

UNIFAC Prediction of Aqueous and Nonaqueous Solubilities of Chemicals with Environmental Interest

A. T. KAN* AND M. B. TOMSON

Department of Environmental Science and Engineering,
Rice University, Houston, Texas 77251

The aqueous and nonaqueous solubilities of a vast number of chemicals with significant environmental roles have been predicted using the latest version of UNIFAC group interaction parameters. A few critical measurements to test specific UNIFAC calculations of nonaqueous solubilities are also reported. The chemicals included in the calculation have aqueous solubilities that span 11 orders of magnitude. Good agreement was observed between the UNIFAC-predicted and literature-reported aqueous solubilities for 11 groups of compounds, i.e., short-chain alkanes, alkenes, alcohols, chlorinated alkanes, alkyl benzenes, chlorinated benzenes, PAHs, PCBs, anilines, phenols, and organohalide insecticides (DDT and lindane). Similarly, UNIFAC successfully predicts the co-solvency of PCB in methanol/water solutions. The error between predicted and literature-reported aqueous solubilities was larger for three groups of chemicals: long-chain alkanes, phthalates, and chlorinated alkenes. The average absolute error in UNIFAC prediction of aqueous solubilities is about 0.5 log unit, but the average absolute error is only about 0.2 log unit for chlorinated aromatic compounds in organic solvents.

Introduction

The fate of organic pollutants in the environment is often determined by their thermodynamic properties in the gas, liquid, and solid phases. Previously, most attention has focused on the aqueous thermodynamic properties of hydrocarbons. Often nonaqueous solvents also play an important role in determining the fate of pollutants, for example, various oxygenated or aromatic additives associated with gasoline spills or leaks into the subsurface; dense nonaqueous phase liquids (DNAPLs); the use of various alcohols, surfactants, etc. to flush contaminants from soils; or PCBs in transformer oils or in natural gas transmission pipes. Due to the large number of organic pollutants, solvents, and solvent mixtures (including water) in common use, there is a need for a simple method to calculate the activity or activity coefficient of essentially any pollutant in any solvent. UNIFAC is a group contribution method that can be used to predict activity coefficients of nonelectrolytes

in liquid mixtures. Originally, UNIFAC was used to predict the activity coefficients of hydrocarbons in other hydrocarbon solvents, but it has been extended to include water as a solute and as a solvent. The fundamental basis of this model is that compounds may be structurally decomposed into functional groups, each functional group having a unique contribution toward the activity coefficient of a compound. The UNIFAC model is attractive because, while there are a large number of organic compounds, the number of functional groups that make up these compounds is small. Hence, it is possible to estimate activity coefficients for a large number of organic compounds from a small number of functional group parameters (1). Unfortunately, the accuracy of the UNIFAC estimation method remains controversial. Discrepancies of up to 4 orders of magnitude have been reported in predicted aqueous solubilities, vapor pressure, and octanol/water partition coefficients using an older version of the interaction parameters (2). Since then, several revisions have been made to the parameters (2, 3). The objective of this study is to evaluate the precision and accuracy of the revised interaction parameters to effect the UNIFAC prediction of the solubilities of a vast number of organic compounds of environmental concerns in both aqueous and nonaqueous solvents.

Fredenslund (1) compared the predicted and observed activity coefficients of a large number of binary solute solvent systems, e.g., hydrocarbons/hydrocarbons, hydrocarbons/nitrogen-containing compounds, hydrocarbon/chlorinated hydrocarbons, and hydrocarbon/carbon disulfide. Limited binary systems containing water were also studied. Generally, the match between the observed and calculated activity coefficients was very good. Later, several authors reported significant error in using UNIFAC to predict parameters of many classes of compounds (2, 4-11). Typically, UNIFAC underestimates the solubility of large hydrophobic compounds, particularly straight-chain alkanes in water (11, 12). Often, reported discrepancies are to be expected based upon simple chemical reasoning. For example, the reported deviation for the aqueous solubility of long-chain alkanes probably is a result of the molecules in solution folding into a coil to reduce the specific repulsion by the water. Since UNIFAC is a simple linear additive model, it would not be expected to yield highly accurate aqueous solubilities in such cases, as will be discussed in greater detail below. Arbuckle (4) concluded that the fugacity correction should not be used for solid/liquid binary system since it gives poorer results, even though the correction is required by theory. Banerjee (6) proposed to use an empirical equation to correct for the error of UNIFAC predictions. These discrepancies indicated that UNIFAC might not be a useful tool for environmental research (2, 7). Such reports coupled with the fact that the calculation procedure is more tedious than can commonly be performed by hand has discouraged its use in environmental chemistry.

The primary reason for the discrepancy appears to be related to the uncertainty of group interaction parameters. Reliable experimental vapor-liquid and liquid-liquid equilibrium data are required to determine the group interaction parameters. Since 1977, the group interaction parameter table has been revised and extended many times.

TABLE 1

Comparison of Calculated Aqueous Solubilities (mol/L) of n-Alkanes, Alkenes, and Cycloalkane Using Three Sets of UNIFAC Methyl/Water Interaction Parameters

