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# The correlation and prediction of the temperature variation of infinite dilution activity coefficients of compounds in water

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ABSTRACT

We list infinite dilution activity coefficients, $\gamma\infty$, in water for 81 compounds from 273.15 to 373.15 K, and we use our linear free energy relationship to obtain equations for log $\gamma\infty$ at 5 K intervals between 273.15 and 373.15 K. These equations, together with Abraham descriptors can then be used to calculate or predict the temperature variation of activity coefficient in water with an estimated error of 0.25–0.30 log unit. If an experimental value of log $\gamma\infty$ is available at 298.15 K (or at any specific temperature) this can be used as a reference point to adjust our calculated values at any other temperature, leading to an estimated error for the temperature variation of around 0.1 log units. This procedure is especially useful in extrapolating limited data on log $\gamma\infty$ over the entire range 273.15–373.15 K. The method requires no complicated software and calculations involve no more than simple arithmetic.



## 1. Introduction

Infinite dilution activity coefficients provide valuable information regarding solute-solvent interactions, and are used in the design of chemical separation processes such as gas stripping, fractional distillation and liquid-liquid extraction. Activity coefficient data for solutes dissolved in water are particularly important in that water is the solvent for many industrial manufacturing processes involving synthesis of new chemical materials. Industrial processes often take place at elevated temperatures. Effective design of industrial processes often requires knowledge of how the activity coefficient varies with temperature. Experimental measurements are not feasible for every solute-water combination, particularly if one has to perform activity coefficient measurements at several temperatures.

There are numerous methods for the prediction of activity coefficients; however, few of these deal with infinite dilution activity coefficients of compounds in water, $\gamma\infty$, and even fewer with their temperature variation [1–18]. Notable exceptions are the work of Brockbank [19] and Dohnal and colleagues [20–30]. However, there still remains the need for a simple method for the correlation and prediction of infinite dilution activity coefficients of compounds in water over a reasonable range of temperature. We have previously used our methods, based on a multiple linear regression equation [31–36] to correlate and predict infinite dilution activity coefficients of compounds in water at 298.15 K [37], and we now attempt to extend this work to cover a range of temperature from 273.15 K to 373.15 K.

## 2. Methods

Our general method has been set out and reviewed several times [31–37] and so we just give a summary. The method revolves round the linear free energy relationship, LFER [37], equation (1).

$$\log \gamma\infty = c + eE + sS + aA + bB + vV + fnF \quad (1)$$

The independent variables in equation (1) are *E* the compound excess molar refractivity in units of ($cm^3$ $mol^{-1}$)/10; *S* the compound dipolarity/polarizability; *A* and *B* the overall or summation hydrogen bond acidity and basicity, *V* the McGowan volume in units of ($cm^3$ $mol^{-1}$)/100 and *nF* the number of aliphatic fluorine atoms in a compound. For pure liquid compounds, *E* is obtained from the refractive index of the compound at 293 K; for gases and solids the refractive index can be estimated or *E* itself can be

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**Abbreviations**

| | |
|---|---|
| $\gamma\infty$ | infinite dilution activity coefficient in water |
| *E* | the compound excess molar refractivity in units of $(cm^3\ mol^{-1})/10$ |
| S | the compound dipolarity/polarizability |
| *A* | overall or summation hydrogen bond acidity |
| *B* | overall or summation hydrogen bond basicity |
| *V* | the McGowan volume in units of (cm3 mol−1)/100 |
| *nF* | the number of aliphatic C-F groups in a compound |
| *SP* | property of a series of compounds in a given system |
| *N* | number of data points (compounds) |
| *SD* | standard deviation |
| *R* | regression correlation constant |
| *F* | the F-statistic |
| *LFER* | linear free energy relationship |
| *PRESS* | the leave-one-out statistic |
| *Q* | the leave-one-out statistic |
| *PSD* | predictive standard deviation |

calculated quite easily [38,39]. For neutral molecules, the descriptors *S*, *A* and *B* can be obtained from various physicochemical measurements [31–36]. The coefficients *c, e, s, a, b, v* and *f* are the equation coefficients obtained by multiple linear regression analysis of the dependent variable, log $\gamma\infty$, against the independent variables in equation (1).

