Prediction of Infinite Dilution Activity Coefficients using COSMO-RS

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Abstract

Infinite dilution activity coefficients (IDACs) are important characteristics of mixtures because of their ability to predict operating behavior in distillation processes. Thermodynamic models are used to predict IDACs since experimental data can be difficult and costly to obtain. The models most often employed for predictive purposes are the Original and Modified UNIFAC Group Contribution Methods (GCMs). COSMO-RS (COnductor-like Screening MOdel for Real Solvents) is an alternative predictive method for a wide variety of systems that requires a limited minimum number of input parameters. A significant difference between GCMs and COSMO-RS is that a given GCMs' predictive ability is dependent on the availability of group interaction parameters, whereas COSMO-RS is only limited by the availability of individual component parameters. In this study COSMO-RS was used to predict infinite dilution activity coefficients. The database assembled by, and calculations with various UNIFAC models carried out by Voutsas et al. (1996) were used as the basis for this comparison. This database contains aqueous and non-aqueous non-electrolyte binary mixtures. In aqueous systems, COSMO-RS provides the best result for systems with alkyl halides or aromatics as solutes in water; all other binary mixtures also gave good results. Overall, COSMO-RS was less successful for non-aqueous systems. Good results from COSMO-RS were obtained for non-aqueous systems involving alkyl halides, alkanes in ethanol, and ketones in alkane.

Introduction and Review

Activity coefficient models first appeared around the turn of the 20th century; Margules and van Laar (1910), among others, realized that liquid-phase nonideality could be represented by phenomenologically plausible algebraic functions that have the correct limiting behavior. Wilson (1964) contributed the all-important "local composition" concept that enabled correlation of activity coefficients in multicomponent systems using only binary parameters. Prausnitz and coworkers subsequently developed the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models that are widely used in the chemical industry today, and are especially useful for highly-nonideal solutions.

Physically, the activity coefficient at infinite dilution (IDAC), γ^∞, is a useful measure of the degree of nonideality in a liquid mixture. Such data may also be used to regress binary interaction parameters for the Margules, van Laar, Wilson, NRTL, and UNIQUAC activity coefficient models. There is a considerable quantity of IDAC data in the literature (Tiegs et al., 1986; Gmehling et al., 1994). Frequently, however, it is necessary to estimate IDACs for systems where no data exists or even for a well-studied system at conditions for which no data has been obtained.

Group Contribution Methods

For correlating thermodynamic properties, it is often convenient to regard a molecule as an aggregate of functional groups; as a result, some thermodynamic properties of pure fluids (e.g., heat capacity, critical properties, and many others) can be calculated by summing group contributions. In any group contribution method, the basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups that make up these compounds, is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecule's functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids, in terms of a much smaller number of parameters. These parameters characterize the contributions of individual groups.

Two particularly useful GCMs that provide reasonable estimates of activity coefficients in nonideal mixtures for which data are sparse or totally absent are UNIFAC (Fredenslund et al., 1975), which is based on the UNIQUAC model, and ASOG (Kojima and Tochigi, 1979), which makes use of the Wilson equation. There are other methods, similar in principle but which differ in the details: LLE-UNIFAC (Magnussen et al., 1981), Modified UNIFAC (Dortmund) (Gmehling et al., 1993), and Modified UNIFAC (Lyngby) (Larsen et al. 1987). VLE data have been used for fitting the required group interaction parameters for the UNIFAC and the ASOG method. The most recent parameter tables have been published respectively in Hansen et al. (1991) and Tochigi et al. (1990). The UNIFAC method has been integrated in almost all process simulators.

Any group contribution method is necessarily approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule. The fundamental assumption of a group contribution method is that the contribution made by one group within a molecule is assumed independent of that made by another group in that molecule. This assumption is valid only when the influence of any one group in a molecule is not affected by the nature of other groups within that molecule. For example, we would not expect the contribution of a carbonyl group in a ketone (say, 2-butanone) to be the same as that of a carbonyl group in an organic acid (say, n-butanoic acid). On the other hand, experience suggests that the contribution of a carbonyl group in, for example, 2-butanone, is close to (although not identical with) the contribution of a carbonyl group in another ketone, say 2-pentanone.

Although the UNIFAC method is well tested, the method still shows some weakness. For example, only poor results are obtained for activity coefficients at infinite dilution (γ^∞) and excess enthalpies (h^E) and systems with compounds very different in size. This should not be too surprising since with the database, of mainly VLE data used for fitting the group interaction parameters, only a limited concentration range (5-95 mole %) is covered and this mostly

accounts for compounds of similar size. Furthermore, no quantitative information about the temperature dependence of activity coefficients can be derived from typical VLE data.

There have been a number of critical evaluations of the ability of group contribution methods at predicting infinite dilution activity coefficient models.

Voutsas et al. (1996) assessed the ability to predict infinite dilution activity coefficients of several different models (mostly variants of UNIFAC):

1. Original UNIFAC with parameters from Hansen et al. (1991).
2. Original UNIFAC with Temperature-Dependent Interaction Parameters (Hansen et al. 1992). For this model, the interaction parameter □ □is calculated with respect to an arbitrary reference temperature .
3. Original UNIFAC Especially Suited for LLE Calculations (Magnussen et al. 1981). No modifications have been made to the Original UNIFAC model; the interaction parameters are obtained by fitting LLE experimental data.
4. Modified UNIFAC (Larsen et al. 1987). There is a modification of the combinatorial term , and reconfiguring the interaction parameter □ so they are temperature dependent.
5. Modified UNIFAC (Gmehling et al. 1993). The segment fraction in the combinatorial term and the interaction parameter are both adjusted.
6. Modified UNIFAC Especially Suited for Infinite Dilution Activity Coefficients (Bastos et al. 1988). The combinatorial term is from Kikic et al., 1980, and the residual term is based upon fitting of experimental data for IDAC.
7. Modified UNIFAC (Hooper et al., 1988). This model is only used for LLE in water/hydrocarbon mixtures. The model is created with a modification to the interaction parameter.
8. The PDD Correlation (Pierotti et al., 1959). This method employs a number of different functional forms that have up to five different parameters plus variables that take into account the number of carbon atoms in the solute and solvent.

