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Authors

Abraham, Michael H.
Gola, Joelle M.R.
Cometto-Muniz, J. Enrique
et al.

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Solvation properties of refrigerants, and the estimation of
their water–solvent and gas–solvent partitions

Michael H. Abraham^a, Joëlle M.R. Gola^a, J. Enrique Cometto-Muñiz^b,
William S. Cain^b

^a The Department of Chemistry, University College London, 20 Gordon Street,
London WC1H OAJ, UK

^b Chemosensory Perception Laboratory, Department of Surgery (Otolaryngology),
University of California, San Diego, Mail Code 0957, La Jolla, CA 92093-0957,
USA

Abstract

We have previously used two general solvation equations to correlate and to interpret a wide variety of physicochemical and biochemical properties of compounds (solutes). Application of these equations requires a knowledge of the relevant solute descriptors, viz. R_2 , the excess molar refraction, π_2^H , the solute dipolarity/polarizability, $\sum\alpha_2^H$, $\sum\beta_2^H$, the solute overall hydrogen bond acidity and basicity, and $\log L^{16}$, where L^{16} is the solute gas–hexadecane partition coefficient at 298 K. We have also shown that these solute descriptors can be obtained from partition coefficients of solutes in various water–solvent and gas–solvent systems. Here, we use this approach to calculate solute descriptors for a series of 18 organofluorocarbons, classed as refrigerants, including chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons and perfluorocarbons, using Henry's law coefficients in water and five organic solvents that we have already measured. These data have been used to calculate Ostwald solubility coefficients, $\log L$. Gas–water and gas–solvent partitions have been then combined to give $\log P$ for partition between water and solvent. A number of $\log P$ and L values have also been taken from the Medchem97 database. There are enough data to obtain the above descriptors for the 18 organofluorocarbons, and then to estimate $\log P$ and L values in a large number of other solvents. The chemosensory properties of the organofluorocarbons are also estimated.

Keywords: Refrigerants, Solvation, Partition, Hydrogen bonding, Molecular interaction, Method of calculation

1. Introduction

Organofluorocarbon fluids are stable, non-flammable, non-corrosive and non explosive. Thanks to these physical properties, they have been used in numerous applications [1]. The chlorofluorocarbons (CFCs) are used as refrigerants, aerosol propellants, foaming agents, solvents and cleaning agents [1]. However, due to their effect on ozone depletion, a complete ban on their production by the year 2000 has been scheduled by the 1987 Montreal protocol and its latest amendments [2]. As a result, attention has turned on the development and assessment of hydrochloro-fluorocarbon (HCFCs), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). HCFCs have much reduced ozone depletion potentials compared with CFCs, nevertheless their production in developed countries is due to be phased out by the year 2030. HFCs and PFCs have zero ozone depletion potentials. Although, CFCs, HCFCs, HFCs and PFCs are still widely used in everyday life, many physicochemical and biochemical properties are not known. Hence, it would be of great interest if it were possible to predict such properties. The solvation parameter method of Abraham [3] is one of the most useful approaches for the analysis and prediction of solute effects in chemical and biochemical systems. This method relies on two linear free energy relationships, LFERs, one for processes within condensed phases, Eq. (1), and one for processes involving gas to condensed phase transfer, Eq. (2).

$$\text{Log SP} = c + r_{\text{pol}}R_2 + s\pi_2^{\text{H}} + a\sum\alpha_2^{\text{H}} + b\sum\beta_2^{\text{H}} + l \log L^{16} \quad (1)$$

$$\text{Log SP} = c + r_{\text{pol}}R_2 + s\pi_2^{\text{H}} + a\sum\alpha_2^{\text{H}} + b\sum\beta_2^{\text{H}} + vVx \quad (2)$$

where subscript 2 refers to a solute. The dependent variable, log SP, is some property of a series of solutes in a fixed phase, and the independent variables, or descriptors, are solute properties as follows: R_2 is an excess molar refraction [4], π_2^{H} is the solute dipolarity/polarizability [5], $\sum\alpha_2^{\text{H}}$ and $\sum\beta_2^{\text{H}}$ are, respectively, the solute overall hydrogen bond acidity and basicity [6]. Vx is the MacGowan characteristic volume in units of ($\text{dm}^3 \text{ mol}^{-1}/100$) [7] and $\log L^{16}$ is a descriptor, where L^{16} is the solute gas–hexadecane partition coefficient at 298 K [8]. The first four descriptors can be regarded as measures of the tendency of a solute to undergo various solute–solvent interactions, all of which are energetically favorable, i.e. exoergic. The $\log L^{16}$ and Vx descriptors are both measures of the size of a solute, and so will be measures of the cavity term that will accommodate the solute. However, general dispersion interactions are related to the size of a solute, and both $\log L^{16}$ and Vx will also describe the general solute–solvent dispersion interactions. The coefficients in Eqs. (1) and (2) are found by the method of multiple linear regression analysis (MLRA). They give information on the particular solvent phase in question [3]. The r_{pol} -coefficient is a measure of the phase polarizability, the s -coefficient measures the phase dipolarity/polarizability and the a - and b -coefficients are measures of the hydrogen bond basicity and hydrogen bond acidity of the phase, respectively.

Both v - and l -coefficients are measures of the phase lipophilicity, and are the resultant of cavity and general dispersion interaction effects. In cases where Eq. (1) is applied to partition between two phases, the coefficients then refer to the difference in properties of the two phases. The LFERs, Eqs. (1) and (2) have been used to correlate and predict solute properties in numerous processes, such as water–solvent partitions [9], high performance liquid chromatography [10], solid phase extraction [11], blood brain distribution [12], gas–liquid [5] and gas–solid chromatography [13], the solubility of gases and vapors in water [14], nasal pungency thresholds in man [15], and eye irritation thresholds [16].

Table 1. Regression coefficients in Eq. (1) for partition from water at 298 K.

