Aromatic Substituent Group Enthalpies of Transfer from Methanol to *N,N*-Dimethylformamide

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Abstract: Enthalpies of solution of 95 aromatic compounds have been measured in methanol (MeOH) and in *N,N*-dimethylformamide (DMF). From these values the enthalpies of transfer (MeOH → DMF) have been determined, which are demonstrated to be additive functions of the substituent groups present, regardless of the relative position of each group on the aromatic ring. Deviations from additivity occur when there exists a possibility for intramolecular hydrogen bonding. Group enthalpies of transfer in kilocalories per gram group weight are: F, −0.1; Cl, −0.1; Br, −0.2; I, −0.6; NO_2, −0.8; $COCH_3$, −1.0; $COOC_2H_5$, −0.6; CN, −1.0; NH_2, −1.8; OH, −1.7; C_6H_5, −0.3; $N(CH_3)_2$, −0.5; OCH_3, −0.6; CF_3, +0.3; α-CH_3, CH_2, and CH, +0.03; β-ω-CH_2 and CH_3, +0.08; CH=CH_2, −0.3; naphthyl, −0.6; and phenoxy, −0.7.

The observations that many nucleophilic displacement reactions proceed at faster rates in dipolar aprotic solvents, such as dimethyl sulfoxide or *N,N*-dimethylformamide, than in protonic solvents, such as water or methanol,[2–7] and that the nucleophilicity of the halide ions in water ($I^- > Br^- > Cl^-$) is reversed[2–5] in dipolar aprotic solvents have led several investigators[8–14] to use enthalpies of transfer ($\Delta\Delta H_s$) from protonic to dipolar aprotic solvents in the study of solvation of ions and nonelectrolytes. In the nucleophilic reaction

$$X^- + RY \longrightarrow [X\text{-}R\text{-}Y]^- \longrightarrow RX + Y^-$$

an increase in solvation of any species involved will result in an increase in stability and a decrease in free energy of that species. Hence, in the transfer from protonic to dipolar aprotic solvent, a net increase in solvation of the reactants should retard the reaction rate, whereas a gain in solvation of the transition state should enhance the rate. Several authors[9,10,11b,12] have used the expression

$$\Delta\Delta H_s^t = \Sigma\Delta\Delta H_s + \Delta\Delta H^{\ddagger}$$

where $\Delta\Delta H_s^t$ is the enthalpy of transfer of the transition state, $\Sigma\Delta\Delta H_s$ is the enthalpy of transfer of the reactants, and $\Delta\Delta H^{\ddagger}$ is the difference in enthalpies of activation of the reaction in the two solvents, to determine enthalpies of transfer of transition states for some SN2 and SNAr reactions. While there has been a substantial amount of data in the literature concerning ionic enthalpies of transfer, relatively few enthalpies of transfer of nonelectrolytes have been reported.[9–13] Until recently no general trends have been noted among the available data, although Friedman[8e] has shown that enthalpies of transfer of aliphatic alcohols and quaternary ammonium salts exhibit a constant methylene group contribution in transfers from dimethyl sulfoxide and DMF to propylene carbonate.

In a preliminary communication,[13] we reported evidence that the enthalpies of transfer of some aromatic compounds from MeOH to DMF are additive functions of the substituent groups present in the molecule and cited $\Delta\Delta H_s$ values for the phenyl, nitro, chloro, and acetyl groups. We now wish to extend this list to include a number of common aromatic substituents. Enthalpies of solution (ΔH_s) and enthalpies of transfer (both observed and calculated) are reported in Table I.

From the enthalpies of transfer of the neutral molecules the enthalpy of transfer for the various functional groups may be calculated as in the following examples.

$$\Delta\Delta H_s(C_6H_5) = \Delta\Delta H_s(\text{benzene}) = {}^1/_2\Delta\Delta H_s(\text{biphenyl}) = {}^1/_3\Delta\Delta H_s(\text{terphenyl})$$

$$\begin{aligned}\Delta\Delta H_s(NO_2) &= \Delta\Delta H_s(\text{nitrobenzene}) - \Delta\Delta H_s(\text{benzene})\\ &= \Delta\Delta H_s(\text{1-nitronaphthalene}) - \Delta\Delta H_s(\text{naphthalene})\\ &= {}^1/_2[\Delta\Delta H_s(\text{dinitrobenzene}) - \Delta\Delta H_s(\text{benzene})]\\ &= \Delta\Delta H_s(\text{nitroiodobenzene}) - \Delta\Delta H_s(\text{iodobenzene}), \text{etc.}\end{aligned}$$