Voutsas et al. report that for asymmetric mixtures of alkanes the modified UNIFAC methods perform very well, whereas the original UNIFAC methods do poorly. The Modified UNIFAC (Dortmund) method gives satisfactory results for non-aqueous polar mixtures, but the PDD method was best for strongly nonideal aqueous systems. The modified UNIFAC type method of Hooper et al. was best of hydrocarbon/water mixtures.

Zhang et al. (1998) evaluated the ability of ASOG and several versions of UNIFAC to predict IDACs in aqueous solutions. Their conclusion was that all models gave rather poor results with mean relative deviations of 45-72% (and that without counting those cases where the mean

relative deviation was greater than 100%). The Modified UNIFAC (Dortmund) method performed well for more highly polar compounds in water. Zhang et al. considered the modified UNIFAC method of Hooper et al. (1988) to be only fair with a mean relative deviation of 36%. They also proposed an improved UNIFAC to account for hydrophobic effects in systems including water for which they obtained satisfactory results.

A more recent paper by Abildskov et al. (2001) has looked at structural effects on infinite dilution activity coefficients of solutes in n-alkanes and other hydrocarbon solvents. They find that the combinatorial term may not be small and the proper modeling of this term can be essential to the success of methods based on UNIFAC. No new model is presented but the authors do suggest ways in which existing methods can be improved.

COnductor like Screening MOdel for Real Solvents (COSMO-RS)

In 1977, Prausnitz said in his "State-of-the-Art Review of Phase Equilibria" talk (in Storvick and Sandler, 1977): "Finally, let us learn to use more the powerful methods of statistical mechanics; let us overcome our fear of partition functions and let us not hesitate to introduce some enlightened empiricism into their construction." Twenty-five years later, we still agree with this statement, especially with the latter part of the sentence. From a practical point of view we cannot wait until theories have advanced to a point where predictions of chemical, physical, and transport properties can be made based on purely theoretical considerations.

Chen and Mathias (2002) expect simulation based on computational molecular science to become an increasingly important tool for the development of applied thermodynamic models. Simulation (or computational molecular science) now has developed to the point where it can be useful for quantitative predictions for certain properties of practical interest. As stated in the Technology Roadmap for Computational Chemistry (1999), "Among other applications, it supplies quantitative estimates of engineering parameters such as heats of formation and heats of reaction, entropies and heat capacities, reaction rate constants, and transport properties like viscosity and thermal conductivity that are needed to construct macro-scale models of complete chemical processes."

However, we believe that many of the simulation-based models have not yet reached a point where they could be used for practical routine work, for example GCMs. Many new models are being developed based on quantum mechanics that do not require the enormous computational burden of molecular dynamics or Monte Carlo simulations. One promising approach has been to use molecular orbital *ab initio* calculations to compute interaction energies between pairs of molecules in a molecular cluster (Sum and Sandler, 1999), which is then used as the energy parameters in the Wilson and UNIQUAC models and to predict phase equilibrium. In another

approach, Lin and Sandler (1999) equated the γ^{∞} expressions from both quantum chemical continuum solvation models and UNIQUAC, for relating the UNIQUAC binary interaction parameters to the charging free energies determined from *ab initio* calculations.

COSMO-RS (Klamt, 1995) is an example of a simulation-based model that is quite close to reaching the point of becoming a practical chemical engineering utility. It is a relatively new prediction method for activity coefficients and other thermophysical properties. COSMO-RS is based solely upon unimolecular quantum chemical calculations of the individual species in the system (i.e., not of the mixture itself). The theory of COSMO-RS has been given elsewhere (Klamt et al., 1998; Klamt and Eckert, 2000) and will not be considered here in detail. However, we want to shortly sketch the practical course of a COSMO-RS calculation and stress the basic differences between COSMO-RS and GCMs. As mentioned above, GCMs are based on the assumption that, with appropriately defined groups, the interaction energy of any system can be well approximated by the sum of functional group interaction energies. That is, a liquid is considered not as a mixture of interacting molecules but as a mixture of interacting structural groups. The properties of a certain mixture can be predicted from previously determined group interaction parameters that have been adjusted to available experimental data of systems containing the same functional groups. Thus, GCMs critically depend on the availability of the appropriate group interaction parameters, and therefore the generality of their applicability is limited.

The COSMO-RS approach starts from a very different point of view, namely, from the complete molecule or, to be more precise, from the molecular surface as computed by quantum chemical methods (QM). COSMO-RS combines an electrostatic theory of locally interacting molecular surface descriptors (which are available from QM calculations) with an exact statistical thermodynamics methodology. In practice, each molecule that is involved in a mixture has to be computed by the quantum chemical conductor-like screening model (COSMO) (Klamt and Schüürmann, 1993). Such calculations are easily done overnight on a single CPU in most cases but can be quite time consuming for very large molecules (more than 70 atoms). However, they have to be done only once per molecule and the results can be stored in a database for subsequent use. The COSMO-RS calculation that predicts the thermodynamic properties (e.g., chemical potentials, activity coefficients, solvent partition coefficients, solubilities, vapor pressures, excess Gibbs free energies, excess enthalpies, etc.) is done in seconds and therefore, for example, can be used in the task of screening a large number of compounds from a database. COSMO-RS depends on a small number of 16 adjustable parameters, some of which are physically predetermined. COSMO-RS parameters are not specific regarding functional groups or molecule types. The parameters have to be optimized only for the QM-COSMO method that is to be used as a basis for the COSMO-RS calculations. Thus, the resulting parameterization is completely general and can be used to predict the properties of almost any imaginable compound mixture or

system (including even experimentally unavailable entities such as reactive intermediates or transition state structures). This is the main practical difference between COSMO-RS and the group contribution methods.

Prediction of Infinite Dilution Activity Coefficients with COSMO-RS

The database assembled by Voutsas et al. (1996) was chosen as the basis for our comparison with COSMO-RS because of its range of systems considered (aqueous and non-aqueous), and because the appendix to their paper provides all the data considered. All of the systems in their study are nonelectrolyte binary mixtures. Systems containing the following compounds were not analyzed because they were not parameterized for COSMO-RS at the time of writing: 1-dodecene, 1,2 dichloropropane, 1,2,3 trichlopropane, cycloheptene, cyclooctene, n-decanoic acid, n-docosane, n-dodecanoic acid, n-dotriacontane, n-eicosane, n-heptadecanol, n-hexatriacontane, n-octadecane, n-tetracosane, n-tetradecanoic acid, n-triacontane, naphthacene, and naphthalene. The system acenaphthene-water was also removed from the database because the temperature, 298 Kelvin, is below the freezing point of acenaphthene.