Process	c	r_{pol}	s	a	b	v	n	r	S.D.	F
Water to solvent										
Gas phase	-0.994	0.577	2.549	3.813	4.841	-0.869	408	0.9976	0.151	16810
Gas phase, 310 K	-0.966	0.698	2.412	3.393	4.577	-1.072	82	0.9945	0.156	1270.8
Olive oil, 310 K	-0.011	0.577	-0.800	-1.470	-4.921	4.173	174	0.9971	0.145	5841
Dry DMF	0.105	0.317	0.462	1.154	-4.843	3.757	68	0.9960	0.140	1525
Dry NMP	-0.071	0.686	0.455	1.547	-5.068	3.899	65	0.9952	0.155	1221
Benzene	0.142	0.464	-0.588	-0.309	-0.625	4.491	213	0.9961	0.143	5317
Tetrachloromethane	0.212	0.602	-1.234	-3.515	-4.528	4.552	173	0.9982	0.119	15658
Dry methanol	0.329	0.299	-0.671	0.080	-3.389	3.512	93	0.9940	0.156	1440
Dry ethanol	0.208	0.409	-0.959	0.186	-3.645	3.928	64	0.9952	0.173	1205
Dry propanol	0.148	0.436	-1.098	0.389	-3.893	4.036	76	0.9975	0.130	2892
Dry butanol	0.152	0.438	-1.177	0.096	-3.916	4.122	88	0.9970	0.125	2719
Dry pentanol	0.080	0.521	-1.294	0.208	-3.908	4.208	59	0.9980	0.112	2597
Dry hexanol	0.044	0.470	-1.153	0.083	-4.057	4.249	46	0.9990	0.114	3775
Dry heptanol	-0.226	0.491	-1.258	0.035	-4.155	4.415	38	0.9986	0.081	2333
Dry decanol	0.008	0.485	-0.974	0.015	-3.798	3.945	45	0.9990	0.123	3843
Dry octanol	0.013	0.550	-1.205	-0.020	-4.262	4.253	99	0.9990	0.103	9536
Wet octanol	0.088	0.562	-1.054	0.034	-3.460	3.814	613	0.9974	0.116	23162
Hexane	0.361	0.579	-1.723	-3.599	-4.764	4.344	173	0.9939	0.207	2721
Heptane	0.325	0.670	-2.061	-3.317	-4.733	4.543	183	0.9923	0.254	2281
Octane	0.223	0.642	-1.647	-3.480	-5.067	4.526	149	0.9922	0.205	1802
Nonane	0.240	0.619	-1.713	-3.532	-4.921	4.482	64	0.9906	0.123	6418
Decane	0.228	0.621	-1.550	-3.535	-5.359	4.533	62	0.9980	0.144	2790
Hexadecane	0.087	0.667	-1.617	-3.587	-4.869	4.433	370	0.9982	0.124	20236
Cyclohexane	0.127	0.816	-1.731	-3.778	-4.905	4.646	180	0.9968	0.131	5512

Table 2. Regression coefficients in Eq. (2) for partition from the gas phase at 298K.

Process	c	r_{pol}	s	a	b	l	n	r	S.D.	F
Gas to solvent										
Water	-1.272	0.822	2.743	3.904	4.814	-0.231	392	0.9962	0.185	10229
Water, 310 K	-1.328	1.058	2.568	3.658	4.533	-0.248	84	0.9920	0.188	863
Olive oil, 310 K	-0.230	0.009	0.795	1.353	0.000	0.888	141	0.9982	0.087	9508
Dry DMF	-0.161	-0.189	2.327	4.756	0.000	0.808	72	0.9977	0.115	3581
Dry NMP	-0.293	0.253	2.210	5.094	0.000	0.818	72	0.9957	0.128	1921
Benzene	0.107	-0.313	1.053	0.457	0.169	1.020	175	0.9987	0.119	12570
Tetrachloromethane	0.282	-0.303	0.460	0.000	0.000	1.047	173	0.9982	0.119	15658
Dry methanol	-0.001	-0.196	1.117	3.671	1.501	0.771	93	0.9976	0.134	3680
Dry ethanol	0.012	-0.221	0.819	3.636	1.249	0.854	74	0.9983	0.145	3534
Dry propanol	-0.028	-0.185	0.648	4.022	1.043	0.869	77	0.9988	0.120	6073
Dry butanol	-0.039	-0.276	0.539	3.781	0.995	0.934	92	0.9983	0.158	5099
Dry pentanol	-0.042	-0.277	0.526	3.779	0.983	0.932	61	0.9997	0.076	19143
Dry hexanol	-0.035	-0.298	0.626	3.726	0.729	0.936	46	0.9998	0.089	18181
Dry heptanol	-0.062	-0.168	0.429	3.541	1.181	0.927	38	0.9999	0.067	23045
Dry octanol	-0.071	-0.119	0.443	3.689	0.589	0.933	99	0.9990	0.030	9535
Wet octanol	-0.222	0.088	0.701	3.478	1.477	0.851	395	0.9939	0.210	6363
Hexane	0.292	-0.169	0.000	0.000	0.000	0.979	119	0.9982	0.102	15683
Heptane	0.275	-0.162	0.000	0.000	0.000	0.983	109	0.9986	0.088	19486
Octane	0.215	-0.049	0.000	0.000	0.000	0.967	105	0.9985	0.098	17429
Nonane	0.200	-0.145	0.000	0.000	0.000	0.980	55	0.9917	0.184	6310
Decane	0.156	-0.143	0.000	0.000	0.000	0.989	60	0.9995	0.065	26396
Hexadecane ^a	0.000	0.000	0.000	0.000	0.000	1.000	-	-	-	-
Cyclohexane	0.216	0.000	-0.179	0.000	0.000	1.019	114	0.9978	0.115	12839

^a Coefficients are defined as such.

Table 3. List of refrigerants.