The *average* values for the functional groups in kilocalories per gram group weight are: F, −0.1; Cl, −0.1; Br, −0.2; I, −0.6; NO_2, −0.8; $COCH_3$, −1.0; $COOC_2H_5$, −0.6; CN, −1.0; NH_2, −1.8;

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Table I. Enthalpies of Solution in MeOH and DMF and Enthalpies of Transfer at 25°

Compd	ΔH_s-(MeOH),[a] kcal/mol	ΔH_s-(DMF),[a] kcal/mol	$\Delta\Delta H_s$-(MeOH → DMF), kcal/mol	$\Delta\Delta H_s$-(calcd),[b] kcal/mol
Benzene[c]	0.36[d]	0.04[e]	−0.32	−0.3
Fluorobenzene	0.03	−0.35	−0.38	−0.4
Chlorobenzene[c]	0.17	−0.25	−0.42	−0.4
Bromobenzene	0.30	−0.19	−0.49	−0.5
Iodobenzene	0.51	−0.40	−0.91	−0.9
o-Dichlorobenzene[c]	0.34	−0.13	−0.47	−0.5
m-Dibromobenzene	0.61	−0.10	−0.71	−0.7
m-Chlorobromobenzene	0.47	−0.15	−0.62	−0.6
p-Fluorobromobenzene	0.00	−0.67	−0.67	−0.6
Nitrobenzene[c]	1.00	−0.19	−1.19	−1.1
o-Dinitrobenzene	5.7	3.9	−1.8	−1.9
m-Dinitrobenzene	4.6	2.9	−1.7	−1.9
p-Dinitrobenzene	6.2	4.2	−2.0	−1.9
o-Chloronitrobenzene[c]	4.7	3.6	−1.1	−1.2
m-Chloronitrobenzene[c]	5.6	4.4	−1.2	−1.2
p-Chloronitrobenzene[c]	4.2	3.0	−1.2	−1.2
o-Bromonitrobenzene	5.1	3.7	−1.4	−1.3
m-Bromonitrobenzene	5.6	4.6	−1.0	−1.3
p-Bromonitrobenzene	5.4	4.2	−1.2	−1.3
o-Iodonitrobenzene	5.1	3.3	−1.8	−1.7
m-Iodonitrobenzene	5.3	3.6	−1.7	−1.7
p-Iodonitrobenzene	6.4	4.6	−1.8	−1.7
o-Fluoronitrobenzene	0.98	−0.30	−1.28	−1.2
m-Fluoronitrobenzene	0.85	−0.33	−1.18	−1.2
2,4-Dinitrofluorobenzene	0.86	−1.06	−1.92	−2.0
2,4-Dinitrochlorobenzene[c]	5.5	3.6	−1.9	−2.0
2,4-Dinitrobromobenzene	5.7	3.4	−2.3	−2.1
2,4-Dinitroiodobenzene	4.7	1.8	−2.9	−2.5
Acetophenone[c]	1.20	−0.14	−1.34	−1.3
p-Chloroacetophenone[c]	1.13	−0.25	−1.38	−1.4
o-Nitroacetophenone[c]	1.75	−0.56	−2.31	−2.1
m-Nitroacetophenone[c]	6.6	4.5	−2.1	−2.1
p-Nitroacetophenone[c]	6.4	4.2	−2.2	−2.1
Ethyl benzoate	1.21	0.27	−0.94	−0.9
Ethyl *o*-nitrobenzoate	6.9	5.2	−1.7	−1.7
Ethyl *m*-nitrobenzoate	7.2	5.6	−1.6	−1.7
Ethyl *p*-nitrobenzoate	5.9	4.2	−1.7	−1.7
Benzotrifluoride	−0.05	−0.01	0.04	0.0
m-Bromobenzotrifluoride	0.14	−0.12	−0.26	−0.2
o-Nitrobenzotrifluoride	4.5	3.8	−0.7	−0.8
Phenol	0.9	−1.1	−2.0	−2.0
o-Nitrophenol	4.8	2.4	−2.4	−2.8
m-Nitrophenol	2.9	0.2	−2.7	−2.8
p-Nitrophenol	1.8	−0.9	−2.7	−2.8
