

New Model to Predict Infinite Dilution Activity Coefficients Based on $(\partial p/\partial x)_{T,x \rightarrow 0}$

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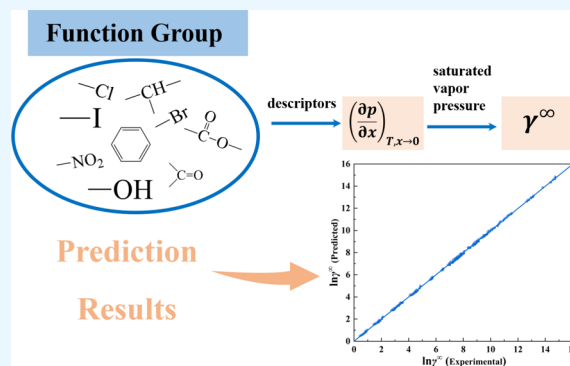


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ABSTRACT: Accurate prediction of infinite dilution activity coefficient (γ^∞) is essential for the calculation of phase equilibria, solubility, and related properties in molecular thermodynamics. Here, we propose a new model to accurately predict the value of γ^∞ . It is applicable to calculate γ^∞ for compounds in aqueous solution at different temperatures. The model is based on the relationship of $(\partial p/\partial x)_{T,x \rightarrow 0}$ with γ^∞ and temperature at low pressure. First, we introduce the new idea of using the group contribution method to estimate $(\partial p/\partial x)_{T,x \rightarrow 0}$ and then obtain the activity coefficient of a solute at infinite dilution in water based on the relationship between $(\partial p/\partial x)_{T,x \rightarrow 0}$ and γ^∞ . The accuracy of this model is verified using experimental data from 46 systems and more than 450 data points. The result shows that the total average relative deviation of the predicted values from the experimental values for training data is 4.73%. Besides, we test the applicability of the model using solutes that are not part of the training data set. The result shows that the model is satisfactory for the prediction of testing data. Compared with other models, the results prove that the developed model outperforms the UNIFAC model, the modified UNIFAC model, and previous predictive models for aqueous systems. The final equation with only simple arithmetic is more easily applied in engineering practices.



1. INTRODUCTION

Infinite dilution activity coefficient (γ^∞) is a physical quantity reflecting solute–solvent interaction. It plays a role in the characterization of thermodynamic behavior for dilute solutions.^{1–4} As early as 1955, $(\partial p/\partial x)_{T,x \rightarrow 0}$ was proposed by Gautreaux and Coates as a variable for calculating γ^∞ .^{5,5} Then, Paolo et al.⁶ reported a differential static cell equilibrium apparatus to measure γ^∞ . In their method, the limiting slope of the pressure–liquid composition at constant temperature, $(\partial p/\partial x)_{T,x \rightarrow 0}$, was determined. In our previous work, we formally proposed to consider $(\partial p/\partial x)_{T,x \rightarrow 0}$ as a thermodynamic function. The relations between $(\partial p/\partial x)_{T,x \rightarrow 0}$ and other thermodynamic functions were derived and summarized.⁷ Based on these relations, the value of $(\partial p/\partial x)_{T,x \rightarrow 0}$ can be determined not only by isothermal vapor–liquid equilibrium (VLE), differential static cell, but also by γ^∞ data.

The value of γ^∞ can be measured by experiments, such as the gas chromatography method,^{8–10} static differential technique,^{11,12} and differential ebulliometry.^{13,14} Moreover, various methods^{15–18} are used to estimate γ^∞ . Among them, the method using the interaction of solute and solvent molecular structure groups to do prediction was first proposed by Pierotti et al.¹⁹ With the introduction of the UNIFAC model,²⁰ the group contribution method has become a hot research topic.^{21–25} The idea behind this method is based on the simplifying assumption that the groups are independent and the molecules are classified as functional groups. And the molecule–molecule interaction is

represented by an appropriately weighted sum of the group–group interaction. Besides, the prediction models of γ^∞ include modified separation of cohesive energy density (MOSCED),^{26–28} conductor-like screening model for real solvent (COSMO-RS),^{29–31} etc. However, these prediction models present large errors in the calculation for γ^∞ of compounds in water. For example, the average relative deviation of γ^∞ for alkanols in water is about 50–70% and almost 100% for alkanes in aqueous solution.^{32,33}

