Hydrogen Bonding. Part 25. The Solvation Properties of Methylene Iodide

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Ostwald solubility coefficients, L, have been determined for 37 gases and vapours in methylene iodide at 298 K, and have been correlated through equation (i), where the solute explanatory

$$\log L = -0.74 + 0.32R_2 + 1.34\pi_2^H + 0.83\alpha_2^H + 1.19\beta_2^H + 0.87 \log L^{16} \qquad (i)$$

variables are R_2 an excess molar refraction, π_2^H the solute dipolarity/polarisability, α_2^H and β_2^H the solute hydrogen-bond acidity and basicity, and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on hexadecane at 298 K. Similar equations have been constructed for solvation of solutes in tetrachloromethane, trichloromethane and 1,2-dichloroethane using literature data. It is shown that polarisability effects favour solvation in methylene iodide, through the R_2 term, but that such effects enhance the solubility of polarisable solutes only moderately: thus the R_2 term contributes 0.4 log units more in methylene iodide than in trichloromethane for the solute benzene. Examination of $\Delta G°$, $\Delta H°$ and $\Delta S°$ for solvation of gaseous solutes suggests also that polarisability effects in methylene iodide are not very much larger than in the other halogenated solvents.

Of all the common organic solvents, methylene iodide has the highest refractive index, η, and hence a particularly large excess molar refraction, R_2, see Table 1. Since the dipole moment, μ, relative permittivity, ε, and E_T value of methylene iodide are rather low in value, it seemed to us that the solvation properties of this solvent might be dominated by non-specific interactions such as dispersion and polarisability, rather than by specific interactions such as hydrogen-bonding. We have therefore determined the solubility of 37 gaseous non-electrolytes in methylene iodide at 298 K in order to investigate the type of solute–solvent interactions that influence solubility. Our method of analysis is based on the general solvation equation, eqn. (1),[1-4] where L is the Ostwald solubility coefficient or gas–liquid partition coefficient (sometimes denoted as K) for a series of gaseous solutes on a given bulk liquid solvent.

$$\log L = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (1)$$

The solute descriptors in eqn. (1) are R_2 an excess molar refraction,[1] π_2^H the solute dipolarity/polarisability,[2-6] α_2^H and β_2^H the solute hydrogen-bond acidity and basicity,[5,6] and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on hexadecane at 298 K.[5-7] The constants in eqn. (1) are found by the method of multiple linear regression analysis (MLRA) and reflect the solvation properties of the solvent as follows: r is the ability of the solvent to interact with π and R electron pairs, s is the solvent dipolarity/polarisability, a is the solvent hydrogen-bond basicity, b is the solvent hydrogen-bond acidity, and l is an interesting parameter that refers to the ability of the solvent to interact with a methylene CH_2 increment,[8] and can be regarded as a measure of the lipophilicity of the solvent.

In order to obtain values of L on methylene iodide for a wide variety of solutes, we used the gas–liquid chromatographic (GLC) method[3,7] in which the stationary phase is methylene iodide coated onto an inert support. However, for very volatile solutes such as the rare gases and lower alkanes, measurements by the GLC method are very difficult to make, and so we determined a few L-values by the classical static method.[9,10] The only previous measurements with methylene iodide are six L-values reported by Carr *et al.*,[11] to which we refer later.

Table 1 Some properties of methylene iodide and other solvents[a]

	CH_2I_2	$CHCl_3$	CCl_4	$ClCH_2CH_2Cl$
η_D^{20}	1.7425	1.4459	1.4601	1.4448
R_2	1.453	0.425	0.458	0.416
μ/D	1.11	1.01	0	1.28
ε^{25}	5.32	4.80	2.23	10.36
E_T	37.5	39.1	32.5	41.9
V_X	76.6	61.7	73.9	63.5

[a] η_D^{20} is the refractive index, R_2 is the excess molar refraction in (cm^3 mol^{-1})/10, μ is the dipole moment in Debyes, ε^{25} is the relative permittivity, E_T is Reichardt's solvent parameter, and V_X is the characteristic volume in cm^3 mol^{-1}.