For this work, we used COSMOtherm Version C1.2, Release 01.02 (Eckert et al., 2002) to predict the activity coefficients of each binary system in the database of Voutsas et al. (1996).

Non-Aqueous Systems

In Table 1, we record the Percent Absolute Deviation (%AAD) for COSMO-RS and UNIFAC for various groups of solutes in non-aqueous solvents. The %AAD is defined as:

$$\% AAD = \frac{1}{NP} \sum_{i=1}^{NP} \frac{\left| \gamma_{i,calc} - \gamma_{i,\exp} \right|}{\gamma_{i,\exp}} \tag{1}$$

where NP is the total number of points for a given group. It must be pointed out that we have relied on the computations of Voutsas et al. (1996) for the different UNIFAC models.

We see from Table 1 that for non-aqueous systems Modified UNIFAC (Dortmund) is the best of the methods considered here. COSMO-RS is, on average, poorer than the UNIFAC methods although it does have some successes. Figure 1 provides a graphical comparison between COSMO-RS and the two Modified UNIFAC models of Gmehling et al. (1993) and Larsen et al. (1987) for non-aqueous systems. The COSMO-RS predictions lie outside the 20% discrepancy lines for many systems. The best predictive model for IDACs in non-aqueous mixtures was the Modified UNIFAC (Dortmund) (Gmehling et al., 1993); indeed, it is apparent that this model performs very well for the systems in Table 1. Modified UNIFAC (Lyngby) (Larsen et al., 1987) is not as good as the model by Gmehling et al. (1993), but still superior to COSMO-RS.

Table 1: %AAD for solutes in non-aqueous solvents. (1) Original UNIFAC (Hansen et al., 1991), (2) Original UNIFAC (Hansen et al., 1992), (3) Original UNIFAC (Magnussen et al., 1981), (4) Modified UNIFAC (Larsen et al., 1987), (5) Modified UNIFAC (Bastos et al., 1988), (6) Modified UNIFAC (Gmehling et al., 1993). UNIFAC results from Voutsas et al. (1996).

| Solute	Solvent	NP	1	2	3	4	5	6	COSMO-RS
Alcohol	Alkane	14	31.77	24.49	62.85	23.26	38.94	15.68	162.55
Alcohol	Cycloalkane	15	19.28	16.33	62.47	22.20	26.86	23.87	137.17
Alkane	Alcohol	17	22.30	23.40	36.59	33.07	76.11	12.58	20.25
Alkane	Alkyl Halide	5	11.48	5.20	83.92	6.90	7.41	2.66	11.31
Alkane	Amine	7	22.70	53.11	19.24	-	21.84	15.12	76.22
Alkane	Carboxylic Acid	4	22.38	39.94	67.82	24.25	-	23.10	132.55
Alkane	Ketone	21	16.98	11.95	22.70	15.20	41.66	12.29	23.17
Alkane	Phenol	24	45.52	36.67	26.63	45.60	13.53	11.44	30.53
Alkene	Amine	15	17.93	12.93	17.57	-	31.72	14.29	75.12
Alkyl Halide	Alkane	23	10.63	7.62	40.35	8.81	9.28	2.44	11.95
Amine	Alkane	11	136.56	54.09	9.52	-	78.57	9.80	46.69
Aromatic	Alkane	28	14.96	13.17	27.80	21.97	29.45	8.44	62.45
Cycloalkane	Alcohol	6	10.31	12.01	19.21	25.21	11.50	7.70	14.58
Cycloalkane	Alkyl Halide	5	3.09	13.06	115.32	1.98	4.35	2.90	0.56
Cycloalkane	Amine	1	51.70	61.45	51.18	-	55.63	58.51	82.86
Cycloalkane	Carboxylic Acid	4	29.93	41.40	63.32	38.59	-	27.89	41.61
Cycloalkane	Phenol	28	39.03	31.80	21.34	39.89	12.76	19.40	22.30
Cycloalkene	Amine	6	22.35	9.79	6.43	-	22.82	16.13	61.70
Ketone	Alcohol	34	11.34	15.20	17.44	15.81	31.48	6.84	32.73
Ketone	Alkane	29	13.76	18.10	13.70	14.40	12.09	12.57	14.07
Weighted average		297	25.46	21.42	30.56	18.34	23.98	12.18	45.57

| | Highest %AAD | | Lowest %AAD | | <15 %AAD |
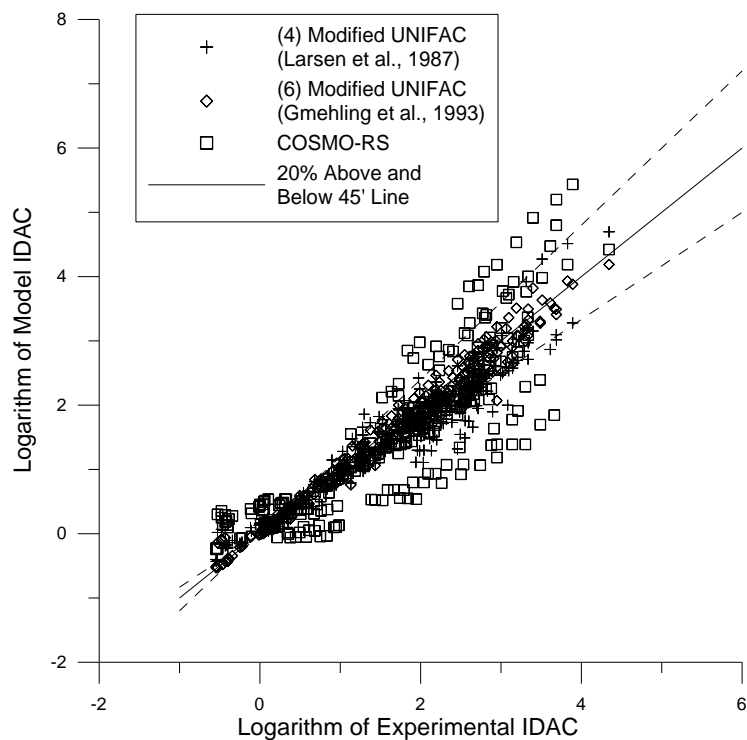
Figure 1: Logarithm of Model IDAC versus Logarithm of Experimental IDAC in Non-Aqueous Systems for models: (4) Modified UNIFAC (Larsen et al., 1987), (6) Modified UNIFAC (Gmehling et al., 1993), and COSMO-RS.