Anisole	0.81	−0.07	−0.88	−0.9
o-Dimethoxybenzene	1.44	−0.10	−1.54	−1.5
p-Bromoanisole	0.82	−0.22	−1.04	−1.1
p-Nitroanisole	5.5	3.8	−1.7	−1.7
Benzonitrile	0.86	−0.48	−1.34	−1.3
o-Tolunitrile	1.14	−0.10	−1.24	−1.3
m-Tolunitrile	1.10	−0.12	−1.22	−1.3
Aniline	−0.62	−2.68	−2.06	−2.1
m-Toluidine	−0.63	−2.68	−2.05	−2.1
o-Nitroaniline	4.2	1.7	−2.5	−2.9
m-Nitroaniline	4.4	1.4	−3.0	−2.9
p-Nitroaniline	3.6	0.0	−3.6	−2.9
2,4-Dinitroaniline	4.8	1.5	−3.3	−3.7
Toluene	0.45[f]	0.16[g]	−0.29	−0.3
Ethylbenzene	0.58[h]	0.43[i]	−0.15	−0.2
1,2-Diphenylethane	5.9	5.2	−0.7	−0.6
Isopropylbenzene	0.66	0.54	−0.12	−0.1
p-Isopropyltoluene	0.89	0.86	−0.03	−0.1
sec-Butylbenzene	0.66	0.64	−0.02	0.0
tert-Butylbenzene	0.71	0.63	−0.08	0.0
p-Diisopropylbenzene	1.11	1.16	0.05	0.1
1,3,5-Triisopropylbenzene	1.23	1.65	0.42	0.3
p-Di-*tert*-butylbenzene	6.1	6.2	0.1	0.2
Hexamethylbenzene	5.7	5.6	−0.1	−0.1
1-Phenyloctane	1.68	1.96	0.28	0.3
Phenylcyclohexane	0.98	1.02	0.04	0.1
Mesitylene	1.04	0.83	−0.21	−0.2
Nitromesitylene	4.9	4.0	−0.9	−1.0
Bromomesitylene	1.32	1.04	−0.28	−0.4
N,*N*-Dimethylaniline	1.03	0.22	−0.81	−0.8
o-Nitro-*N*,*N*-dimethylaniline	1.91	0.21	−1.70	−1.6
m-Nitro-*N*,*N*-dimethylaniline	6.1	4.7	−1.4	−1.6
p-Nitro-*N*,*N*-dimethylaniline	7.0	5.4	−1.6	−1.6
Biphenyl[c]	4.3	3.7	−0.6	−0.6
p-Nitrobiphenyl[c]	5.6	4.2	−1.4	−1.4
p,*p*′-Dinitrobiphenyl[c]	6.1	4.1	−2.0	−2.2
o-Terphenyl[c]	4.6	3.6	−1.0	−0.9
Naphthalene[c]	4.5	3.9	−0.6	−0.6
1-Chloronaphthalene[c]	0.55	−0.19	−0.74	−0.7
1-Nitronaphthalene[c]	5.3	3.9	−1.4	−1.4
1-Bromonaphthalene	0.72	−0.12	−0.84	−0.8
α-Naphthylamine	2.30	−0.19	−2.49	−2.4
β-Naphthol	2.30	0.0	−2.3	−2.3
Acetonaphthone	5.6	4.0	−1.6	−1.6
Styrene	0.35	−0.21	−0.56	−0.6
α-Methylstyrene	0.58	0.06	−0.52	−0.5
1,1-Diphenylethylene	1.12	0.35	−0.77	−0.9
cis-Stilbene	1.14	0.22	−0.92	−0.9
trans-Stilbene	5.9	4.9	−1.0	−0.9
Diphenyl ether	4.7	3.7	−1.0	−1.0
p-Nitrodiphenyl ether	6.3	4.4	−1.9	−1.8

[a] Calorimetric values ±0.1 kcal/mol (solid samples), ±0.05 kcal/mol (liquid samples). [b] Calculated $\Delta\Delta H_s$ values based on best values for all groups. [c] Values from ref 13. [d] 0.37 (ref 8e). [e] 0.06 (ref 8e). [f] 0.45 (ref 8e). [g] 0.16 (ref 8e). [h] 0.56 (ref 8e). [i] 0.37 (ref 8e).