Experimental

Gas–Liquid Chromatography.—Methylene iodide (1 g) and chromosorb GAWDMCS 40–60 mesh (10 g) were weighed into a round bottomed flask, toluene (40 cm^3) added, the mixture swirled to dissolve the methylene iodide, and the solvent carefully removed using a rotary evaporator at room temperature. The coated inert support was packed into glass columns, 3 mm i.d., 80 cm long, and the latter purged with nitrogen for 30 min at 298 K. Relative retention times were obtained using a Perkin–Elmer F11 chromatograph equipped with a liquid thermostat bath (±0.05 K) and Negretti and Zambra flow controllers. Solutes used were of commercial grade.

Static Measurements.—Ostwald solubility coefficients were obtained using an apparatus described in detail elsewhere,[9] and which is based on a design by Ben Naim and Baer.[10] It consists

Table 2 Values of log L for solutes on methylene iodide at 298 K

Solute	log τ	log L
Argon		−1.46
Methane		−1.07
Ethane		−0.25
Hexane	−1.86	1.51
Heptane	−1.28	2.09
Octane	−0.90	2.47
Nonane	−0.45	2.92
Decane	0.00	3.37
Undecane	0.45	3.82
Dichloromethane	−1.32	2.05
Tetrachloromethane	−1.07	2.30
1,2-Dichloroethane	−0.64	2.73
1,4-Dioxane	0.25	3.62
Acetone	−0.94	2.43
Butanone	−0.56	2.81
Pentan-2-one	−0.28	3.09
Methyl formate	−1.50	1.87
Ethyl formate	−1.18	2.19
Methyl acetate	−1.05	2.32
Nitromethane	−0.59	2.78
Nitroethane	−0.23	3.14
Methanol	−1.49	1.88
Ethanol	−1.24	2.13
Propan-1-ol	−0.78	2.59
Propan-2-ol	−1.20	2.17
Butan-1-ol	−0.34	3.03
Butan-2-ol	−0.71	2.66
Pentan-1-ol	0.13	3.50
2,2,2-Trifluoroethanol	−1.51	1.86
1,1,1,3,3,3-Hexafluoropropan-2-ol	−1.57	1.80
Benzene	−0.56	2.81
Toluene	−0.08	3.29
Ethylbenzene	0.30	3.67
1,3,5-Trimethylbenzene	0.59	3.96
Butylbenzene	0.94	4.31
3-Chlorotoluene	0.75	4.12
4-Chlorotoluene	0.63	4.00

Table 3 Comparison of log L and log τ on methylene iodide at 298 K

Solute	log L[a]	log τ[b]	Δ
Octane	2.46	−0.90	3.36
Nitromethane	2.75	−0.59	3.39
Butanone	2.82	−0.56	3.37
Toluene	3.32	−0.08	3.40
Dioxane	3.60	0.25	3.35
	Average		3.37
Ethanol	2.08	−1.24	3.32

[a] From ref. 11. [b] This work, relative to decane.

essentially of a burette system, a manometer and a solution vessel (40 cm^3). As the vapour pressure of the methylene iodide solvent is small, 0.17 kPa, the solution vessel was used for solvent degassing. The total pressure was chosen so that the partial pressure of the gas under study was about 101.33 kPa. The temperature of the air thermostat bath holding the apparatus was controlled to within ±0.2 K and temperature control of the solution vessel was to within ±0.05 K. The gases were from *Sociedad Española del Oxigeno*, and their mol percentage purities were Ar; 99.9990, CH_4; 99.90, and C_2H_6, 99.0. The methylene iodide was an Aldrich product with 99% purity. The mean precision in the Ostwald coefficients is ± 3%.

Results and Discussion

Since methylene iodide boils at 454 K, we thought that it would be involatile enough to use as a GLC stationary phase at 298 K. In the event, we found that methylene iodide was readily leached from the stationary phase even at 298 K, so that it was quite impossible to determine absolute L-values. We therefore made up several GLC columns with methylene iodide, and by using each column for only a few hours before discarding it, we were able to obtain relative retention times, τ, of a reasonable number of solutes (Table 2). Fortunately, Carr *et al.*[11] have determined absolute L-values for six solutes on methylene iodide at 298 K using a static head-space analysis method, and so we were able to match our relative retention times with his absolute L-values, Table 3. With the exception of ethanol solute, probably rather difficult to deal with by either method, there is excellent agreement, with $\log L = \log \tau + 3.37$, so that all our $\log \tau$ values can be converted into absolute $\log L$ values, Table 2, with a standard deviation of 0.02 log units.

