

Thermodynamics of Transfer of Nonelectrolytes from Light to Heavy Water. I.* Linear Free Energy Correlations of Free Energy of Transfer with Solubility and Heat of Melting of a Nonelectrolyte

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The solubilities of twenty-four slightly soluble nonelectrolytes were measured in light and heavy water. From these solubility values the changes in the standard free energy of transfer from H₂O to D₂O could be calculated for all compounds at 298.15 K. The determined transfer free energies are generally rather small in magnitude and positive in sign. They are, however, significant having a standard error less than 10 %.

A satisfactory linear free energy correlation was obtained between the free energy of transfer of nonelectrolytes from H₂O to D₂O and the free energy of transfer of the corresponding nonelectrolytes from the gas phase to the hypothetical one aquamolal solution in H₂O. In addition, a linear correlation was found between the free energy of transfer from H₂O to D₂O and the heat of melting at the melting point of the various compounds.

When studying the structure of aqueous solutions, further informations are obtained from additional studies in deuterium oxide.² Among the earliest studies in this field with nonelectrolytes as solutes is that of Swain and Thornton,³ who employed methyl halides and determined their thermodynamic transfer properties from H₂O to D₂O in order to get their kinetic studies more complete. Gaseous nonelectrolytes have been studied by Scheraga *et al.*⁴ and by Ben Naim.⁵ Some interesting works in this field have recently been published by Dahlberg,⁶ by Ben Naim *et al.*,⁷ and by Jolicoeur and Lacroix.⁸ These all are dealing with thermodynamic

parameters of transfer of nonelectrolytes from H₂O to D₂O with special reference to the free energy of transfer. The survey by Jolicoeur and Lacroix⁸ is interesting in the sense that it deals with a series of isomeric ketones and attaches importance also to the structural changes of solutes. Transfer and exchange effects have not been adequately separated in some of these surveys.^{2,6}

In the present study the solubilities of twenty-four slightly soluble nonelectrolytes were determined in H₂O and D₂O. From these solubility values the standard free energy change of dissolution could be calculated for each solute separately in H₂O and D₂O. The difference in the obtained values represents the change in the free energy of transfer of the various nonelectrolytes from H₂O to D₂O. One of the most important criteria when choosing the solutes was that they did not contain any exchangeable hydrogen atoms. The group of nonelectrolytes which was chosen for this study consisted therefore of compounds having moderately different structures and internal polarizabilities.

The main aspect of this work was the search for possible linear free energy correlations where the free energy of transfer from H₂O to D₂O would participate. This type of possible correlations would undoubtedly be useful when solute-solvent interactions in nonelectrolyte-water solutions are considered.

* An abridgement of A. Vesala's dissertation.¹

EXPERIMENTAL

Reagents. The water employed in the experiments was distilled water which was passed through an Amberlite CG 120+CG 400 ion-exchange column. The deuterium oxide used in the experiments with sulfur dioxide, iodine, and triethylamine was a product of the Norsk Hydro-elektrisk Kvaestofaktieselskab. In the remaining experiments heavy water from the New England Nuclear Company was employed. The deuterium content in both these waters was 99.7%. Some portions of solutions containing deuterium oxide were distilled and the distillate reused. The deuterium content of the distillate was determined from its density according to the method proposed by Kirshenbaum.^{9a} Both light and heavy water were degassed by boiling under reduced pressure prior to the equilibration experiments.

The reagents used in the solubility measurements were commercial except 1,3-dinitrobenzene which was synthesized from benzene in a nitric acid-sulfuric acid mixture in the usual way.¹⁰ The commercial reagents were at least of analytical grade. The solid compounds were recrystallized twice and sublimated if possible. The liquids were generally distilled through a column. All the organic compounds were checked by gas chromatography and found more than 99% pure. Sulfur dioxide was bubbled through conc. H₂SO₄ before equilibration. The radioactive naphthalene-1-C-14 was purchased from the Radiochemical Centre and had a specific activity of 200 mCi/mmol and a radiochemical purity of 99%. The naphthalene used in the experiments was prepared by mixing inactive naphthalene and active naphthalene and by recrystallizing the mixture from absolute ethanol.

