$\tilde{g}$ = gravitational acceleration
Gr_x = $\tilde{g}\bar{\beta}(T_w - T_\infty)X^3/\nu$
$\bar{h}$ = heat transfer coefficient
k = thermal conductivity
Nu_x = $\bar{h}x/k$
Pr = Prandtl number
T = temperature variable
u = velocity in the x-direction
v = velocity in the y-direction
x = coordinate along the plate
y = coordinate normal to the plate
α = thermal diffusivity
$\tilde{\beta}$ = wall temperature variation parameter as defined in Eq. 9
$\bar{\beta}$ = coefficient of volumetric expansion
$\epsilon(\gamma)$ = $4\xi \frac{d\gamma}{d\xi}$
ψ = stream function
ξ = transformed stream-wise coordinate
η = transformed normal coordinate
θ = $(T - T_\infty)/(T_w - T_\infty)$
ν = kinematic viscosity

Subscripts

w = surface condition
∞ = conditions in the ambient
0 = zero order solution
1 = first order solution

Superscript

= derivative with respect to the independent variable

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Correlation of Activity Coefficients of Hydrocarbons in Water at Infinite Dilution with Molecular Parameters

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Hydrocarbon solubilities in water are directly related to the prediction of activity coefficients at infinite dilution. Mackay and Shiu (1977) correlated the activity coefficients of polynuclear aromatic hydrocarbons in water at infinite dilution with the number of carbon atoms and Yalkowsky and Valvani (1979) related solubilities to molecular surface areas. These correlations, limited to a single hydrocarbon family and solvent, predict activity coefficients at infinite dilution where the generally accepted UNIQUAC and UNIFAC equations fail.

The present study correlates the activity coefficients at infinite dilution of aromatic and aliphatic hydrocarbons in water reported by Mackay and Shiu (1975, 1977) with physical properties of the hydrocarbon molecules, Table 1. A suitable physical property should reflect the size, shape and charge distribution of the molecule. A single parameter cannot fulfill all these characteristics and multiparametric correlations are necessary.

The data for the activity coefficients at infinite dilution of these hydrocarbons in water at 25°C, and the values of the parameters used are given in Tables 2, 3 and 4. The variations of the natural logarithm of the activity coefficient with the molecular connectivity of first order are represented in Figure 1. Similar linear trends would be obtained with the other selected physical parameters.

The multiple linear regression analysis, the calculation of the standard error of estimate (STD) and the multiple correlation coefficient (r) have been performed according to the method described by Cooley and Lohnes (1962) and Ostle (1954).

CORRELATIONS?

Aliphatic Hydrocarbons

The correlations of the natural logarithm of the activity coefficient at infinite dilution of aliphatic hydrocarbons with the molecular connectivity of first order, the acentric factor, and the number of carbon atoms, with the dipole moment as second parameter, are summarized in Table 5. The dipole moment has been selected since it accounts for the differences in molecular polarity. However, the corrective effect of the dipole moment is not sufficient to incorporate the cyclic hydrocarbons. The data for this

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Table 1. Molecular Parameters

Molecular Parameter	Symbol	Molecular Property	Reference
Number of Carbon Atoms	N_c	Size	
Surface Area	SA	Size and Shape	Yalkowsky and Valvani (1979)
Molecular Connectivity of First Order	χ	Size and Topology*	Kier (1977)
Total Electronic Energy	E_T	Size and Topology	Carbó (1970) and Streitwieser (1961)
Acentric Factor	ω	Noncentral Intermolecular Forces	Reid et al. (1977)
Dipole Moment	μ	Polarity	Reid et al. (1977)

* χ is a count of the bonds weighted by the degree of branching.

Table 2. Activity Coefficient at Infinite Dilution in Water, Molecular Connectivity, Acentric Factor and Dipole Moment of Aliphatic Hydrocarbons.