Solute	Refrigerant code
Difluoromethane	R32
Trifluoromethane	R23
Tetrafluoromethane	R14
Trichlorofluoromethane	R11
Dichlorodifluoromethane	R12
Chlorotrifluoromethane	R13
1,1-Difluoroethane	R152a
1,1,1,2-Tetrafluoroethane	R134a
Pentafluoroethane	R125
1,1-Dichloro-1-fluoroethane	R141b
1-Chloro-1,2-difluoroethane	R142b
1-Chloro-1,1,2-trifluoroethane	R133a
1-Chloro-1,2,2,2-tetrafluoroethane	R124
1,2-Dichloro-1,1,2,2-tetrafluoroethane	R114
1-Chloro-1,1,2,2,2-pentafluoroethane	R115
1,1,1,2,3,3,3-Heptafluoropropane	R227
1-Chloro-2,2-difluoroethene	R1122
Perfluoropropene	R1216

Table 4. Gas/solvent and water/solvent partition coefficients calculated from Henry's law coefficients

Code	$\log L^{w298}$	$\log L^{w310}$	$\log L^{woct}$	$\log P^{woct}$	$\log L^{oct}$	$\log P^{oct}$	$\log L^{NMP}$	$\log P^{NMP}$	$\log L^{DMF}$	$\log P^{DMF}$	$\log L^{non}$	$\log P^{non}$
R32	0.235	0.124	0.427	0.192	0.413	0.178	1.242	1.007	1.241	1.007	0.267	0.033
R23	-0.510	-0.622	0.130	0.640	0.148	0.658	0.993	1.502	0.632	1.141	-0.046	0.463
R14	-2.306	-2.386	-0.950	1.356	-0.913	1.385	-1.324	0.982	-1.142	1.164	-0.590	1.716
R11	-0.451	-0.641	1.809	2.260	1.885	2.335	1.875	2.326	1.851	2.302	2.083	2.534
R12	-1.129	-1.275	0.920	2.049	0.982	2.111	0.978	2.107	0.994	2.123	1.233	2.362
R13	-1.670	-1.777	0.005	1.679	0.043	1.711	-0.174	1.496	-0.059	1.610	0.338	2.008
R152a	0.090	-0.041	2.369	0.690	0.782	0.692	1.479	1.390	1.553	1.463	0.791	0.701
R134a	-0.408	-0.547	0.648	1.056	0.647	1.055	1.442	1.849	1.616	2.024	0.558	0.996
R125	-1.059	-1.203	0.391	1.450	0.419	1.477	1.159	2.218	1.126	2.185	0.290	1.348
R141b	-0.148	-0.336	1.804	1.952	1.949	2.097	-	-	-	-	-	-
R142b	-0.449	-0.605	1.168	1.617	1.189	1.638	1.562	2.011	1.528	1.977	1.274	1.724
R133a	1.011	-0.165	1.451	1.446	1.476	1.471	-	-	-	-	1.348	1.344
R124	-0.569	-0.737	1.180	1.749	1.220	1.789	1.749	2.318	1.786	2.355	1.104	1.674
R114	-1.652	-1.788	1.126	2.778	1.181	2.833	1.093	2.745	1.165	2.817	1.474	3.126
R115	-2.116	-2.212	0.227	2.344	1.903	2.395	-0.045	2.071	1.127	2.212	0.643	2.579
R227	-1.468	-1.636	0.754	2.222	0.821	2.289	1.606	3.074	1.537	3.005	-	-
R1122	-0.380	-0.544	1.136	1.516	1.236	1.616	1.656	2.035	1.463	1.843	-	-
R1216	-1.772	-1.895	0.209	1.981	0.160	1.932	-	-	-	-	0.582	2.354

Table 5. The dependent variables for processes in Tables 1 and 2 for R32^a

Solvent	Observed		Calculated	
	$\log L$	$\log P$	$\log L$	$\log P$
Octanol wet	0.427	0.192	0.430	0.306
Dry DMF	1.241	1.006	1.375	1.123
Dry octanol	0.413	0.178	0.491	0.241
Olive oil, 310 K [23]	0.350	0.226	0.279	0.255
Dry NMP	1.242	1.007	1.068	0.882
Nonane	0.268	0.033	0.286	0.002
Water, 298 K	0.235	0.235	0.300	0.317
Water, 310 K	0.124	0.124	0.052	0.141

^a Calculation of descriptors: $R_2 = -0.316$, $\pi_2^H = 0.487$, $\sum \alpha_2^H = 0.065$, $\sum \beta_2^H = 0.052$, $\log L^{16} = 0.042$, $V_x = 0.2849$, S.D. = 0.091.

2. Methodology

Of the descriptors used in Eqs. (1) and (2), V_x can be obtained for any given solute from atomic and bond contributions, using a simple computer program [7]. R_2 can be easily calculated from the liquid refractive index at 293 K [4]. In the case of solid solutes, R_2 can be obtained either from the hypothetical refractive index of the liquid, or through addition of fragments or substructures. For gaseous compounds at 293 K, R_2 is better added to the list of descriptors to be determined, viz. π_2^H , $\sum \alpha_2^H$, $\sum \beta_2^H$ and $\log L^{16}$.

Table 6. The dependent variables for processes in Tables 1 and 2 for R23^a

Solvent	Observed		Calculated	
	$\log L$	$\log P$	$\log L$	$\log P$
Octanol wet	0.131	0.640	0.068	0.695
Dry DMF	0.632	1.141	0.647	1.153
Dry octanol	0.149	0.659	0.231	0.697
Olive oil, 310 K [23]	-0.092	0.531	-0.183	0.530
Dry NMP	0.993 ^b	1.503 ^b	0.340	0.897
Nonane	0.046	0.463	-0.007	0.463
Water, 298 K	-0.510	-0.510	-0.469	-0.453
Water, 310 K	-0.622	-0.622	-0.685	-0.618

^a Calculation of descriptors: $R_2 = -0.427$, $\pi_2^H = 0.183$, $\sum \alpha_2^H = 0.110$, $\sum \beta_2^H = 0.034$, $\log L^{16} = -0.274$, $V_x = 0.3026$, S.D. = 0.051.