## 3. Results and discussion

For a few compounds we calculated log $\gamma\infty$ at various temperatures from known values of gas-water partition coefficients [40] and the corresponding vapor pressures. For most of the compounds we collected data on activity coefficients over a wide range of temperature [5,6,17,19,20,22–26,29,30,41–44] so that with minimal extrapolation we could cover the range 273 K–373 K. The list of 81 compounds and their descriptors is in Table 1.

We then applied the LFER equation (1) to values of log $\gamma\infty$ for the 81 compounds at 5 K intervals, leading to the coefficients given in Table 2. We give also the statistics of the equations, noting that the number of data points, *N*, is 81 in all cases. *SD* is the standard deviation, *R* is the equation correlation coefficient, *F* is the *F*-statistic, and *PRESS* and $Q^2$ are the leave-one-out statistics. Rather than use a training set and a test set to assess the predictive power of our model, we prefer to use the predictive standard deviation, *PSD*, which is derived from the leave-one-out statistics but which uses all the data and is much easier to calculate [45]. .

We have only 81 compounds instead of the 655 compounds that we previously used to obtain an equation for log $\gamma\infty$ (298), but we can compare coefficients in equation (1) for the two data sets in Table 3. The sets of coefficients are reasonably close enough to suggest that the 81 data set is a representative subset of the 655 data set.

The coefficients in Table 2 are for equations that are only 5 K apart, and so it should be quite easy to interpolate coefficients at any other temperature. To aid this, we have fitted each coefficient in equation (1) to equation (2), where *W*, *X*, *Y* and *Z* are given in Table 4. Note that *Z* was not significant. We do not give the statistics because in all cases, $R^2 = 1.000$ and $Q^2 = 1.000$

