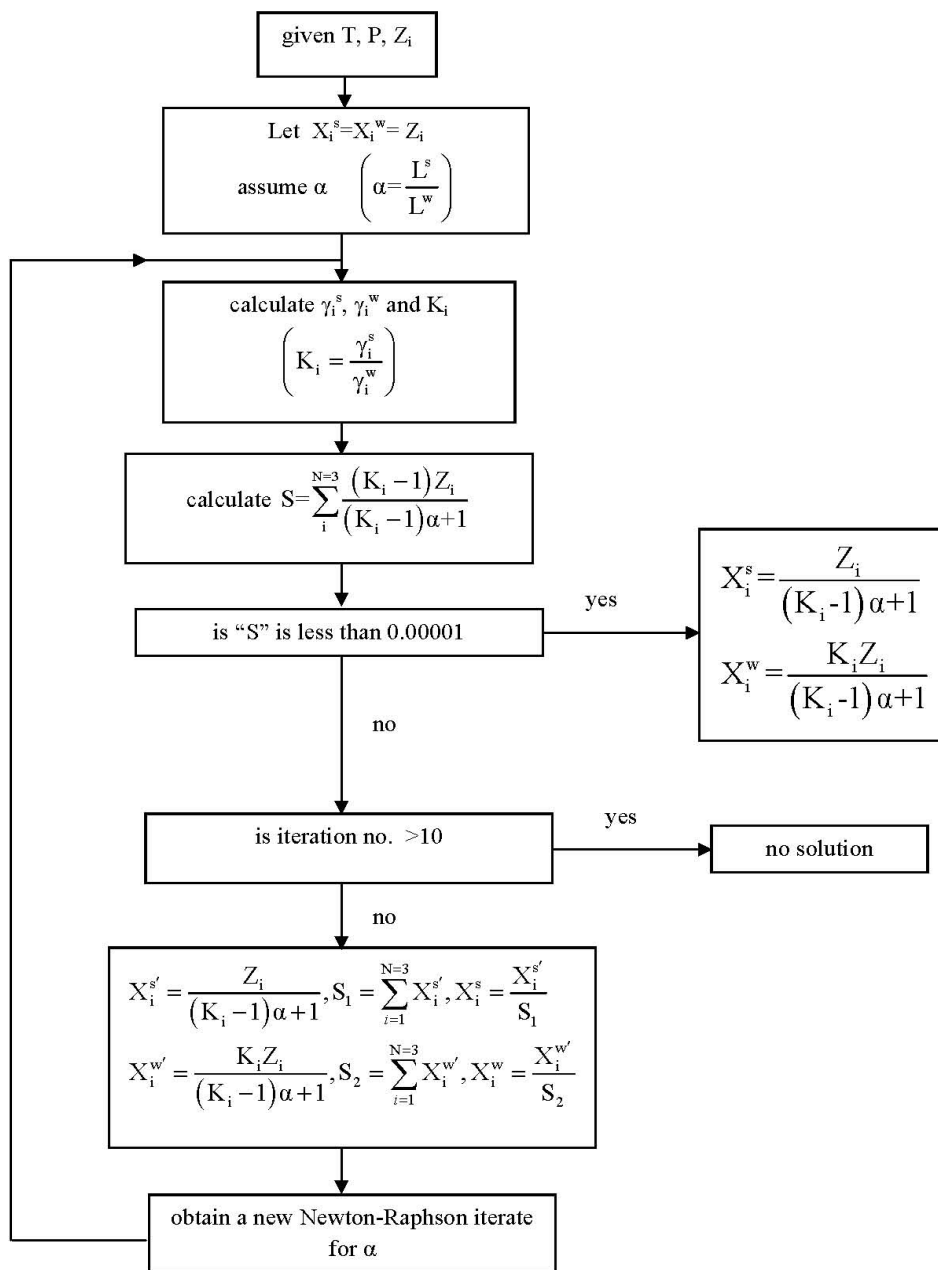


Fig. 1. Flowchart of ternary LLE calculation

Calculated D_{sw} values were obtained from the ratio of activity coefficient of a solute in an aqueous phase to that of the solute in the solvent phase at infinite dilution when the solute–feed composition was extrapolated to zero (i.e., $Z_i=0$). The UNIQUAC (Abrams and Prausnitz, 1975) equation used for calculations. The parameters of all binary pairs are obtained from literature (Sorensen and Arlt, 1980b).