Equilibrations. The equilibrations were carried out in vessels which were modified from those constructed by Franks *et al.*¹¹ The stirring was arranged with the aid of a magnetic stirrer. When liquids were treated, equilibrium was usually obtained in 48 h, whereas it took several days to reach the equilibrium state for the solid substances. The samples were filtered through glass-wool plugs prior to analysis.

The temperature of the water baths was maintained constant with Lauda or Termomix thermostats, the temperature varying within ± 0.05 K. The apparatus and flasks were kept in darkness to prevent possible decomposition of solutes by light.

A simple vacuum line system was applied when the solubility (the constant of Henry's law) of sulfur dioxide was determined. In this case the equilibrating vessel was directly connected to a vacuum pump and a manometer by which the pressure of the system, *i.e.* the sum of partial pressures of water and sulfur dioxide, could be measured.

Methods of analyzing solutes in saturated solutions. Three different methods were applied

when the solubilities were determined, titrimetry, spectrophotometry, and radiochemistry. The solutes which were analyzed titrimetrically were sulfur dioxide, iodine, the tertiary amines, and the nitrobenzenes.

The samples of sulfur dioxide were titrated with a standard iodine solution in a phosphate buffer of pH 7. The end point of the titrations was determined visually. The pressure readings were corrected with respect to the vapor pressure of water. The vapor pressure of D₂O used in the calculations was that given by Kirshenbaum.^{9b} The system followed Henry's law provided the concentration of the formed dissociation products of sulfurous acid was subtracted from the total concentration of SO₂.¹² This correction was carried out by means of the dissociation constant of sulfurous acid previously determined.¹³

Water samples containing iodine were titrated with a standard sodium thiosulfate solution. The end point of the titration was indicated by the dead-stop method using a Metrohm 350 B potentiometer equipped with a Metrohm Polarizer E 371.

The tertiary amines were titrated with standard HCl solutions. The titration mixture comprising tripropylamine and tributylamine contained about 75% of acetone. All the amine titrations were performed with a Metrohm Combi titrator type 3 D.

The concentrations of the nitrobenzenes were also determined by a volumetric method.¹⁴ In this procedure the nitro group was reduced by the Ti³⁺ ion. The titrations were carried out manually.

Most of the studied water solubilities were analyzed spectrophotometrically using a direct method of measurements or an extraction method. The employed procedures principally resembled those of Bohon and Claussen¹⁵ and Wauchope and Getzen.¹⁶ The standard solutions were prepared in water or in 2,2,4-trimethylpentane for the direct method and the extraction method, respectively. The measured molar and molal absorptivities are presented in Table 1.

The solubility of naphthalene was determined radiochemically using the technique of liquid scintillation counting. The measuring apparatus was an LKB-Wallac 81000 liquid scintillation counter in which it was possible to choose the counting channels so that the tritium in D₂O could be dropped down to the lower channel. The C-14 pulses in the upper channel were proportional to the concentration of naphthalene-C-14 in the sample. The cpm values were corrected to the same quenching using the method proposed by Reunanen and Soini.¹⁷ The cpm value of the naphthalene used in the solubility experiments was measured in a standard solution in ethanol.

At least five parallel determinations were performed in each case, or alternatively two or

Table 1. Molar and molal absorptivities and values of λ_{\max} for solutes at 298.15 K.