$$\text{Coefficient} = W + X/\text{T} + Y \log \text{T} + Z\text{T} \quad (2)$$

**Table 1**
Compounds used in the calculations, and their descriptors.

| Compound | Ref | *E* | *S* | *A* | *B* | *V* | *nF* |
|---|---|---|---|---|---|---|---|
| Propane | [40] | 0.000 | 0.00 | 0.00 | 0.00 | 0.5313 | 0 |
| Butane | [40] | 0.000 | 0.00 | 0.00 | 0.00 | 0.6722 | 0 |
| Neopentane | [40] | 0.000 | −0.08 | 0.00 | 0.00 | 0.8131 | 0 |
| Fluoromethane | [40] | 0.066 | 0.35 | 0.00 | 0.09 | 0.2672 | 1 |
| Tetrafluoromethane | [40] | −0.550 | −0.25 | 0.00 | 0.00 | 0.3203 | 4 |
| Difluorochloromethane | [40] | −0.056 | 0.38 | 0.04 | 0.05 | 0.4073 | 2 |
| Tetrafluoroethene | [40] | −0.310 | −0.21 | 0.00 | 0.14 | 0.4182 | 4 |
| Hexafluoropropene | [40] | −0.500 | −0.17 | 0.00 | 0.10 | 0.5945 | 6 |
| Butanone | [22,41] | 0.166 | 0.70 | 0.00 | 0.51 | 0.6879 | 0 |
| Cyclopentanone | [22] | 0.373 | 0.86 | 0.00 | 0.52 | 0.7202 | 0 |
| Cyclohexanone | [22] | 0.403 | 0.86 | 0.00 | 0.56 | 0.8611 | 0 |
| Methyl vinyl ketone | [30] | 0.291 | 0.76 | 0.00 | 0.48 | 0.6449 | 0 |
| Acetylacetone | [22] | 0.412 | 0.80 | 0.00 | 0.62 | 0.8445 | 0 |
| Diethyl ether | [5,24] | 0.041 | 0.25 | 0.00 | 0.45 | 0.7309 | 0 |
| Tetrahydrofuran | [24] | 0.289 | 0.52 | 0.00 | 0.48 | 0.6223 | 0 |
| Tetrahydropyran | [24] | 0.296 | 0.50 | 0.00 | 0.47 | 0.7632 | 0 |
| Dimethoxymethane | [24] | 0.099 | 0.46 | 0.00 | 0.52 | 0.6487 | 0 |
| 1,3-Dioxolane | [24] | 0.298 | 0.61 | 0.00 | 0.59 | 0.5401 | 0 |
| 1,4-Dioxane | [24] | 0.329 | 0.75 | 0.00 | 0.64 | 0.681 | 0 |
| Furfural | [30] | 0.690 | 1.13 | 0.00 | 0.45 | 0.6929 | 0 |
| 2-Methylfuran | [30] | 0.368 | 0.51 | 0.00 | 0.14 | 0.6772 | 0 |
| 2,3-Dimethylfuran | [30] | 0.369 | 0.51 | 0.00 | 0.16 | 0.8181 | 0 |
| Methyl acetate | [22] | 0.142 | 0.64 | 0.00 | 0.45 | 0.6057 | 0 |
| Ethyl acetoacetate | [22] | 0.208 | 0.80 | 0.00 | 0.86 | 1.0441 | 0 |
| 2-Methoxyethyl acetate | [22] | 0.166 | 0.79 | 0.00 | 0.81 | 0.9462 | 0 |
| 2-Ethoxyethyl acetate | [22] | 0.099 | 0.79 | 0.00 | 0.79 | 1.0871 | 0 |
| Methyl methoxyacetate | [22] | 0.181 | 0.62 | 0.00 | 0.81 | 0.8053 | 0 |
| Dimethylcarbonate | [26] | 0.142 | 0.59 | 0.00 | 0.53 | 0.6644 | 0 |
| Diethylcarbonate | [26] | 0.061 | 0.69 | 0.00 | 0.50 | 0.9462 | 0 |
| Vinyl acetate | [26] | 0.223 | 0.55 | 0.00 | 0.43 | 0.7036 | 0 |
| Methyl methacrylate | [26] | 0.245 | 0.55 | 0.00 | 0.42 | 0.8445 | 0 |
| Acetonitrile | [17] | 0.237 | 0.90 | 0.07 | 0.32 | 0.4042 | 0 |
| Proprionitrile | [17] | 0.162 | 0.90 | 0.02 | 0.36 | 0.5451 | 0 |
| Acrylonitrile | [26] | 0.297 | 0.83 | 0.03 | 0.30 | 0.5021 | 0 |
| N-Methylformamide | [25] | 0.405 | 1.36 | 0.40 | 0.55 | 0.5059 | 0 |