^b Omitted.

Table 7. The dependent variables for processes in Tables 1 and 2 for R14^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	-0.950	1.357	-1.083	1.268
Cyclohexane [24]	-0.633	1.673	-0.606	1.620
Benzene [24]	-0.804	1.502	-0.824	1.474
Dry decanol [25]	-0.994	1.312	-0.973	1.269
Dry DMF	-1.142	1.165	-1.312	1.016
Dry ethanol [25]	-0.717	1.589	-0.774	1.485
Hexadecane [26]	-0.820	1.486	-0.819	1.551
Dry hexanol [25]	-0.855	1.421	-0.797	1.440
Dry methanol [25]	-0.732	1.574	-0.814	1.460
Dry octanol	-0.921	1.386	-0.920	1.314
Olive oil, 310 K [23]	-1.284	1.103	-1.165	1.211
Dry pentanol [25]	-0.854	1.452	-0.787	1.470
Dry propanol [25]	-0.762	1.544	-0.803	1.480
Dry butanol [25]	-0.801	1.505	-0.789	1.531
Dry heptanol [25]	-0.914	1.392	-0.838	1.438
Tetrachloromethane [21]	-0.525	1.781	-0.526	1.733
Dry NMP	-1.324 ^b	0.982 ^b	-1.666	0.683
Nonane	-0.590	1.716	-0.523	1.771
Hexane [23]	-0.364	1.942	-0.417	1.872
Heptane [23]	-0.456	1.850	-0.441	1.936
Octane [23]	-0.531	1.775	-0.550	1.738
Decane [23]	-0.632	1.674	-0.575	1.747
Water, 298 K	-2.306	-2.306	-2.250	-2.241
Water, 310 K	-2.386	-2.386	-2.413	-2.310

^a Calculation of descriptors: $R_2 = -0.550$, $\pi_2^H = -0.250$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.000$, $\log L^{16} = -0.819$, $V_x = 0.3203$, S.D. = 0.071.

^b Omitted.

Table 8. The dependent variables for processes in Tables 1 and 2 for R11^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.809	2.260	1.727	2.129
Dry DMF	1.851	2.302	1.934	2.326
Dry octanol	1.885	2.335	1.871	2.237
Dry NMP	1.876	2.327	1.885	2.299
Nonane	2.083	2.534	2.080	2.456
Water	-0.451	-0.451	-0.521	-0.475
Water, 310 K	-0.641	-0.641	-0.659	-0.602

^a Calculation of descriptors: $R_2 = 0.207$, $\pi_2^H = 0.240$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.070$, $\log L^{16} = 1.950$, $V_x = 0.6344$, S.D. = 0.065.

Table 9. The dependent variables for processes in Tables 1 and 2 for R12^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	0.920	2.049	0.825	1.992
Dry DMF	0.994	2.123	1.033	2.161
Dry octanol	0.982	2.111	1.030	2.130
Dry NMP	0.978	2.108	0.910	2.070
Nonane	1.233	2.362	1.297	2.417
Water, 298 K	-1.129	-1.129	-1.145	-1.120
Water, 310 K	-1.275	-1.275	-1.257	-1.213

^a Calculation of descriptors: $R_2 = 0.027$, $\pi_2^H = 0.125$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.000$, $\log L^{16} = 1.124$, $V_x = 0.5297$, S.D. = 0.052.

The most common procedure for the estimation of descriptors uses Eq. (1) with water–solvent partition, P , in the dependent variable $\log P$, and Eq. (2) with gas solvent partition, L , in the dependent variable $\log L$. Equations in $\log P$ and L are constructed for various water–solvent and gas–solvent systems; the coefficients for Eq. (1) are given in Table 1, and the coefficients for Eq. (2) are listed in Table 2. Then for a given solute, if values of $\log P$ and L are known in several systems, the entire set of equations can be solved to yield the solute descriptors that best reproduce the experimental $\log P$ and L values. As a criterion of the ‘best-fit’ we use S.D. in the experimental and calculated values. Although there will be only one ‘best-fit’ solution, there may be a number of other solutions with almost the same S.D. value. In such a case, the solution that best agrees with the chemical structure of the solute may be chosen instead of the ‘best-fit’ solution. The general method has recently been detailed by Abraham and coworkers for the determination of descriptors for terpenes [17] and Buckminsterfullerene [18]. In the present study, we use this approach to calculate the descriptors for a series of 18 organofluorocarbon fluids, classed as refrigerants, including CFCs, HCFCs, HFCs and PFCs; names and abbreviations are in Table 3. Arlt and coworkers have recently measured Henry’s law coefficient, $H_{2,S}$, for these refrigerants [19–21]. Values of $H_{2,S}$ were determined in the solvents (S) octan-1-ol (dry octanol), *n*-nonane, *N*-methylpyrrolidone (dry NMP) and dimethylformamide (dry DMF) and in water and water/octan-1-ol mixture (wet octanol). The Henry’s law coefficient can be easily transformed into the gas–solvent partition coefficient, $L_{2,S}$.

$$L_{2,S} = RT \frac{\rho_s}{H_{2,S} M_S} \quad (3)$$

where R is the gas constant ($\text{dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$), T the temperature (K) and ρ_s

and M_S the density (g cm^{-3}) and the molecular weight (g mol^{-1}) of the pure solvent. Values of ρ_S at T were taken from the literature [22]. For simplicity, we refer to $L_{2,S}$ just as L_S . If the gas–water (w) and gas–solvent (S) partitions, $\log L_w$ and L_S , are known, then the water–solvent partition coefficient, $\log P_S$, can be deduced from

$$\log P_S = \log L_S - \log L_w \quad (4)$$

Table 10. The dependent variables for processes in Tables 1 and 2 for R13^a.

