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Application of the Unified Functional Activity Coefficient (UNIFAC) and Analytical Solution of Groups (ASOG) for the Calculation of Mutual Solubilities in Water Systems of Alkanes, Arenes, and Alkanols

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ABSTRACT: The recommended solubilities taken from the International Union of Pure and Applied Chemistry/National Institute of Standards and Technology (IUPAC-NIST) Solubility Data Series were used as testing data for the prediction of the solubilities in water systems of alkanes, arenes, and alkanols with various versions of unified functional activity coefficient (UNIFAC) and analytical solution of groups (ASOG) methods. It was strongly confirmed that parameters aimed at the prediction of vapor−liquid equilibria (VLE) are not applicable for predictions of liquid−liquid equilibria (LLE) in the water systems. The average relative error of the predicted solubility for alkane−water systems is equal to hundreds or even thousands of percent. For arene−water and alkanol−water systems it is usually about 100 %. Much better accuracy can be obtained with parameters adjusted to the solubility data. The UNIFAC version developed by Voutsas and Tassios, VT-UNIFAC, predicts mutual solubilities in alkane−water systems with an average relative error equal to about 40 %. This modification supplemented with temperature-dependent parameters for a pair of groups, $ACCH_2-H_2O$, predicts the mutual solubilities in alkylbenzene−water systems with 20 % accuracy. For alkanol−water systems, the VT-UNIFAC was not applied because of lack of group-interaction parameters for the OH group.

INTRODUCTION

Group contribution methods such as unified functional activity coefficient (UNIFAC) and analytical solution of groups (ASOG) are widely used for the calculation of phase equilibria in various systems. The calculation of mutual solubility in water systems of organic substances is probably the most demanding task. Several papers were devoted to this problem. Aqueous systems with a liquid−liquid phase split are of particular interest for the chemical and petrochemical industry. Such data are also of interest in environmental protection, for example, for the modeling of environmental fate of pollutants. The original UNIFAC[1] method, its (Dortmund[2] and Lyngby[3]) modifications, and the ASOG[4] method are mostly intended to represent primarily vapor−liquid equilibria (VLE) data and are not suitable for the quantitative prediction of liquid−liquid equilibria (LLE) in aqueous systems. Among the Dortmund and Lyngby modifications, the most elaborated is the first one. New versions with corrected and/or extended group-parameters are systematically published. Most of these works are performed/coordinated by the UNIFAC Consortium. In the case of the Lyngby version, extensions are relatively rare and are given by “volunteers”. So, it can be expected that the Dortmund method should be the best one for VLE prediction.

At least one among above methods is included in any chemical process simulator software.

There are numerous pertinent modifications and/or extensions to the above methods. Examples can be the A-UNIFAC (UNIFAC plus an association term according to Wertheim theory) proposed by Mengarelli et al.[5] or KT-UNIFAC (second-order group contributions included) proposed by Kang et al.[6] We have not included these methods since neither of them was implemented into process simulators and, what was crucial, for systems under considerations we have not observed substantial improvement in the representation of solubilities in aqueous systems discussed below.

Magnussen et al.[7] developed the UNIFAC-LLE method. Unfortunately, this version of the classical UNIFAC has temperature-independent group-interaction parameters and therefore was recommended for very narrow range of temperatures [(283 to 313) K]. Results in many cases were only semiquantitative.

Authors of the methods usually reported some short estimation (indication) of accuracy of LLE prediction in different classes of mixtures as well as some illustrative examples. There are also some independent revisions like that of Gupte and Danner[8] or Kan and Tomson.[9] In such critical reviews, the key value is the quality of reference experimental data used. The experimental data on solubility in water systems are often scattered and influenced by systematic errors. There does not exist a thermodynamic consistency test for LLE data. Thus the crude data are not very useful for testing these methods. Fortunately, a series of works devoted to the selection of recommended solubility data was published in the IUPAC-NIST Solubility Data Series. The volumes published in years 2004−2007 are devoted to water systems of alkanes,[10,13,16,17,19−21] arenes,[11,14,15,18,19] and alkanols.[12,22−26] These data are used here for testing UNIFAC and ASOG methods. The recommended data used in this paper enable a more complex and thorough investigation and make conclusions.

In this work three types of binary systems are investigated: alkanes + water, arenes + water, and alkanols + water. These

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systems include substances which behave differently in respect to water: alkanes do not associate, arenes weakly crossassociate with water, and alkanols exhibit strong autoassociation and cross-association. These substances are built from a relatively small number of the functional groups, which are confronted with large amounts of recommended solubility data taken from papers.[10−26] The systems selected for the tests fulfill following criteria:

(1) The experimental points cover the tested temperature range (270 to 400) K.
(2) Homologous series are preferred to show trends of the prediction.