compd	-log S_{obs} (mol/L)	Fredenlund et al. (7) $a_{\text{CH}_2-\text{H}_2\text{O}} = 1318$ $a_{\text{H}_2\text{O}-\text{CH}_2} = 580.6$		Yalkowsky and Banerjee (18) $a_{\text{CH}_2-\text{H}_2\text{O}} = 1318$ $a_{\text{H}_2\text{O}-\text{CH}_2} = 550$		Arburkle (4) $a_{\text{CH}_2-\text{H}_2\text{O}} = 500$ $a_{\text{H}_2\text{O}-\text{CH}_2} = 575$		Hansen et al. (3) Chen et al. (2) $a_{\text{CH}_2-\text{H}_2\text{O}} = 1318$ $a_{\text{H}_2\text{O}-\text{CH}_2} = 300$	
		-log S_{pred} (mol/L)	EF	-log S_{pred} (mol/L)	EF	-log S_{pred} (mol/L)	EF	-log S_{pred} (mol/L)	EF
n-hexane	3.83	3.37	0.46	3.69	0.14	3.53	0.30	2.28	1.55
n-heptane	4.51	4.03	0.48	4.39	0.12	4.22	0.29	2.79	1.72
n-octane	5.20	4.69	0.51	5.09	0.11	4.90	0.30	3.30	1.90
n-nonane	5.94	5.34	0.60	5.79	0.15	5.57	0.37	3.79	2.15
n-decane	6.57	5.99	0.58	6.48	0.09	6.24	0.33	4.29	2.28
n-dodecane	7.52	7.27	0.25	7.85	-0.33	7.57	-0.05	5.27	2.25
n-hexadecane	7.80	9.81	-2.01	10.56	-2.76	10.20	-2.40	7.19	0.61
n-octadecane	8.08	11.06	-2.98	11.91	-3.83	11.50	-3.42	8.14	-0.06
cyclohexane	3.15	2.96	0.19	3.23	-0.08	3.10	0.05	2.05	1.10
1-hexene	3.15	3.63	-0.48	3.10	0.05	3.00	0.15	2.20	0.95
1-octene	4.52	4.93	-0.41	4.51	0.01	4.37	0.15	3.21	1.31

In 1991, a fifth revision (3) of the parameters was published in which the backbone of the data set was taken from a 1982 version (13) with revision and addition of parameters from five other sources (3, 14–17). In addition, several other authors have reported different values for individual pairs of parameters, e.g., the $\text{CH}_2\text{--H}_2\text{O}$ pair (4, 18), the $\text{OH--H}_2\text{O}$ pair and oxygenated alkane– H_2O pairs (2), and the aromatic $\text{Cl--H}_2\text{O}$ pair (2, 4, 18, 19). Also, the present authors traced the origin of some reports of UNIFAC failure to an apparent typographical error in a commonly used data set, for example, the $\text{ArCl--H}_2\text{O}$ interaction (20). In this paper, the precision of UNIFAC calculation is determined using the latest set of group interaction parameters to test the reliability and the accuracy of the UNIFAC approach as a semiquantitative screening tool for environmental applications of a wide range of solutes and solvents.

Background

In UNIFAC, the reference state for all solutes and solvents is taken to be the pure liquid at 1 atm total pressure at the temperature of the calculation, typically 298 K (i.e., Raoult's law convention). The activity coefficient γ_i is calculated from two parts:

$$\ln \gamma_i = \ln \gamma_i^{\text{C}} + \ln \gamma_i^{\text{R}} \quad (1)$$

where γ_i is the activity coefficient for the component i , γ_i^{C} is the combinatorial part, and γ_i^{R} is the residual part. The combinatorial term takes into account entropy effects and depends on size and shape of molecule i . In the combinatorial part, the group surface volume (R_k) and area (Q_k) for each functional group are used as model parameters (see ref 21 for the origin of R_k and Q_k). The residual term, $\ln \gamma_i^{\text{R}}$, is mainly governed by the energetic interaction of pairs of functional groups in different molecules. The group interaction parameters, a_{mn} and a_{nm} , are introduced in this term (note that $a_{mn} \neq a_{nm}$).

For sparingly soluble liquid solutes, the solubility of an organic compound in a solvent is approximated by the following equations (22):

$$X_{\text{predicted}} = 1/\gamma_i^{\infty} \quad (2a)$$

or

$$S_{\text{predicted}} (M) = 1000/V\gamma_i^{\infty} \quad (2b)$$

where X is the mole fraction solubility, γ_i^{∞} is the UNIFAC-derived activity coefficient of compound solute i extrapolated to an infinitely dilute solution, S is the molar solubility, M is molarity (mol/L), V is the molar volume (cm^3/mol) of the solvent, and the "1000" term converts from cm^3 to L.

For compounds that are either solids or gases at 1 atm and the temperature of interest, such as naphthalene (a solid) or chloromethane (a gas), the reference state for the use of UNIFAC is still the pure liquid (now a hypothetical liquid) at 1 atm and the temperature of interest. When the solubility of a solid is calculated by using infinite dilution activity coefficients, the "energy cost" of a solid to its subcooled liquid state is given by the ratio of the fugacity of the pure solid (f_s) to the fugacity of the subcooled liquid (the reference state, f_l). When assuming ideal gas behavior, the ratio of the fugacity is equal to the ratio of vapor pressure between the solid state and that in the reference state; this changes eqs 2a and 2b to the following for a solid:

$$X_{\text{predicted}} = \frac{(f_s/f_l)}{\gamma_i^{\infty}} \cong \frac{P_s^{\circ}/P_l^{\circ}}{\gamma_i^{\infty}} \quad (3a)$$

or

$$S_{\text{predicted}} (M) = \frac{1000(f_s/f_l)}{V\gamma_i^{\infty}} \cong \frac{1000(P_s^{\circ}/P_l^{\circ})}{V\gamma_i^{\infty}} \quad (3b)$$

The fugacity ratio (f_s/f_l) can be evaluated for the pure solute from their thermodynamic properties as discussed in many texts, such as Hildebrand and Scott (23), and summarized below. Preston and Prausnitz (24) simplified the theoretical approach to yield the following equation:

$$\ln \frac{f_s}{f_l} = \frac{\Delta S_f}{R} \left(1 - \frac{T_m}{T} \right) \quad (4)$$

where ΔS_f is the molar entropy of fusion at melting point, R is the gas constant, and T_m is the melting point. The fugacity ratio or molar entropy fusion is available for many compounds of interest (22, 25). If the molar entropy of fusion is not readily available, Yalkowsky (26) has shown the entropy of fusion to be approximately the same for