Solute	λ_{\max} /nm.	ϵ	Solvent	N ^a
Methylbenzene	261.0	248.8 ± 2.0 ^b	Water	6
Ethylbenzene	260.0	233.5 ± 2.7	»	3
1,3-Dimethylbenzene	264.0	249.1 ± 8.5	»	4
1,3,5-Trimethylbenzene	264.0	299 ± 15	»	7
Diphenyl	247.0	16810 ± 590	»	5
Benzene	254.0	150.0 ^c ± 5.5	2,2,4-Tri-	8
Chlorobenzene	264.5	198.7 ^c ± 1.5	methylpen-	10
Bromobenzene	265.0	141.3 ^c ± 0.92	tane	7
Iodobenzene	257.5	471.7 ^c ± 6.5	»	5
1,3-Dichlorobenzene	270.5	325.1 ^c ± 4.5	»	9
1,4-Dichlorobenzene	273.0	371.6 ^c ± 4.0	»	9
Methoxybenzene	277.5	1633 ^c ± 6	»	4
Ethoxybenzene	271.0	1382 ^c ± 8	»	4
Diphenylether	271.0	1385 ^c ± 16	»	4
Acenaphthene	288.5	4676 ^c ± 24	»	4
Phenanthrene	292.0	9822 ^c ± 91	»	4

^a Number of measurements. ^b Mean and standard deviation. ^c Molal absorptivity.

three measurements at five or more temperatures, from which the values at 298.15 K could be calculated by the method of least squares.

RESULTS

The measured solubilities in H₂O as well as those reported previously are presented in Table 2. It is seen that the agreement of the determined values with the literature values is good. The solubilities are expressed in aquamolal units, *i.e.* in numbers of mol of solute dissolved in 55.51 mol of water. This unit is comparable with the mol fraction and has the advantage of being free from temperature and density effects.

When the solubility of a substance is relatively low, nearly ideal conditions can be assumed to exist in the solution. In this case the change in the free energy when the substance is transferred from the gas phase to the solution is

$$\Delta G_s^\circ = -RT \ln m \quad (1)$$

The standard state for a solute is defined as a hypothetical one-aquamolal solution, where the vapour pressure of the solute is one atmosphere (1 atm = 101.325 kPa). The letter *m* denotes thus aquamolality in the above equation. ΔG_s° can then be considered as the standard free energy change of the process

substance (g, 1 atm) = substance (aq, hypoth. 1 m soln) (2)

When the solute is a gas, both its vapor pressure and solubility have to be determined. In the case of the solute being a solid or a liquid at 298.15 K, the ΔG° values for processes (3) and (4) must be known to allow the desired changes in free energy for process (2) to be calculated from the measured free energy changes in processes (5) and (6).

substance (l) = substance (g, 1 atm) (3)

substance (s) = substance (g, 1 atm) (4)

substance (l) = substance (aq, hypoth. 1 m soln) (5)

substance (s) = substance (aq, hypoth. 1 m soln) (6)

The changes in the free energy of transfer of a solute from H₂O to D₂O in process (7) is simply defined by eqn. (8).

subst. (H₂O, hypoth. 1 m soln) = subst. (D₂O, hypoth. 1 m soln) (7)

$$\Delta G_t^\circ = \Delta G^\circ(\text{D}_2\text{O}) - \Delta G^\circ(\text{H}_2\text{O}) \quad (8)$$

ΔG_t° can as well be calculated by eqn. (9)

$$\Delta G_t^\circ = -RT \ln (m_{\text{D}_2\text{O}}/m_{\text{H}_2\text{O}}) \quad (9)$$

Table 2. Solubilities of nonelectrolytes in light water determined in this work and reported in literature, respectively. (The values refer to 298 K if not otherwise stated.)