Also given in Table 2 are the absolute values for argon, methane and ethane obtained by the usual gas volumetric technique. These are quite important, because they extend the range of experimental log L values by no less than 3 log units, *i.e.* from 2.8 log units to 5.8 log units.

Before analysing results by the full eqn. (1), it is useful to compare our GLC and static log L values. Now for the rare gases and alkanes, all the solute descriptors in eqn. (1) are zero, except for $\log L^{16}$. Hence a plot according to the reduced eqn. (2)

$$\log L = c + l \log L^{16} \qquad (2)$$

should be a straight line for rare gases and alkanes. This is indeed so, as shown in eqn. (3), so we can take it that our two

$$\log L = -0.78 + 0.887 \log L^{16} \qquad (3)$$

$$n = 9 \quad \rho = 0.9996 \quad \text{s.d.} = 0.057$$

very different methods for obtaining L-values have yielded quite compatible results. In eqn. (3), and elsewhere, n is the number of data points, ρ is the overall correlation coefficient, and s.d. is the standard deviation.

We can now analyse the full set of 37 compounds, using eqn. (1). The descriptors needed are in Table 4 and result in eqn. (4). It is noteworthy that the c- and l-constants in eqn. (4) are very close to those in eqn. (3), as required by the method of analysis.

$$\log L = -0.74 + 0.32R_2 + 1.34\pi_2^H + 0.83\alpha_2^H + 1.19\beta_2^H + 0.866 \log L^{16} \qquad (4)$$

$$n = 37 \quad \rho = 0.9979 \quad \text{s.d.} = 0.089 \quad F = 1461$$

The fit of the log L values to eqn. (4) is as good as could be expected, with an overall correlation coefficient of 0.9979 and a standard deviation in log L of 0.089 log units, and certainly good enough for interpretive purposes. Chemically, the constants in eqn (4) are reasonable. For example, the a-value of 0.83 indicates that methylene iodide is somewhat basic, and the b-value of 1.19 shows that the solvent is a hydrogen-bond acid, as expected. However, it would be useful to be able to compare the constants in eqn. (4) with those obtained for other solvents, but this requires knowledge of a rather large number of values of log L for an assorted collection of solutes in a given solvent. These values of log L can be obtained directly in the case of gaseous or volatile solutes, but for most organic solutes this direct method is not convenient. In these cases, it is possible to calculate Henry's constants, and thence L-values, from infinite dilution Raoult's law activity coefficients, γ^∞, and the compound saturated vapour pressure, especially if the assumption is made (*c.f.* ref. 11) that the vapour is ideal. We have gathered together log L values obtained by these methods for a number of halogenated solvents. In the event, enough values of log L to

Table 4 Solute descriptors used in the regression equations

Solute	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
Argon	0.000	0.000	0.000	0.000	−0.688
Methane	0.000	0.000	0.000	0.000	−0.323
Ethane	0.000	0.000	0.000	0.000	0.492
Hexane	0.000	0.000	0.000	0.000	2.668
Heptane	0.000	0.000	0.000	0.000	3.173
Octane	0.000	0.000	0.000	0.000	3.677
Nonane	0.000	0.000	0.000	0.000	4.182
Decane	0.000	0.000	0.000	0.000	4.686
Undecane	0.000	0.000	0.000	0.000	5.191
Dichloromethane	0.387	0.570	0.100	0.050	2.019
Tetrachloromethane	0.458	0.380	0.000	0.000	2.823
1,2-Dichloroethane	0.416	0.640	0.100	0.110	2.573
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892
Propanone	0.179	0.700	0.040	0.490	1.696
Butanone	0.166	0.700	0.000	0.510	2.287
Pentan-2-one	0.143	0.680	0.000	0.510	2.755
Methyl formate	0.192	0.680	0.000	0.380	1.285
Ethyl formate	0.146	0.660	0.000	0.380	1.845
Methyl acetate	0.142	0.640	0.000	0.450	1.911
Nitromethane	0.313	0.950	0.060	0.310	1.892
Nitroethane	0.270	0.950	0.020	0.330	2.414
Methanol	0.278	0.440	0.430	0.470	0.970
Ethanol	0.246	0.420	0.370	0.480	1.485
Propan-1-ol	0.236	0.420	0.370	0.480	2.031
Propan-2-ol	0.212	0.360	0.330	0.560	1.764
Butan-1-ol	0.224	0.420	0.370	0.480	2.601
Butan-2-ol	0.217	0.360	0.330	0.560	2.338
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106
2,2,2-Trifluoroethanol	0.015	0.600	0.570	0.250	1.224
1,1,1,3,3,3-Hexafluoropropan-2-ol	−0.240	0.550	0.770	0.100	1.392
Benzene	0.610	0.520	0.000	0.140	2.786
Toluene	0.601	0.520	0.000	0.140	3.325
Ethylbenzene	0.613	0.510	0.000	0.150	3.778
1,3,5-Trimethylbenzene	0.649	0.520	0.000	0.190	4.344
Butylbenzene	0.600	0.510	0.000	0.150	4.730
3-Chlorotoluene	0.736	0.670	0.000	0.070	4.179
4-Chlorotoluene	0.705	0.670	0.000	0.070	4.205