TABLE 2

Comparison of UNIFAC-Based and Observed Aqueous Solubility of Aliphatic and Substituted Aliphatic Compounds^a

compd	$-\log S_{\text{obs}}$ (mol/L)	$-\log S_{\text{pred}}^{b,c}$ (mol/L) (A)	EF ^b (A)	$-\log S_{\text{pred}}^b$ (mol/L) (B)	EF ^b (B)
Alkane					
<i>n</i> -hexane	3.83	3.69	0.14	see Table 1	
<i>n</i> -heptane	4.51	4.39	0.12		
<i>n</i> -octane	5.20	5.09	0.11		
<i>n</i> -nonane	5.94	5.79	0.15		
<i>n</i> -decane	6.57	6.48	0.09		
<i>n</i> -dodecane	7.52	7.85	-0.33		
Alkenes/Cycloalkane					
1-hexene	3.15	3.10	0.05	2.21	0.94
1-octene	4.52	4.51	0.01	3.23	1.29
cyclohexane	3.15	3.23	-0.08	3.23	-0.08
Alcohols/Ketone					
1-butanol	0.07	0.89 (0.87)	-0.82	-0.14	0.21
1-hexanol	0.88	2.16	-1.28	0.75	0.13
1-octanol	2.35	3.44	-1.09	1.64	0.71
1-octanone	2.05	2.88	-0.83	1.49	0.56
Chlorinated Alkanes					
dichloromethane	0.64	0.65 (0.63)	-0.01	0.59	0.05
tetrachloromethane	2.20	2.27	-0.07	2.30	-0.10
1,1-dichloroethane	1.30	1.46	-0.16	1.11	0.19
1,2-dichloroethane	1.07	1.07 (1.07)	0.00	1.02	0.05
1,1,1-trichloroethane	2.07	1.94	0.13	1.54	0.53
1,1,2,2-tetrachloroethane	1.74	2.30	-0.56	2.20	-0.46
Chlorinated Alkenes					
vinyl chloride	1.35	0.60 (0.59)	0.75	0.14	1.21
trichloroethene	2.04	1.36	0.68	1.29	0.75
tetrachloroethene	3.04	1.89	1.15	1.81	1.23
hexachlorobutadiene	4.90	3.51	1.39	3.39	1.51

^a The UNIFAC-based aqueous solubilities are based on both the group interaction parameters of (A) Hansen et al. (12) and Yalkowsky and Banerjee (18) and (B) Chen et al. (2). ^b The A set of data was calculated using the interaction parameters of Hansen et al. (12) with the parameters for (CH₂-H₂O) from Yalkowsky and Banerjee (18). The B set of data was calculated using the group interaction parameters of Chen (2). ^c Values were calculated using eq 2b. Values in parentheses were calculated with method of Lyman (27) for more soluble solutes ($\gamma_i^\infty < 1000$).

many compounds, and therefore the fugacity ratio can be approximated with a function of melting point and temperature so that at 25 °C:

$$\ln(f_s/f_l) = -0.023(T_m - 25) \cong (P_s^0/P_l^0) \quad (5)$$

where T_m is in °C. If the compound of interest is a gas, a similar correction term is used to correct the difference between between the gas and reference state (22).

The above equations may not be valid when the binary solute/solvent pair are significantly soluble in each other; this notation is tested below. In such a binary system, the mutual solubility of the solute and solvent in each phase can also be calculated from UNIFAC activity coefficients at various combinations of solute/solvent mole fraction ratios. For sample numerical details of the UNIFAC calculation procedure, the interested reader is referred to ref 27.

Methods

The solubility of a wide range of organic chemicals in both aqueous and organic solvent media was calculated via eqs 2 and 3. The method of Lyman et al. (27) was used to determine the solubility of the more soluble compounds for the compounds with $\gamma_i^\infty < 1000$. The list of compounds was selected to be representative rather than exhaustive. Most of the UNIFAC calculations were done with a computer program written in FORTRAN by Professor Prausnitz's research group at the University of California at Berkeley, which incorporated the equations of Fredenslund et al.

(28). Group interaction parameters were those of Hansen et al. (3), which consisted of revised data from five previous revisions. In addition, the methyl/water parameters in refs 1, 4, 6, and 18; the chlorinated alkane/water and hydroxyl/water parameters in ref 2; the aromatic chlorine/water parameters in ref 19; and the phenol/water parameters in refs 2, 18, and 27 were compared to that of Hansen et al. (3). The literature-reported solubility data of refs 22, 23, 29, and 30 were used in comparison. The literature-reported fugacity ratio data in refs 22, and 25 are used in the calculation of the solubility of a solid.

The solubilities of three PCBs (2,2',4,5'-tetrachlorobiphenyl, 2,2',4,4',6,6'-hexachlorobiphenyl, and decachlorobiphenyl) in 2,2,4-trimethylpentane and a terpene-based industrial solvent were measured. A small excess of PCB isomers (Ultra Scientific, Kingstown, RI) was dissolved in 5 mL of solvent. An aliquot of the solution was filtered through a 0.45- μ m nylon membrane filter (Nylon Acrodisc, Gelman). The concentration of PCB isomer in the solution was analyzed with a HP 5890 GC/ECD detector.

In the following discussion, the term "error factor (EF)" is defined as follows:

$$EF \equiv \log_{10} \left(\frac{S_{\text{predicted}}(M)}{S_{\text{observed}}(M)} \right) \quad (6)$$

Therefore, the predicted value is identical to the observed value, when $EF = 0$. When $EF > 0$, the predicted value overestimates the solubility. Likewise, the predicted value