The following systems were used for the tests:

(1) Systems of water with alkanes: pentane, hexane, heptane, octane, decane, 2-methylpentane, cyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane.
(2) Systems of water with arenes: benzene, methylbenzene, ethylbenzene, propylbenzene, butylbenzene, 1,3-dimethylbenzene, and 1,3-diethylbenzene.
(3) Systems of water with alkanols: pentan-1-ol, hexan-1-ol, heptan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, 2-methylbutan-1-ol, 2-ethylbutan-1-ol, 3-methylbutan-1-ol, pentan-2-ol, hexan-2-ol, heptan-2-ol, octan-2-ol, pentan-3-ol, hexan-3-ol, 4-methylpentan-2-ol, 5-methylhexan-2-ol, and 2-methylbutan-2-ol.

■ SOLUBILITIES OF THE INVESTIGATED SUBSTANCES IN WATER

This section presents a comparison of the experimental solubilities of the investigated substances in water with the solubilities calculated with the above selected versions of UNIFAC and ASOG. To this end, the experimental recommended data points are used together with corresponding recommended lines, henceforth called reference lines. The reference lines are not adjusted to the recommended points shown in the plots. They are predicted from thermodynamic equations and association models reported in papers.[10−12] These models and equations allow us to reproduce a large body of experimental material with a relatively small number of physically sensible parameters. The parameters are optimized to reproduce simultaneously all solubility data reported for a given type of systems. The resulting solubility values are used as a reference for evaluation of experimental points in papers.[13−26]

Alkanes in Water. Deviations of the calculated values with respect to the experimental solubilities increase slowly in a series of normal alkanes. The results for isomeric alkanes are almost the same as for corresponding normal alkanes. Therefore the only solubility of hexane in water is shown as an example in Figure 1. The isomeric hexane is shown in Figure 2. The solubility of cyclohexane in water is shown in Figure 3 as an example. Results for all investigated alkanes, isomeric alkanes, and cycloalkanes are shown in Table 1. Because of the large variation in the solubility, errors of the prediction given in Table 1 are measured using the root-mean-square deviation (rmsd) of natural logarithms of solubility

$$\mathrm{rmsd}(\ln x_i) = \sqrt{\sum_{i=1}^{N} [\ln x_i(\mathrm{calc}) - \ln x_i(\mathrm{ref})]^2 / N} \qquad (1)$$

where N is the number of compared points per system, and calc and ref denote the data calculated by relevant group-contribution method or reference data, respectively.

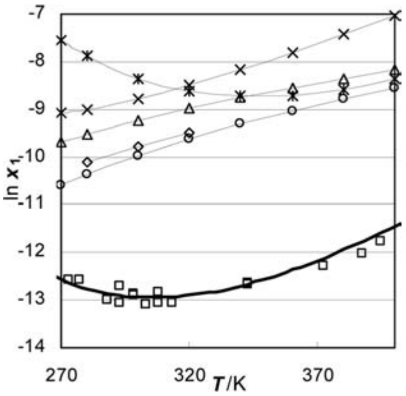

Figure 1. Solubility of hexane in water. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

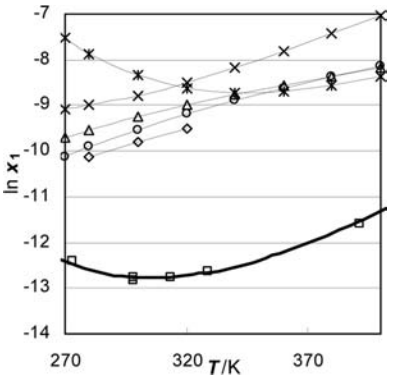

Figure 2. Solubility of 2-methylpentane in water. For symbols see Figure 1.

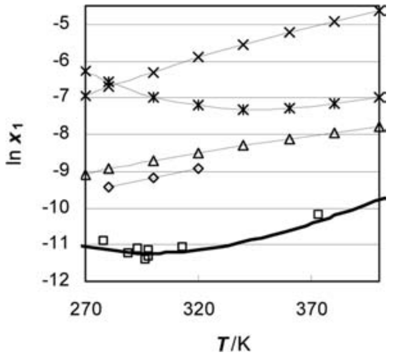

Figure 3. Solubility of cyclohexane in water. The predicted values: △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

Arenes in Water. Classical UNIFAC and its Lyngby version predict the solubility of benzene, as shown in Figure 4, quite well. Unfortunately, both of the methods do not reproduce the minimum of solubility. For other arenes, investigated in this paper, the prediction is much worse. The example is shown in Figure 5. It should be noted that for these arenes