OH, −1.7; C_6H_5, −0.3; α-CH_3, CH_2, CH, 0.03; β-ω-CH_2, CH_3, 0.08; $N(CH_3)_2$, −0.5; OCH_3, −0.6; CF_3, +0.3; naphthyl, −0.6; phenoxy, −0.7; and —CH=CH$_2$, −0.3.

Discussion

As previously noted,[13] substituent $\Delta\Delta H_s$ values are not dependent on the overall molecular dipole moment. The solvents apparently interact with each functional group without interference from ortho substituents, which results in additive values of $\Delta\Delta H_s$. There is good agreement between calculated and observed $\Delta\Delta H_s$ values for all compounds in Table I with the exceptions: 2,4-dinitroiodobenzene (the deviation of 0.4 kcal is not due to steric effects since *o*-nitroiodobenzene does not show the same effect and is thus attributed to experimental error); *o*-nitrophenol (the deviation of 0.4 kcal may be due to experimental error but could also be attributed to possible intramolecular hydrogen bonding between the two groups which may be disrupted to different extents in the two solvents); *o*-nitroaniline and 2,4-dinitroaniline (same explanation as for *o*-nitrophenol but it should be noted that the $\Delta\Delta H_s$ value for 2,4-dinitroaniline is the sum of $\Delta\Delta H_s$ for *o*-nitroaniline plus the normal increment of -0.8 kcal for another nitro group); *p*-nitroaniline (the observed $\Delta\Delta H_s$ value for this compound is 0.7 kcal more exothermal than the calculated value of -2.9 kcal; this cannot reasonably be attributed to the altered electron distribution, bond angles,[15] or bond lengths resulting from the direct resonance interaction between the amino nitrogen atom and the nitro group, because *p*-nitro-*N*,*N*-dimethylaniline, in which similar interactions occur, shows no such deviations in $\Delta\Delta H_s$; since *p*-nitrophenol does not exhibit the same type of deviation, we do not attribute the difference to the enhanced acidity of the amino protons through a direct resonance interaction with the nitro group and can offer no convincing explanation for the deviation at this time).

Enthalpies of solution are the resultant of several energy terms. The dissolution process of a solute in a solvent has an exothermic term due to solvent–solute interactions. Overcoming solute–solute interactions in the pure solid or liquid is endothermic, as is the energy required to overcome solvent–solvent interactions to make "holes" in the solvent structure to accommodate solute molecules. Consideration of enthalpies of transfer rather than enthalpies of solution removes the solute–solute term from consideration. The types of solvent–solute interactions which may occur include: (1) dispersion forces; (2) charge transfer complexation; (3) dipole–dipole interactions; (4) dipole–induced dipole interactions; (5) hydrogen bonding (a dipole–dipole interaction of very small physical size). Of these 1 probably does not vary greatly from solvent to solvent, and 2 has been avoided by the choice of solvents and solutes. Solvent "hole" energy and interactions 3–5 are the main differences between MeOH and DMF. Of the two solvents DMF is believed to be more strongly associated[16] and should therefore have a more endothermic "hole" energy than MeOH. DMF also has a greater dipole moment (3.85 D) than MeOH (1.70 D) and should be the better solvent with respect to interactions 3 and 4. DMF is also said to be a stronger hydrogen bond acceptor than MeOH.[17–19] Dipole moments and polarizabilities of some monosubstituted benzene compounds are given in Table II.

