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The performance of UNIFAC and related group contribution models
Part II. Prediction of Henry's law constants

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Abstract

Henry's law constants for 24 different systems have been determined using UNIFAC and related group contribution models. The results obtained from original, modified and free-volume effect UNIFAC models are compared with experimental results. Empirical relationships for the temperature-dependency of Henry's constant for the chloroform(1)–water(2) system are also determined.

Keywords: Activity coefficients; Infinite dilution; Henry's law constants; UNIFAC

1. Introduction

The Henry's law constant is an important physical property that represents the ability of a chemical to partition between two phases. Knowledge of reliable Henry's law constants is necessary in many areas. For environmental purposes, it gives a direct measure of the partitioning between air and water and between water and soil. In toxicology, anaesthesiology and physiology partitioning between air and blood is related to the Henry's law constant [1]. Designing of gas–liquid contacting processes to clean contaminated waters with organic materials requires reliable information on phase equilibria of organic pollutants in water, which can be described by Henry's law constants. Temperature is the most important parameter that affects the extent of

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removal of volatile solutes in these processes [2]. Therefore data on Henry's law constants at different temperatures is required.

Major water pollutants may be present at infinitely high dilutions and be sparingly soluble in water. Furthermore, it is difficult to measure the necessary data because of the low vapour pressures and limited solubilities. These are the main reasons for the limited data on Henry's law constants found in the literature [3]. Therefore in the following work, Henry's law constants for 24 systems have been calculated using infinite dilution activity coefficients calculated by the UNIFAC and related models. The reliability of the models' predictions is discussed. The temperature-dependency of Henry's law constants for some of the compounds is also obtained.

2. Theoretical background

For a given solute i at constant pressure and temperature, equilibrium exists between two phases when the fugacities, f_i in the phases α and β are equal.

$$f_i^{\alpha} = f_i^{\beta} \tag{1}$$

For vapour–liquid phase equilibria, α corresponds to vapour phase, v, and β corresponds to the liquid phase, L. At low pressure and ambient temperature the vapour phase is assumed to behave ideally, so that the partial pressure, p_i, is equivalent to the vapour phase fugacity, f_i^{v}

$$f_i^{v} = p_i = y_i p \tag{2}$$

where p is the system pressure and y_i is the mole fraction of component i in the vapour phase. The liquid phase fugacity of component i, f_i^{L} can be expressed in several forms depending on the reference state chosen.

$$f_i^{L} = x_i \gamma_i f_i^{0} \tag{3}$$

where x_i is the mole fraction of component i in the liquid phase, f_i^{0} is the pure component reference fugacity in the liquid state and γ_i is the activity coefficient at the system temperature and pressure. Normally the reference fugacity is the vapour pressure of the pure component i, p_i^{vap}, if it is a liquid at the system temperature and pressure. As a result the phase equilibrium equation takes the form:

$$x_i \gamma_i p_i^{vap} = y_i p \tag{4}$$

When the solute mole fraction is very low, the activity coefficient can be taken as the infinite dilution activity coefficient, γ_i^{∞}. Henry's law constant, H_i, of solute i at ambient pressures is:

$$H_i = \gamma_i^{\infty} p_i^{vap} \tag{5}$$

where H_i is the Henry's law constant in atm.

With the knowledge of γ_i^{∞} and p_i^{vap}, the Henry's law constant for volatile different solutes in different solvents can be calculated.

3. Results and discussion

The free volume contribution in original and modified UNIFAC models in predicting γ_i^∞ was found to be significant, especially for asymmetric systems where the solvent is water (Part I of this paper). Therefore infinite dilution activity coefficients calculated from original and modified UNIFAC with free volume contributions are used to calculate the Henry's law constants using Eq. (5) for 24 systems. The vapour pressure is calculated according to Antoine's equation:

$$\ln p_i^{\mathrm{vap}} = A_i - \frac{B_i}{C_i + T} \qquad (6)$$

where A_i, B_i, C_i are Antoine constants for component i taken from Reid et al. [4]. In Table 1 calculated Henry's law constants and vapour pressures are given. Henry's law constants are also calculated using measured infinite dilution activity coefficients found in the literature. As the volatility of the components increases, Henry's law constants also increase. Calculated Henry's law constants for chloroform(1)–water(2) system are between 146 and 397 atm in the temperature range 293.15–313.15 K. In the same temperature range the vapour pressure of chloroform changes between 0.206 and 0.467 atm. For the tetrahydrofuran(1)–water(2) system the Henry's law constant for tetrahydrofuran is between 3.6 and 38.6 atm in the temperature range of 298.15–313.15 K. In this range the vapour pressure of tetrahydrofuran is between 0.213 and 1.138 atm. The volatilities of chloroform and tetrahydrofuran are similar, but in their mixtures with water the Henry's law constant for chloroform is about ten times higher than that for tetrahydrofuran. This shows that volatility alone is not the only factor that effects the Henry's law constant. The molecular structure and interaction between the molecules are also important. The UNIFAC models used in calculating the activity coefficients have residual and combinatorial parts which take these properties of components into account.