COSMO-RS does have some successes in non-aqueous systems: alkyl halides in most solvents being a case in point. Figures 2 and 3 show Chloroform in n-alkanes and cyclohexane in carbon tetrachloride. N-Alkanes in ethanol are shown in Figure 4 and n-alkanes in 2-butanone in Figure 5. COSMO-RS has almost the correct slope for acetone in n-alkanes (Figure 6) although the UNIFAC methods do better than COSMO-RS when there are not too many carbon atoms in the n-alkane.

COSMO-RS provided very poor estimates of IDACs for DMF as well as the general amine group in mixtures. This unexpected error with DMF is most likely due to the special liability of the planar (sp2) hybridization of DMF (and other doubly N-substituted amides) with respect to the pyramid structure of these molecules (sp3). The special problems for amines have been reported and discussed by Klamt et. al. (1998).
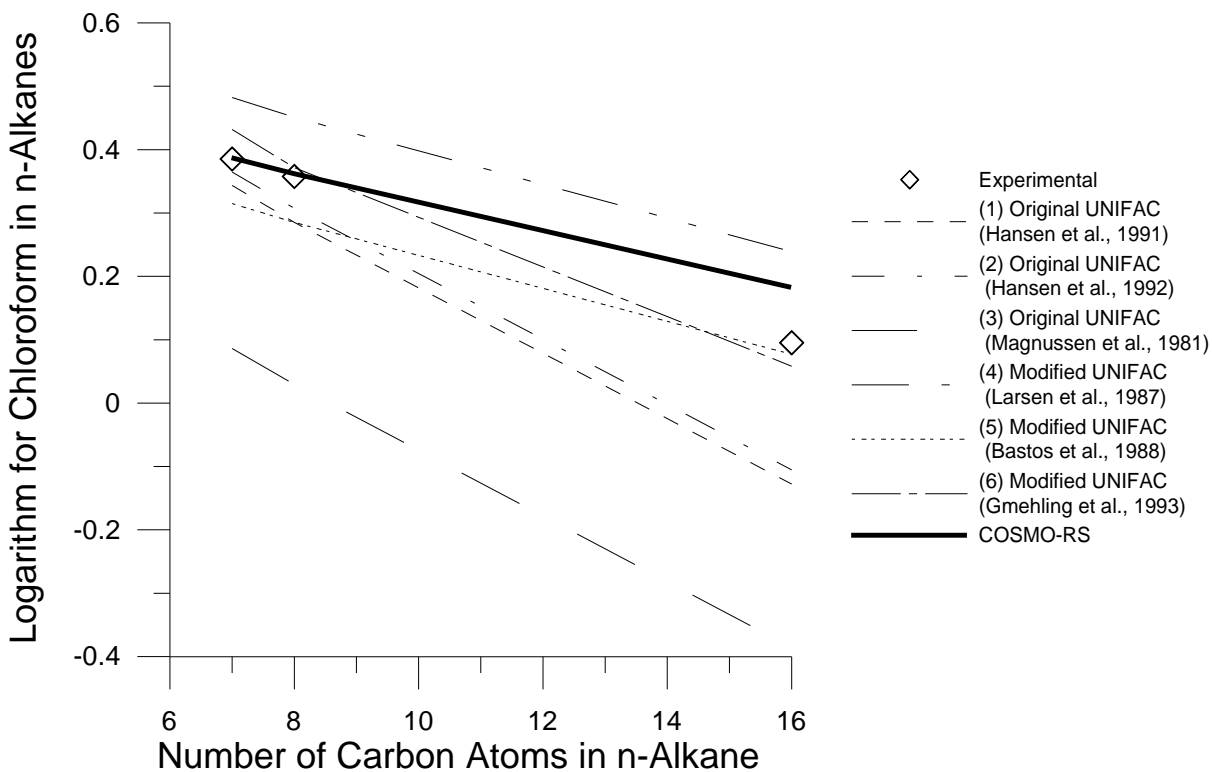
Figure 2: Logarithm of IDAC versus Number of Carbon Atoms in n-Alkane for Chloroform in n-Alkane at T=293 K.
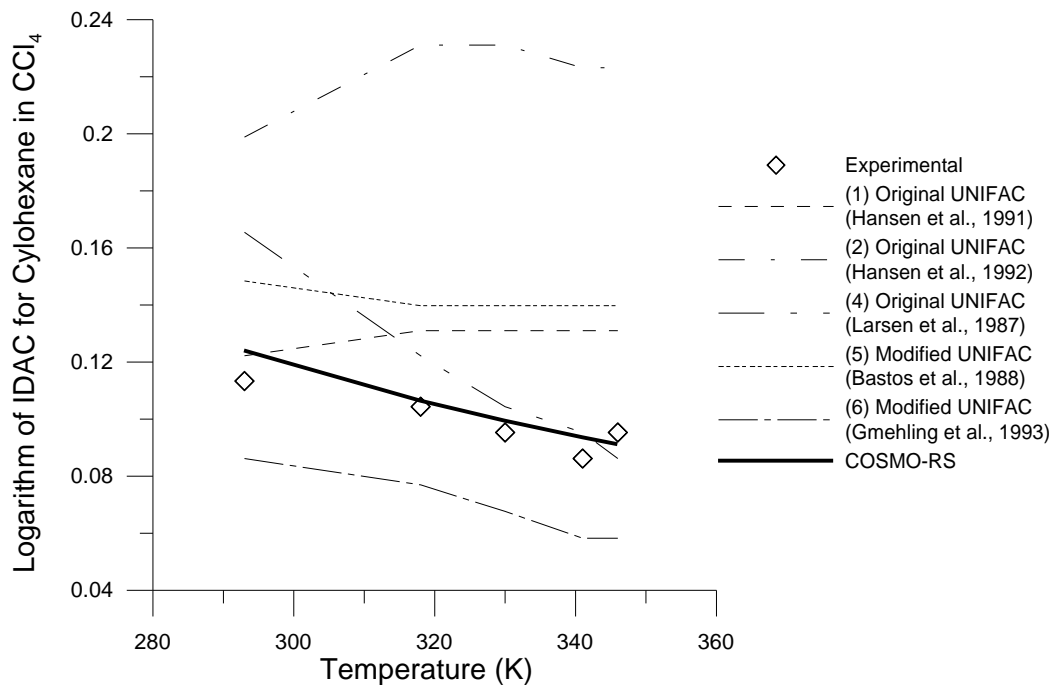