| Dimethylformamide | [25] | 0.367 | 1.31 | 0.00 | 0.74 | 0.6468 | 0 |
| N-Methylacetamide | [25] | 0.350 | 1.28 | 0.40 | 0.71 | 0.6468 | 0 |
| Nitrobenzene | [23] | 0.871 | 1.11 | 0.00 | 0.28 | 0.8906 | 0 |
| Aniline | [23] | 0.955 | 0.96 | 0.26 | 0.41 | 0.8162 | 0 |
| Butan-1-ol | [42] | 0.224 | 0.42 | 0.37 | 0.48 | 0.7309 | 0 |
| Isobutanol | [42] | 0.217 | 0.39 | 0.37 | 0.48 | 0.7309 | 0 |
| Pentan-2-ol | [29] | 0.195 | 0.36 | 0.33 | 0.56 | 0.8718 | 0 |
| Pentan-3-ol | [29] | 0.218 | 0.36 | 0.33 | 0.56 | 0.8718 | 0 |
| 2-Methylbutan-1-ol | [29] | 0.219 | 0.39 | 0.37 | 0.48 | 0.8718 | 0 |
| 3-Methylbutan-1-ol | [29] | 0.192 | 0.39 | 0.37 | 0.48 | 0.8718 | 0 |
| 2-Methylbutan-2-ol | [29] | 0.194 | 0.30 | 0.31 | 0.63 | 0.8718 | 0 |
| 3-Methylbutan-2-ol | [29] | 0.194 | 0.33 | 0.33 | 0.56 | 0.8718 | 0 |
| Cyclopentanol | [22,42] | 0.427 | 0.54 | 0.26 | 0.57 | 0.7632 | 0 |
| Cyclohexanol | [22,42] | 0.459 | 0.59 | 0.29 | 0.59 | 0.9041 | 0 |
| Allyl alcohol | [30] | 0.342 | 0.46 | 0.38 | 0.48 | 0.5470 | 0 |
| Phenol | [20,43] | 0.805 | 0.89 | 0.60 | 0.30 | 0.7751 | 0 |
| o-Cresol | [5,20] | 0.840 | 0.86 | 0.52 | 0.30 | 0.9160 | 0 |
| m-Cresol | [6,20] | 0.822 | 0.88 | 0.57 | 0.34 | 0.9160 | 0 |
| p-Cresol | [6,20] | 0.820 | 0.87 | 0.57 | 0.31 | 0.9160 | 0 |
| Thiophene | [44] | 0.687 | 0.57 | 0.00 | 0.15 | 0.6411 | 0 |
| Propanethiol | [44] | 0.385 | 0.42 | 0.00 | 0.21 | 0.6948 | 0 |
| Isopropylthiol | [44] | 0.336 | 0.35 | 0.00 | 0.25 | 0.6948 | 0 |
| Butanethiol | [44] | 0.382 | 0.43 | 0.00 | 0.21 | 0.8357 | 0 |
| Mesitylene | [19] | 0.649 | 0.52 | 0.00 | 0.19 | 1.1391 | 0 |
| Butyl butanoate | [19] | 0.044 | 0.56 | 0.00 | 0.45 | 1.3102 | 0 |
| Pyrene | [19] | 2.808 | 1.71 | 0.00 | 0.28 | 1.5846 | 0 |
| Phenanthrene | [19] | 2.055 | 1.29 | 0.00 | 0.29 | 1.4544 | 0 |
| Ethyl acetate | [19] | 0.106 | 0.62 | 0.00 | 0.45 | 0.7466 | 0 |
| Propyl acetate | [19] | 0.092 | 0.60 | 0.00 | 0.45 | 0.8875 | 0 |
| Butyl acetate | [19] | 0.071 | 0.60 | 0.00 | 0.45 | 1.0284 | 0 |
| Cyclooctane | [19] | 0.409 | 0.10 | 0.00 | 0.00 | 1.1272 | 0 |
| o-Xylene | [19] | 0.663 | 0.56 | 0.00 | 0.16 | 0.9982 | 0 |
| Benzonitrile | [19] | 0.742 | 1.11 | 0.00 | 0.33 | 0.8711 | 0 |
| 1,2-Dichloropropane | [19] | 0.369 | 0.63 | 0.00 | 0.17 | 0.7761 | 0 |
| 1,1-Dichloroethane | [19] | 0.322 | 0.49 | 0.10 | 0.10 | 0.6352 | 0 |
| 1,2-Dichloroethane | [19] | 0.416 | 0.64 | 0.10 | 0.11 | 0.6352 | 0 |
| Nitrobenzene | [19] | 0.871 | 1.11 | 0.00 | 0.28 | 0.8906 | 0 |
| Nitroethane | [19] | 0.270 | 0.95 | 0.02 | 0.33 | 0.5646 | 0 |
| Nitropropane | [19] | 0.242 | 0.95 | 0.00 | 0.31 | 0.7055 | 0 |