Figs. 1–4 show changes of Henry's law constants with temperature calculated from original and modified UNIFAC models with free volume effects and measured infinite dilution activity coefficients for the systems methanol(1)–cyclohexane(2), methyl tertiarybutyl ether(1)–cyclohexane(2), methyl tertiarybutyl ether(1)–hexane(2), and diisopropyl ether(1)–cyclohexane(2). Henry's law constants increase with temperature in Figs. 1, 3 and 4, but for methyl tertiarybutyl ether(1)–cyclohexane(2) in Fig. 2 the Henry's law constant decreases above 323 K. In Figs. 2 and 3 the solute is methyl tertiarybutyl ether, but the solvents are cyclohexane in Fig. 2 and hexane in Fig. 3. The effect of solvent activity on the Henry's law constant can be seen. In Fig. 4 there is a trend of decreasing Henry's law constant above 333 K. For phase splitting purposes in particular, knowledge of the Henry's law constant is essential for determining the right solvent for the solute at the corresponding temperature range.

In Figs. 2 and 4, the solvent is cyclohexane and the solutes are different ethers. The Henry's law constant for methyl tertiarybutyl ether in the methyl tertiarybutyl ether(1)–cyclohexane(2) system increases with temperature to a maximum, then decreases. Fig. 4 shows that the Henry's law constant for diisopropyl ether in diisopropyl

Table 1
Experimental and calculated infinite dilution Henry's constants from UNIFAC models.

Solute (1)–Solvent (2) Ref.	T/K	Original + FV		Modified + FV		Experimental***		Vapour Pressure	
		$H1^{*}$/Atm	$H2^{**}$/Atm	$H1$/Atm	$H2$/Atm	$H1$/Atm	$H2$/Atm	$P1$/Atm	$P2$/Atm
Methanol/cyclohexane [5,6]	283.15	2.143	–	8.969	–	8.66052	–	0.073	0.0632
	293.15	3.327	–	11.510	–	9.9584	–	0.128	0.102
	308.15	6.058	3.018	16.112	4.247	14.9592	3.742	0.276	0.198
	313.15	7.282	–	17.840	–	22.2759	–	0.350	0.243
	318.15	8.700	4.378	19.686	6.040	16.7086	5.150	0.440	0.296
	333.15	14.307	7.243	25.870	9.683	22.9625	8.499	0.835	0.512
Methanol/Cyclopentane [6]	288.15	2.997	3.298	11.250	4.348	16.4754	4.487	0.097	0.277
Pyridine/Water [5]	343.15	2.491	0.709	2.233	0.766	5.3874	0.884	0.219	0.308
	363.15	5.896	1.669	4.728	1.820	9.06	1.938	0.453	0.692
	373.15	8.673	2.463	6.550	2.680	10.7032	2.800	0.630	1.00
1,4-Dioxane–*n*-heptane [7]	353.15	1.159	3.910	1.951	2.346	1.33962	2.128	0.498	0.563
1,4-Dioxane–*n*-octane [7]	353.15	2.506	1.950	1.592	1.040	1.24002	0.984	0.498	0.230
1,4-Dioxane–*n*-nonane [7]	353.15	2.410	0.980	1.402	0.470	1.0956	0.453	0.498	0.096
1,4-Dioxane–water [7]	308.15	0.409	0.060	0.566	0.217	0.51128	0.383	0.077	0.056
	323.15	6.603	0.138	9.315	0.458	8.1357	0.782	1.154	0.122
	343.15	2.135	0.365	3.177	1.087	2.52269	1.500	0.347	0.308
1,4-Dioxane–chloroform [7]	323.15	0.032	0.236	0.021	0.250	0.04466	0.310	0.154	0.673
Tetrahydrofuran–*n*-hexane [7]	313.15	0.659	0.681	0.886	0.688	0.69147	0.714	0.397	0.368
	333.15	1.315	1.345	1.770	1.313	1.33823	1.357	0.821	0.754
Tetrahydrofuran–water [7]	298.15	7.314	0.083	3.628	0.484	6.16209	0.551	0.213	0.031
	323.15	19.851	0.352	9.521	1.475	15.1552	1.144	0.578	0.122
	343.15	38.597	0.929	18.386	3.089	35.0845	2.402	1.138	0.308
Tetrahydrofuran–chloroform [7]	303.15	0.094	0.116	0.080	0.102	0.04488	0.060	0.264	0.315
	313.15	0.146	0.179	0.129	0.165	0.0794	0.103	0.397	0.467
	323.15	0.221	0.267	0.198	0.257	0.12716	0.175	0.578	0.673
Tetrahydrofuran–cyclohexane [7]	313.15	0.747	0.478	0.656	0.412	0.71857	0.428	0.397	0.243
	333.15	1.489	0.976	1.270	0.815	0.3007	0.001	0.821	0.512
1-Butanol–water [5]	343.15	5.901	1.242	5.663	1.236	8.8818	1.007	0.131	0.308