Figure 3: Logarithm of IDAC versus Temperature for Cyclohexane in CCl$_4$.
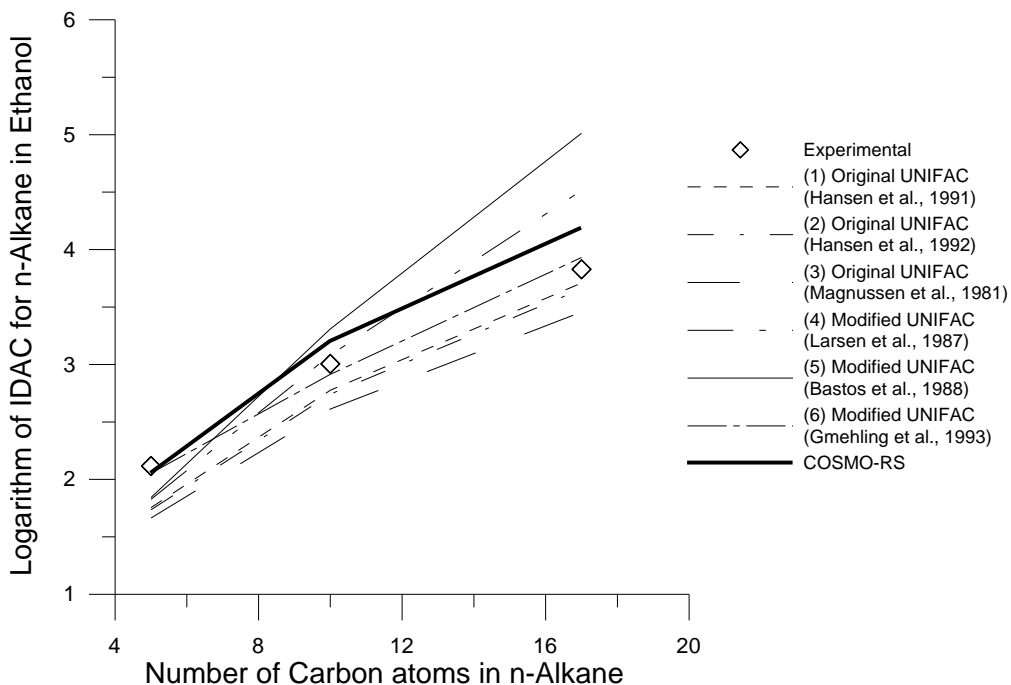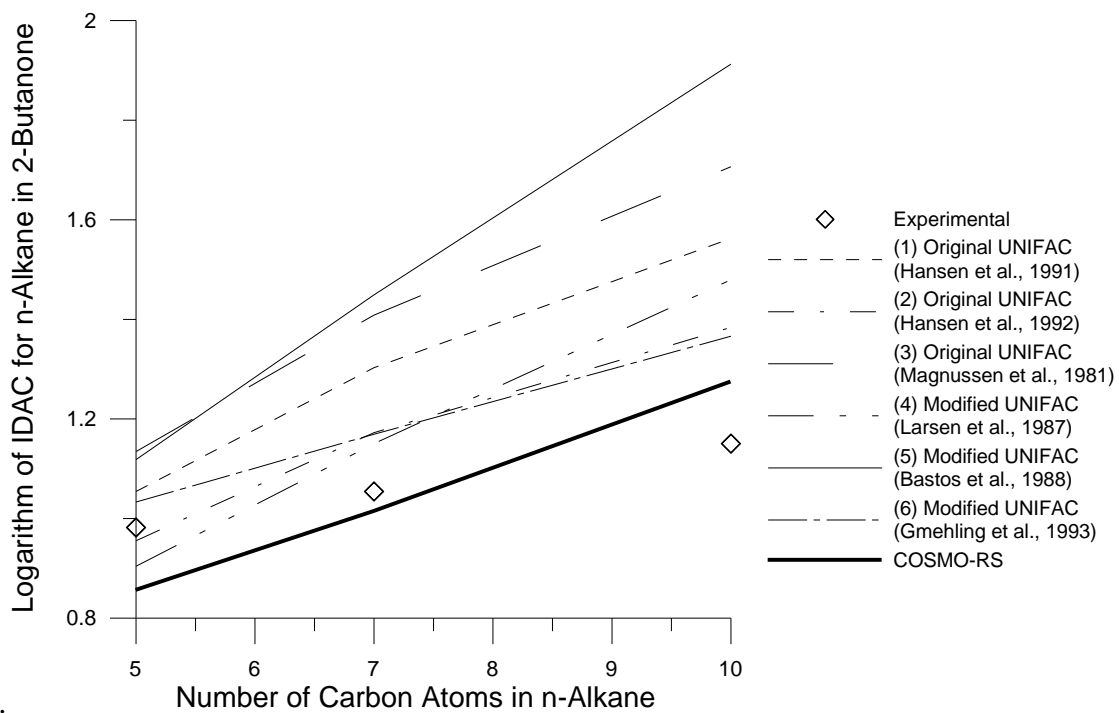
Figure 4: Logarithm of IDAC versus Number of Carbon Atoms in n-Alkane for n-Alkane in ethanol at T=323

K.