Compound	γ^∞	χ	ω	μ (Debyes)
Propane (C_3H_8)	4.23×10^3	1.414	0.152	—
n-Butane (C_4H_{10})	2.19×10^4	1.919	0.193	—
n-Pentane (C_5H_{12})	1.04×10^5	2.414	0.251	—
n-Hexane (C_6H_{14})	5.04×10^5	2.914	0.296	—
n-Heptane (C_7H_{16})	1.90×10^6	3.414	0.351	—
n-Octane (C_8H_{18})	9.62×10^6	3.914	0.394	—
n-Nonane (C_9H_{20})	3.24×10^7	4.414	0.444	—
n-Decane ($C_{10}H_{22}$)	1.58×10^8	4.914	0.490	—
iso-Butane (C_4H_{10})	1.96×10^4	1.732	0.176	—
iso-Pentane (C_5H_{12})	8.39×10^4	2.270	0.227	—
iso-Hexane (C_6H_{14})	3.47×10^5	2.770	0.279	—
iso-Heptane (C_7H_{16})	2.19×10^6	3.270	0.330	—
3-Methylpentane (C_6H_{14})	3.74×10^5	2.808	0.275	—
3-Methylhexane (C_7H_{16})	1.12×10^6	3.308	0.324	—
3-Methylheptane (C_8H_{18})	8.01×10^6	3.808	0.369	—
2,2-Dimethylpropane (C_5H_{12})	7.42×10^4	2.000	0.197	—
2,2-Dimethylbutane (C_6H_{14})	2.60×10^5	2.561	0.231	—
2,3-Dimethylbutane (C_6H_{14})	2.13×10^5	2.643	0.247	—
2,2-Dimethylpentane (C_7H_{16})	1.27×10^6	3.061	0.289	—
2,3-Dimethylpentane (C_7H_{16})	1.06×10^6	3.181	0.299	—
3,3-Dimethylpentane (C_7H_{16})	9.37×10^5	3.121	0.270	—
2,4-Dimethylpentane (C_7H_{16})	1.37×10^6	3.126	0.306	—
2,2,5-Trimethylpentane (C_8H_{18})	6.20×10^6	3.561	0.338	—
2,2,4-Trimethylpentane (C_8H_{18})	2.60×10^6	3.417	0.303	—
2,3,4-Trimethylpentane (C_8H_{18})	2.76×10^6	3.553	—	—
Ethylene (C_2H_4)	1.99×10^2	0.500	0.085	0.0
Propene (C_3H_6)	1.15×10^2	0.986	0.148	0.4
1-Butene (C_4H_8)	5.07×10^2	1.524	0.187	0.3
1-Pentene (C_5H_{10})	2.63×10^4	2.024	0.245	0.4
1-Hexene (C_6H_{12})	9.35×10^4	2.524	0.285	0.4
1-Octene (C_8H_{18})	2.31×10^6	3.524	0.386	0.3
2-Heptene (C_7H_{14})	3.64×10^5	3.026	—	0.3*
3-Methyl-1-Butene (C_5H_{10})	2.50×10^4	1.896	0.209	0.3*
2-Methyl-1-Pentene (C_6H_{12})	5.99×10^4	2.414	—	0.3*
4-Methyl-1-Pentene (C_6H_{12})	9.74×10^4	2.379	—	0.3*
2-Methyl-Propene (C_4H_8)	4.65×10^3	1.354	0.190	0.5
1,3-Butadiene (C_4H_6)	4.09×10^3	1.150	0.195	0.0
1,4-Pentadiene (C_5H_8)	6.78×10^3	1.633	0.104	0.4
2-Methyl-1,3-Butadiene (C_5H_8)	5.90×10^3	1.550	0.164	0.3
Propyne (C_3H_4)	1.04×10^2	0.789	0.218	0.7
1-Butyne (C_4H_6)	5.83×10^2	1.349	0.050	0.8
1-Pentyne (C_5H_8)	2.41×10^3	1.849	0.164	0.9

* Estimated values.

Table 3. Activity Coefficient at Infinite Dilution in Water, Molecular Connectivity and Total Electronic Energy of Monocyclic Aromatic Hydrocarbons

Compound	γ^∞	χ	E_T
Benzene (C_6H_6)	2.40×10^3	2.000	26.106
Toluene (C_7H_8)	9.90×10^3	2.411	32.721
Ethylbenzene (C_8H_{10})	3.88×10^4	2.971	39.327
p-Xylene (C_8H_{10})	2.98×10^4	2.821	39.337
m-Xylene (C_8H_{10})	3.01×10^4	2.821	39.337
o-Xylene (C_8H_{10})	2.90×10^4	2.827	29.337
1,2,4-Trimethylbenzene (C_9H_{12})	1.17×10^5	3.238	45.952
1,3,5-Trimethylbenzene (C_9H_{12})	6.90×10^4	3.232	45.952
Propylbenzene (C_9H_{12})	1.27×10^5	3.471	45.930
Isopropylbenzene (C_9H_{12})	1.34×10^5	3.354	45.935
Butylbenzene ($C_{10}H_{14}$)	5.92×10^5	3.971	52.533
tert-Butylbenzene ($C_{10}H_{14}$)	2.19×10^5	3.661	52.545

Table 4. Activity Coefficient at Infinite Dilution in Water, Molecular Connectivity and Surface Area of Polynuclear Aromatic Hydrocarbons