Table 1. Comparison of Accuracy in the Prediction of Solubility Data in Organic (1)/Water (w) Systems by Different Group-Contribution Methods[a]

		rmsd(ln x_i)						
		UNIFAC					UNIFAC	
substance	i	v. 6	Dortmund	Lyngby	LLE	ASOG	VT	Mod-VT
pentane	1	3.27	3.97	3.83	2.84	2.83	0.16	0.04
	w	1.15	2.16	2.35	0.40	5.09	0.63	0.22
hexane	1	3.56	4.24	4.16	3.08	2.97	0.18	0.03
	w	1.00	2.25	2.20	0.41	4.85	0.40	0.02
heptane	1	3.88	4.52	4.50	3.34	3.14	0.22	0.06
	w	0.91	2.31	2.09	0.46	4.67	0.23	0.19
octane	1	4.32	4.91	4.96	3.74	3.44	0.36	0.23
	w	0.85	2.34	2.01	0.50	4.53	0.11	0.32
decane	1	5.39	5.85	6.03	4.72	4.23	0.90	0.78
	w	0.77	2.40	1.90	0.58	4.32	0.13	0.52
2-methylpentane	1	3.40	4.08	4.01	2.91	3.23	0.19	0.16
cyclopentane	1	2.37	4.76	3.94	2.15		0.78	0.74
cyclohexane	1	2.36	5.01	3.85	2.01		0.43	0.39
	w	0.91	1.76	1.78	0.48		0.03	0.40
methylcyclohexane	1	2.63	5.48	4.17	9.51		0.47	0.43
	w	0.90	0.33	1.85	0.45		0.04	0.39
ethylcyclohexane	1	2.74	5.52	4.32	2.32		0.34	0.31
	w	0.83	0.87	1.77	0.51		0.12	0.53
benzene	1	0.21	0.47	0.22	0.86	2.25	0.10	(0.10)
	w	0.92	1.00	0.18	4.19	2.18	0.04	(0.04)
methylbenzene	1	0.46	0.38	0.44	0.25	2.21		0.03
	w	1.14	0.72	0.18	0.31	2.14		0.00
ethylbenzene	1	0.36	0.39	0.58	0.18	2.27		0.36
	w	0.96	0.96	0.24	0.27	2.09		0.08
propylbenzene	1	0.32	0.43	0.76	0.21	2.27		0.50
butylbenzene	1	0.32	0.49	0.96	0.27	2.23		0.59
	w	0.78	1.12	0.34	0.20	2.02		0.18
1,3-dimethylbenzene	1	0.65	0.36	0.91	0.62	2.13		0.15
	w	1.44	0.51	0.38	0.55	2.09		0.04
1,3-diethylbenzene	1	0.42	0.39	1.17	0.21	2.22		0.43
	w	1.05	1.01	0.50	0.41	2.00		0.16
pentan-1-ol	1	0.57	0.53	1.09	0.34	0.43		
	w	0.14	0.31	0.30	0.16	0.32		
pentan-2-ol	1	0.69	0.38	0.45	0.80	0.53		
	w	0.10	0.35	0.20	0.04	0.25		
2-methylbutan-2-ol	1	1.28	0.73	0.70	1.63	0.71		
	w	0.33	0.56	0.25	0.33	0.16		
nonan-1-ol	1	1.56	1.24	2.18	1.23	0.87		
	w	0.14	0.55	0.27	0.06	0.32		
decan-1-ol	w	0.18	0.62	0.37	0.15	0.34		
hexan-1-ol	1	0.77	0.71	1.29	0.50	0.50		
	w	0.16	0.35	0.25	0.16	0.34		
heptan-1-ol	1	1.02	0.89	1.57	0.73	0.60		
	w	0.16	0.39	0.22	0.14	0.34		
octan-1-ol	1	1.29	1.07	1.88	0.98	0.73		
	w	0.15	0.50	0.23	0.02	0.34		
2-methylbutan-1-ol	1	0.48	0.25	0.53	0.39	0.62		
	w	0.25	0.09	0.32	0.34	0.44		
2-ethylbutan-1-ol	1	0.47	0.32	0.94	0.32	0.50		
	w	1.00	1.29	0.99	1.05	1.05		
3-methylbutan-1-ol	1	0.48	0.25	0.53	0.39	0.62		
	w	0.15	0.21	0.24	0.21	0.35		
hexan-2-ol	1	0.60	0.43	0.66	0.56	0.56		
	w	0.16	0.28	0.25	0.19	0.33		
heptan-2-ol	1	0.65	0.51	0.89	0.45	0.60		
	w	0.18	0.30	0.22	0.21	0.34		
octan-2-ol	1	0.79	0.61	1.14	0.42	0.66		
	w	0.18	0.33	0.18	0.20	0.32		
pentan-3-ol	1	0.69	0.38	0.45	0.49	0.53		
	w	0.28	0.07	0.48	0.36	0.46		
hexan-3-ol	1	0.61	0.39	0.56	0.66	0.54		
	w	0.38	0.03	0.49	0.49	0.53		
4-methylpentan-2-ol	1	0.63	0.37	0.51	0.73	0.67		
	w	0.18	0.25	0.28	0.23	0.39		
5-methylhexan-2-ol	1	0.59	0.40	0.73	0.56	0.71		
	w	0.20	0.28	0.24	0.23	0.38		

[a] Empty cells result from a lack of relevant group-interaction parameters. The rmsd is given by eq 1.