TABLE 3

Comparison of Observed and UNIFAC-Based Aqueous Solubilities of Substituted Aromatic Compounds, Biphenyls, PAHs, Phthalates, and Organohalide Insecticides Using the Interaction Parameters of Ref 12 with Modifications with Refs 2, 18, and 19

compd	$\log \gamma_i^\infty$	T_m^b ($^\circ\text{C}$)	$-\log S_{\text{pred}}^a$ (mol/L)	$-\log S_{\text{obs}}$ (mol/L)	EF
Methyl-Substituted Benzene					
benzene	3.37	5.5	1.63	1.64	0.01
toluene	4.08	-95.0	2.25	2.25	0.00
ethylbenzene	4.83	-95.0	3.09	2.80	-0.29
1,2-dimethylbenzene	4.74	-25.2	3.00	2.76	-0.24
1,4-dimethylbenzene	4.74	13.2	3.00	2.77	-0.23
1,2,4-trimethylbenzene	5.40	-43.8	3.65	3.33	-0.32
1,3,5-trimethylbenzene	5.40	-44.7	3.65	3.40	-0.25
Chlorinated Benzene					
1,2-dichlorobenzene	4.33	-17.0	2.59	3.20, 3.01	0.61, 0.42
1,4-dichlorobenzene	4.33	53.1	2.87	3.39	0.52
1,2,4-trichlorobenzene	4.84	16.9	3.09	3.65	0.56
1,3,5-trichlorobenzene	4.84	63.0	3.47	4.53	1.06
1,2,3,4-tetrachlorobenzene	5.34	47.5	3.82	4.42	0.60
1,2,3,5-tetrachlorobenzene	5.34	54.5	3.88	4.83	0.95
pentachlorobenzene	5.84	86.0	4.71	5.56	0.85
hexachlorobenzene	6.35	230.0	6.66	7.69	1.03
Polycyclic Aromatic Hydrocarbons					
naphthalene	5.13	80.6	3.94	3.61	-0.33
fluorene	9.33	113.0	5.70	4.96	-0.74
phenanthrene	6.85	99.5	5.85	5.25	-0.60
anthracene	6.85	217.5	7.09	6.46	-0.67
pyrene	7.76	156.0	6.84	6.17	-0.63
benz[a]pyrene	9.42	176.5	9.19	8.22	-0.97
benz[a]anthracene	9.42	159.8	7.62	7.31	-0.31
Phthalates					
dimethyl phthalate	3.66	<25	1.91	1.66	-0.25
diethyl phthalate	5.34	<25	3.60	2.38	-1.21
di- <i>n</i> -butyl phthalate	7.84	<25	6.09	4.47	-1.62
Phenol and Substituted Phenols					
phenol	1.79	43.0	0.22	0.20	-0.02
3-methylphenol	3.41	11.5	1.66	1.59	-0.07
2,4-dimethylphenol	2.98	27.5	1.26	1.19	-0.08
chlorophenol	2.14	9.0	0.40	1.05	-0.65
Aniline and Substituted Anilines					
aniline	2.09	-6.3	0.34 (0.32)	0.41	0.07
methylaniline	2.85	-57.0	1.11 (1.10)	1.28	0.17
dimethylaniline	3.66	2.5	1.92	2.04	0.12
Polychlorinated Biphenyls					
2,5-PCB	6.93	23.0	5.19	5.06	-0.13
4,4'-PCB	6.93	149.0	6.43	6.53	0.10
2,4,6-PCB	7.41	62.0	6.03	6.07	0.04
2,2',5,5'-PCB	7.89	87.0	7.11	7.06	-0.05
2,3',4,4'-PCB	7.89	128.0	7.18	7.70	0.52
2,2',4,4',5,5'-PCB	8.85	103.0	7.93	7.82	-0.11
2,2',3,3',4,4'-PCB	8.85	151.9	8.38	8.78	0.40
2,2',3,3',5,5',6,6'-PCB	9.79	161.0	9.30	9.29	-0.01
decachloro-PCB	10.72	305.8	11.41	10.55	-0.86
Organohalide Insecticides					
p,p'-DDT	9.33	109.0	8.43	7.85	-0.58
lindane	6.46	112.9	5.60	4.59	-1.01

^a Values are calculated by eqs 2b and 3b with fugacity ratios of ref 22. Values in parentheses are calculated by method in Lyman et al. (27) to correct for mutual solubility effect. ^b Melting point data are from refs 22 and 25.

underestimates when $EF < 0$. Average error factor is the mean of the absolute value of $EF \pm 1$ SD.

Results and Discussion

Aqueous Solubility. In Table 1, the calculated aqueous solubilities using the four sets of methyl/water interaction parameters are compared to the observed solubilities. For short-chain hydrocarbons, interaction parameters from Fredenslund et al. (1), Yalkowsky and Banerjee (18), or Albuckle (4) were better than those from Hansen (3).

However, the calculated solubility values for long-chain alkanes ($> C_{12}$) based on the first three sets of parameters are not as good as when Hansen parameters were used. None of the above four sets of parameters are universally applicable to all alkane hydrocarbons, and the possible cause of discrepancy has been discussed in the Introduction. Kikic et al. (11) recommended a modified combinatorial term to correct the problem, while Park and Carr (12) believed the origin of the problem was the crudeness in equating interaction parameters of CH_3 , CH_2 , CH , and C .

TABLE 4

Comparison of Observed and UNIFAC-Based Mole Fraction Solubilities of 10 Aromatic and Chlorinated Aromatic Compounds in 13 Different Nonaqueous Solvents

