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Enthalpy of solvation correlations for organic solutes and gases dissolved in *N*,*N*-dimethylformamide and *tert*-butanol

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ABSTRACT

Data have been assembled from the published literature on the enthalpies of solvation for 159 compounds dissolved in *N*,*N*-dimethylformamide and for 84 compounds dissolved in *tert*-butanol. It is shown that an Abraham solvation equation can be used to correlate the experimental enthalpies of solvation in *N*,*N*-dimethylformamide and *tert*-butanol to within standard deviations of 3.08 kJ/mol and 2.48 kJ/mol, respectively. The derived correlations provide very accurate mathematical descriptions of the measured enthalpy of solvation data at 298 K, which in the case of *N*,*N*-dimethylformamide span a range of about 108 kJ/mol. Mathematical correlations have also been derived for predicting the enthalpies of solvation in both solvents based on the Goss modified version of the Abraham model. Expressions based on this latter model were found to correlate the experimental enthalpies of solvation to within an overall average standard deviation of 2.82 kJ/mol for the two solvents studied.

1. Introduction

Solvent extraction is a common purification technique used in the chemical and pharmaceutical industries to remove synthesized compounds from aqueous reaction media. Solvent selection is a crucial factor in the extraction optimization process because extraction efficiency, as measured by both separation selectivity and product recovery, is determined to a large extent by both the desired product's and unwanted impurity's affinities for the organic versus aqueous phase. The partition coefficient quantifies the affinity differences. Historically, many of the very early studies focused on measuring and developing predictive correlations for the 1-octanol and water system. This system is thought to mimic several important biological processes. As additional experimental data became available, researchers expanded their studies to include more organic solvents and temperatures other than 298 K and 310 K (body temperature). Many commercial extraction and separation processes occur at much higher temperatures and there is need of enthalpy data and computation methods for adjusting partition coefficients measured at 298 K to the higher temperatures employed in manufacturing processes.

The general solvation parameter model of Abraham [1–5] is one of the most useful approaches for the analysis and prediction of free energies and enthalpies for solute transfer between two phases. The method relies on two linear free energy relationships (LFERs), one for processes within condensed phases

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \quad (1)$$

and one for processes involving gas-to-condensed phase transfer

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + 1 \cdot \mathbf{L} \quad (2)$$

The dependent variable, SP, is some property of a series of solutes in a fixed phase. The independent variables, or descriptors, are solute properties as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarizability descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity, **V** is the McGowan volume of the solute and **L** is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The set of coefficients, *c*, *e*, *s*, *a*, *b* and *v* (or *l*) characterize the system and are determined by multiple linear regression analysis. For any fully characterized system/process (those with calculated values for the equation coefficients) further values of SP can be estimated for solutes with known values for the solute descriptors. This is a major advantage in using Eqs. (1) and (2) to correlate partition coefficients and enthalpies of solvation. The same set of solute descriptors needed in the partition coefficient prediction can then be used in estimating the enthalpy data needed to correct the partition coefficient to higher temperatures.

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Table 1
Experimental values of the gas to *N*,*N*-dimethylformamide solvation enthalpy, $\Delta H_{Solv,DMF}$ (kJ/mol), for 159 solutes, together with the solute descriptors