Figure 5: Logarithm of IDAC versus Number of Carbon Atoms in n-Alkane for n-Alkane in 2-butanone at T=363 K.
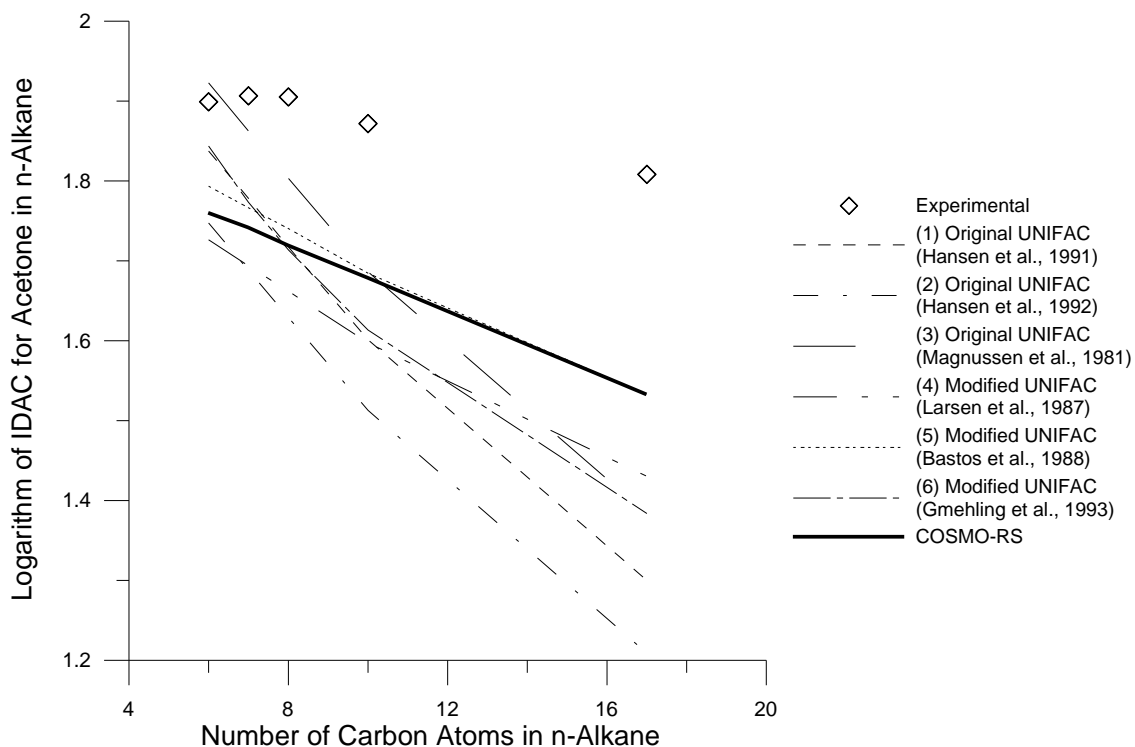
Figure 6: Logarithm of IDAC versus Number of Carbon Atoms in n-Alkane for Acetone in n-Alkane at T=298 K.

Aqueous Systems

For aqueous systems on the other hand, Table 2 and Figure 7 show that, on average, COSMO-RS performs better than the UNIFAC methods. In Figure 2, the comparison is with the two best UNIFAC methods: the original UNIFAC (with parameters from Hansen et al., 1991) and LLE UNIFAC (Magnussen et al., 1981). In 5 out of 11 types of systems, COSMO-RS has either the lowest error or no more than 1.2 times the lowest error. In 8 out of 11 types of system, COSMO-RS is no worse than 1.5 times the model with the lowest error. Even for those types of system for which COSMO-RS may not provide the best %AAD, it does provide a reasonable approximation to all aqueous mixtures tested. This is something that cannot be claimed for the UNIFAC models.

Table 2: %AAD for solutes in water or water in solvents. (1) Original UNIFAC (Hansen et al., 1991), (2) Original UNIFAC (Hansen et al., 1992), (3) Original UNIFAC (Magnussen et al., 1981), (4) Modified UNIFAC (Larsen et al., 1987), (5) Modified UNIFAC (Bastos et al., 1988), (6) Modified UNIFAC (Gmehling et al., 1993), (7) Modified UNIFAC (Hooper et al., 1993). UNIFAC results from Voutsas et al. (1996).

Solute Type	NP	1	2	3	4	5	6	7	COSMO-RS
Alcohol	15	69.33	75.07	56.66	58.95	95.31	51.21	-	71.60
Aldehyde	7	42.81	38.21	45.42	-	-	37.97	-	41.65
Alkane	15	97.77	97.05	96.08	99.14	99.55	98.57	31.12	52.32
Alkyl Halide	7	46.94	43.07	36.21	62.73	-	59.81	-	28.06
Aromatic	5	20.31	99.45	65.22	52.13	-	62.87	444.10	9.73
Multi Ring Aromatics	5	758.20	99.49	915.56	52.34	-	1998.63	27.07	75.96
Carboxylic Acid	6	40.42	27.39	34.38	59.83	-	33.68	-	41.93
Cycloalkane	4	92.66	89.91	87.35	98.95	98.19	99.42	53.58	77.34
Ketone	6	57.70	56.44	57.88	62.04	92.25	46.29	-	60.32
Water	35	31.51	52.39	35.50	382.80	76.17	146.18	50.42	37.13
Weighted Average	106	51.43	60.79	52.67	188.10	87.14	88.57	79.09	44.40

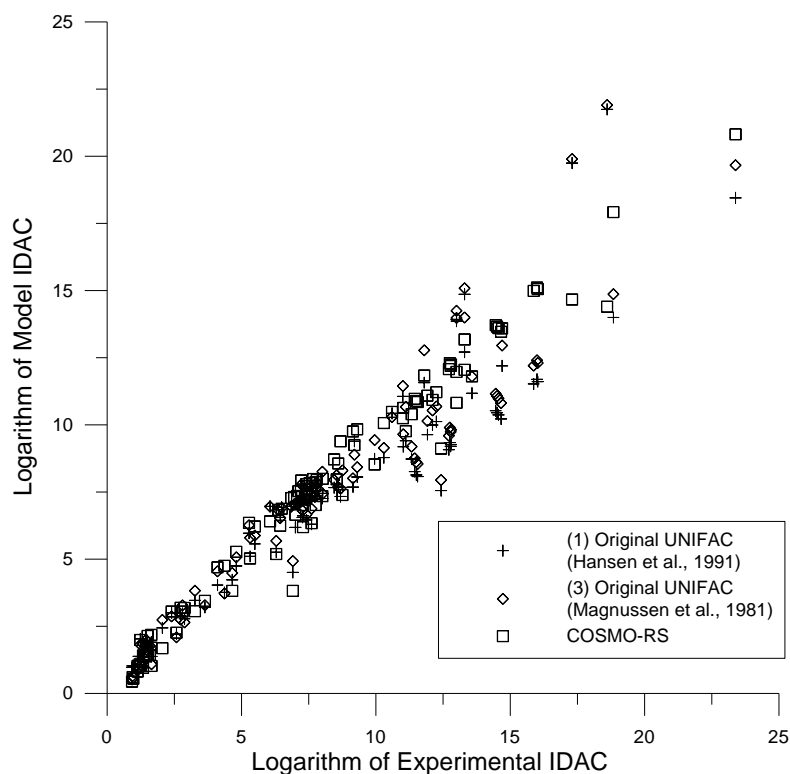|	Highest %AAD			Lowest %AAD			<1.2*Lowest %AAD

Figure 7: Logarithm of Model IDAC versus Logarithm of Experimental IDAC in Aqueous Systems for models: (1) Original UNIFAC (Hansen et al., 1991), (3) Original UNIFAC (Magnussen et al., 1981), COSMO-RS.