In this study, we propose a novel model for predicting γ^∞ of compounds in highly nonideal aqueous solution. Following this model, γ^∞ is obtained in two steps. First, $(\partial p/\partial x)_{T,x \rightarrow 0}$ is estimated by the group contribution method. Then, γ^∞ is calculated from $(\partial p/\partial x)_{T,x \rightarrow 0}$ and the saturation vapor pressure. This method's outstanding feature is the generalization of the model parameters using the idea of group contribution. Compared with other prediction models, our model gives more reliable results. The rest of the article is organized as follows. Section 2 is devoted to the model description. Section 3

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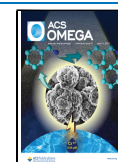





Table 1. Compounds Used in the Calculations and the Parameters in eq 6

solutes	a	b_1	b_2	e	f
<i>n</i> -alkanes	1.63×10^1	1.93×10^{-4}	3.82×10^{-1}	1.00×10^0	1.00×10^0
alkyl aromatics	8.35×10^0	-4.74×10^{-4}	3.60×10^{-1}	1.00×10^0	1.00×10^0
halogenides	1.78×10^1	-3.42×10^{-3}	2.37×10^{-1}	1.24×10^1	1.30×10^{-3}
<i>n</i> -alcohols	3.48×10^0	2.20×10^{-3}	9.54×10^{-1}	1.77×10^0	2.61×10^1
ketones	2.37×10^1	-9.61×10^{-3}	2.44×10^{-1}	-8.94×10^0	-9.27×10^{-5}
esters	1.97×10^1	-8.80×10^2	2.39×10^{-1}	9.42×10^2	4.91×10^{-3}
nitro compounds	1.52×10^1	-9.92×10^{-3}	2.49×10^{-1}	1.45×10^1	3.42×10^{-4}
carboxylic acids	3.28×10^0	3.00×10^{-3}	3.76×10^{-1}	-2.23×10^0	1.14×10^0

Table 2. Contribution of the Groups in eq 6

Groups	c_i	d_i
—CH ₃	-3.19E-04	-5.71E-01
—CH ₂ —	1.66E-05	7.64E-02
—CH— 	2.29E-04	6.51E-01
	1.55E-04	-3.70E-01
—Cl	3.77E-05	-3.79E-01
—Br	1.28E-04	-2.75E-01
—I	1.59E-04	6.39E-02
—F	-1.40E-03	-1.02E-01
—OH	-2.22E-03	-1.10E+00
	1.16E-02	2.59E-01
	8.79E+02	5.78E-01
—NO ₂	6.97E-03	-4.58E-02

introduces the data set and methods. Section 4 illustrates the prediction results and compares the predicted performances with the traditional thermodynamic models. Finally, the conclusion is described in Section 5.

2. MODEL DESCRIPTION

At low pressure, the relationship between $(\partial p/\partial x)_{T,x \rightarrow 0}$ and γ^∞ in a binary liquid mixture of species 1 (solute) and 2 (solvent) under constant temperature conditions can be expressed as^{5,7}

$$\gamma_1^\infty = \frac{1}{p_1^s} \left[\left(\frac{\partial p}{\partial x_1} \right)_{T,x_1 \rightarrow 0} + p_2^s \right] \quad (1)$$

where p^s is the saturated vapor pressure and x_1 is the molar fraction of the solute. For convenience, x is equivalent to x_1 and γ^∞ is equal to γ_1^∞ in the latter.

