Correlation between Molecular Size and Packing Density of Solvents

Masato Kodaka*

Institute for Biological Resources and Functions, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 6, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8566, Japan

Received: September 9, 2003

There is a general correlation between packing density and molecular diameter for various solvents. Molecular diameters are estimated by three methods, in which two diameters are on the basis of the scaled particle theory (SPT) and the third one is obtained from actual molecular volumes assuming a spherical molecule shape. Hydrophobicity or solvophobicity can be reasonably explained by the large deviation of packing density from a hypothetical solvent with the same size and less cohesive energy density (ced).

Introduction

Hydrophobicity is one of the fundamental properties controlling biological phenomena. On the basis of the scaled particle theory (SPT),[1] the author previously concluded that hydrophobicity (or solvophobicity) is caused by the packing density of water (or organic solvents such as ethylene glycol) higher than that expected for a solvent with the same size and less cohesive energy density (ced).[2] Here the term, solvophobicity, is ordinarily used for the phenomenon that solutes associate in nonaqueous polar solvents, such as micelle formation and polymer folding.[3,4] The remarkable finding was that there is a correlation between the diameter of solvents (a_1) and the packing density ($y = \pi a_1^3\rho/6$, ρ: number density of solvent molecules); that is, y has a tendency to increase with a_1 depending on the magnitude of ced at constant temperature and pressure. The objective of the present study is to show that this unique correlation between the packing density and the diameter of solvents generally holds irrespective of SPT. Hydrophobicity (or solvophobicity) is correlated to the deviation of the packing density of water (or organic solvents) from the a_1-y curves of typical organic solvents.

Calculation Method

In the present study, a solvent molecule was assumed to be a sphere, whose diameter was defined by the following three methods. Two types of a solvent diameter (a_β and a_σ) were obtained from experimental values of compressibility (β)[1] and surface tension (σ),[5] using eqs 1 and 2 derived from SPT[1]

$$\beta = (\pi a_\beta^3/6kT)\{(1 - y_\beta)^4/y_\beta(1 + 2y_\beta)^2\} \quad (1)$$

$$\sigma = (kT/4\pi a_\sigma^2)[12y_\sigma/(1 - y_\sigma) + 18\{y_\sigma/(1 - y_\sigma)\}^2] - pa_\sigma/2 \quad (2)$$

where y_β is equal to $\pi a_\beta^3\rho/6$, y_σ is equal to $\pi a_\sigma^3\rho/6$, k is the Boltzmann constant, T is the absolute temperature, and p is the pressure. The number density of solvent molecules (ρ) was also cited from ref 5. The third type of a solvent diameter (a_w) was determined from the actual molecular volume (V_w) without using SPT. Molecular volume (V_w) can be determined by the method of Edward, in which V_w is regarded as the summation of individual volume of molecular fragments.[6] This method reproduces well the actual molecular volume. Since it is assumed that solvent molecule is a sphere in SPT, a_β and a_σ obtained from eqs 1 and 2 are the defined parameters.[1] On the other hand, as a_w was obtained from V_w, this quantity is supposed to be the parameter correctly reflecting the actual molecular volume, whether the solvents are spherical or not. Cohesive energy density (ced) was obtained from eq 3[7]

$$\text{ced} = \Delta U_{vap}/V \cong \Delta H_{vap}/V \quad (3)$$

where ΔU_{vap} and ΔH_{vap} are, respectively, the energy and the heat of evaporation, and V is the molar volume of solvents.

Results and Discussion

Correlation among Three Types of Diameters. The three diameters (a_β, a_σ, a_w), the corresponding packing density (y_β, y_σ, y_w), and cohesive energy density (ced) are summarized in Table 1. First, correlation among a_β, a_σ, and a_w was investigated as illustrated in Figures 1 and 2, where the values of a_β inside the bracket in Table 1 were used for the plot. Figure 1 shows that a good linearity exists between a_β and a_w, where the regression line is given by eq 4 with a correlation coefficient 0.9959.

$$a_\beta = 1.140a_w - 1.143 \quad (4)$$

This good linearity means that one can estimate a_β values from a_w using eq 4, when a_β cannot be determined by eq 1 owing to the lack of experimental β values.