3. RESULTS AND DISCUSSION

From the investigated systems, 26 ternary systems have been found for which the distribution coefficient at infinite dilution and the ternary data at finite concentration could be related within the deviation of 1 order of magnitude (<100%) using the UNIQUAC model. Here deviation means, $Deviation = \frac{(literature - calculated)}{calculated} \cdot 100$. These systems have been classified as consistent systems

(i.e., a ternary system for which the UNIQUAC parameters given in literature can be used to predict ternary data as well as partition coefficient at infinite dilution). Table 2 lists the consistent systems along with their experimentally determined D_{sw} values and calculated D_{sw} values. All D_{sw} values correspond to the middle components of each ternary system.

Table 2. List of consistent Systems

Ternary System	Literature D_{sw}	Calculated D_{sw}
benzene – ethanol – water	0.19*	0.21
benzene – 2-methyl-1-propanol – water	4.11	8.02
benzene – 2-methyl-2-propanol – water	1.33	1.84
benzene – pyridine – water	14.94	16.46
benzene – acetone – water	4.41	4.14
butanol – succinic acid – water	2.67	2.85
butanol – 2-hydroxy propanoic acid – water	2.2	2.75
2-butanone – acetic acid – water	3.33	3.11
diethyl ether – acetic acid – water	3.0	2.28
ethyl acetate – ethanol – water	1.79	1.71
tetrachloromethane – 2-propanone – water	2.45	2.39
toluene – aniline – water	45.97	50.16
toluene – pyridine – water	11.54	14.83
toluene – acetone – water	2.90	3.74
toluene – methanol – water	0.04	0.05
toluene – ethanol – water	0.11	0.09
toluene – 2-propanone – water	2.88	3.75
trichloro methane – formic acid – water	0.02	0.02
hexane – ethanol – water	0.04	0.03
heptane – aniline – water	6.36	7.73
heptane – ethanol – water	0.065	0.05
cyclohexane – ethanol – water	0.03	0.03
diethyl ether – acetic acid – water	2.31	3.00
diethyl ether – acetone – water	3.20	4.50
butanol – acetic acid – water	3.43	4.50
octanol – 2-hydroxy propanoic acid – water	1.59	1.50

* sample calculation: $D_{sw} = \frac{\hat{V}^S}{\hat{V}^W} K_{sw} = \frac{89.68}{18.04} \cdot 10^{-1.42} = 0.19$ ($\log K_{sw} = -1.42$)

In the case of some systems the distribution coefficient at infinite dilution and the ternary data at finite concentration were found to be deviated greater than 1 order of magnitude (>100%). These are classified as inconsistent systems. For these systems, the UNIQUAC parameters are not sufficient for predicting infinite dilution properties and finite ternary data simultaneously. Table 3 lists the 29 inconsistent systems. The wide disparity between the D_{sw} values indicates that the model UNIQUAC cannot be used to predict D_{sw} at infinitely dilute concentrations.

For extensive analysis, the calculated D_{sw} values of the ternary systems, namely, hexane–butanol–water, CCl_4 –PA(propanoic acid)–water and hexane–PA–water, were compared with the measured data. The data for these three systems only are available in literature (Sorensen and Arlt, 1979, 1980a, 1980b) at finite concentration; in our laboratory the data corresponding to very dilute region to finite

concentrations are measured. Complete experimental procedures and ternary LLE data are reported in the theses of Javvadi (2000) and Rizvi (2003). The parameters used for calculations for these three systems are listed in Tables 4 and 5.