Table II. Dipole Moments and Polarizabilities of Monosubstituted Benzene Compounds

Compd	μ, D[a]	Group polarizability[b]	Group molar vol[c]	Group $\Delta\Delta H_s$
Benzene	0.0			
Aniline	1.56	4.4	2.3	−1.8
Phenol	1.55	1.6[d]		−1.7
Acetophenone	2.96	10.3	28.0	−1.0
Benzonitrile	3.93	5.3	14.2	−1.0
Nitrobenzene	3.93	6.7	13.5	−0.8
Ethyl benzoate	1.87	16.4	53.9	−0.6
Anisole	1.25	6.7	20.4	−0.6
N,*N*-Dimethylaniline	1.57	14.7	37.9	−0.5
Iodobenzene	1.30	13.1	23.0	−0.6
Bromobenzene	1.52	7.2	16.2	−0.2
Chlorobenzene	1.58	5.0	12.9	−0.1
Fluorobenzene	1.35	0	5.0	−0.1
Toluene	0.43	4.9	17.5	0.03
α,α,α-Trifluorotoluene	2.56	4.6	34.1	+0.3

[a] "Table of Experimental Dipole Moments," W. H. Freeman, Ed., San Francisco, Calif., 1963. [b] Values calculated from Lorenz–Lorentz equation. Polarizability $C_6H_5X - C_6H_6$. [c] Group molar volume (in ml) = $MV(C_6H_5X) - MV(C_6H_6)$. [d] Calculated from polarizability of *m*-cresol − toluene.

Group Enthalpies of Transfer. Although a complete discussion of solvent–group interactions would require a consideration of free energies of transfer, our comparisons of $\Delta\Delta H_s$ and the limited number of $\Delta\Delta G$ values[18] available for aromatic and aliphatic molecules suggest that the two quantities are rather closely parallel for MeOH to DMF transfers. It therefore appears that, unlike transfers from water to organic solvents,[11] the present systems involve solvation phenomena determined primarily by enthalpy rather than entropy terms. Discussion of changes in group solvation upon solvent transfer in terms of $\Delta\Delta H_s$ values are, therefore, quite reasonable.

In the transfer from MeOH to DMF the endothermal $\Delta\Delta H_s$ values for $-CH_3$, $-CH_2-$, and $-CF_3$ probably reflect the greater "hole" energy in the more strongly associated DMF. In the alkylbenzenes the apparent alkyl group volume (calculated as the molar volume of $C_6H_5R - C_6H_6$) increases linearly with the number of carbon atoms in the side chain (or chains) as follows: $C_6H_5CH_3$, 17.5 ml (17.5 ml/C); $C_6H_5CH_2CH_3$, 33.6 ml (16.8 ml/C); *sec*-BuC_6H_5, 66.8 ml (16.7 ml/C); and MeC_6H_4-*i*-Pr, 67.7 ml (16.9 ml/C). There is, of course, a small increase in polarizability (about 4.8) for each additional side chain carbon and increased dispersion interactions, but the latter are not likely to be greatly different in MeOH and in DMF. If the "hole" energy

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(15) P. J. Krueger, *Can. J. Chem.*, **40**, 2300 (1962).

(16) This is suggested by the higher molar heat of vaporization for DMF and by our unpublished $\Delta\Delta H_s$ values (MeOH → DMF) and those of Friedman (ref 8e) for nonpolar compounds of low polarizability, such as alkanes and cycloalkanes, which exhibit endothermic $\Delta\Delta H_s$ values.

(17) C. D. Ritchie, "Solute—Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 4.

(18) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(19) From ^{19}F chemical shifts for *p*-fluorophenol in various solvents it has been concluded that DMF is a stronger hydrogen bond acceptor than oxygen bases such as THF, cyclohexanone, and diethyl ether, with which MeOH is probably comparable: D. Gurka and R. W. Taft, *J. Amer. Chem. Soc.*, **91**, 4794 (1969).