Lyngby version does predict the minimum solubility, though it is considerably shifted with respect to the experimental minimum. Results for all investigated arenes are shown in Table 1.

Alkanols in Water. The errors of the predicted solubilities increase in the series of primary alkanols from pentanol until nonanol. The results for the first and the last members of this series are shown in Figures 6 and 7. The branched isomeric alkohols give similar results.

The results obtained for secondary alkanols change systematically within the homologous series, but in all cases the error of the prediction is too high. Figures 8 and 9 show results obtained for secondary and ternary pentanol to be compared with results for pentan-1-ol as shown in Figure 6. Results for all investigated alkanols are shown in Table 1.

It is useless to analyze the behavior of ASOG and the investigated modifications of UNIFAC. Figures 1 to 9 show that the errors of the prediction are too high. In some cases a particular equation works relatively well, but it is worse in other systems. All of the investigated substances exhibit a minimum of solubility at a room temperature. Except for the Lyngby modification, no other method is able to reproduce this minimum for "normal" substances. But also in this case the minimum is shifted to the right. For branched alkanols also the Dortmund version predicts minima but shifted to left in this case.

SOLUBILITY OF WATER

This section describes water solubilities obtained with the selected versions of UNIFAC and ASOG, where parameters are optimized for VLE prediction. Results for all investigated systems are shown in Table 1. Typical cases are discussed below.

Water in Alkanes. The experimental solubility of water in various normal alkanes is almost the same especially at room temperatures. Also the predicted curves does not change very much in the series of the alkanes. As the example results obtained for octane are shown in Figure 10. Solubilities of water in ethylcyclohexane having the same number of carbon atoms as octane are shown in Figure 11. The experimental solubility curves in Figures 10 and 11 are almost equal, but the predicted values are different.

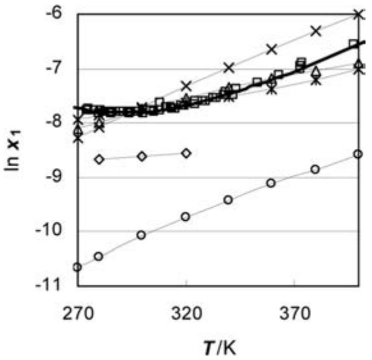

Figure 4. Solubility of benzene in water. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

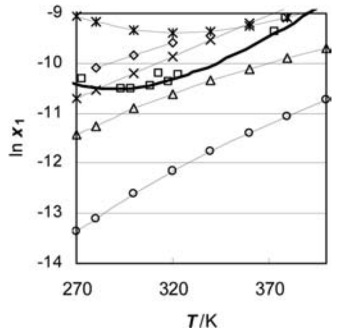

Figure 5. Solubility of 1,3-dimethylbenzene in water. For symbols see Figure 4.

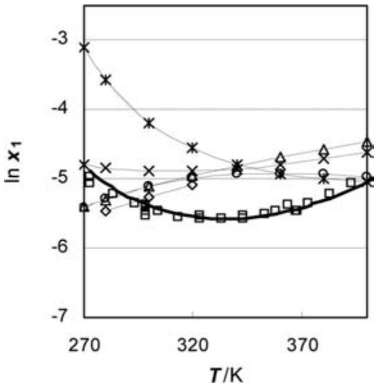

Figure 6. Solubility of pentan-1-ol in water. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

Water in Arenes. It was found that the solubility of water in benzene and its monoalkyl derivatives is well-predicted with the Lyngby version of UNIFAC but the error is bigger for dialkylbenzenes. The other methods give much worse results in all investigated systems. The examples are shown in Figures 12 and 13.

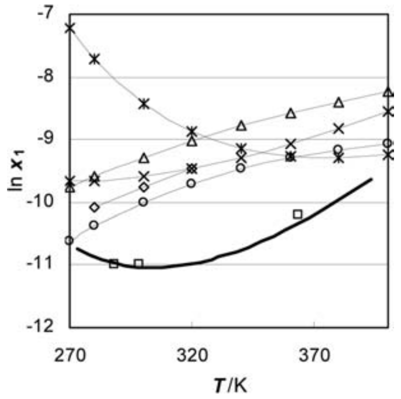

Figure 7. Solubility of nonan-1-ol in water. For symbols see Figure 6.