Solute	Solubility/mol 10^{-6} g $^{-1}$ This work ^a		Previously reported	Ref.
1. Sulfur dioxide	1100	± 20	1230 1270	12 18
2. Iodine	1.29	± 0.01	1.33	19
3. Nitrobenzene	14.6	± 0.4	16.7 ^b	20
4. 1,3-Dinitrobenzene	5.12	± 0.05	3.98 ^b 4.82	20 21
5. Triethylamine	728	± 28	762	22
6. Tripropylamine	5.22	± 0.10		
7. Tributylamine	0.765	± 0.015	0.2 ^c	23
8. Benzene	24.4	± 0.1	22.0 23.0 22.4 22.9	24 15 25 26
9. Methylbenzene	6.81	± 0.08	6.2 6.84 5.78 6.00 5.62	20 15 25 27 26
10. 1,3-Dimethylbenzene	1.94	± 0.01	1.86 1.48	15 28
11. 1,3,5-Trimethylbenzene	0.328	± 0.005		
12. Ethylbenzene	1.91	± 0.02	1.97 1.43	15 26
13. Chlorobenzene	4.11	± 0.07	4.45 4.95 4.33 ^b	27 29 20
14. Bromobenzene	2.84	± 0.03	2.84 ^b	20
15. Iodobenzene	1.12	± 0.03	1.7 ^b	30
16. 1,3-Dichlorobenzene	0.700	± 0.007	0.840	31
17. 1,4-Dichlorobenzene	0.580	± 0.008	0.565 0.52	16 20
18. Methoxybenzene	14.2	± 0.4	14	32
19. Ethoxybenzene	4.66	± 0.04	4.5	32
20. Diphenylether	0.110	± 0.005		
21. Diphenyl	0.0491	± 0.0004	0.0459 0.0486	16 15
22. Naphthalene	0.251	± 0.002	0.244 0.270	16 15
23. Acenaphthene	0.0233	± 0.0003	0.0252	16
24. Phenanthrene	0.00677	± 0.00008	0.00662	16

^a Mean and standard deviation. ^b 303 K. ^c 291 K.

The results are listed in Table 3, where as well ΔG°_t values obtained by other investigators are collected.

DISCUSSION

It is seen that the values of ΔG°_t for nonelectrolytes are rather small and varying in sign and it is difficult to draw any direct conclusions from these values. When the free

energies of transfer are plotted against the free energies of dissolution for the thirty-four different nonelectrolytes, a fairly good linear correlation is obtained (Fig. 1). The ΔG° values for process (2) were evaluated from the values determined in this study and from values found in literature.³⁷⁻³⁹ When the ΔG° values for processes (3) or (4) were not found in literature, they were evaluated by means of the values of vapor pressure. For three of the compounds,

Table 3. Free energies of transfer of nonelectrolytes from light to heavy water at 298.15 K.

Solute	$\Delta G^{\circ}_t/\text{J mol}^{-1}$	Ref.
1. Sulfur dioxide	93 ± 150^a	This work
2. Iodine	544 ± 33	»
	451	19
3. Nitrobenzene	218 ± 92	This work
	238	33
4. 1,3-Dinitrobenzene	314 ± 46	This work
5. Triethylamine	533 ± 93	»
6. Tripropylamine	138 ± 33	»
7. Tributylamine	-188 ± 25	»
8. Benzene	195 ± 25	»
	0 ± 63	6
	196 ± 73	7
9. Methylbenzene	287 ± 12	This work
	105 ± 63	6
10. 1,3-Dimethylbenzene	203 ± 25	This work
	188 ± 50	6
11. 1,3,5-Trimethylbenzene	463 ± 46	This work
12. Ethylbenzene	135 ± 17	»
13. Chlorobenzene	103 ± 125	»
14. Bromobenzene	322 ± 33	»
15. Iodobenzene	429 ± 29	»
16. 1,3-Dichlorobenzene	246 ± 33	»
17. 1,4-Dichlorobenzene	278 ± 50	»
18. Methoxybenzene	660 ± 134	»
19. Ethoxybenzene	290 ± 33	»
20. Diphenylether	460 ± 138	»
21. Diphenyl	574 ± 46	»
	-109 ± 148	7
22. Naphthalene	343 ± 38	This work
	452 ± 63	6
23. Acenaphthene	468 ± 46	This work
24. Phenanthrene	804 ± 58	»
25. Argon	-211	5
26. Methane	-134	7
27. Ethane	-147	7
28. Propane	-60	4
29. Butane	-73	4
30. Carbon dioxide	2	34
	8	13
31. Methyl fluoride	-58^b	3
32. Methyl chloride	76^b	3
33. Methyl bromide	151^b	3
34. Methyl iodide	230^b	3
35. <i>t</i> -Butyl chloride	-68^c	35
36. 1,2-Dimethylbenzene	351	6
37. 1,3,5-Trinitrobenzene	481	36