no.	solvent ^a	solute ^b	T ^c (°C)	γ^{∞}	X _{pred} (mole fraction)	X _{obs} (mole fraction)	EF ^d	ref
Biphenyl and PCBs^e								
1	isooctane	Te-PCB	25.0	6.469	0.064	0.065	-0.01	this work
2	isooctane	D-PCB	25.0	29.289	0.000057	0.000183	-0.51	this work
3	terpenes ^f	H-PCB	25.0	2.518	0.052	0.136	-0.42	this work
4	<i>n</i> -heptane	biphenyl	25.0	3.034	0.116	0.129	-0.05	21
5	methanol	biphenyl	19.5	15.734	0.0222	0.0135	0.21	27
6	methanol	M-PCB	25.0	16.214	0.0185	0.0143	0.11	28
7	methanol	T-PCB	25.0	20.362	0.0210	0.00899	0.37	28
8	methanol	H-PCB	25.0	33.258	0.00394	0.00234	0.23	28
9	ethanol	biphenyl	19.5	19.166	0.0184	0.0346	-0.27	27
10	ethanol	M-PCB	25.0	19.663	0.0153	0.0328	-0.33	28
11	1-propanol	M-PCB	25.0	12.434	0.0241	0.0415	-0.24	28
12	benzene	biphenyl	25.0	0.817	0.430	0.389	0.05	21
13	DCB	biphenyl	25.0	1.256	0.280	0.398	-0.15	21
14	dioxane	biphenyl	26.4	1.0522	0.335	0.398	-0.08	27
			25.0			0.386	-0.06	21
15	CCl ₄	biphenyl	28.1	1.2623	0.279	0.372	-0.12	27
			25.0			0.340	-0.09	21
16	CS ₂	biphenyl	28.4	1.382	0.255	0.251	0.05	27
			25.0			0.371	-0.16	21
PAHs and Chlorobenzenes^g								
17	<i>n</i> -hexane	naphthalene	20.0	2.745	0.104	0.090	0.06	21
18	<i>n</i> -hexane	phenanthrene	25.0	3.661	0.049	0.048	0.01	21
19	<i>n</i> -hexane	anthracene	25.0	3.661	0.004	0.0018	0.35	21
20	methanol	naphthalene	20.0	13.026	0.0219	0.018	0.09	21
21	ethanol	phenanthrene	25.0	36.869	0.0049	0.0125	-0.41	21
22	ethanol	anthracene	25.0	36.869	0.000404	0.0009	-0.35	21
23	acetone	naphthalene	20.0	2.527	0.113	0.183	-0.21	21
24	benzene	naphthalene	20.0	0.952	0.300	0.241	0.10	21
25	benzene	phenanthrene	25.0	0.840	0.215	0.207	0.02	21
26	benzene	anthracene	25.0	0.840	0.0177	0.0081	0.34	21
27	CCl ₄	naphthalene	20.0	1.396	0.204	0.205	0.00	21
28	CCl ₄	phenanthrene	25.0	1.650	0.110	0.186	-0.23	21
29	CCl ₄	anthracene	25.0	1.650	0.009	0.0063	0.16	21
30	CS ₂	phenanthrene	25.0	1.470	0.123	0.255	-0.32	21
31	CS ₂	anthracene	25.0	1.470	0.0101	0.0112	-0.04	21
32	cymene	HCB	23.5	1.916	0.005	0.0134	-0.43	27
33	benzene	HCB	19.9	2.336	0.004	0.0102	-0.40	27

^a Isooctane is 2,2,4-trimethylpentane; DCB is dichlorobenzene. ^b M-PCB is 4-chlorobiphenyl; T-PCB is 2,4,6-trichlorobiphenyl; Te-PCB is 2,2',4,5'-tetrachlorobiphenyl; H-PCB is 2,2',4,4',6,6'-hexachlorobiphenyl; D-PCB is *p*-dechlorobiphenyl (Data extrapolated from the eutectic point, 27.7 °C); and HCB is hexachlorobenzene. ^c T is the temperature at which the experimental solubility were measured. The UNIFAC-predicted solubility is calculated at 25 °C. ^d EF = log₁₀(X_{pred}/X_{obs}). ^e Fugacity ratios of Mackay et al. (23) are used. ^f Terpenes is an industrial-grade solvent (RE-Entry KNI 2000, by Environmental Solvents Co., Jacksonville, FL) containing multiple components of the terpenes family. UNIFAC calculation is based on Terpinolene, one of the typical components in natural terpene extract. ^g Fugacity ratios of Schwarzenbach et al. (20) are used.

The authors had not evaluated either approach, and interested readers should review the work of Kikic et al. and Park and Carr (11, 12) for further details.

Chen et al. (2) have revised a number of interaction parameters using the data from the Dortmund Data Bank. In particular, they had modified most of the interaction parameters with H₂O and oxygenated and chlorinated hydrocarbon groups. Table 2 is a list of the predicted and observed aqueous phase solubilities of short-chain aliphatic and substituted aliphatic compounds. The UNIFAC calculation uses the parameters of either (a) Hansen et al. (3) with modification from Yalkowsky and Banerjee (18) for the (CH₂-H₂O) parameters or (b) Chen et al. (2). Chen et al. used the same set of parameters for (CH₂-H₂O) as in Hansen et al., and the problem with that set of parameters was illustrated in Table 1. The prediction for the aqueous solubility of short-chain alkanes, alkenes, and halogenated alkanes are better when the parameters of Hansen et al. (3) and Yalkowsky and Banerjee (18) are used. As might be expected, the solubility prediction for alcohols and ketones using Chen's parameters is better than using Hansen's parameters. The predicted solubilities of halogenated

alkenes are about 0.7–1.5 orders of magnitude higher than the experimental measurements using either method. The error is much smaller than that reported in ref 9 (1.6–2.5 orders of magnitude) for this group of compounds. The prediction may be improved if the interaction parameters for functional groups containing a chlorine atom next to a double bond (vinyl) were available. The overall error factor for all the data points in Table 2 is 0.43 ± 0.46.

Table 3 is a list of observed and UNIFAC-based aqueous solubility data for compounds containing aromatic ring and organohalide insecticides (DDT and lindane). The chlorinated aromatic/water parameters of either Hansen et al. (3) or Chen et al. (2) failed to predict the PCB aqueous solubility accurately. Therefore, the aromatic chlorine/water parameters of Burkhard (19) ($a_{\text{water-organic chlorine}} = 526$; $a_{\text{aromatic chlorine-water}} = 92.04$) were used in the calculation of the solubility of chlorinated compounds. Preliminary evaluation of Chen's parameters showed that the solubility prediction using Hansen's parameters is more accurate for most of the compounds listed in Table 3 except for the groups of phenols and phthalates. Therefore, Chen's interaction parameters for aromatic OH-H₂O and CCOO-