Compound	γ^∞	χ	SA (A^2)
Indan (C_9H_{10})	6.00×10^4	3.535	151.5
Naphthalene ($C_{10}H_8$)	6.42×10^4	3.405	155.8
1-Methylnaphthalene ($C_{11}H_{10}$)	2.82×10^5	3.821	172.5
2-Methylnaphthalene ($C_{11}H_{10}$)	2.65×10^5	3.815	176.3
1,3-Dimethylnaphthalene ($C_{12}H_{12}$)	1.09×10^6	4.232	192.9
1,4-Dimethylnaphthalene ($C_{12}H_{12}$)	7.63×10^5	4.238	189.2
1,5-Dimethylnaphthalene ($C_{12}H_{12}$)	7.45×10^5	4.238	189.2
2,3-Dimethylnaphthalene ($C_{12}H_{12}$)	5.02×10^5	4.232	193.1
2,6-Dimethylnaphthalene ($C_{12}H_{12}$)	6.53×10^5	4.226	196.7
1-Enthylnaphthalene ($C_{12}H_{12}$)	8.06×10^5	4.376	187.4
Biphenyl ($C_{12}H_{10}$)	4.33×10^5	4.071	182.0
Acenaphthene ($C_{12}H_{10}$)	4.33×10^5	4.445	175.0
Fluorene ($C_{13}H_{10}$)	5.93×10^5	4.612	193.6
Phenanthrene ($C_{14}H_{10}$)	1.50×10^6	4.815	198.0
Anthracene ($C_{14}H_{10}$)	1.72×10^6	4.809	202.2
2-Methylanthracene ($C_{15}H_{12}$)	4.17×10^6	5.220	222.6
9-Methylanthracene ($C_{15}H_{12}$)	1.14×10^7	5.232	215.1
9,10-Dimethylanthracene ($C_{16}H_{14}$)	5.77×10^6	5.655	228.0
Pyrene ($C_{16}H_{10}$)	3.87×10^6	5.893	213.0
Fluoranthene ($C_{16}H_{10}$)	6.02×10^6	5.565	218.0
1,2-Benzofluorene ($C_{17}H_{12}$)	6.73×10^6	6.022	237.4
2,3-Benzofluorene ($C_{17}H_{12}$)	1.60×10^7	6.017	239.9
Chrysene ($C_{18}H_{12}$)	3.41×10^7	6.226	241.0
Triphenylene ($C_{18}H_{12}$)	5.65×10^6	5.020	236.0
Naphthacene ($C_{18}H_{12}$)	1.43×10^7	6.214	248.0
1,2-Benzanthracene ($C_{18}H_{12}$)	4.24×10^7	6.220	244.3
Perylene ($C_{20}H_{12}$)	1.15×10^8	6.976	251.5
3,4-Benzopyrene ($C_{20}H_{12}$)	1.21×10^8	6.970	256.0
3-Methylcholanthrene ($C_{21}H_{16}$)	1.61×10^8	7.677	282.7
Benzo(g,h,i) perylene ($C_{22}H_{12}$)	1.89×10^8	7.720	266.9

family, which are only included in Figure 1, have not been considered in the equations presented in Table 5.

The correlation with the molecular connectivity of first order presents the best multiple correlation coefficient and a standard error of estimate 2 to 3.8 times smaller. The maximum relative error of the activity coefficient predicted with the equation based on molecular connectivity of first order is of 95% for ethylene and propyne, while with the N_c and ω relative errors as high as 300% and 800% are obtained for several olefines, respectively. It should be noted that errors involved in the experimental determination of activity coefficients of hydrocarbons in water at infinite dilution may also be considerably large.

It may be concluded that for aliphatic hydrocarbons the molecular connectivity of first order represents the data much better than the number of carbon atoms while the acentric factor gives a very poor correlation. This was expected since the molecular connectivity of first order distinguishes among saturated isomers as butane and iso-butane, and between saturated and unsaturated hydrocarbons of the same number of carbon atoms.

The UNIFAC equation with the parameters published by Fredenslund et al. (1977) for the hydrocarbons listed in Table 2, gives an average relative error of 73% for the activity coefficients at infinite dilution. This is 3 times higher than the one obtained with the correlation based on molecular connectivity and dipole moment.