Table 3. List of inconsistent ternary systems

Ternary System	Literature D_{sw}	Calculated D_{sw}
hexane – acetic acid – water	0.011	0.091
hexane – propanoic acid – water	0.020	1.651
hexane – propanol – water	0.221	9.984
hexane – butanol – water	1.450	14.634
hexane – acetone – water	0.879	1.847
benzene – methanol – water	0.064	0.112
benzene – 2-propanol – water	0.543	4.448
benzene – butanol – water	2.260	6.650
benzene – 2-butanol – water	3.841	20.653
benzene – acetic acid – water	0.031	0.213
benzene – propanoic acid – water	0.211	4.989
butyl acetate – methanol – water	0.110	0.740
ethyl acetate – methanol – water	0.089	1.040
toluene – acetic acid – water	0.075	0.222
toluene – propanoic acid – water	0.201	5.946
toluene – 1-propanol – water	0.896	10.500
trichloro methane – ethanol – water	0.628	1.138
trichloro methane – 2-propanol – water	1.985	8.182
trichloro methane – formic acid – water	0.014	0.022
trichloro methane – acetic acid – water	0.122	0.582
trichloro methane – propanoic acid – water	0.487	10.060
tetrachloro methane – acetic acid – water	0.0428	0.148
tetrachloro methane – propanoic acid – water	0.068	3.534
tetrachloro methane – 2-propanol – water	0.325	4.281
tetrachloro methane – nicotine – water	46.929	19.977
heptane – propanoic acid – water	0.284	1.892
heptane – 1-propanol – water	0.247	2.345
cyclohexane – 1-propanol – water	0.182	7.006
cyclohexane – acetic acid – water	3.110	7.100

Table 4. Common parameters (Sorensen and Arlt, 1980b)

Pair ($i-j$)	A_{ij}	A_{ji}
hexane – butanol	201.69	-64.52
hexane – water	1297.1	572.51
hexane – PA	218.31	-81.23
butanol – water	-9.18	267.10
CCl ₄ – water	1204.80	502.85
CCl ₄ – PA	235.30	-156.26
PA – water	-104.24	78.99

Table 5. Specific parameters (Sorensen and Arlt1, 1980a, 1980b)

System	Pair (<i>i-j</i>)	A_{ij}	A_{ji}
hexane – butanol – water	hexane – butanol	374.4	-151.16
	hexane – water	1318.1	633.83
	butanol – water	-16.397	285.51
CCl ₄ – PA – water	CCl ₄ – water	1470.0	1021.2
	CCl ₄ – PA	525.16	-250.92
	PA – water	810.8	-225.5
hexane – PA – water	hexane – PA	-185.07	41.43
	PA – water	266.96	-409.04
	hexane – water	1176.8	244.17

The mole fraction of the solute in the solvent/water phase is plotted against the mole fraction of the solute in feed, as shown in Figures 2a, 2b, and 2c. In these figures, phase L_1 refers to top phase and phase L_2 refers to the bottom phase.

Hexane is the top phase and water is the bottom phase in hexane–butanol–water and hexane–PA–water systems since hexane is lighter than water. Water is the top phase and CCl₄ is the bottom phase in CCl₄–PA–water system since water is lighter than CCl₄. Using the plots shown in Figures 2a–2c, it can be clearly explained why there is an order–of–magnitude difference between the experimental and calculated D_{sw} values. In Figure 2a, the ratio of the slopes of two most dilute butanol concentration in L_1 and L_2 phases is 1.42 (1.176/0.823). This is the experimental D_{sw} (literature value: 1.45). On the other hand, the calculated D_{sw} is 14.63. The inability to calculate acceptable D_{sw} values confirms that the calculated results cannot represent experimental data at dilute concentrations. As seen in the figures, the calculated results do not improve even when the calculations are performed using specific parameters. The specific parameters are the UNIQUAC parameters fitted individually to each ternary system. Good predictions are obtained by using both common and specific parameters as the concentrations increase.

As shown in Figures 2b and 2c, the behavior of the UNIQUAC model is the same for both CCl₄–PA–water and hexane–PA–water systems. The calculated results show large deviations at dilute concentrations, resulting an order–of–magnitude difference between the experimental and calculated D_{sw} values. Interestingly, the behaviors of the solutes in these two systems show differ from that in hexane–butanol–water. The different behavior is called cross behavior.

In cross behavior, the initial solute concentration in the aqueous phase is higher than in the solvent phase, and upon increasing the mole fraction of the solute in both phases, the solute concentration in the solvent phase becomes higher than that in the water phase. The UNIQUAC model fails to represent this behavior, as can be seen clearly in Figure 2b. From the compilations of Macedo and Rasmussen (1987) and Sorensen and Arlt (1979, 1980a, 1980b) 45 ternary systems were identified that show cross behavior. These systems are listed in Table 6. In fact, these are the systems in which the solutes are mainly lower alcohols (propanol, 2-propanol, etc.) and lower acids (formic acid, acetic acid, etc.). In the case of these systems, in the dilute concentration range, the solubility of the solute, *i.e.*, lower alcohol or acid, in the aqueous phase becomes higher than that in the organic phase as the concentration increases. Since alcohols and acids are highly soluble in organic solvents, in higher concentration ranges, the solubility of lower alcohols/ acids in the organic phase solutes is much higher than that in the aqueous phase. This is known as cross behavior. Not all lower alcohols/acids used as solutes show this behavior; in particular, in the low–concentration range, the solutes are more soluble in nonaqueous solvents than in water.