	353.15	9.229	1.893	9.071	1.800	9.9045	0.100	0.213	0.468
	363.15	14.01	2.805	14.017	2.545	–	2.124	0.336	0.692
	372.15	19.824	3.915	19.973	3.405	13.279	2.866	0.490	0.965
	383.15	29.399	5.734	29.699	4.732	–	4.101	0.754	1.414
Chloroform–water [8]	293.15	192,782	–	146,982	–	168,696	–	0,206	–
	303.15	264,173	–	198,831	–	263,367	–	0,315	–
	308.15	306,179	–	228,844	–	326,391	–	0,385	–
	313.15	352,697	–	261,784	–	397,188	–	0,467	–
Methyl tertiarybutyl ether–2-Methylpentane [9]	303.15	10.982	0.516	9.118	0.437	8.85162	0.433	0.289	0.341
	323.15	0.941	1.052	0.780	0.889	0.74494	0.870	0.625	0.713
Methyl tertiarybutyl ether–*n*-Hexane [9]	303.15	0.448	0.371	0.371	0.314	0.36414	0.285	0.289	0.246
	323.15	0.939	0.785	0.778	0.661	0.7500	0.613	0.625	0.533
Methyl tertiarybutyl ether–*n*-heptane [9]	313.15	0.770	0.319	0.747	0.311	0.56592	0.123	0.432	0.122
	323.15	1.092	0.472	1.058	0.459	0.76372	0.176	0.626	0.187
Methyl tertiarybutyl ether–cyclohexane [9]	313.15	0.800	0.559	0.737	0.484	0.60912	0.294	0.432	0.243
	323.15	1.132	0.802	1.038	0.678	0.825	0.383	0.625	0.358
Methyl tertiarybutyl ether–cyclopentane [9]	313.15	0.860	1.591	0.769	1.357	0.51408	0.847	0.432	0.730
	323.15	1.215	2.181	1.083	1.826	0.700	1.126	0.625	1.024
Diisopropyl ether–*n*-heptane [9]	313.15	0.390	0.131	0.386	0.130	0.42716	0.132	0.362	0.122
	333.15	0.811	0.297	0.802	0.293	0.88686	0.283	0.758	0.277
Diisopropyl ether–cyclohexane [9]	313.15	0.408	0.267	0.453	0.279	0.45974	0.231	0.362	0.243
	333.15	0.850	0.560	0.930	0.630	0.93234	0.471	0.758	0.512
Ethylene glycol–water [10]	297.50	0.00012	–	0.00012	–	0.00013	–	0.00016	0.02983
	308.20	0.00030	–	0.00029	–	0.00030	–	0.00037	0.05540
	317.90	0.00065	–	0.00063	–	0.00077	–	0.001	0.093
	328.20	0.00138	–	0.00132	–	0.00156	–	0.002	0.156
	338.10	0.00273	–	0.00259	–	0.00297	–	0.003	0.246
	348.10	0.00519	–	0.00487	–	0.00654	–	0.005	0.380
Isopropanol–water [6]	288.15	0.671	0.054	0.366	0.057	0.40635	0.095	0.032	0.017
Isopropanol–ethyl acetate [6]	288.15	0.100	0.238	0.084	0.187	0.14585	0.274	0.032	0.077

* *H*1 - Henry's law constant of component 1 at infinite dilution.