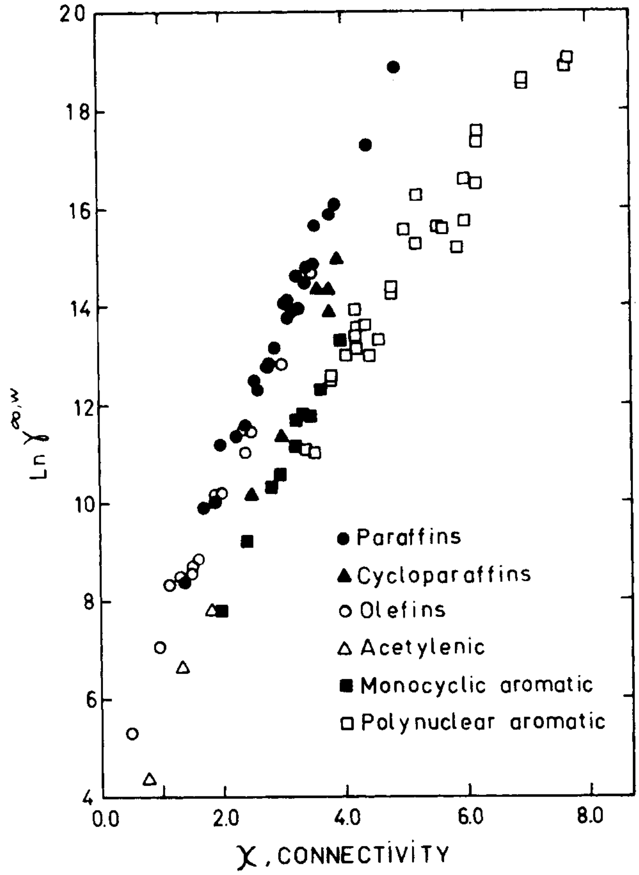

Figure 1. Variations of the natural logarithm of the activity coefficient at infinite dilution of hydrocarbons in water with the molecular connectivity of first order.

Aromatic Hydrocarbons

The parameters considered in the prediction of activity coefficients of aromatic hydrocarbons at infinite dilution in water are the molecular connectivity of first order, the total electronic energy, the number of carbon atoms and the acentric factor. As for aliphatic hydrocarbons the acentric factor is a poor correlating parameter and is not further discussed.

The molecular connectivity is linearly related to the total electronic energy according to Carbó and Ferrer (1980) and therefore will give, in general, very similar results. However, for monocyclic aromatic hydrocarbons the equation based on the molecular connectivity of first order presents a higher correlation coefficient and a standard error of estimate 1.6 times smaller than the total electronic energy. The predictions based on the number of carbon atoms and total electronic energy are equivalent. These equations are included in table 5.

For polinuclear aromatic hydrocarbons the molecular connectivity of first order, the total electronic energy and the number of carbon atoms yield comparable results. The adoption of the correlation proposed by Mackay and Shiu (1977) based on the number of carbon atoms and extended with a second order term does not improve the goodness of the fit.

In order to compare with the results obtained by Yalkowsky and Valvani (1979) the molecular surface area has also been considered for the polinuclear aromatic hydrocarbons. The equation otained with this parameter is compared with the one based on the molecular connectivity of first order and both are included in Table 5. The correlation coefficient is practically identical for both equations and the standard error of estimate is only slightly inferior for the one based on the molecular surface area. From a practical point of view it may be preferable to use the molecular connectivity of first order since it is very easily calculated and has been extensively used in pharmacology and medical sciences.

TABLE 5. ACTIVITY COEFFICIENT CORRELATIONS

Correlation	r	STD	Hydrocarbon Family
$ln\ \gamma^{\infty} = 4.51 + 2.98\ \chi - 3.16\ \mu^2$	0.995	0.336	Aliphatic
$ln\ \gamma^{\infty} = 4.46 + 29.4\ \omega - 3.47\ \mu^2$	0.933	1.26	
$ln\ \gamma^{\infty} = 2.85 + 1.59\ N_c - 4.72\ \mu^2$	0.983	0.620	
$ln\ \gamma^{\infty} = 2.63 + 2.69\ \chi$	0.993	0.180	Monocyclic Aromatic
$ln\ \gamma^{\infty} = 2.99 + 0.187\ E_T$	0.982	0.292	
$ln\ \gamma^{\infty} = 0.458 + 1.24\ N_c$	0.982	0.291	
$ln\ \gamma^{\infty} = 5.52 + 1.82\ \chi$	0.970	0.558	Polinuclear Aromatic
$ln\ \gamma^{\infty} = 1.07 + 0.066\ SA$	0.971	0.545	

It may be concluded that for the two aromatic families the molecular connectivity of first order is the most suitable correlating parameter and the equation obtained is

$$ln\gamma^{\infty} = 5.08 + 1.90_{\chi} \quad r = 0.982 \quad STD = 0.533$$

The consideration of the dipole moment as a second parameter never improves the results.

As reported by Yalkowsky and Valvani (1979), the incorporation of the melting point as a second parameter significantly improves the correlation of hydrocabon solubilities in water, but it does not affect the predictions of the activity coefficients at infinite dilution.

As for the aliphatic hydrocarbons, the UNIFAC equation predicts the activity coefficients at infinite dilution of aromatic hydrocarbons with an average relative error 3 times higher than any of the correlations based on the molecular connectivity of first order.

The method presented in this work is less general than the UNIFAC equation but is able to predict, for a definite solvent and family, activity coefficients at infinite dilution more accurately.

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