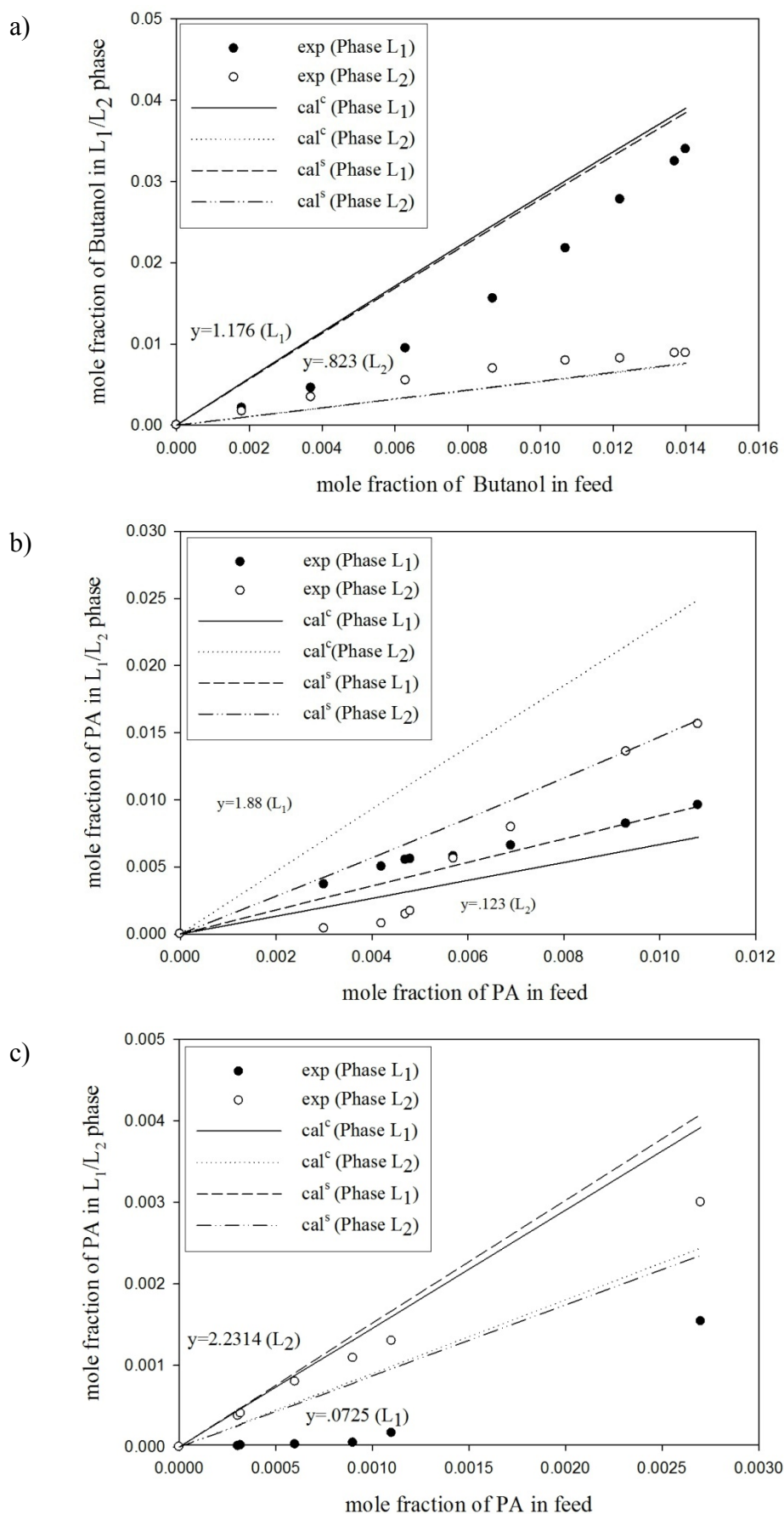


Fig. 2. Comparison of experimental data and results calculated from UNIQUAC model for (a) hexane – butanol – water, (b) CCl_4 – PA – water, and (c) hexane – PA – water systems in very dilute region. (exp – experimental, cal – calculated, superscript c and refers calculated by common and specific parameters respectively)