There are mixed results with UNIFAC for many of the aqueous mixtures. Some of the UNIFAC models are not even able to make predictions when water is present. COSMO-RS is better able to predict the IDACs in aqueous systems because of its ability to account for polarity and hydrogen bonding. Many of the IDACs calculated using COSMO-RS are superior to or not very different from the "best" of all UNIFAC model predictions for a given aqueous mixture.

Figure 8 shows that COSMO-RS provides excellent predictions for water in n-alkanes even though the approximation worsens slightly as the number of carbon atoms increases. The opposite is true in n-alcohol systems as shown in Figure 9; the COSMO-RS prediction improves as the number of carbon atoms increases. Very good predictions are also obtained for aromatics in water (see Figure 10).
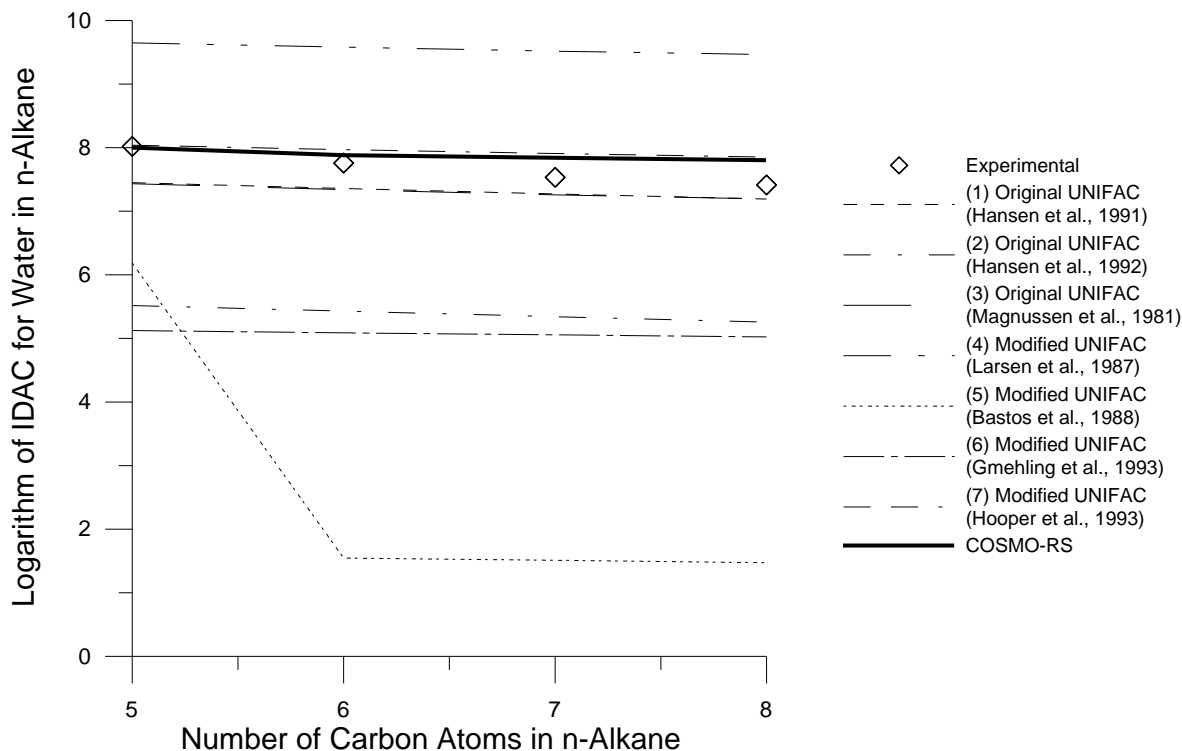
Figure 8: Logarithm of IDAC versus Number of Carbon Atoms in n-Alkane for Water in n-Alkane System at T=293 K.
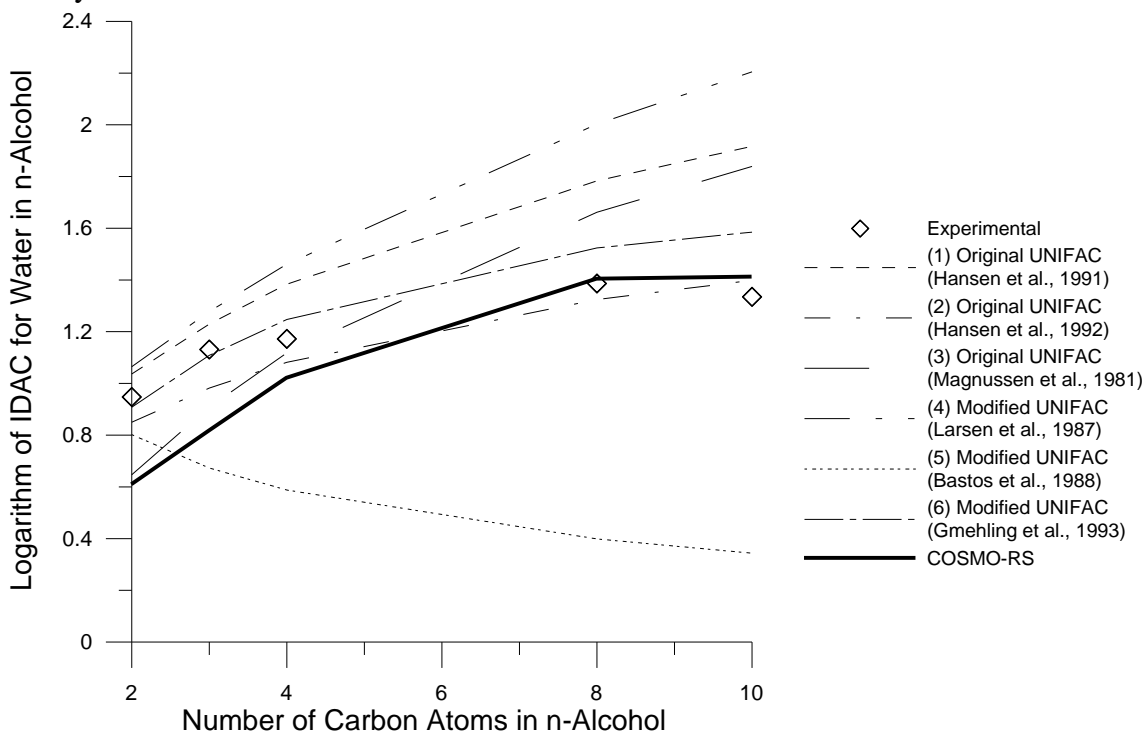