Figure 2 also gives a good linearity between a_σ and a_w, whose regression line is given by eq 5 with a correlation coefficient 0.9866.

$$a_\sigma = 1.147a_w - 1.211 \quad (5)$$

It is surprising that a_β, a_σ, and a_w have good correlation, that is, the slopes of eqs 4 and 5 (ca. 1.14) are both close to unity, while the intersections with the a_β and a_σ axes are both near −1. As indicated by eqs 1 and 2, the diameters a_β and a_σ are defined within the framework of SPT which assumes that a solvent molecule is a sphere.[1] On the other hand, a_w is the quantity directly reflecting the actual molecular volume (V_w), whether a solvent molecule is a sphere or not, because V_w is

* Tel: +81-29-861-6124; fax: +81-29-861-6123; e-mail: m.kodaka@aist.go.jp.

10.1021/jp031056t CCC: $27.50
Published on Web 12/18/2003

TABLE 1: Diameter (Å), Packing Density, and Cohesive Energy Density (ced) (Pa) of Various solvents[a]

solvent	a_β		a_σ	a_w	y_β	y_σ	y_w	ced × 10^{-8}	solvent	a_β	a_σ	a_w	y_β	y_σ	y_w	ced × 10^{-8}
water	2.74	[2.72]	2.88	3.40	0.360	0.418	0.688	24.35	3-methyl-1-butanol	5.52	5.35	5.84	0.486	0.442	0.574	5.10
ethylene glycol	4.43	[4.45]	4.42	4.88	0.489	0.488	0.655	10.18	2-methyl-2-butanol	5.52	5.30	5.84	0.485	0.429	0.572	4.59
methanol	3.54	[3.47]	3.31	4.10	0.343	0.280	0.534	9.19	3-methyl-2-butanol	5.52	5.30	5.84	0.490	0.433	0.579	4.79
ethanol	4.18	[4.13]	3.96	4.66	0.393	0.333	0.545	7.21	1-hexanol	5.87	5.69	6.14	0.508	0.463	0.582	4.95
1-propanol	4.70	[4.63]	4.50	5.12	0.435	0.383	0.562	6.30	2-methyl-1-pentanol	5.87		6.14	0.511		0.586	
2-propanol	4.70	[4.64]	4.47	5.12	0.425	0.366	0.549	5.92	4-methyl-2-pentanol	5.87	5.67	6.14	0.501	0.453	0.574	
carbon disulfide	4.14	[4.26]	4.32	4.63	0.368	0.418	0.514	4.54	2-ethyl-1-butanol	5.87	5.66	6.14	0.517	0.464	0.592	
acetone	4.55	[4.49]	4.45	4.98	0.400	0.375	0.527	4.17	*cis*-2-methylcyclo-hexanol	5.97		6.23	0.548		0.623	
ethyl bromide	4.53	[4.55]	4.51	4.97	0.390	0.385	0.515	3.62	*trans*-2-methylcyclo-hexanol	5.97		6.23	0.542		0.615	
chloroform	4.72	[4.77]	4.77	5.13	0.410	0.425	0.528	4.13	*cis*-3-methylcyclo-hexanol	5.97		6.23	0.536		0.609	
ethyl iodide	4.76	[4.81]	4.82	5.17	0.421	0.436	0.539	3.89	*trans*-3-methylcyclo-hexanol	5.97		6.23	0.540		0.613	
1,2-dichloroethane	4.79	[4.81]	4.86	5.20	0.437	0.456	0.558	4.31	1-octanol	6.47	6.34	6.67	0.539	0.507	0.590	4.54
benzene	4.97	[5.01]	5.03	5.36	0.433	0.449	0.541	3.79	2-ethyl-1-hexanol	6.47		6.67	0.543		0.595	
ethyl acetate	5.16	[5.17]	5.09	5.52	0.439	0.421	0.538	3.57	benzyl alcohol	5.55	5.61	5.86	0.519	0.536	0.612	
carbon tetrachloride	5.08	[5.15]	5.16	5.45	0.426	0.445	0.526	3.34	*m*-cresol	5.56	5.59	5.87	0.516	0.526	0.608	5.88