** *H*2 - Henry's law constant of component 2 at infinite dilution.

***Experimental - calculated from measured infinite dilution activity coefficients.

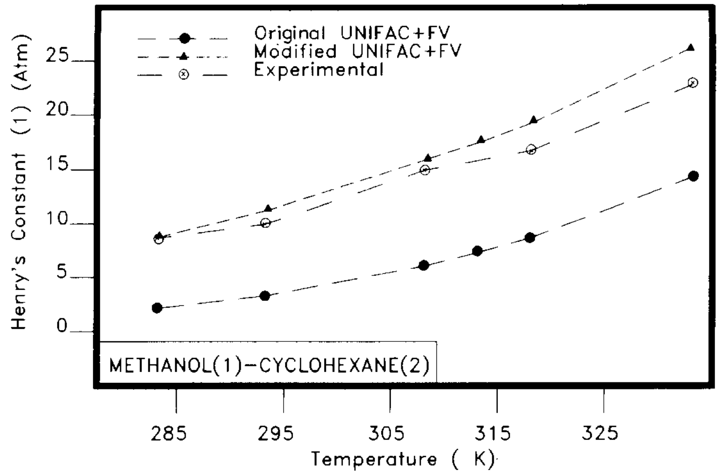

Fig. 1. Change of Henry's law constant with temperature for methanol(1)–cyclohexane(2).

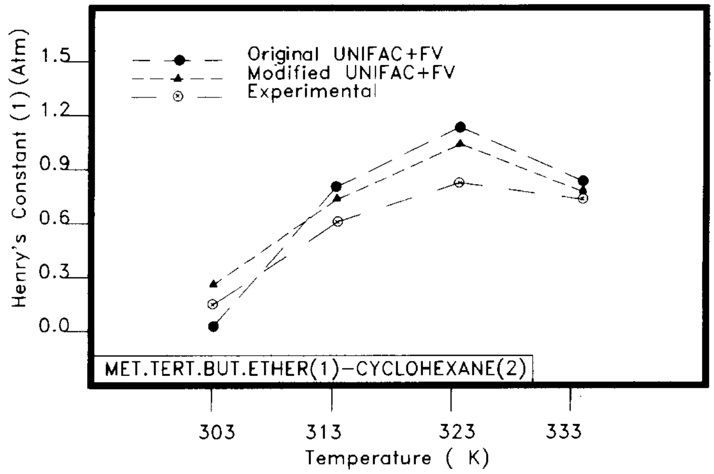

Fig. 2. Change of Henry's law constant with temperature for methyl tertiarybutyl ether(1)–cyclohexane(2).

ether(1)–cyclohexane(2) decreases above 333 K; a maximum is not observed in this temperature range.

The performance of the models used to predict Henry's law constants can be compared in Figs. 1–4; it can be seen that modified UNIFAC with free volume contribution gives better results.

The literature contains very limited data on the direct measurement of Henry's law constants. In Fig. 5 Henry's law constants found in the literature [11,12] for chloro-

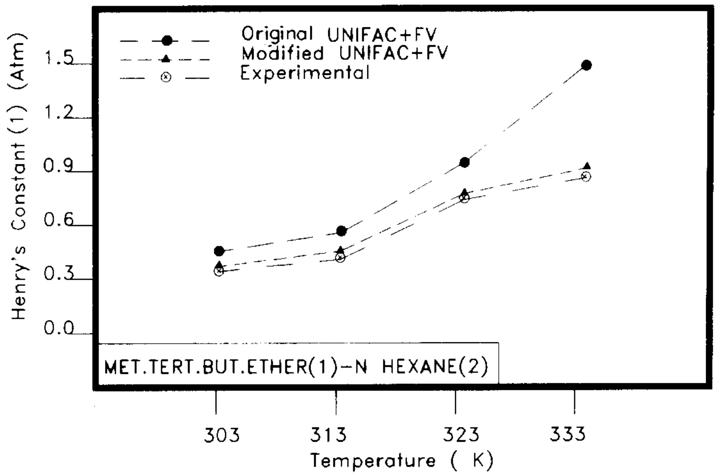

Fig. 3. Change of Henry's law constant with temperature for methyl tertiarybutyl ether(1)–*n*-hexane(2).

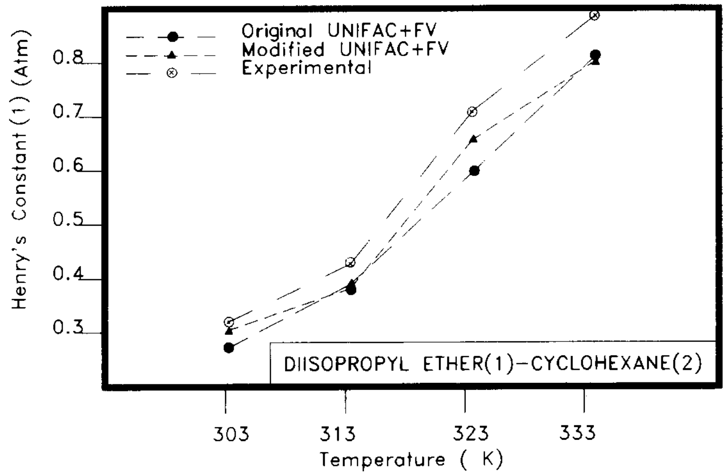

Fig. 4. Change of Henry's law constant with temperature for diisopropyl ether(1)–cyclohexane(2).