Solvent	Observed		Calculated	
	$\log L$	$\log P$	$\log L$	$\log P$
Wet octanol	0.006	1.676	-0.098	1.619
Dry DMF	-0.060	1.611	-0.052	1.602
Dry octanol	0.041	1.712	0.133	1.740
Dry NMP	-0.174	1.496	-0.286	1.396
Nonane	0.338	2.008	0.440	2.071
Water, 298 K	-1.670	-1.670	-1.645	-1.623
Water, 310 K	-1.777	-1.777	-1.759	-1.705

^a Calculation of descriptors: $R_2 = -0.247$, $\pi_2^H = -0.046$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.000$, $\log L^{16} = 0.209$, $V_x = 0.4250$, S.D. = 0.073.

Values of $\log L_S$, P_S and L_w obtained from the data of Arlt and coworkers [19–21] are given in Table 4. In addition, Eger and coworkers [23] determined gas–olive oil partition coefficients, $\log L_{oil}$, for a number of HFCs and PFCs at 310 K. Values of $\log L_w$ at 310K are available (see Table 4), so that $\log P_{oil}$ at 310K can be obtained from Eq. (4). Finally, a number of directly determined water–solvent partition coefficients for R14, R134a, R125 and R114 were obtained either from the Medchem97 database [24] or literature surveys [25–28], and the corresponding $\log L$ values were deduced from Eq. (4). Note that we distinguish between ‘dry’ and ‘wet’ solvents. The former are solvents that are miscible with water and for which $\log P$ values are for the hypothetical partition between water and the pure dry solvent, obtained from Eq. (4). The ‘wet’ solvents are those for which partitions have been obtained by direct experiments in which the solvent is saturated with water. In Tables 5–23 are given the values of $\log P_S$ and L_S that we have used to determine descriptors. Since enough dependent variables were obtained, we were able to calculate descriptors for all the 18 refrigerants listed in Table 3. At the heading of Tables 5–23, the ‘chemically’ significant descriptor set that best reproduces the dependent variables is given.

Table 11. The dependent variables for processes in Tables 1 and 2 for R152a^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	0.780	0.690	0.771	0.779
Dry DMF	1.553	1.463	1.641	1.540
Dry octanol	0.782	0.692	0.856	0.765
Olive oil, 310 K [23]	0.637	0.678	0.668	0.792
Dry NMP	1.480	1.390	1.324	1.298
Nonane	0.795	0.702	0.758	0.635
Water, 298 K	0.090	0.090	0.158	0.161
Water, 310 K	-0.041	-0.041	-0.110	-0.039

^a Calculation of descriptors: $R_2 = -0.250$, $\pi_2^H = 0.498$, $\sum \alpha_2^H = 0.040$, $\sum \beta_2^H = 0.050$, $\log L^{16} = 0.517$, $V_x = 0.4258$, S.D. = 0.105.

Table 12. The dependent variables for processes in Tables 1 and 2 for R134a^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	0.634	1.042	0.517	1.016
Dry DMF	1.413 ^b	1.821 ^b	1.568	1.929
Dry octanol	0.842	1.250	0.715	1.078
Hexadecane [27]	0.331	0.739	0.288	0.741
Dry NMP	1.267 ^b	1.670 ^b	1.133	1.612
Olive oil, 310 K	0.480 ^b	1.027 ^b	-0.230	-0.011
Nonane	0.613	1.021	0.572	0.906
Water, 298 K	-0.408	-0.408	-0.326	-0.326
Water, 310 K	-0.540	-0.547	-0.636	-0.563

^a Calculation of descriptors: $R_2 = -0.410$, $\pi_2^H = 0.342$, $\sum \alpha_2^H = 0.060$, $\sum \beta_2^H = 0.040$, $\log L^{16} = 0.318$, $V_x = 0.4612$, S.D. = 0.081.

^b Omitted.

3. Discussion

The final list of solute descriptors for 18 organofluorocarbons, classed as refrigerants, is given in Table 23. It is not easy to calculate the error in the descriptors obtained by our method, because all the descriptors are calculated simultaneously. However, we can take the errors as those suggested before [17], viz. 0.03 U for π_2^H , $\sum \alpha_2^H$, $\sum \beta_2^H$ and 0.02 U for $\log L^{16}$.

Inspection of the descriptors shows that the refrigerants interact with the neighboring solvent molecules through very weak interaction forces. These forces become smaller as the number of fluorine atoms in the molecule increases. The R_2 term describes the polarizability of a solute; R_2 values for most of the refrigerants are small and even negative. The negative value means that such compounds have less polarizability ability than the corresponding hydrocarbons, for which $R_2 = 0$ [4]. This is in agreement with characteristics of the fluorine atom. Even though hydrogen and fluorine atoms have almost the same atomic size, the latter shields the carbon-backbone due to its electron withdrawing capability. The π_2^H descriptor measures the ability of a molecule to stabilize a neighboring charge or dipole. The PFCs of the set, R14 and R1216, have negative π_2^H values -0.250 and -0.166, respectively. Hence, R14 is less dipolar than the homologous hydrocarbon (CH₄, $\pi_2^H = 0$). R1216 is more polar than octafluoropropane ($\pi_2^H = -0.45$) due to presence of a double bond in R1216. In partially fluorinated alkanes, HFCs, the dipolar effect is more important than in PFCs because of the net C–F dipole that is absent in PFCs. We find also that organofluorocarbons are not important hydrogen bond acids or bases. Finally, the $\log L^{16}$ descriptor is a measure of the dissolution of the gaseous solute into *n*-hexadecane. A large positive value means that the dissolution of the solute in *n*-hexadecane is easy, and therefore that the solute can be called as lipophilic. A negative value for $\log L^{16}$ suggests that the dissolution in *n*-hexadecane is unfavored and that the solute has little lipophilic character. This is the case for the perfluorocarbon R14 and the hydrofluorocarbon R23. The remaining compounds have small $\log L^{16}$ values, and hence are slightly lipophilic. For some classes of solute, it is possible to estimate various descriptors, as shown.