In our previous work, we proposed that the relationship between $(\partial p/\partial x)_{T,x \rightarrow 0}$ and temperature can be written as follows:⁷

$$\ln \left(\frac{\partial p}{\partial x} \right)_{T,x \rightarrow 0} = \frac{A}{T} + B \quad (2)$$

where T is the temperature and A and B are the model parameters, which are determined by the structure and properties of the solute and solvent. When the solvent is water, A and B are only related to the property of the solute. Therefore, we consider estimating parameters by the group contribution of solutes.

The relationship between parameter A and the contribution of the group is expressed as

$$A = \frac{e}{(b_1 + \sum_i N_i c_i)} \quad (3)$$

where N_i is the number of groups i in the solute, c_i is the contribution of group i to parameter A , and b_1 and e are constants.

Parameter B can be linked to the contribution of the group by eq 4

$$B = a + \frac{f}{b_2 + \sum_i N_i d_i + (\sum_i N_i d_i)^2} \quad (4)$$

where d_i is the contribution of group i to parameter B and a , b_2 and f are constants.

Substituting eqs 3 and 4 to eq 2, the final $(\partial p/\partial x)_{T,x \rightarrow 0}$ can be written as follows:

$$\ln \left(\frac{\partial p}{\partial x} \right)_{T,x \rightarrow 0} = a + \frac{e}{T(b_1 + \sum_i N_i c_i)} + \frac{f}{b_2 + \sum_i N_i d_i + (\sum_i N_i d_i)^2} \quad (5)$$

Therefore, the final equation can be written as follows:

$$\gamma^\infty = \frac{1}{p_1^s} \left[\exp \left(a + \frac{e}{T(b_1 + \sum_i N_i c_i)} + \frac{f}{b_2 + \sum_i N_i d_i + (\sum_i N_i d_i)^2} \right) + p_2^s \right] \quad (6)$$

The new model is applicable to predict γ^∞ of compounds in water at different temperatures. The prediction here is to correlate a set of data with eq 6 and then apply the same model to both the training data and the testing data. Notably, we estimate parameters A and B using the group contribution method. The outstanding feature of this model is that the calculation involves only simple arithmetic, and the method requires no complex software.

3. MATERIALS AND METHODS

The data sources for this paper are collected from Gmehling and Menke.³⁴ Different methods, such as gas chromatography, dilution technique, and static differential technique, were used to obtain them. However, different experimental methods show different values of γ^∞ at the same temperature and pressure conditions. In fact, the infinite dilution activity coefficient is a thermodynamic property at infinite dilution, which is only related to temperature and pressure. It implies that there are erroneous data points in the literature data. In this case, we use eq 2 to screen the literature data. Notably, due to the limitations of the fluoride data set, we choose the infinite dilution activity coefficient at 298.15 K for modeling. 1stopt6.0 software is used for correlation fitting. We use universal global optimization to solve the nonlinear regression problem. The maximum number of iterations is 5000, which guaranteed the convergence of the algorithm in most cases.

4. RESULTS AND DISCUSSION

4.1. Predictive Model Results. Infinite dilution activity coefficient data of 46 groups are selected to test the new model in this work, which are listed in Table 1. It has 8 types of systems, including 5 groups of *n*-alkanes, 3 groups of alkyl aromatics, 15 groups of halohydrocarbons, 6 groups of *n*-alcohols, 5 groups of ketones, 5 groups of esters, 4 groups of nitro compounds, and 3 groups of carboxylic acids. The model described in eq 6 is fitted using 1stopt6.0 software, leading to the parameters and group contribution values given in Tables 1 and 2, respectively.

As can be seen from Table 1, for nonpolar molecules like *n*-alkanes and alkyl aromatics, the constants e and f are both 1, while for polar molecules like ketones and esters, e and f are adjusted to some extent.

According to Tables 1 and 2, $(\partial p/\partial x)_{T,x \rightarrow 0}$ can be calculated using eq 5. Then, γ^∞ is calculated using eq 6, where p^s is calculated by the Antoine equation, and the parameters are from the NIST database (<https://webbook.nist.gov/>). The average relative deviations of the predicted results with respect to experimental values for the training data are listed in Table 3.