Solute	E	S	A	B	L	V	Exp	Ref
Methane	0.000	0.000	0.000	0.000	−0.323	0.2500	−2.36	51
Propane	0.000	0.000	0.000	0.000	1.050	0.5313	−13.44	51
Butane	0.000	0.000	0.000	0.000	1.615	0.6722	−16.00	23
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	−19.29	21
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	−23.05	21
Heptane	0.000	0.000	0.000	0.000	3.173	1.0950	−27.28	21
Octane	0.000	0.000	0.000	0.000	3.677	1.2360	−30.96	21
Nonane	0.000	0.000	0.000	0.000	4.182	1.3767	−34.60	21
Decane	0.000	0.000	0.000	0.000	4.686	1.5180	−37.86	21
Undecane	0.000	0.000	0.000	0.000	5.191	1.6585	−41.94	24
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	−45.43	21
Tetradecane	0.000	0.000	0.000	0.000	6.705	2.0810	−52.68	22
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	−60.25	21
2-Methylpentane	0.000	0.000	0.000	0.000	2.503	0.9540	−22.22	25
2,2-Dimethylbutane	0.000	0.000	0.000	0.000	2.352	0.9540	−19.25	22
3-Ethylpentane	0.000	0.000	0.000	0.000	3.091	1.0950	−26.30	33
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.106	1.2358	−25.19	22
2-Methyloctane	0.000	0.000	0.000	0.000	3.966	1.3767	−32.05	22
3,3-Diethylpentane	0.000	0.000	0.000	0.000	3.820	1.3767	−31.30	22
2,2,4,4-Tetramethylpentane	0.000	0.000	0.000	0.000	3.512	1.3767	−27.78	39
2,2,5,5-Tetramethylhexane	0.000	0.000	0.000	0.000	4.039	1.5176	−28.83	22
Cyclopentane	0.263	0.100	0.000	0.000	2.477	0.7045	−22.34	22
Cyclohexane	0.305	0.100	0.000	0.000	2.964	0.8454	−25.36	22
Cyclooctane	0.413	0.100	0.000	0.000	4.329	1.1272	−34.06	22
Methylcyclohexane	0.244	0.060	0.000	0.000	3.319	0.9863	−27.07	22
cis-1,2-Dimethylcyclohexane	0.281	0.240	0.000	0.000	3.847	1.1272	−30.84	22
1-Butene	0.100	0.080	0.000	0.070	1.491	0.6292	−18.40	23
1-Pentene	0.093	0.080	0.000	0.070	2.047	0.7701	−21.34	22
1-Hexene	0.078	0.080	0.000	0.070	2.572	0.9110	−25.52	22
1-Heptene	0.092	0.080	0.000	0.070	3.063	1.0520	−29.46	22
1-Octene	0.094	0.080	0.000	0.070	3.568	1.1930	−32.76	22
1-Nonene	0.090	0.080	0.000	0.070	4.073	1.3340	−36.65	22
1-Decene	0.090	0.080	0.000	0.070	4.554	1.4750	−40.50	39
1-Dodecene	0.089	0.080	0.000	0.070	5.515	1.7570	−48.16	22
1-Tridecene	0.087	0.080	0.000	0.070	6.020	1.8973	−52.01	22
1-Tetradecene	0.085	0.080	0.000	0.070	6.513	2.0382	−56.11	22
1-Pentadecene	0.083	0.080	0.000	0.070	7.006	2.1791	−59.79	22
cis-2-Octene	0.135	0.080	0.000	0.070	3.683	1.1928	−32.05	22
trans-2-Octene	0.123	0.080	0.000	0.070	3.600	1.1928	−31.92	22
cis-4-Octene	0.133	0.080	0.000	0.070	3.607	1.1928	−31.46	22
trans-4-Octene	0.144	0.080	0.000	0.070	3.593	1.1928	−31.21	22
Cyclopentene	0.335	0.200	0.000	0.100	2.402	0.6610	−24.56	22
Cyclohexene	0.395	0.200	0.000	0.100	3.021	0.8020	−28.12	22
1-Methylcyclohexene	0.391	0.200	0.000	0.100	3.483	0.9860	−32.05	22
1,3-Butadiene	0.320	0.230	0.000	0.100	1.543	0.5862	−20.40	23
1,5-Hexadiene	0.191	0.150	0.000	0.100	2.450	0.8680	−27.91	22
Benzene	0.610	0.520	0.000	0.140	2.786	0.7176	−33.68	30
Toluene	0.601	0.520	0.000	0.140	3.325	0.8570	−37.32	30
Ethylbenzene	0.613	0.510	0.000	0.150	3.778	0.9982	−40.57	26
Isopropylbenzene	0.602	0.490	0.000	0.160	4.084	1.1391	−42.84	26
sec-Butylbenzene	0.603	0.480	0.000	0.160	4.506	1.2800	−46.82	26
tert-Butylbenzene	0.619	0.490	0.000	0.180	4.413	1.2800	−44.96	26
1,4-Dimethylbenzene	0.613	0.520	0.000	0.160	3.839	0.9982	−40.75	30
1,3,5-Trimethylbenzene	0.649	0.520	0.000	0.190	4.344	1.1391	−44.20	30
Hexamethylbenzene	0.950	0.720	0.000	0.210	6.557	1.5618	−62.67	26
Octylbenzene	0.579	0.480	0.000	0.150	6.714	1.7027	−59.20	26
4-Isopropyltoluene	0.607	0.490	0.000	0.190	4.590	1.2800	−46.70	26
1,2-Diphenylethane	1.200	1.030	0.000	0.280	6.764	1.6060	−69.64	26
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3240	−64.37	26
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	−56.57	26
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	−79.50	33
Styrene	0.849	0.650	0.000	0.160	3.856	0.9550	−44.38	26
α-Methylstyrene	0.851	0.640	0.000	0.190	4.290	1.0960	−48.65	26
Trans-Stilbene	1.450	1.050	0.000	0.340	7.520	1.5630	−79.10	26
Acetone	0.179	0.700	0.040	0.490	1.696	0.5470	−31.38	36
2-Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	−34.27	36
2-Pentanone	0.143	0.680	0.000	0.510	2.755	0.8288	−37.40	28
3-Pentanone	0.154	0.660	0.000	0.510	2.811	0.8288	−37.61	28
2-Hexanone	0.136	0.680	0.000	0.510	3.286	0.9697	−41.30	28
3-Hexanone	0.136	0.660	0.000	0.510	3.310	0.9697	−40.54	28
2-Heptanone	0.123	0.680	0.000	0.510	3.760	1.1106	−45.23	36
4-Heptanone	0.110	0.660	0.000	0.510	3.705	1.1106	−43.72	36
2-Octanone	0.108	0.680	0.000	0.510	4.257	1.2515	−49.08	28
2-Nonanone	0.119	0.680	0.000	0.510	4.735	1.3924	−52.55	36
5-Nonanone	0.103	0.660	0.000	0.510	4.698	1.3924	−50.33	36