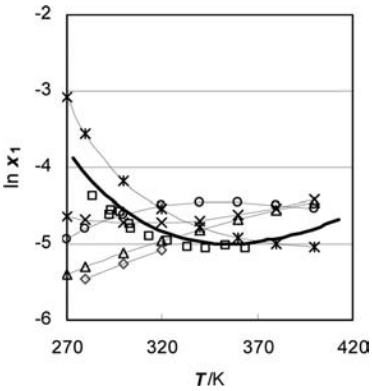

Figure 8. Solubility of pentan-2-ol in water. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

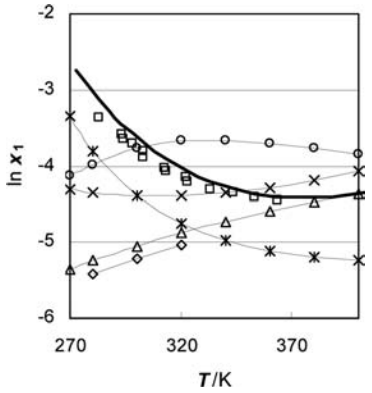

Figure 9. Solubility of 2-methylbutan-2-ol in water. For symbols see Figure 8.

Water in Alkanols. Errors of the prediction changes systematically in the homologous series of primary alkanols. The examples are shown in Figures 14 and 15. Its branched isomers behave in a similar way.

Two isomeric pentanols are shown in Figures 16 and 17 to be compared with pentan-1-ol, shown in Figure 14. The behavior

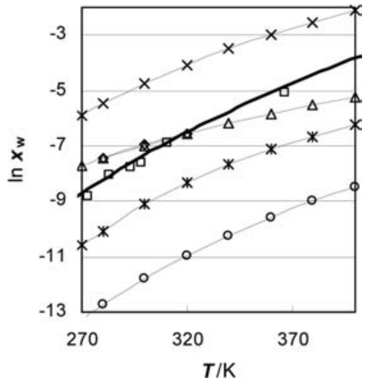

Figure 10. Solubility of water in octane. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

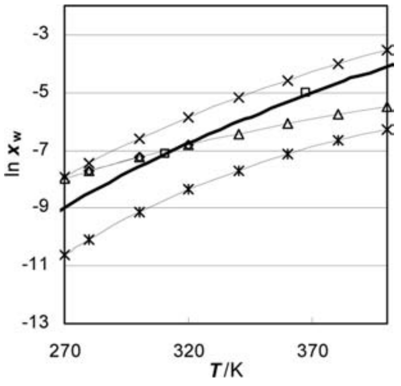

Figure 11. Solubility of water in ethylcyclohexane. For symbols see Figure 10.

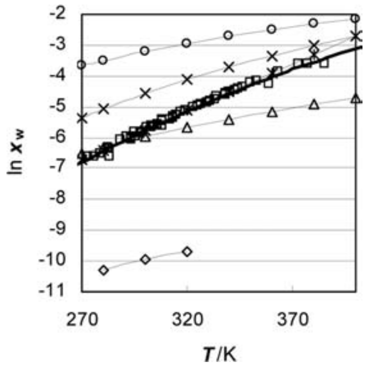

Figure 12. Solubility of water in benzene. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

of secondary and ternary alkanols deviates from the corresponding primary alkanols, while the predicted lines are almost the same.

The obtained results presented in the two above sections are not surprising, because parameters of the investigated equations are optimized for prediction of VLE. Better results can be achieved with parameters adjusted to LLE data. The corresponding results are presented in the next section.

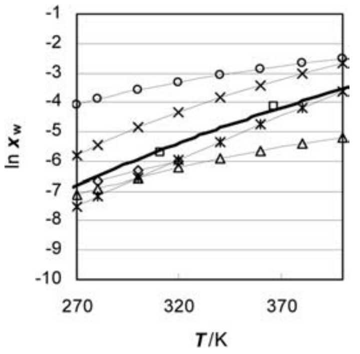

Figure 13. Solubility of water in 1,3-diethylbenzene. For symbols see Figure 12.

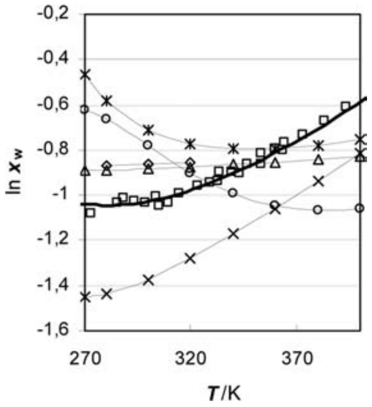

Figure 14. Solubility of water in pentan-1-ol. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◊, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