Table 13. The dependent variables for processes in Tables 1 and 2 for R125^a.

Solvent	Observed		Calculated	
	$\log L$	$\log P$	$\log L$	$\log P$
Wet octanol	0.392	1.450	0.242	1.430
Dry DMF	1.127	2.186	0.830	1.898
Dry octanol	0.418	1.477	0.510	1.546
Hexadecane [27]	-0.018	1.242	0.064	1.203
Olive oil, 310K [22]	0.182	1.442	0.075	1.371
Dry NMP	1.160 ^b	2.218 ^b	0.450	1.607
Nonane	0.290	1.349	0.350	1.401
Water, 298 K	-1.059	-1.059	-0.989	-1.003
Water, 310 K	1.203	1.203	-1.241	-1.208

^a Calculation of descriptors: $R_2 = -0.510$, $\pi_2^H = -0.019$, $\sum \alpha_2^H = 0.105$, $\sum \beta_2^H = 0.064$, $\log L^{16} = 0.100$, $V_x = 0.4789$, S.D. = 0.095.

^b Omitted.

Table 14. The dependent variables for processes in Tables 1 and 2 for R141b^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.804	1.952	1.818	1.985
Dry octanol	1.948	2.097	1.951	2.088
Hexadecane [27]	1.932	2.080	1.920	2.061
Water, 298 K	0.148	0.148	-0.152	-0.136
Water, 310 K	-0.336	-0.336	-0.348	-0.306

^a Calculation of descriptors: $R_2 = 0.084$, $\pi_2^H = 0.430$, $\sum \alpha_2^H = 0.005$, $\sum \beta_2^H = 0.054$, $\log L^{16} = 1.920$, $V_x = 0.6529$, S.D. = 0.047.

Table 15. The dependent variables for processes in Tables 1 and 2 for R142ba.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.168	1.618	1.151	1.689
Dry DMF	1.528	1.978	1.571	2.048
Dry octanol	1.189	1.638	1.308	1.771
Dry NMP	1.562	2.011	1.407	1.930
Nonane	1.275	1.724	1.270	1.749
Water, 298 K	-0.449	-0.449	-0.405	-0.405
Water, 310 K	-0.605	-0.605	-0.591	-0.571

^a Calculation of descriptors: $R_2 = -0.080$, $\pi_2^H = 0.240$, $\sum \alpha_2^H = 0.060$, $\sum \beta_2^H = 0.056$, $\log L^{16} = 1.081$, $V_x = 0.5482$, S.D. = 0.128.

Table 16. The dependent variables for processes in Tables 1 and 2 for R133aa.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.451	1.447	1.367	1.437
Dry octanol	1.476	1.471	1.511	1.499
Nonane	1.349	1.344	1.383	1.355
Water, 298 K	0.005	0.005	0.048	0.048
Water, 310 K	-0.165	-0.165	-0.220	-0.172

^a Calculation of descriptors: $R_2 = -0.160$, $\pi_2^H = 0.350$, $\sum \alpha_2^H = 0.060$, $\sum \beta_2^H = 0.080$, $\log L^{16} = 1.186$, $V_x = 0.5659$, S.D. = 0.098.

Table 17. The dependent variables for processes in Tables 1 and 2 for R124^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.180	1.749	1.081	1.727
Dry DMF	1.786 ^b	2.355 ^b	1.483	2.054
Dry octanol	1.220	1.789	1.283	1.825
Dry NMP	1.749 ^b	2.318 ^b	1.240	1.871
Water, 298 K	-0.569	-0.569	-0.528	-0.532
Water, 310 K	-0.737	-0.737	-0.761	-0.741

^a Calculation of descriptors: $R_2 = -0.300$, $\pi_2^H = 0.170$, $\sum \alpha_2^H = 0.097$, $\sum \beta_2^H = 0.071$, $\log L^{16} = 0.904$, $V_x = 0.5860$, S.D. = 0.047.

^b Omitted.

Table 18. The dependent variables for processes in Tables 1 and 2 for R114^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.126	2.778	1.011	2.621
Dry DMF	1.165	2.817	1.144	2.720
Dry octanol	1.181	2.833	1.305	2.851
Dry NMP	1.093	2.745	0.937	2.574
Water, 298 K	-1.652	-1.652	-1.594	-1.592
Water, 310 K	-1.789	-1.789	-1.755	-1.735

^a Calculation of descriptors: $R_2 = -0.190$, $\pi_2^H = 0.050$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.000$, $\log L^{16} = 1.427$, $V_x = 0.7060$, S.D. = 0.110.

Table 19. The dependent variables for processes in Tables 1 and 2 for R115^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	0.227	2.344	0.125	2.306
Dry DMF	0.095	2.212 ^b	0.067	2.195
Dry octanol	0.279	2.395	0.426	2.517
Dry NMP	-0.045	2.071 ^b	-0.205	1.972
Nonane	0.643	2.760	0.784	2.918
Water, 298 K	-2.116	-2.116	-2.012	-2.030
Water, 310 K	-2.212	-2.212	-2.152	-2.151

^a Calculation of descriptors: $R_2 = -0.360$, $\pi_2^H = -0.120$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.000$, $\log L^{16} = 0.543$, $V_x = 0.6013$, S.D. = 0.109.

^b Omitted.

Table 20. The dependent variables for processes in Tables 1 and 2 for R227^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	0.755	2.223	0.611	2.160
Dry DMF	1.537 ^b	3.005 ^b	0.861	2.331
Dry octanol	0.821	2.289	0.918	2.349
Olive oil, 310 K [22]	1.606	3.074 ^b	0.480	2.140
Dry NMP	0.443 ^b	1.910 ^b	0.512	2.063
Water, 298 K	-1.468	-1.468	-1.425	-1.442
Water, 310 K	-1.637	-1.637	-1.665	-1.653

^a Calculation of descriptors: $R_2 = -0.557$, $\pi_2^H = -0.012$, $\sum \alpha_2^H = 0.070$, $\sum \beta_2^H = 0.030$, $\log L^{16} = 0.688$, $V_x = 0.6552$, S.D. = 0.070.