The average relative deviation (A.R.D. (%)) is used to evaluate the accuracy of the developed model, as given in eq 7

$$\text{A. R. D. (\%)} = \frac{100}{N_p} \left(\frac{|\gamma_{\text{cal.}}^\infty - \gamma_{\text{exp.}}^\infty|}{\gamma_{\text{exp.}}^\infty} \right) \quad (7)$$

In Table 3, we can see that the A.R.D. (%) of the correlation is 3.08%, while the A.R.D. (%) of the prediction model is only

Table 3. Average Relative Deviation between Model Calculation Results and Experimental Values

solute	N_p	temperature range, K	A.R.D., %	
			cor. ^a	pre. ^b
propane	19	[298.05, 355.25]	4.32	4.85
butane	8	[298.15, 344.25]	7.46	7.66
pentane	12	[293.15, 333.25]	4.23	4.83
hexane	14	[298.15, 342.85]	2.76	3.27
heptane	5	[298.15, 372.15]	5.50	5.64
methanol	22	[293.15, 372.55]	3.55	3.71
ethanol	28	[298.15, 372.15]	5.63	5.68
propanol	18	[303.15, 373.15]	5.26	5.38
1-butanol	15	[318.15, 353.15]	2.68	5.48
hexanol	10	[313.15, 343.15]	3.99	5.92
octanol	11	[298.15, 333.15]	4.82	5.79
acetone	10	[293.15, 303.25]	3.65	4.84
2-butanone	6	[297.85, 303.25]	1.17	1.35
2-pentanone	4	[298.15, 323.25]	2.67	7.91
2-heptanone	14	[292.95, 363.65]	5.01	6.01
2-octanone	6	[302.85, 364.15]	3.95	6.75
2-nonanone	4	[303.45, 354.35]	3.60	3.71
methyl acetate	6	[293.15, 323.25]	2.53	3.21
methyl formate	2	[298.15, 303.25]	0.00	4.17
ethyl acetate	6	[298.15, 343.25]	4.74	5.05
propyl acetate	2	[333.25, 343.25]	0.00	5.14
butyl acetate	6	[333.15, 363.65]	7.93	7.99
benzene	80	[288.15, 377.95]	4.92	5.09
toluene	14	[303.05, 333.15]	3.90	4.86
ethylbenzene	5	[339.85, 413.65]	1.99	2.55
1,1,1,2-tetrachloroethane	7	[303.15, 343.15]	3.16	5.45
1,1,2,2-tetrachloroethane	3	[302.85, 312.75]	0.13	6.86
1,1,2-trichloroethane	12	[303.15, 354.85]	3.23	4.04
1,2-dibromoethane	13	[283.25, 353.45]	1.95	4.27
1,1-dichloroethane	17	[283.15, 323.15]	3.96	4.51
1,2-dichloroethane	9	[283.15, 313.15]	1.38	1.59
1,2-dichloropropane	5	[298.15, 343.65]	1.84	4.85
1-bromopropane	4	[292.65, 303.15]	2.14	5.29
2-chloropropane	5	[283.15, 303.15]	2.43	7.54
1-iopropane	5	[283.15, 303.15]	2.35	5.72
1-bromobutane	3	[289.15, 303.15]	1.56	2.60
1,2-dichlorobenzene	11	[293.15, 372.95]	3.50	5.00
nitromethane	5	[293.15, 323.15]	2.27	4.37
nitroethane	5	[293.15, 323.15]	1.62	1.68
1-nitropropane	5	[293.15, 323.15]	2.03	3.65
2-nitropropane	4	[293.15, 323.15]	1.36	1.66
formic acid	2	[298.15, 323.15]	0.00	1.04
acetic acid	9	[298.15, 383.55]	4.37	4.56
propionic acid	2	[323.15, 373.15]	0.00	6.45
average			3.08	4.73

^aWe use eq 2 to correlate $(\partial p/\partial x)_{T,x \rightarrow 0}$ and then use eq 1 to calculate the value of γ^∞ . ^bWe use eq 6 to predict the value of γ^∞ .