carry out an analysis *via* eqn. (1) were collected for three halogenated aliphatic solvents, *viz.* trichloromethane, tetrachloromethane and 1,2-dichloroethane as set out in Table 5. An analysis of the various sets of $\log L$ values through eqn. (1) results in equations that are summarised in Table 6.

Bearing in mind the scattered nature of the γ^∞ values used, the equations listed in Table 6 are quite reasonable, with correlation constants ranging from 0.9969 to 0.9993 and standard deviations in $\log L$ from 0.069 to 0.153 log units. The goodness-of-fit of these equations means that they can, indeed, be used as a comparison with results for methylene iodide. Before so doing, we examine the equations in Table 6 to check that the constants are chemically reasonable. In the case of tetrachloromethane, the very small values of the *s*-, *a*-, and *b*-constants are all compatible with the lack of dipolarity or of hydrogen-bond strength in this solvent, whereas the rather large *l*-constant indicates a large lipophilicity, again exactly as expected. With both trichloromethane and 1,2-dichloroethane, the higher *s*-constants indicate some dipolarity as expected from the dipole moments given in Table 1. These two solvents are both weak bases, with very similar *a*-constants, but trichloromethane is an appreciably stronger hydrogen-bond acid, with a reasonably large *b*-constant. All this is in accord with the chemical nature of the chlorinated solvents, and so we can conclude that application of eqn. (1) does lead to reasonable correlation equations.

Comparison of the constants for methylene iodide with those for the chlorinated solvents does not reveal any striking difference. The *s*-, *a*-, and *b*-constants for methylene iodide are about as expected from the dipolarity and the hydrogen-bond properties of this solvent. Thus, although the $s.\pi_2^H$ term reflects a mixture of dipolarity and polarisability, for the solvents in Table 6 there seems to be a reasonable connection between the *s*-constant and dipolarity only. The only term in eqn. (1) that reflects the very high polarisability of methylene iodide is the $r.R_2$ term, in which the *r*-constant for methylene iodide is considerably more positive than those for the chlorinated solvents. This has the effect of increasing the solubility of polarisable solutes in methylene iodide, although not by a great amount. Thus the $r.R_2$ term contributes about 0.4 log units more to the solubility of benzene in methylene iodide than it does to solubility in trichloromethane. Although such effects are in the direction expected, they are comparatively small, and our conclusion is that the large polarisability of solvent methylene iodide does not lead to any large increase in the solubility of polarisable solutes.

We can quantify the various factors leading to the solubility of gaseous solutes by calculating the influence of each term in eqn. (1) on the overall $\log L$ values. Results are in Table 7 for some representative solutes. In all cases the $l \log L^{16}$ term makes the largest contribution. Bearing in mind that this term includes a cavity effect that makes a negative contribution to $\log L$ and a general dispersion effect that makes a positive contribution, it is clear that largest solute–solvent interaction term aiding solvation is this general dispersion effect in all cases. Although hydrogen-bonding is important, for example the acidity of ethanol contributes 0.31 log units and the basicity of ethanol contributes 0.57 log units to solvation in methylene iodide, it is a much smaller effect than that of general dispersion. As mentioned above, the large polarisability of methylene iodide is