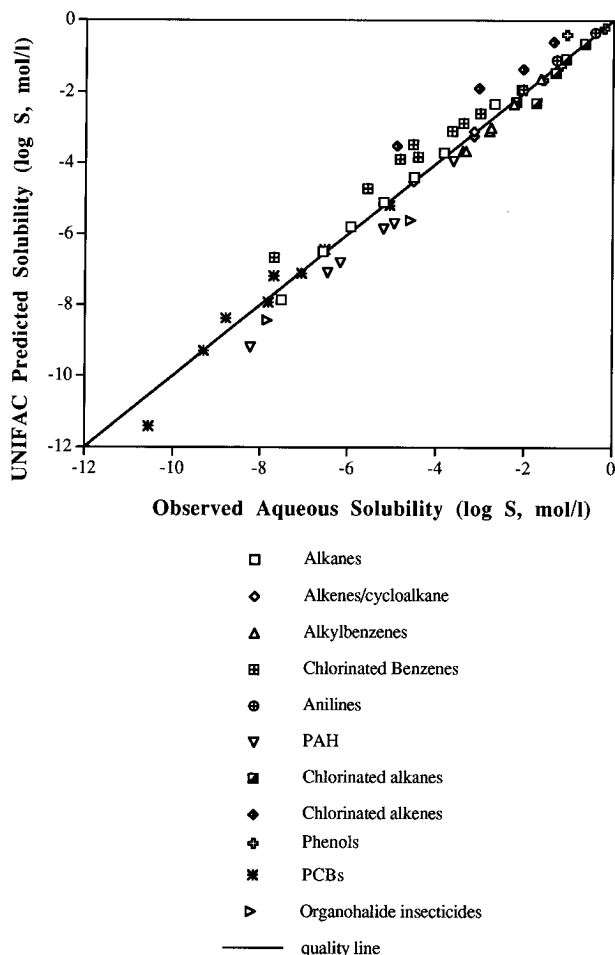


FIGURE 1. Plot of the observed versus UNIFAC-predicted aqueous solubilities [in $\log S$, (mol/L)] of 11 groups of organic compounds listed in Tables 1–3.

H₂O replaced that of Hansen et al. in calculating the predicted solubilities of a number of aromatic compounds listed in Table 3. The agreement between the calculated and predicted solubilities are good with the exception of the phthalate group. The problem with phthalate may reflect the need of the aromatic methyl ester group parameters. The average error factor is 0.50 ± 0.47 for all the data in Table 3, which is comparable to that shown in Table 2. For the more soluble compounds ($\gamma_i^\infty < 1000$), the solubility predicted with the more rigorous approach of Lyman (27) was included in parentheses of Tables 2 and 3. This more laborious approach only corrects the solubility calculation by about 0.02 log unit, which is probably not warranted due to the larger error factor inherent in the UNIFAC approach. Figure 1 is plot of the observed versus predicted solubilities of 11 groups of compounds listed in Tables 2 and 3. Small systematic deviations of the predicted versus observed values are observed with PAHs, chlorinated benzenes, aliphatic alcohols, and chlorinated alkenes. The overall agreement between the observed and the calculated values are good, considering that the chemicals span 11 orders of magnitude in aqueous solubility.

Co-solvency Effect. The activity coefficient and solubility of an organic chemical in solvent/water mixtures can be calculated with UNIFAC and eqs 2 and 3 as long as the mole fractions of solvent and water are known or are assumed. Li and Andren (30) have determined the solubility of three PCB isomers in several alcohol/water mixtures. The methanol volume fraction tested ranges from 0.05 to

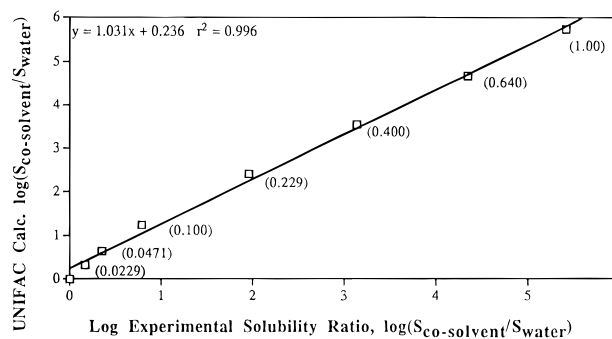


FIGURE 2. Plot of the experimentally observed versus the UNIFAC-predicted co-solvency effect, where the solvent is methanol and the chemical is 2,4,6-trichlorobiphenyl. The x-axis is the logarithm of the experimentally observed solubility ratio, while the y-axis is the logarithm of the UNIFAC predicted solubility ratio. The number in parentheses under the symbol indicates the mole fraction of methanol used in the experiment. The experimental data are that of ref 28.

1.0. Li and Andren's experimental data for 2,4,6-trichlorobiphenyl in methanol are used herein to test the UNIFAC calculations. The corresponding UNIFAC predicted solubility of 2,4,6-trichlorobiphenyl in various methanol/water mixtures has been calculated and compared with the corresponding solubility measurements (see Figure 2). As shown in Tables 3 and 4, UNIFAC can predicted the solubility of 2,4,6-trichlorobiphenyl in both water and in neat methanol with an error factor of 0.04 and 0.37 log unit, respectively. Figure 2 is a plot of the observed versus UNIFAC-predicted logarithmic solubility enhancement due to various ratios of co-solvent content. In Figure 2, the numbers in parentheses next to the symbols are the mole fractions of methanol used in each experiment. Clearly, UNIFAC calculations can be used to predict the solubility of this PCB in methanol/water co-solvent mixtures. Similar results have been obtained by the authors for other co-solvent systems.

Nonaqueous Solvents. The solubility of 10 different compounds in 13 organic solvents is reported in Table 4. The first three solubilities were determined by the present authors. The solutes include PAHs, PCBs, and chlorinated benzenes. The solvents include alkanes, alcohols, benzene, tetrachloromethane, CS₂, and several other miscellaneous solvents. Figure 3 is a plot of the observed and predicted solubility of the data listed in Table 4. Agreement between the observed and predicted values is good for these compounds, which represent a solubility span of 3.33 orders of magnitude. The average error factor for these compounds is 0.18 ± 0.14 , which is better than those listed in Tables 2 and 3 for the aqueous system, indicating that UNIFAC is more reliable for predicting the solubility of chlorinated aromatic compounds in various organic solvents than for the corresponding aqueous solubilities.