form(1)–water(2) are compared with calculated Henry's law constants from UNIFAC models. The original UNIFAC model with free volume contribution gives a better fit at low temperatures than the modified UNIFAC model with free volume contribution. The measured Henry's law constants in Fig. 5 were obtained by EPICS (equilibrium partitioning in closed systems), which is believed to have a low accuracy [13]. This may be the reason for the fair agreement between the measured values and those calculated.

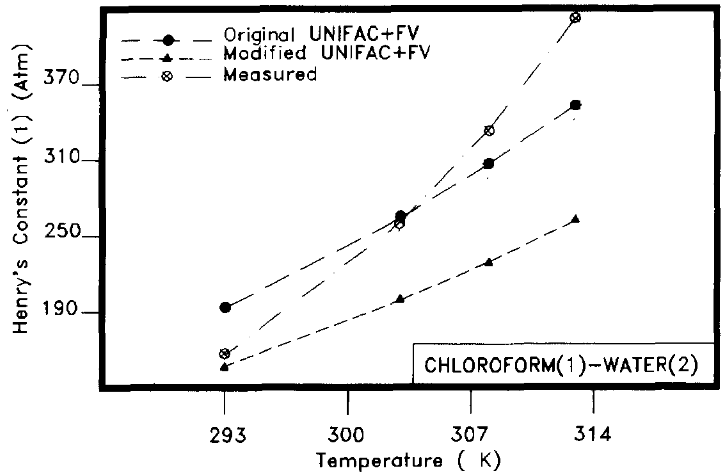

Fig. 5. Change of Henry's law constant with temperature for chloroform(1)–water(2).

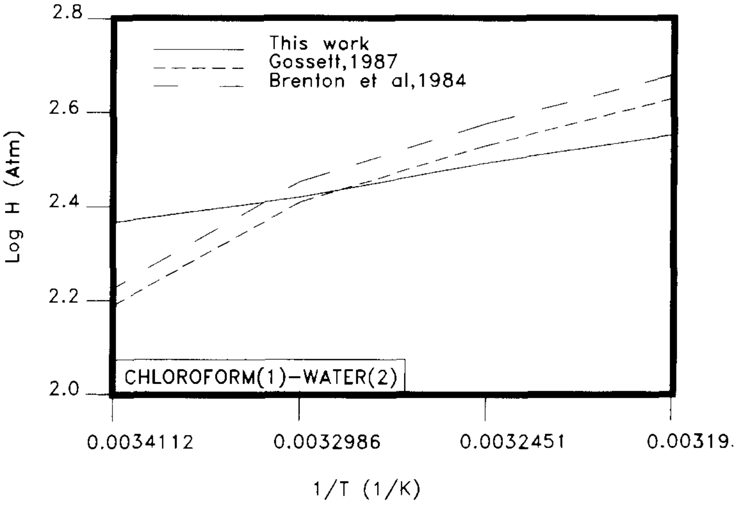

Fig. 6. Comparison of empirical relationships for changes of Henry's law constants given in the literature and obtained in this work of chloroform(1)–water(2).

An empirical relationship for the temperature dependency of the Henry's law constant is usually given by:

$$\log H_i = C_1 - \frac{C_2}{T} \tag{7}$$

where C_1 and C_2 are constants and T is the temperature in K. We obtained an empirical relationship for the chloroform(1)–water(2) system using calculated values from the original UNIFAC model with free volume contribution. In the temperature range 293.15 to 313.15 K, the constants C_1 and C_2 in Eq. (7) are 2.222 and 0.0851, respectively. The correlation coefficient for this relationship is 0.999. In Fig. 6, this relationship is compared with other relationships found in the literature [12,14].

4. Conclusions

In part I of this work, infinite dilution activity coefficients were calculated using UNIFAC and related models. These coefficients are used in this work to calculate the Henry's law constants of 24 binary mixtures including highly non-ideal and moderately non-ideal systems. Data on Henry's law constants, especially at infinite dilution, are very scarce. Using the modified UNIFAC model with free volume contribution when experimental data is not available gives satisfactory results for Henry's law constants for most of the systems studied in this work. The model also enables determination of the temperature dependency of Henry's law constants.

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