Table 5 Values of log *L* for solutes in some chlorinated solvents at 298 K

Solute	$CHCl_3$	CCl_4	CH_2ClCH_2Cl	Solute	$CHCl_3$	CCl_4	CH_2ClCH_2Cl
Helium		-1.56^{a}		Trifluorochloromethane		0.44^{s}	
Neon		-1.37^{a}		Difluorodichloromethane		1.41^{s}	
Argon		-0.47^{b}		1,1,2-Trifluorotrichloroethane	2.37^{m}	2.40^{m}	2.05^{m}
Krypton	0.01^{b}	0.12^{b}		Diethyl ether		2.58^{t}	
Xenon	0.53^{b}	0.52^{b}		Dipropyl ether		3.54^{t}	
Radon	1.12^{b}			Diisopropyl ether		3.10^{e}	
Hydrogen	-1.18^{b}	-1.11^{a}	-1.26^{b}	Dibutyl ether		4.60^{t}	4.38^{u}
Oxygen		-0.52^{a}		Methyl butyl ether		3.22^{t}	
Nitrogen	-0.87^{b}	-0.79^{a}		Ethyl butyl ether		3.60^{t}	
Nitrous oxide	0.71^{b}	0.63^{b}		Dimethoxymethane		2.68^{t}	
Carbon monoxide	-0.71^{b}	-0.66^{a}	-0.84^{b}	Diethoxymethane		3.64^{t}	
Methane		-0.14^{a}		1,2-Dimethoxyethane		3.40^{t}	
Tetrafluoromethane		-0.60^{a}		1-Methoxy-2-ethoxyethane		4.29^{t}	
Sulfur hexafluoride		0.02^{a}		Bis(2-methoxyethyl) ether		4.89^{t}	
Ethane		0.73^{b}		Tetrahydrofuran	3.86^{f}	3.13^{v}	
Propane		1.34^{b}		Dioxane	4.44^{h}	3.64^{h}	
Butane		1.96^{c}		Propanone	3.44^{f}	2.38^{s}	3.13^{e}
Isobutane		1.74^{c}		Butanone		2.99^{f}	3.64^{h}
Pentane		2.36^{d}	1.99^{e}	Hexan-2-one		3.93^{w}	
Hexane	2.87^{f}	2.98^{d}	2.51^{f}	Octan-2-one		4.91^{w}	
Heptane		3.48^{d}	2.98^{g}	Cyclopentanone		4.06^{x}	
Octane	3.90^{h}	4.05^{h}	3.44^{h}	Cyclohexanone		4.57^{x}	
Hexadecane		8.36^{j}	7.08^{i}	Ethyl acetate			3.45^{f}
Cyclohexane		3.22^{d}	2.79^{i}	Acetonitrile	3.28^{f}	2.22^{e}	3.23^{f}
Ethane		0.57^{c}		Proprionitrile		2.77^{e}	3.65^{f}
Propene		1.35^{c}		Ammonia	1.72^{b}		
But-1-ene		1.83^{c}		Methylamine		1.71^{b}	
Isobutene		1.79^{c}		Dimethylamine		2.11^{b}	
Pent-1-ene			2.10^{e}	Trimethylamine	2.78^{y}	2.12^{b}	
3-Methylbut-1-ene			1.99^{e}	Triethylamine	4.01^{r}	3.54^{r}	3.21^{r}
2-Methylbut-1,3-diene		2.56^{e}	2.42^{e}	Nitromethane	3.25^{h}	2.54^{h}	3.57^{h}
Chloromethane	1.82^{k}	1.61^{k}		2-Nitropropane		3.35^{f}	
Chloropropane	2.66^{e}	2.71^{e}		Methanol	2.51^{f}	1.50^{v}	2.16^{f}
2-Chloro-2-methylpropane		2.68^{l}	2.62^{l}	Ethanol	2.94^{h}	2.06^{h}	2.63^{h}
Dichloromethane	2.69^{m}	2.46^{e}	2.73^{e}	Propanol		2.59^{v}	3.15
Trichloromethane	3.07^{m}	2.94^{e}	3.06^{e}	Butanol		3.26^{v}	
Tetrachloromethane	3.25^{m}	3.24^{n}	3.04^{e}	2-Methylpropan-2-ol		2.58^{v}	
1,1-Dichloroethane	3.01^{m}	2.77^{m}	2.95^{m}	Carbon disulfide		2.66^{e}	
1,2-Dichloroethane	3.44^{m}	3.15^{m}	3.47^{n}	Dimethyl sulfoxide	6.56^{aa}		
1,1,1-Trichloroethane	3.24^{m}	3.11^{m}	3.11^{m}	Tetramethyltin	3.00^{bb}	3.24^{cc}	2.64^{bb}
1,1,2-Trichloroethane	3.87^{m}	3.71^{m}	4.01^{m}	Benzene	3.51^{f}	3.24^{p}	3.32^{j}
1,2-Dichloropropane		3.41^{o}		Toluene	4.07^{h}	3.82^{h}	3.89^{h}
1,3-Dichloropropane		3.81^{o}		*o*-Xylene			4.49^{dd}
Chlorobutane		3.16^{p}		*m*-Xylene			4.38^{dd}
Bromoethane	2.78^{f}	2.53^{e}	2.64^{e}	*p*-Xylene		4.20^{ee}	4.37^{dd}
Bromopropane		3.06^{p}		Naphthalene		5.59^{w}	
2-Bromo-2-methylpropane		3.03^{l}	2.95^{l}	Anthracene		8.17^{w}	
Bromobutane		3.48^{p}		Chlorobenzene		4.14^{w}	
Iodomethane	2.78^{q}	2.53^{q}	2.65^{e}	*o*-Dichlorobenzene		4.98^{w}	
Iodoethane	3.25^{r}	3.06^{r}	3.08^{r}	Bromobenzene		4.57^{w}	
Iodopropane		3.64^{p}		Iodobenzene		4.99^{w}	
Iodobutane		4.08^{p}					