UNIFAC has been used to predict the fate and status of PCBs in the natural gas pipelines and for selection of a decontamination solvent. The natural gas pipeline is often contaminated with PCBs due to previous use of PCBs as valve grease or compressor oil. Large quantities of PCB lubricant were suspected to have leaked into the pipeline over the past 30 years. The predominant PCBs in the pipelines are Aroclor 1242 (compressor oil) and Aroclor 1268 (valve grease). Aroclor 1242 has an average chlorine number of 3.0, and Aroclor 1268 has an average chlorine number of 8.7 (31). Natural gas pipeline liquid hydrocarbons are predominantly C-7–C-15 hydrocarbons with

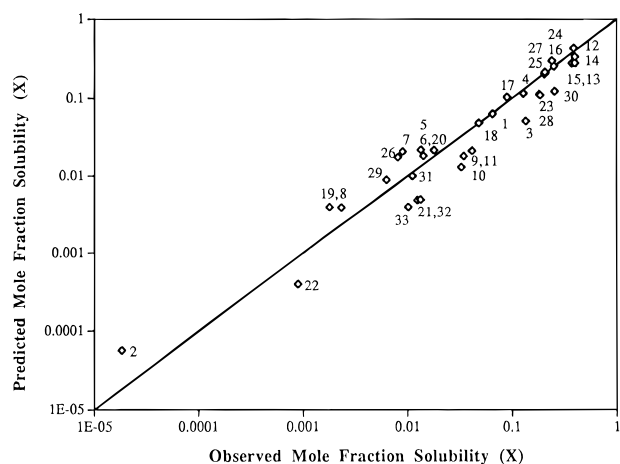


FIGURE 3. Plot of the observed versus predicted mole fraction solubilities of 10 aromatic and aromatic chlorinated compounds in 13 organic solvents (Table 4). The number next to the symbol corresponds to the data entry number listed in column 1 of Table 4.

mostly paraffin, isoparaffin, and traces of olefins, naphthene, and aromatics. Water and dehydration agents, e.g., methanol and triethylene glycol, are also present in the pipeline liquids. Figure 4 is a plot of the UNIFAC-calculated solubility of representative PCB homologs in various common hydrocarbons and dehydration agents. The eight-carbon members of the straight and branched alkanes, alkenes, cycloalkanes, and aromatic hydrocarbons are selected to represent the common members of hydrocarbon liquids in pipelines. The vertical axis is the UNIFAC-calculated solubility in units of weight percent of PCB per unit volume of liquid. As expected, PCB solubility does not vary too much among the nonaromatic hydrocarbons. Since natural gas pipeline condensate is not expected to have a substantial volume of aromatics, the solubility of PCBs in the pipeline liquid may be represented by the nonaromatic hydrocarbons. Therefore, the solubility of Aroclor 1242 is expected to be in the neighborhood of 10–15% (wt/vol) while the solubility of Aroclor 1268 is expected to be in the neighborhood of less than 1%. Based on UNIFAC calculations, terpene-based industrial solvents made from citrus, pine, or other plants have better solvency than the conventional hydrocarbon-based solvents such as hexane, octane, etc. Preliminary laboratory testing has concurred with the model predictions and supports the use of terpenes for PCB removal from natural gas pipelines.

In conclusion, UNIFAC calculation based on the core UNIFAC parameters from that of Hansen (3) with modification from Yalkowsky and Banerjee [$a_{\text{CH}_2-\text{H}_2\text{O}}$ (18)], Burkhard [$a_{\text{AC}-\text{Cl}}$ (19)], and Chen et al. [$a_{\text{OH}-\text{H}_2\text{O}}$, $a_{\text{ACOH}-\text{H}_2\text{O}}$, $a_{\text{CCOO}-\text{H}_2\text{O}}$ (2)] successfully predicts the aqueous solubilities of 11 out of 14 groups of common organic chemicals. The 11 groups of chemicals include short-chain alkanes, alkenes, alcohols, chlorinated alkanes, alkylbenzenes, chlorinated benzenes, PAHs, PCBs, anilines, phenols, and organohalide insecticides. The groups of chemicals less successfully predicted are chlorinated alkenes, phthalates, and long-chain alkanes. New interaction parameters for these groups may be needed for better results. UNIFAC can also be used to predict the solubility of PAHs, PCBs, and chlorinated benzenes in 11 different organic solvents with good accuracy and to estimate the co-solvency of solvent/water solutions. The solubility of Aroclor 1242 is about 10–15% (wt/vol),