4.73%. The results of both calculations are generally comparable. This indicates that the new model proposed in this paper to predict γ^∞ is accurate and reliable. In the prediction model, A.R.D. (%) is 5.25% for the *n*-alkane system, 4.17% for the alkyl aromatic system, 4.81% for the halogenide system, 5.33% for the *n*-alcohol system, 5.10% for the ketone system, 5.11% for the ester compound, 2.84% for the nitro compound, and 4.00% for the carboxylic acids. Given these results, the predicting accuracy of the new model is satisfactory, especially for alkyl aromatic systems and nitro compounds.

Table 4. Experimental and Predicted $\ln\gamma^\infty$ for the Solutes in Water at Different Temperatures

solute	T , K	exp.	pre.	ref
1-propanol	298.15	2.62	2.81	34
1-butanol	298.15	3.92	4.26	34
1-pentanol	323.15	5.44	5.56	34
1-pentanol	333.15	5.40	5.55	34
1-heptanol	333.15	8.19	8.30	34
1-heptanol	343.15	8.06	8.26	34
1-heptanol	353.15	8.24	8.24	34
octane	342.85	15.76	15.75	34
nonane	298.15	17.88	18.01	34
nonane	372.25	16.65	16.15	34
decane	298.15	19.81	19.77	34
2-nonanone	293.15	9.94	10.06	34
butyl acetate	363.65	7.20	7.14	34
propyl formate	293.15	5.01	4.77	34
propyl formate	303.15	5.12	4.85	34
propyl formate	313.15	4.88	4.94	34
1-chlorobutane	285.65	8.96	8.56	34
1-chlorobutane	293.15	8.52	8.49	34
2-bromopropane	291.15	7.78	7.83	34
2-bromopropane	293.15	7.67	7.82	34
2-bromopropane	298.15	7.65	7.80	32
2-iopropane	283.15	8.79	8.75	34
1-bromo-2-chloroethane	303.15	7.05	7.87	35
bromoethane	298.15	6.52	6.70	35
Iodoethane	298.15	7.69	7.64	32
butyric acid	298.15	3.97	3.97	32
pentanoic acid	298.15	4.84	5.78	35
1,2-dichlorotetrafluoroethane	298.15	11.15	11.30	35
dichlorofluoromethane	298.15	9.17	10.01	35

Besides, we test the applicability of the model with solutes that are not part of the training data. The results are shown in Table 4. It indicates that the model has good predictive ability not only on the training data but also on the testing data.

4.2. Model Comparison. There have been many prediction models for γ^∞ , the most common of which is the UNIFAC model. We select five models for comparison with the proposed new model:

- (1) Original UNIFAC²⁰ with parameters from Hansen et al.²¹
- (2) Modified UNIFAC (Bastos),¹⁸ especially suited for γ^∞ calculations. The combined term is from the model proposed by Kikic et al.,²³ and the residual term is fitted using the experimental value of γ^∞ .
- (3) Modified UNIFAC (Gmehling).²⁵ The segment fraction in the combinatorial term and the interaction parameter are adjusted.
- (4) The PDD correlation.¹⁹ This model considers the number of carbon atoms in the solute and the solvent. It employs many different functional forms.
- (5) The AJ correlation.³⁶ This model uses linear free energy relationship to obtain equations for $\log \gamma^\infty$. It includes 6 descriptors, such as excess molar refractivity and McGowan volume of the compound, and 7 model parameters.

Figure 1 shows the calculation results of γ^∞ for different models in 4 systems, including 1-butanol, 2-heptanone, ethyl acetate, and propane. We present the A.R.D. (%) of the predicted and experimental values for different models in Table S1.