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Table 6 Analysis of log L values into halogenated solvents at 298 K using eqn. (1)

Solvent	c	r	s	a	b	l	n	ρ	s.d.	F
CH_2I_2	−0.74	0.32	1.34	0.38	1.19	0.866	37	0.9979	0.089	1461
$CHCl_3$	0.10	−0.35	1.26	0.60	1.18	0.994	35	0.9969	0.153	754
CCl_4	0.23	−0.20	0.35	0.07	0.27	1.041	89	0.9993	0.069	11877
CH_2ClCH_2Cl	−0.01	−0.28	1.72	0.73	0.59	0.926	40	0.9977	0.096	1443

Table 7 Contributions of the terms in eqn. (1) to log L values at 298 K

Term	rR_2	$s\pi_2^H$	$s\alpha_2^H$	$b\beta_2^H$	$l \log L^{16}$
CH_2I_2					
Hexane	0.00	0.00	0.00	0.00	2.31
Benzene	0.20	0.70	0.00	0.17	2.41
Propanone	0.06	0.94	0.03	0.58	1.47
Ethanol	0.08	0.56	0.31	0.57	1.29
Anthracene	0.73	1.80	0.00	0.31	6.55
$CHCl_3$					
Hexane	0.00	0.00	0.00	0.00	2.65
Benzene	−0.21	0.66	0.00	0.17	2.77
Propanone	−0.06	0.88	0.02	0.58	1.69
Ethanol	−0.09	0.53	0.22	0.57	1.48
Anthracene	−0.80	1.69	0.00	0.31	7.52
CCl_4					
Hexane	0.00	0.00	0.00	0.00	2.78
Benzene	−0.12	0.18	0.00	0.04	2.90
Propanone	−0.04	0.25	0.00	0.13	1.77
Ethanol	−0.05	0.15	0.03	0.13	1.55
Anthracene	−0.46	0.47	0.00	0.07	7.88
$(CH_2Cl)_2$					
Hexane	0.00	0.00	0.00	0.00	2.47
Benzene	−0.17	0.89	0.00	0.08	2.58
Propanone	−0.05	1.20	0.03	0.29	1.57
Ethanol	−0.07	0.72	0.27	0.28	1.38
Anthracene	−0.64	2.30	0.00	0.15	7.01

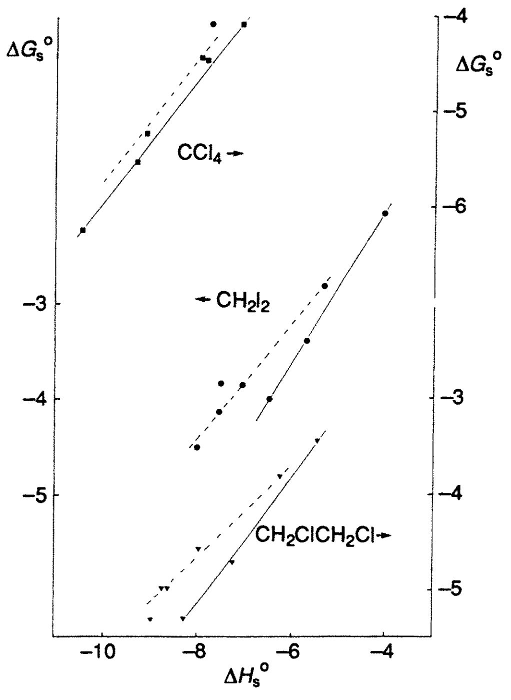

Fig. 1 Plot of ΔG_s^0/kcal mol^{-1} against ΔH_s^0/kcal mol^{-1}. Full lines are for n-alkanes, broken lines for the remaining solutes in Table 8.