^b Omitted.

Table 21. The dependent variables for processes in Tables 1 and 2 for R1122^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	1.136	1.516	1.085	1.528
Dry DMF	1.463 ^b	1.843 ^b	1.865	2.200
Dry octanol	1.236	1.616	1.324	1.628
Dry NMP	1.656	2.036	1.608	2.028
Water, 298 K	-0.380	-0.380	-0.336	-0.330
Water, 310 K	-0.544	-0.544	-0.585	-0.547

^a Calculation of descriptors: $R_2 = -0.340$, $\pi_2^H = 0.285$, $\sum \alpha_2^H = 0.150$, $\sum \beta_2^H = 0.000$, $\log L^{16} = 0.723$, $V_x = 0.5052$, S.D. = 0.044.

^b Omitted.

Table 22. The dependent variables for processes in Tables 1 and 2 for R1216^a.

Solvent	Observed		Calculated	
	log <i>L</i>	log <i>P</i>	log <i>L</i>	log <i>P</i>
Wet octanol	0.210	1.981	0.052	1.903
Dry octanol	0.161	1.933	0.288	2.040
Nonane	0.602	2.388	0.602	2.388
Water, 298 K	-1.728	-1.738	-1.728	-1.738
Water, 310 K	-1.914	-1.895	-1.914	-1.895

^a Calculation of descriptors: $R_2 = -0.500$, $\pi_2^H = -0.166$, $\sum \alpha_2^H = 0.000$, $\sum \beta_2^H = 0.100$, $\log L^{16} = 0.337$, $V_x = 0.5945$, S.D. = 0.084.

Table 23. Descriptors of the refrigerants.

Code	R_2	π_2^H	$\sum \alpha_2^H$	$\sum \beta_2^H$	log L^{16}	V_x
R32	-0.316	0.487	0.065	0.052	0.040	0.2849
R23	-0.427	0.183	0.110	0.034	-0.274	0.3026
R14	-0.550	-0.250	0.000	0.000	-0.819	0.3203
R11	0.207	0.240	0.000	0.070	1.950	0.6344
R12	0.027	0.125	0.000	0.000	1.124	0.5297
R13	-0.247	-0.046	0.000	0.000	0.209	0.4250
R152a	-0.250	0.498	0.040	0.050	0.517	0.4258
R134a	-0.410	0.342	0.060	0.040	0.318	0.4612
R125	-0.510	-0.019	0.105	0.064	0.100	0.4789
R141b	0.084	0.430	0.005	0.054	1.920	0.6530
R142b	-0.080	0.240	0.060	0.056	1.081	0.5482
R133a	-0.160	0.350	0.060	0.080	1.186	0.5659
R124	-0.309	0.170	0.097	0.071	0.904	0.5860
R114	-0.190	0.050	0.000	0.000	1.427	0.7060
R115	-0.360	-0.120	0.000	0.000	0.543	0.6013
R227	-0.557	0.012	0.070	0.030	0.688	0.6552
R1122	-0.340	0.285	0.150	0.000	0.723	0.5052
R1216	-0.500	-0.166	0.000	0.100	0.337	0.5945

3.1. Halogenated *n*-alkanes

The excess molar refractivity, R_2 , describes the polarizability of a solute. This property correlates well with the size of atoms contained in a molecule, and also with the electron distribution. There are over 200 R_2 values of *n*-halogenated alkanes available in our database. To these, can be added the R_2 values obtained in this study. A regression of R_2 against the number of iodine, bromine, chlorine and fluorine atoms, nI , nBr , nCl and nF , respectively, in halogenated *n*-alkanes, yields Eq. (5).

$$R_2 = 0.641nI + 0.328nBr + 0.140nCl - 0.0984nF \quad (5)$$

where $n = 221$ and S.D. = 0.083. In this equation, n is the number of data points and S.D. the standard deviation in the independent variable. Because we constrained the intercept to be zero in Eq. (5), we give no values of the correlation coefficient, r , or of the Fisher F -statistic, F , which have no meaning under this circumstance. As expected, the number of carbon atoms was found to be not significant. Eq. (5) could certainly be used to estimate further values of R_2 . The π_2^H descriptor is a blend of polarizability and dipolarity, therefore in order to estimate π_2^H values for chlorinated and fluorinated *n*-alkanes (with $n < 3$), it is useful to dissect π_2^H values into contributions from these two factors. A regression of π_2^H values against the number of chlorine and fluorine atoms nCl and nF and the square of the dipole moment, μ_0^2 yields

$$\pi_2^H = 0.108 \mu_0^2 + 0.108nCl - 0.053nF \quad (6)$$

where $n = 39$ and S.D. = 0.091. Again, we give no r or F value because we have constrained the equation to have a zero intercept. Eq. (6) is just about good enough to use to estimate further values of π_2^H .

Table 24. Calculated $\sum \alpha_2^H$ and σ_1 values.

Code	$\sum \alpha_2^H$	σ_1 [29]
R32	0.065	0.32
R23	0.110	0.43
R152a	0.040	0.25
R134a	0.060	0.30
R125	0.105	0.39
R141b	0.005	0.14
R142b	0.060	0.30
R133a	0.060	0.29
R124	0.097	0.37
R227	0.070	0.31