Figure 9: Logarithm of IDAC versus Number of Carbon Atoms in n-Alcohol for Water in n-Alcohol at T=373 K.
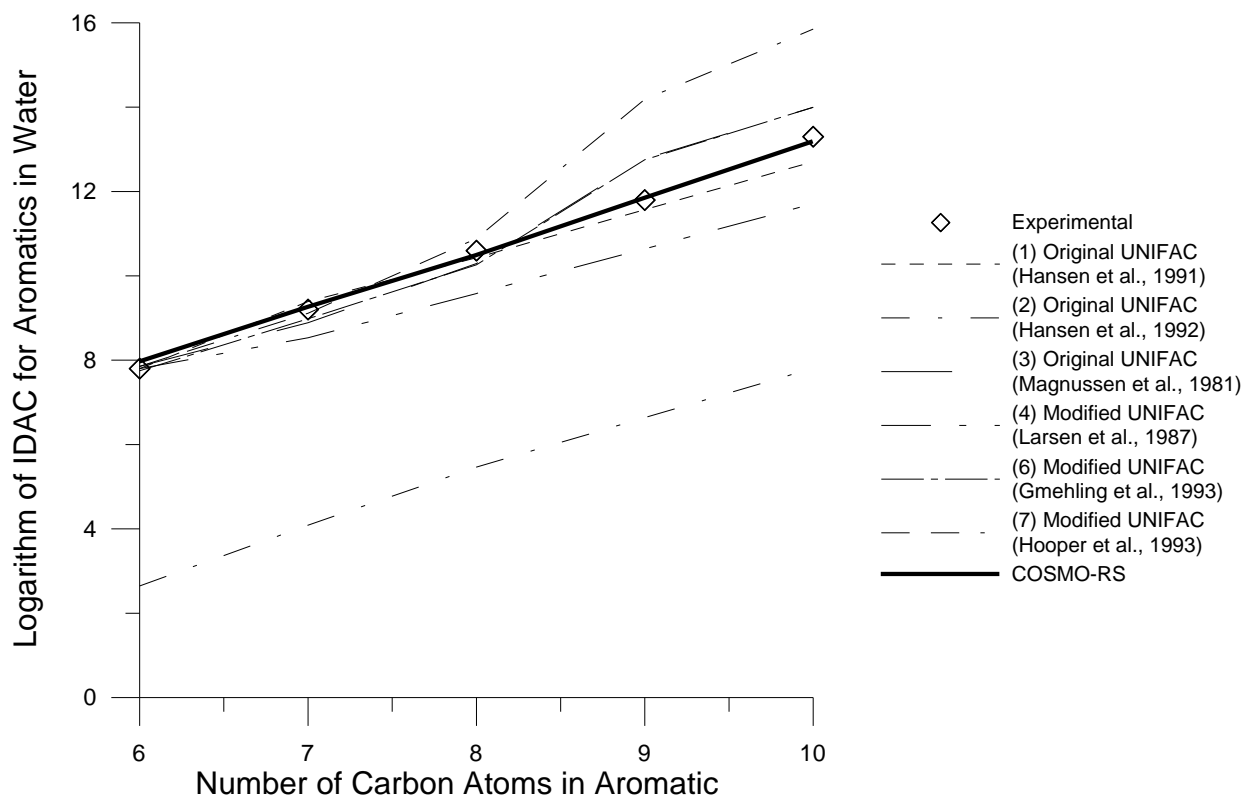
Figure 10: Logarithm of IDAC versus Number of Carbon Atoms in Aromatic molecule for Aromatic in Water at T=298 K.

Conclusions

Infinite dilution activity coefficients were predicted using the COSMO-RS model for over 400 binary systems. The version of COSMO-RS used in this evaluation was COSMOTherm vC1.2 r01.02. The database of Voutsas et al. (1996) was used as the basis for the comparison with various UNIFAC-type models.

COSMO-RS consistently gives very good estimates for most of the aqueous solutions tested. There were no extremely poor results (as seen in most of the UNIFAC models). The best COSMO-RS aqueous systems were those with the aldehydes, alkyl halides, and aromatics in water, as well as systems where water is a solute.

For approximately half of the non-aqueous solute-solvent systems tested, COSMO-RS gave good results. For the other half, the results were poor. Good systems for COSMO-RS involve alkanes in alcohols, alkyl halides in alkanes, ketones in alkanes, and alkanes in alkyl halides.

The binary systems used in this evaluation include relatively simple mono-functional compounds that, to a large degree, have been used for fitting the parameters in many of the different versions of UNIFAC. Thus, this comparison is not true test of the predictive abilities of the UNIFAC methods. On the other hand, COSMO-RS has been fitted only to pure component vapor

pressures and to aqueous partition coefficients, and this study represents a more genuine test of its predictive abilities. With this in mind, it is reasonable that COSMO-RS performs especially well for aqueous systems.

This leads to our conclusion that currently, the overall quality of the COSMO-RS predictions cannot reach that of group contribution methods in their core region in which they are well parameterized (i.e., VLE data of simple organic solvents). However, often COSMO-RS predictions can be applied to problems where group contribution methods and other prediction tools cannot be used at all (e.g., because of unknown interaction parameters, unknown group increments, reactive systems, unstable components, or proximity effects).

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