in DMF is the principle energy term determining $\Delta\Delta H_s$ for alkyl groups, this would be consistent with the observed $\Delta\Delta H_s$ increment of +0.08 per CH_2 or CH_3 group. Molar volumes may not be perfect measures of relative molecular sizes, because of the failure to take into account variations in the size of the voids between the molecules in various pure liquids. However, we find the molar volume increment per carbon too persistently constant to be coincidental. The observed $\Delta\Delta H_s$ value for an α-CH_2 or CH_3 (+0.03) is slightly less endothermic, perhaps because of a small increase in dipole–dipole interactions in DMF associated with the dipole moment (about 0.4 D) of the phenyl to α-carbon bond. The "hole" energy factor is also operative with other groups, but is masked by other larger energy terms. The large exothermal $\Delta\Delta H_s$ values for -OH and -NH_2 reflect the greater ability of DMF to accept hydrogen bonds. Hydrogen bonding from methanol to these groups is a relatively minor interaction.[20] Solvent–solute dipole–dipole interactions, which are larger in DMF, are probably primarily responsible for the fairly large $\Delta\Delta H_s$ (−1.0 to −0.8) for the highly polar groups -NO_2, -$COCH_3$, and -CN, all of which have dipole moments greater than 3 D when attached to the benzene ring. It appears that interactions of a solvent dipole with a substituent group (Z) are most effective if the dipole moment of C_6H_5Z arises mainly from only one or two relatively unhindered polar bonds in Z. α,α,α-Trifluorotoluene, which has a sizable dipole moment (μ = 2.56 D), shows no indication of strong interactions with the DMF dipole according to the $\Delta\Delta H_s$ value of the CF_3 group. The same conclusion must be drawn on the basis of ^{19}F chemical shifts[21] of appropriately substituted fluorobenzenes, which are essentially unaffected by transfer from MeOH to DMF.

The remaining groups which are moderately polar (μ = 1.38–1.75 D), and of varying polarizability, have $\Delta\Delta H_s$ values from −0.1 to −0.7. Dipole–dipole interactions are not likely to be sufficiently large to be of major importance, and $\Delta\Delta H_s$ values reflect mainly the polarizability of the groups. The large dipole of DMF is capable of inducing substantial dipoles into the -I, -COOEt, and -NMe_2 groups and appreciable dipole–induced dipole interactions result. The less polarizable -F and -Cl substituents show substantially less exothermal enthalpies of transfer. A similar interaction accounts for the more exothermal transfer of the vinyl group compared with ethyl, although the smaller vinyl group volume plays a minor role. Polar groups in the solutes may also induce dipoles in solvent molecules (DMF > MeOH), but relatively minor interactions are likely to result, due to the limited polarizability of the solvent molecules. A possibility exists for hydrogen bonding from MeOH to -NO_2, -CN, -COOEt, -OEt, and especially to -NMe_2, but since each of these groups is exothermally transferred to DMF, these interactions must be relatively weak.

The observed enthalpies of group transfer (<2 kcal/g group wt) represent interaction changes too small to cause major perturbations in the electron distribution of the molecules. Nevertheless, the small electronic changes which do result when a group is transferred from MeOH to DMF are reflected in a rough correlation of $\Delta\Delta H_s$ with values for the change in the Taft σ_I substituent constants[21] upon transfer of the substituent from a "normal" aprotic solvent to a "weakly protonic" solvent such as methanol.

Experimental Section

Reagents. The methanol was MCB reagent grade stated to contain 0.02% water. The DMF was Fisher reagent grade stated to contain 0.05% water. The solvents were further dried by storing over 3A and 4A molecular sieve, respectively. All solutes were commercial samples. Liquid compounds were purified by distillation whenever appreciable impurities were detected by capillary gc. The solid samples were recrystallized when necessary from suitable solvents and dried by vacuum when possible. All melting points of solids agreed well with literature values.

Calorimetry. Except as noted below, the calorimetric procedure was that described previously.[22] Solid samples were weighed into a sample holder consisting of a short piece of glass tubing to which a polyethylene cap had been fitted. The cap was attached to the glass tubing with a polypropylene thread. The sample holder was attached to an extension tube using a short section of rubber tubing (which is not immersed in solvent) and a close fitting polypropylene rod was inserted through the extension tube into the sample holder. The sample was introduced into the calorimeter by depressing the polypropylene rod to dislodge the polyethylene cap.

A thermistor inside the calorimeter served as one arm of a Wheatstone bridge. The bridge imbalance signal was fed to a digital multimeter (Keithley Model 160) which served as the null meter, and the amplified output voltage was recorded. The calorimeter was immersed in a water bath maintained at 25.00° with regulation to ±0.001°. Samples were weighed to 0.01 mg on a microbalance. Phenol samples were weighed to 0.1 mg on an analytical balance inside a nitrogen filled drybox. Liquid samples were introduced into the calorimeter from a 20-μl syringe with the needle tip immersed in solvent. Sample concentrations were 10^{-4}–10^{-3} *M*; ΔH_s values were not concentration dependent within this range.

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