^a Standard error. ^b 302.5 K. ^c 287 K.

namely, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, and tributylamine, the ΔG° values could not be estimated because their vapor pressures at 298 K were difficult to evaluate and no reliable values could be found in the literature. It must also be noted that some points in the plot do not refer to measurements at 298 K.

When taken into account the varying type of compounds studied the correlation may appear satisfactory. The correlation becomes still better when the compounds which are highly polarizable like sulfur dioxide and nitrobenzene are omitted.

A correlation that closely resembles the free

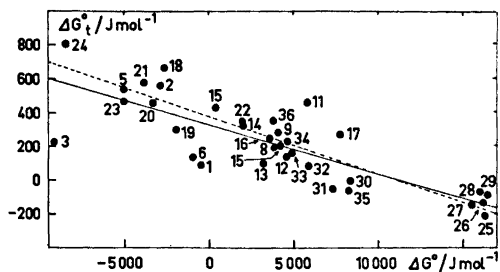


Fig. 1. Correlation between the free energy of transfer from H₂O to D₂O (ΔG°_t) and the free energy of dissolution (ΔG°) of some nonelectrolytes (For numbers, see Table 3)

slope	-0.0287	-0.0338 ^a
intercept	331	380 ^a
corr. coeff.	-0.814	-0.902 ^a

^a Dotted line (points 1, 3, and 6 omitted).

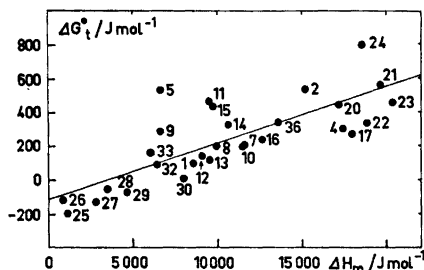


Fig. 2. Correlation between the free energy of transfer from H₂O to D₂O (ΔG°_t) and the heat of melting (ΔH_m) of some nonelectrolytes (For numbers, see Table 3)

slope	0.0332
intercept	-113
corr. coeff.	0.774

energy correlation mentioned above is that between partition coefficients and aqueous solubility of organic liquids reported by Hansch *et al.*⁴⁰ in their study on partition coefficients between water and octanol. Different slopes and intercepts are found for the different types of organic liquids but the overall correlation is good.

It is to be expected that in this kind of ideal case there exists a linear correlation between solubilities and heats of melting. It is therefore natural to assume that there must exist a linear correlation between the free energies of transfer and the heats of melting. It is, however, to be expected that polarization effects do not appear in this kind of correlation. The heats

of melting at melting points for twenty-nine compounds were taken from literature.^{27b,40} When plotting ΔG°_t against ΔH_m a fairly good linear correlation is indeed obtained (Fig. 2). The values for sulfur dioxide and nitrobenzene (and 1,3-dinitrobenzene) appear to fit satisfactorily into the plot. Since the value of the heat of melting for 1,3,5-trinitrobenzene was not found in literature the value of ΔH_m for trinitrotoluene (22 500 J mol⁻¹) may be considered as a rough estimate. By so doing, a rather good fit is obtained (ΔG°_t for 1,3,5-trinitrobenzene is 481 J mol⁻¹). The point for triethylamine deviates most from the correlation line. If the ΔH_m value for triethylamine were replaced by that for (C₂H₅)₃N·3H₂O, 15 000–16 000 J mol⁻¹, evaluated by Kohler *et al.*,⁴¹ a better fit could be obtained. As for the other deviations there is no such uniform group of compounds whose members would systematically deviate. The anomalies observed may thus be regarded as fortuitous.

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