Table 6. List of ternary systems which show cross behavior

Cross behavior ternary systems	
1. CHCl ₃ – methanol – water	24. heptane – 1-propanol – water
2. CHCl ₃ – acetic acid – water	25. diphenyl ether – 1-propanol – water
3. CHCl ₃ – ethanol – water	26. ethyl acetate – 2-propanol – water
4. CCl ₄ – PA(propanoic acid) – water	27. benzene – 2-propanol – water
5. methane, dichloro-acetic acid – water	28. cyclohexene – 2-propanol – water
6. furfural – formic acid – water	29. cyclohexane – 2-propanol – water
7. 2-pentanol, 4-methyl-formic acid – water	30. hexane – 2-propanol – water
8. propanoic acid, nitril-methanol – water	31. toluene – 2-propanol – water
9. propane, 1-nitro-methanol – water	32. ethyl benzene – 2-propanol – water
10. ethyl acetate – methanol – water	33. hypochlorous acid, tert, butyl ester – 2-propanol, 2 methyl – water
11. di butyl ether – acetic acid – Water	34. benzene – morpholine – water
12. benzene – ethanol – water	35. acetic acid, 1-ethenylethyl ester – 2,3-butanediol – water
13. heptane – ethanol – water	36. dihydroxy – aniline – amine, diethyl, 2, 2' – water
14. dibutyl ether – ethanol – water	37. nathalene, 1-methyl – 2-pyrrolidone, 1-methyl – water
15. acetic acid, benzyl ester – ethanol – water	38. benzene – hexanoic acid, 6 amino, lactum – water
16. furfural – 1,2-ethane-diol – water	39. cycloheptane, 1-aza -hexanoic acid, 6-amino, lactam – water
17. diethyl eter – malonic acid – water	40. toluene – 2-propanol, 1,3 - bis (dimethyl amino) – water
18. cyclohexane – propanoic acid – water	41. terpene – propanol – water
19. hexane – propanoic acid – water	42. dibasic ester – acetic acid – water
20. heptane – propanoic acid – water	43. tert methyl butyl ether – acetic acid – water
21. furfural – formic acid, amide, n,n-dimethyl – water	44. methyl iso propyl ketone – acetic acid – water
22. cyclohexane – 1-propanol – water	45. methyl ethyl ketone – acetic acid – water
23. toluene – 1-propanol – water	

4. CONCLUDING REMARKS

In this study we have investigated literature and calculated partition coefficients by UNIQUAC for a number of ternary systems and classified them into so-called consistent and inconsistent categories. For the consistent systems the results are within 1 order of magnitude while for inconsistent systems the deviations are even more than 8000% using both common and specific parameters and failed completely to predict the finite concentration and infinite dilution behavior simultaneously. Throughout this study we have also observed some cross behavior systems. Especially for the inconsistent systems it is very necessary to develop appropriate models that can represent the solute behavior in different concentration ranges from finite to infinitely dilute, and also can demonstrate cross behavior. In our series study (Islam et al., 2011; Islam and Kabadi, 2011) we have already examined one of these systems, hexane – butanol – water, very extensively and have proposed a scheme to solve the issue by applying current existing models. However, rest of the systems is still kept rooms for the future researchers.

SYMBOLS

C_i^s	molar concentrations of component i in solvent phase, mol/l
C_i^w	molar concentrations of component i in aqueous phase, mol/l
K_i	ratio of activity coefficient of component i in solvent phase (γ_i^s) to that of component i in aqueous phase (γ_i^w), -
M_w^s	mole percent of water in solvent, % mol
M_s^w	mole percent of solvent in water, , % mol
V^s	molar volumes of pure solvent, mol
\hat{V}^s	molar volumes of solvent phase, mol
\hat{V}^w	molar volumes of aqueous phase, mol
X_i^s	molar composition of component i in solvent phase, mol/mol
X_i^w	molar composition of component i in aqueous phase, mol/mol
Z_i	molar composition of component i in feed, mol/mol

Greek symbols

α	ratio of solvent phase (L^s) to aqueous phase (L^w)
γ_i^s	activity coefficient of component i in solvent phase
γ_i^w	activity coefficient of component i in aqueous phase

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Received 09 November 2011

Received in revised form 16 April 2012

Accepted 16 April 2012