3.2. Estimation of $\sum\alpha_2^H$ values

In solvation situation, $\sum\alpha_2^H$ the 'effective' or 'summation' solute hydrogen bonding acidity must be considered [6]. Here, the solute is surrounded by solvent molecules and undergoes multiple hydrogen bonding. For volatile solutes, the gas chromatographic method can in principle be used to obtain $\sum\alpha_2^H$ values through the measurements on highly basic stationary phases. However, the use of the partition coefficients for various water–solvent or gas–solvent systems is often preferred. Here, the last approach was used to estimate $\sum\alpha_2^H$ for several CFCs and HCFs. In a previous study, Abraham and coworkers [6] highlighted a relationship between the 1:1 hydrogen bond acidity, α_2^H and the Hammett inductive parameter, σ_1 for a few halogenated compounds. We use the same approach to establish a correlation between $\sum\alpha_2^H$ and σ_1 for a few CFCs and HFCs. We expected to find the same type of relationship between $\sum\alpha_2^H$ and σ_1 . $\sum\alpha_2^H$ values calculated in this study were plotted against σ_1 values recently determined by Taylor [29] (see Table 24). Hence, it appeared that a correlation between these parameters could be drawn.

$$\sum\alpha_2^H = -0.0535 + 0.389\sigma_1 \quad (7)$$

where $r = 0.977$, S.D. = 0.03 and $n = 10$. Such a correlation is certainly good enough to estimate further values of $\sum\alpha_2^H$ for aliphatic halogenated compounds.

4. Estimation of physicochemical and biochemical properties

In Tables 1 and 2 are given the coefficients in Eqs. (1) and (2) for partition from water and from the gas phase into a wide variety of solvents. Once the descriptors for the refrigerants are available (see Table 23), it is a trivial matter to calculate the $\log P$ and L values at 298 K, simply by inserting values of the descriptors into Eqs. (1) and (2), using the coefficients in Tables 1 and 2.

In a similar way, any property that has been correlated through Eqs. (1) and (2) can be predicted, once the relevant descriptors are available. Because of the widespread use of refrigerants, it is of some consequence to estimate biological properties such as chemosensory perception. We have already obtained equations derived from Eq. (1) for nasal pungency thresholds [15] and eye irritation thresholds [16] in humans. These are defined as the minimum vapor concentration in ppm that a subject can just detect, and are measures of the chemosensory potency of gaseous solutes. The nasal pungency thresholds, NPT, follow Eq. (8) and the eye irritation thresholds, EIT follow Eq. (9).

$$\log \frac{1}{\text{NPT}} = -8.519 + 2.154\pi_2^H + 3.522\sum\alpha_2^H + 1.397\sum\beta_2^H + 0.860 \log L^{16} \quad (8)$$

Table 25. Estimation of chemosensory potency of the refrigerants.

Code	NPT (ppm)	EIT (ppm)	P^0 (ppm) ^a
R32	13600000	863000	16700000
R23	84200000	694000	46300000
R14	5780000000	2170000	
R11	1690000	488000000	1050000
R12	19200000	106000000	6420000
R13	274000000	16600000	35200000
R152a	6180000	3100000	5900000
R134a	17400000	2570000	6570000
R125	103000000	2790000	13600000
R141b	705000	213000000	775000000
R142b	6060000	28600000	3340000
R133a	2640000	21800000	2010000
R124	8600000	12600000	
R114	15300000	213000000	2120000
R115	204000000	40300000	9000000
R227	41000000	14100000	4580000
R1122	5690000	4130000	4670000
R1216	280000000	18800000	7530000
3-Methylpentane	1990000	138000	250000
Toluene	29500 ^b	25700 ^b	37400
Propan-1-ol	3090 ^b	6920 ^b	26900
Heptan-2-one	812 ^b	309 ^b	4990
Octan-1-ol	98 ^b	60 ^b	99
Decyl acetate	5 ^b	20 ^b	30

^a Taken from [20,30].

^b Observed values [15,16].

$$\log \frac{1}{\text{EIT}} = -7.918 - 0.482R_2 + 1.420 \pi_2^H + 4.025 \sum \alpha_2^H + 1.219 \sum \beta_2^H + 0.853 \log L^{16} \quad (9)$$

We use 1/NPT and 1/EIT in Eqs. (8) and (9) because then the larger the value of log 1/NPT and 1/EIT the more potent is the solute. It is again straightforward to insert the relevant values of the descriptors into Eqs. (8) and (9) to deduce the chemosensory properties.

We have all the descriptors in Eqs. (8) and (9) for the 18 refrigerants listed in Table 23, so that it is possible to calculate log(1/NPT) and (1/EIT) values. The

corresponding NPT and EIT values themselves are in Table 25 together with observed values for a selection of other solutes. Comparing these data with those obtained for the refrigerants, it can be concluded that the latter have only a small chemosensory effect on man. Values of NPT and EIT are all larger than those for 3-methylpentane and toluene that are very weak irritants. Furthermore, values of the saturated vapor pressure, P^0 , in ppm at 298K [20,30] are also given in Table 25. For some refrigerants the saturated vapor pressure at 298K is less than the threshold values, in which case these will be no perceived effect, anyway.

List of symbols

a	phase hydrogen-bond acidity
b	phase hydrogen-bond basicity
c	constant of the regression equation
DMF	dimethylformamide
F	Fisher's F -statistic
$H_{2,S}$	Henry's coefficient of a solute 2 in a solvent (S)
l, v	phase lipophilicity
L	gas/solvent partition coefficient
L^{16}	solute gas/hexadecane partition coefficient or Oswald solubility coefficient in hexadecane at 298K
MS	molecular weight of pure solvent (S)
n	number of data points
NMP	<i>N</i> -methylpyrrolidone
non	<i>n</i> -nonane
oct	dry octan-1-ol solvent
P	water/solvent partition coefficient
r	correlation coefficient
r_{pol}	phase polarizability
R_2	solute excess molar refraction
s	phase dipolarity/polarizability
S.D.	standard deviation
SP	solute property in a fixed phase
V_x	MacGowan's characteristic volume
w298	water solvent at 298K
w310	water solvent at 310K
woct	wet octan-1-ol solvent

Greek letters

$\sum \alpha_2^H$	solute overall hydrogen-bond acidity
$\sum \beta_2^H$	solute overall hydrogen-bond basicity
π_2^H	solute dipolarity/polarizability
ρ_s	density of pure solvent (S)

Subscripts

S solvent
2 solute

For further reading see [31–34].

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