■ SOLUBILITY CALCULATED WITH UNIFAC ADJUSTED TO LLE

It was clear just from the original paper[27] on the UNIFAC method that interaction parameters fitted to VLE data are not suitable for the quantitative prediction of solubility data. Magnussen et al. elaborated on a particular interaction parameter matrix based on solubility data. Unfortunately, the UNIFAC-LLE was recommended for a very narrow range of temperatures [(283 to 313) K], and results in many cases were only semiquantitative. This is confirmed by our results shown in the previous sections. Many attempts have been made to improve the interaction parameters of water with nonpolar groups, particularly for alkane and arene groups. Hooper et al.[28] developed the modified UNIFAC method aimed at the prediction of liquid−liquid equilibria for water−organic liquid systems over a wide temperature range. This modified UNIFAC represents successfully the hydrocarbon-rich phase but cannot correctly reproduce the minimum solubility of hydrocarbon in water. One drawback of this method consists in a limited number of available groups. Voutsas and Tassios[29] examined and modified this version of

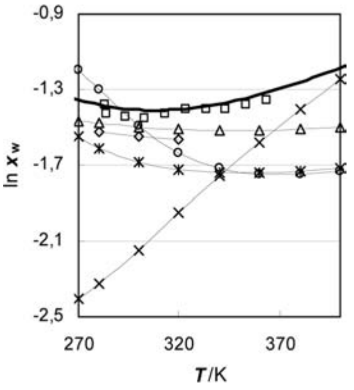

Figure 15. Solubility of water in decan-1-ol. For symbols see Figure 14.

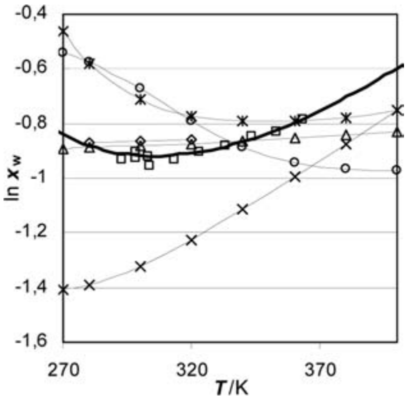

Figure 16. Solubility of water in pentan-2-ol. The predicted values: ○, ASOG; △, classical UNIFAC (revision 6); ×, modified UNIFAC (Dortmund); ∗, modified UNIFAC (Lyngby); ◇, UNIFAC-LLE by Magnussen et al.; □, the experimental recommended points; the bold line, reference line (described in text).

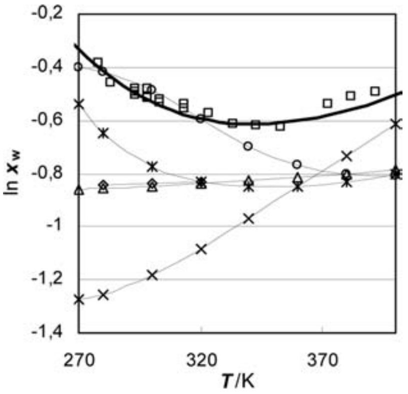

Figure 17. Solubility of water in 2-methylbutan-2-ol. For symbols see Figure 16.

Table 2. Coefficients for Temperature-Dependent Organic Group (1)/Water (2) Interaction Parameters a_{12} and a_{21} Given by Equation 2 for the VT-UNIFAC

interaction	$a_{12}{}^{(0)}$/K	$a_{12}{}^{(1)}$	$a_{12}{}^{(2)}$/K^{-1}	$a_{21}{}^{(0)}$/K	$a_{21}{}^{(1)}$	$a_{21}{}^{(2)}$/K^{-1}
			Voutsas and Tassios[a]			
CH_2−H_2O	2812.5	−3.982		−1481.52	13.490	−0.016659
ACH−H_2O	1907.3	−2.437		−629.84	8.231	−0.008953
			This Work[a]			
CH_2−H_2O	2055.17	0.6704	−0.007852	−1446.26	12.928	−0.015217
$ACCH_2$−H_2O	−349.78	12.031	−0.020876	−1964.80	16.098	−0.021150

[a] $r(H_2O) = 0.591$; $q(H_2O) = 1.4$.

the UNIFAC method. They introduced the Flory−Huggins combinatorial contribution with adjusted r and q structural parameters for water and developed new interaction parameters for the H_2O−CH_2 and H_2O-ACH groups with extended temperature dependence. The interaction parameters are given by eq 2

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)}T + a_{ij}^{(2)}T^2 \qquad (2)$$

where T is in kelvin. This is probably the best attempt. The method was tested only for five systems including relatively low hydrocarbons, pentane, hexane, octane, and cyclohexane as well as for benzene. Results of the prediction achieved with the described modifications are shown below. Parameters reported by Voutsas and Tassios are given in Table 2. Figure 18 shows the solubility of alkanes in water. The reference and predicted values at some discrete temperatures are represented here by the corresponding symbols. The approximating lines are not used to differentiate between the overlapping values. For pentane and hexane the reference and predicted solubility almost coincide, because data for these alkanes (and octane) were used for adjusting the VT-UNIFAC parameters. For other members of the homologous series deviations systematically increase. In the second coexisting liquid phase the reference solubility values for water in various normal alkanes almost overlap. Therefore only results for water in pentane and water in decane are shown in Figure 19. The accuracy of the solubility prediction is good both in systems shown in Figure 19 and in other hydrocarbon systems shown in Table 1.