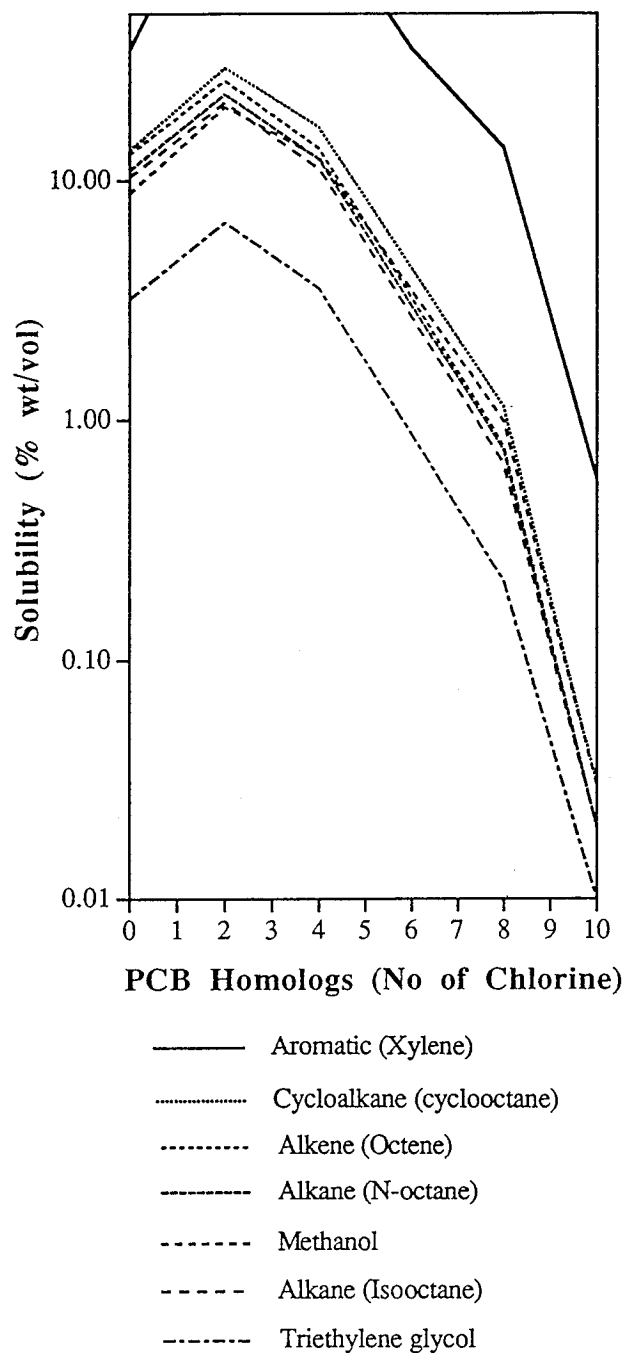


FIGURE 4. UNIFAC-calculated PCB solubilities in various hydrocarbon and organic solvents. The x-axis is the number of chlorine molecules on the PCB homologs, and the y-axis is the calculated solubility in units of % (wt/vol). The solvents are hydrocarbons and additives commonly present in natural gas pipeline liquids. The fugacity ratios used in calculation are that of biphenyl, 2,4'-PCB, 2,2',4,4'-PCB, 2,2',4,4',6,6'-PCB, 2,2',3,3',5,5',6,6'-PCB, and decachlorobiphenyl from ref 23.

and the solubility of Aroclor 1268 is about 0.1% (wt/vol) in natural gas pipeline liquids (aliphatic hydrocarbons).

Acknowledgments

Funding from the Gas Research Institute through Roy F. Weston, Inc. and the U.S. EPA under the Hazardous Substance Research Center/South & Southwest Region to support this research is greatly appreciated. However, this publication does not necessarily reflect the views of EPA or GRI, and no official endorsement should be inferred.

Literature Cited

- (1) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-liquid equilibria using UNIFAC*; Elsevier Scientific Publishing Co.: Amsterdam, 1977.
- (2) Chen, F.; Holten-Andersen, J.; Tyle, H. *Chemosphere* **1993**, *26*, 1325–1354.
- (3) Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352–2355.
- (4) Arbuckle, W. B. *Environ. Sci. Technol.* **1986**, *20*, 1060–1064.
- (5) Arbuckle, W. B. *Environ. Sci. Technol.* **1983**, *17*, 537–542.
- (6) Banerjee, S. *Environ. Sci. Technol.* **1985**, *19*, 369–370.
- (7) Burkhard, L. P.; Armstrong, D. E.; Andren, A. W. *Environ. Sci. Technol.* **1985**, *19*, 590–596.
- (8) Campbell, J. R.; Luthy, R. G. *Environ. Sci. Technol.* **1985**, *19*, 980–985.
- (9) Tse, G.; Orbey, H.; Sandler, S. I. *Environ. Sci. Technol.* **1992**, *26*, 2017–2022.
- (10) Nielsen, F.; Olsen, E.; Fredenslund, A. *Environ. Sci. Technol.* **1994**, *28*, 2133–2138.
- (11) Kikic, I.; Alessi, P.; Rasmussen, P.; Fredenslund, A. *Can. J. Chem. Eng.* **1980**, *58*, 253–258.
- (12) Park, J. H.; Carr, P. W. *Anal. Chem.* **1987**, *59*, 2596–2602.
- (13) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118–127.
- (14) Herskowitz, M.; Gottlieb, M. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *20*, 407–409.
- (15) Macedo, E. A.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem. Res.* **1983**, *22*, 676–678.
- (16) Tiegs, D.; Rasmussen, P.; Gmehling, J.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1987**, *26*, 159–161.
- (17) Zarkarian, J. A.; Anderson, F. E.; Boyd, J. A.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 657–661.
- (18) Yalkowsky, S. H.; Banerjee, S. *Aqueous solubility—Method of estimation for organic compounds*; Marcel Dekker: New York, 1992.
- (19) Burkhard, L. P.; Andren, A. W.; Loux, N. T.; Armstrong, D. E. *Environ. Sci. Technol.* **1986**, *20*, 527–528.
- (20) Prausnitz, J. M. Personal communication, 1994.
- (21) Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; Wiley: New York, 1968.
- (22) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1993.
- (23) Hildebrand, J. H.; Scott, R. L. *The solubility of nonelectrolytes*, 3rd ed.; Dover Publications: New York, 1964.
- (24) Preston, G. T.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1970**, *9*, 264–271.
- (25) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*; Lewis Publishers: Ann Arbor, MI, 1992; Vol. 1.
- (26) Yalkowsky, S. H. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 108.
- (27) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of chemical property estimation methods*; McGraw-Hill: New York, 1982.
- (28) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
- (29) Stephen, H.; Stephen, T. *Solubilities of inorganic and organic compounds, Volume 1 Binary Systems, Part 2*; The MacMillan Company: New York, 1963; Vol. 1.
- (30) Li, A.; Andren, A. W. *Environ. Sci. Technol.* **1994**, *28*, 47–52.
- (31) Erickson, M. D. *Analytical Chemistry of PCBs*; Butterworth: Boston, 1986.

Received for review August 31, 1995. Revised manuscript received December 12, 1995. Accepted December 14, 1995.®

ES950638O

® Abstract published in *Advance ACS Abstracts*, February 15, 1996.