In Figure 1, the solid blue lines indicate the best fits to the experimental data (this work), while both the original UNIFAC model and the modified UNIFAC model show poor results, especially for the propane–water system, where the A.R.D. (%)

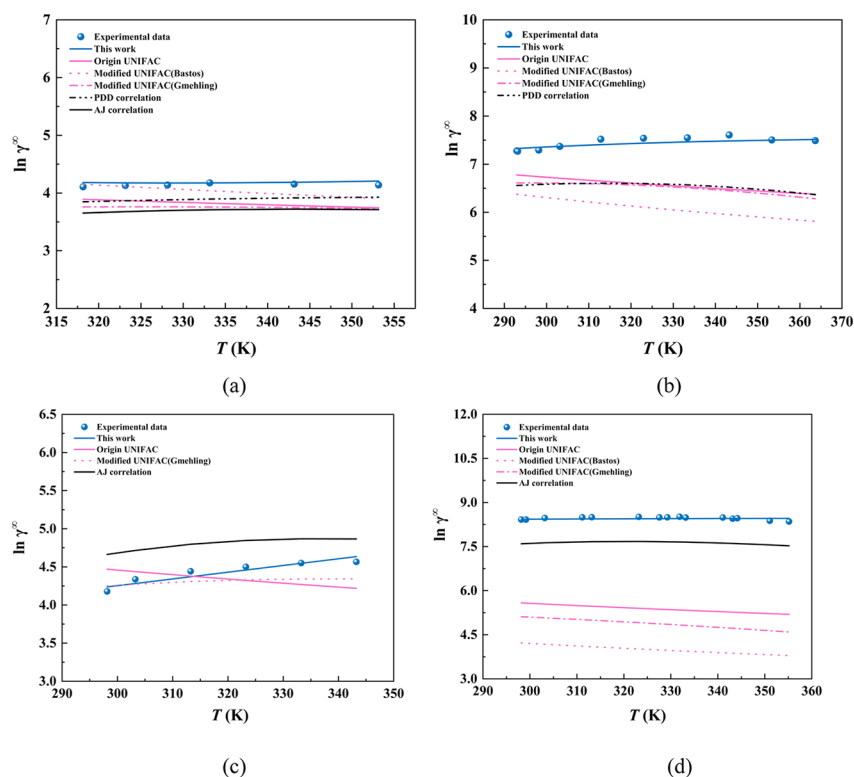


Figure 1. Values of γ^∞ for solutes in aqueous solutions at different temperatures. (a) 1-butanol; (b) 2-heptanone; (c) ethyl acetate; and (d) propane.

is greater than 90%. The PPD model¹⁹ and the AJ model³⁶ correlate well for aqueous systems with strong nonidealities in the published results. However, comparisons in Figure 1 and Table S1 reveal that the new proposed model outperformed these models. Therefore, it can be deduced that the proposed model in this work fits better with experimental data.

5. CONCLUSIONS

We propose a novel method to predict γ^∞ based on $(\partial p/\partial x)_{T,x\rightarrow 0}$. First, $(\partial p/\partial x)_{T,x\rightarrow 0}$ is estimated using the group contribution method; then, the saturated vapor pressure of the solute and solvent is used to calculate γ^∞ . This model is particularly suitable for calculating the value of γ^∞ for compounds in the nonideality of the aqueous solution at different temperatures. We use the presented model to predict the value of γ^∞ for 46 organic compounds in aqueous solution. The result shows that the total average relative deviation of the new model is only 4.73%. Compared with other prediction models, this model could predict γ^∞ more accurately, which provides a new idea for accurately calculating the value of γ^∞ . Moreover, the unique feature of the model is that the calculations involve only simple arithmetic. It has positive practical applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c00368>.

List of compounds and experimental and predicted infinite dilution activity coefficients of aqueous systems at different temperatures (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

A, B, a, b_1, b_2, e, f the model constants for the model

c_i	the contribution of group i to parameter A
d_i	the contribution of group i to parameter B
N_i	the number of groups i
N_p	the number of experimental points
p_i^s	the saturated vapor pressure of component i [kPa]
T	temperature [K]
x_i	mole fraction of component i
γ^∞	infinite dilution activity coefficient

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