Some explanation should be given for those who compared results for octane presented in Figure 18 with corresponding results in Figure 4 shown in the paper of Voutsas and Tassios. In the latter case the predicted curve nearly overlaps the experimental points. In our figure there is a small but systematically increasing gap between predicted and recommended data. In the Voutsas and Tassios paper using inconsistent experimental data causes this difference. We have fitted interaction parameters for pair CH_2−H_2O using recommended data for hexane. New parameters, reported in Table 2, result in the reproduction of solubility curves for pentane, hexane, and heptane as shown in Figure 20. For octane and decane predictions are near similar to that of Voutsas and Tassios. In this attempt only parameters for one pair were modified by adjusting them to one chosen system.

For arenes Voutsas and Tassios fitted interaction parameters for ACH−H_2O pair of groups using LLE data for benzene with water. It is clear that in this case solubilities in this system can be well-predicted. Unfortunately, a single ACH group is not sufficient to represent alkylbenzenes correctly. To this end parameters for the group $ACCH_2$ with water are needed. Parameters reported by Hooper et al. cannot be used for this purpose. We have fitted temperature-dependent parameters for $ACCH_2$−H_2O groups using recommended data for methylbenzene. These parameters are reported in Table 2. Parameters for $ACCH_2$−H_2O groups fitted in this work were used together with the

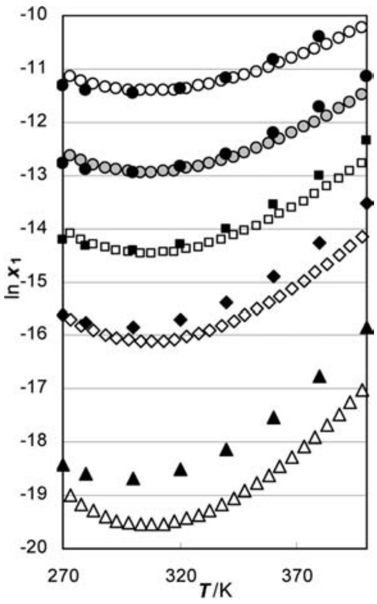

Figure 18. Solubility of alkanes in water and prediction with the VT-UNIFAC. Reference curves for the solubility of: ○, pentane; gray ●, hexane; □, heptane; ◊, octane; and △, decane. The corresponding predicted values (calculated with the original parameters reported by Voutsas and Tassios) are denoted with the same but black symbols.

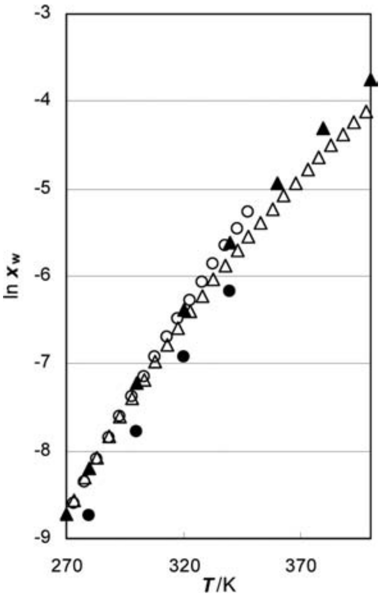

Figure 19. Solubility of water in alkanes. Reference curves for of water in ○, pentane and △, decane. The corresponding predicted values (calculated with the original parameters reported by Voutsas and Tassios) are denoted with the same but black symbols.

original parameters for CH_2-H_2O and $ACH-H_2O$ reported by Voutsas and Tassios. Temperature-independent interaction parameters between organic groups (CH_2, ACH, and $ACCH_2$) were those as reported by Hooper et al. Thus for solubility of benzene and methylbenzene in water the reference and predicted curves almost coincide, because these arenes were used for adjusting the VT-UNIFAC parameters. For other members of

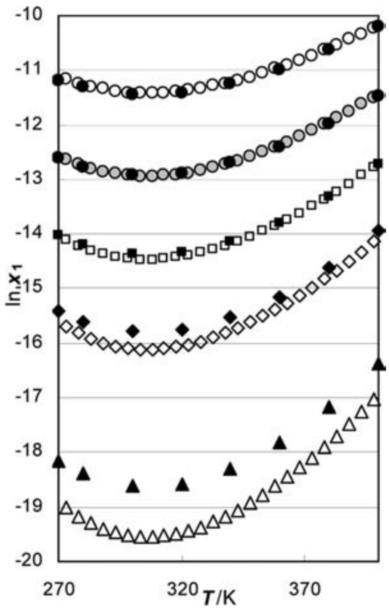

Figure 20. Solubility of alkanes in water and prediction with the VT-UNIFAC with interaction parameters for pair CH_2-H_2O modified by the authors. Reference curves for the solubility of: ○, pentane; , hexane; □, heptane; ◊, octane, and △, decane. The corresponding predicted values are denoted with the same but black symbols.