Table 8 Thermodynamics of solvation of solutes in halogenated solvents at 298 K[a]

Solute	ΔG_s^0	ΔH_s^0	ΔS_s^0
CH_2I_2			
Hexane	−2.06	−4.06	−6.7
Octane	−3.37	−5.70	−7.8
Nonane	−3.98	−6.51[b]	−8.5
Cyclohexane	−2.81[b]	−5.34	−8.5
Benzene	−3.83	−7.08	−10.9
Toluene	−4.49	−8.00	−11.8
Butanone	−3.83	−7.51	−12.3
Butan-1-ol	−4.13	−7.55	−11.5
CCl_4			
Hexane	−4.07	−7.11	−10.2
Octane	−5.53	−9.36	−12.8
Nonane	−6.24[b]	−10.47	−14.2
Cyclohexane	−4.39	−7.70	−11.1
Benzene	−4.42	−7.96	−11.9
Toluene	−5.21	−9.12	−13.1
Butanone	−4.08	−7.73	−12.2
Butan-1-ol	−4.45	−7.87	−11.5
$(CH_2Cl)_2$			
Hexane	−3.42	−5.45	−6.8
Octane	−4.69	−7.23	−8.5
Nonane	−5.29[b]	−8.25	−9.9
Cyclohexane	−3.81	−6.13	−7.8
Benzene	−4.53	−7.97	−11.5
Toluene	−5.31	−8.98	−12.3
Butanone	−4.97	−8.69	−12.5
Butan-1-ol	−4.96[b]	−8.61	−12.2

[a] Standard states unit concentration gas and unit concentration solution; ΔG_s^0 and ΔH_s^0 in kcal mol^{-1} and ΔS_s^0 in cal K^{-1} mol^{-1}. 1 cal = 4.184 J. [b] Estimated values.

reflected only in the rR_2 term which contributes some 0.4 log units more to solvation of benzene in methylene iodide than to solvation in trichloromethane. However, if extraordinarily polarisable solutes are considered, this effect can be quite large. We give in Table 7 results for anthracene, with an excess molar refraction of 2.29 units. Now the rR_2 term leads to an extra 1.53 log units to solvation in methylene iodide over solvation in trichloromethane.

Although polarisability effects in methylene iodide generally are rather small over those in the other halogenated solvents, this is in terms of log L, or the equivalent standard solvation Gibbs energy, ΔG_s^0. It is possible that larger effects might be observed on other thermodynamic parameters, and so we set out in Table 8 values of ΔG_s^0, ΔH_s^0 and ΔS_s^0 for solvation of gaseous solutes. The ΔH_s^0 values are all from the work of Fuchs *et al.*[12,13] and so represent a coherent data set. It is not easy to assess the results in Table 8 by inspection, but plots of ΔG_s^0 against ΔH_s^0 are instructive. We note that it would not be correct to plot ΔS_s^0 against ΔH_s^0 because these two quantities are not experimentally independent. However, ΔG_s^0 and ΔH_s^0 are experimentally completely independent. Plots of ΔG_s^0 against ΔH_s^0 are in Fig. 1. In all three cases, the line for the n-alkanes differs to a greater or lesser extent from the line for the other solutes, with the difference increasing from CCl_4 to CH_2ClCH_2Cl to CH_2I_2. By comparison with 'alkane' line, a polarisable solute such as toluene has ΔH_s^0 on CH_2I_2 more negative than expected by some 0.9 kcal mol^{-1}.* Corresponding values are 0.6 and 0.3 kcal mol^{-1} in CH_2ClCH_2Cl and CCl_4. The more-negative-than-expected ΔH_s^0 values for toluene, and benzene, in CH_2I_2, may be due to polarisability effects on general dispersion interactions, but just as our analysis of log L values suggests, these polarisability effects are very small in relation to the large refractive index of methylene iodide.

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* 1 cal = 4.184 J.

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