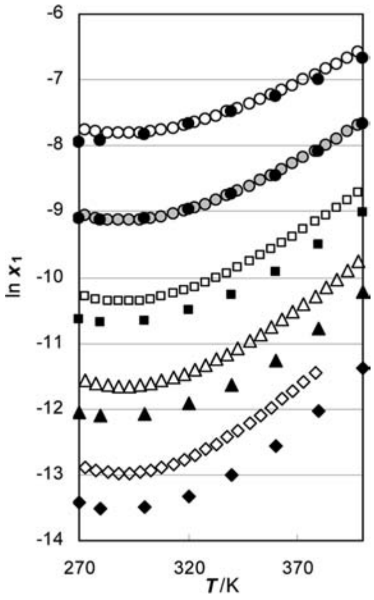

Figure 21. Solubility of arenes in water and prediction with the original VT-UNIFAC supplemented with interaction parameters for pair $ACCH_2-H_2O$ estimated by the authors. Reference curves for the solubility of: ○, benzene; gray ●, methylbenzene; □, ethylbenzene; △, propylbenzene, and ◊, butylbenzene. The corresponding predicted values are denoted with the same but black symbols.

the homologous series deviations systematically increase as is shown in Figure 21.

In the second coexisting liquid phase solubility curves of water in the arenes almost overlap. Therefore only results for water in benzene and water in butylbenzene are shown in Figure 22. The accuracy of the prediction for these two arenes is quite good.

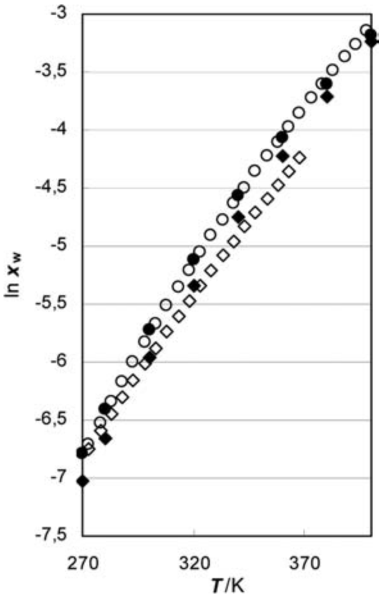

Figure 22. Solubility of water in arenes. Prediction with the original VT-UNIFAC supplemented with interaction parameters for pair AC-CH_2−H_2O estimated by the authors. Reference curves for water in ○, benzene, and ◇, butylbenzene. The corresponding predicted values are denoted with the same but black symbols.

Similar accuracy is observed for solubility of water in other investigated arenes such as ethylbenzene, propylbenzene, dimethylbenzenes, and diethylbenzenes. The obtained accuracy is given in Table 1.

VT-UNIFAC does not include parameters necessary for alkanol−water systems. Thus the corresponding LLE calculations were not made.

Special attention should be paid to particular solubility data, namely, aqueous solubility at 298 K, denoted as *S*. These data, and more precisely log *S*, are of special interest in environmental applications. Kan and Tomson[9] reviewed attempts to improve application of the UNIFAC for prediction of aqueous solubility *S*. Many other methods (for example, correlation with amended solvation equation, correlation with molecular connectivity index, and a polarizability factor or QSPR methods) were used to predict the *S* values. Unfortunately conclusions from comparisons with experiment very often are confusing due to unreliable reference data. It should be also noted that solubilities of arenes predicted by some versions of UNIFAC intersect recommended data at room temperatures. Some authors who limited their interest to these temperatures could conclude that UNIFAC gives good predictions, but this is not generally correct.

CONCLUSIONS

Generally it has been confirmed that all commonly used UNIFAC and ASOG methods for solubilities of water with alkanes, arenes, and alkanols are not suitable for quantitative prediction. However, when interaction parameters are fitted to suitable recommended LLE data, quantitative predictions are possible when sacrificing generality of the method, that is, restricting the application of the parameters for the calculation of LLE. For predictions in a wider temperature range, temperature-dependent interaction parameters are needed. It can be expected that further improvement can be achieved by exploring other modifications. This however is out of scope of this paper.

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