1-butanol	5.14	[5.13]	4.97	5.50	0.465	0.421	0.570	5.71	*trans*-2-buten-1,4-diol	4.49		4.93	0.481		0.638	
acetic anhydride	5.22	[5.18]	5.26	5.57	0.471	0.483	0.573	4.02	1,2-propanediol	4.91		5.30	0.505		0.636	9.12
toluene	5.38	[5.41]	5.43	5.72	0.461	0.472	0.551	3.56	1,3-propanediol	4.91	4.91	5.30	0.513	0.516	0.646	
chlorobenzene	5.32	[5.39]	5.45	5.66	0.464	0.498	0.559	4.16	glycerol	5.10		5.47	0.571		0.703	
aniline	5.27	[5.33]	5.38	5.62	0.504	0.536	0.610	6.09	propyl ether	5.84	5.76	6.11	0.455	0.438	0.523	2.59
bromobenzene	5.42	[5.51]	5.58	5.75	0.477	0.519	0.569	4.31	isopropyl ether	5.84	5.71	6.11	0.441	0.413	0.506	2.29
1,1,2,2-tetrachloro-ethane	5.47	[5.54]	5.58	5.79	0.488	0.518	0.579	4.25	butylvinyl ether	5.71		6.00	0.453		0.526	
cyclohexanol	5.64	[5.51]	5.50	5.94	0.547	0.507	0.639	6.00	butylethyl ether	5.84	5.76	6.11	0.457	0.440	0.525	
nitrobenzene	5.50	[5.59]	5.64	5.82	0.510	0.549	0.604	5.11	butyl ether	6.44	6.43	6.64	0.495	0.491	0.543	2.58
m-xylene	5.75	[5.76]	5.78	6.04	0.486	0.492	0.562	3.46	pentyl ether	6.97	6.99	7.10	0.525	0.529	0.556	
acetophenone	5.79	[5.84]	5.89	6.07	0.521	0.548	0.601	4.55	isopentyl ether	6.97	6.94	7.10	0.521	0.516	0.552	
ethyl ether	5.10	[5.03]	4.91	5.47	0.399	0.356	0.492	2.60	1,2-dimethoxyethane	5.25		5.60	0.436		0.529	
cyclohexane	5.48	[5.33]	5.36	5.80	0.476	0.446	0.565	3.04	cineole	6.62	6.65	6.80	0.546	0.552	0.591	
hexane	5.71	[5.65]	5.54	6.01	0.447	0.408	0.519	2.40	*p*-dioxane	4.97	5.06	5.36	0.452	0.476	0.565	
heptane	6.04	[5.97]	5.92	6.29	0.471	0.445	0.533	2.48	tetrahydropyran	5.23		5.58	0.460		0.559	3.56
octane	6.34	[6.32]	6.26	6.55	0.491	0.473	0.543	2.54	benzylethyl ether	6.18	6.27	6.41	0.516	0.539	0.576	
cyclopentane	5.09		4.95	5.46	0.438	0.403	0.540	3.01	anisole	5.52	5.64	5.83	0.485	0.519	0.573	
pentane	5.35		5.09	5.69	0.417	0.357	0.500	2.28	phenetole	5.86		6.14	0.500		0.573	
2-methylbutane	5.35		5.04	5.69	0.412	0.344	0.495	2.12	benzyl ether	7.01		7.14	0.569		0.601	
2,2-dimethylpropane	5.35		4.89	5.69	0.392	0.299	0.471	1.77	dimethoxymethane	4.83	4.75	5.23	0.398	0.379	0.505	3.24
methylcyclopentane	5.48		5.35	5.80	0.458	0.427	0.543	2.79	propionaldehyde	4.55		4.98	0.404		0.532	
2-methylpentane	5.71		5.51	6.01	0.443	0.396	0.514	2.25	butylaldehyde	5.01	5.11	5.39	0.437	0.465	0.544	
3-methylpentane	5.71		5.51	6.01	0.450	0.404	0.523	2.32	isobutylaldehyde	5.01		5.39	0.430		0.535	
2,2-dimethylbutane	5.71		5.46	6.01	0.440	0.384	0.511	2.07	benzaldehyde	5.44		5.76	0.498		0.593	
2,3-dimethylbutane	5.71		5.48	6.01	0.449	0.395	0.521	2.22	2-butanone	5.01	4.92	5.39	0.439	0.416	0.546	
methylcyclohexane	5.83		5.72	6.10	0.486	0.459	0.558	2.76	3-pentanone	5.41	5.33	5.74	0.468	0.447	0.559	
2-methylhexane	6.04		5.90	6.29	0.468	0.436	0.528	2.34	cyclohexanone	5.53		5.84	0.511		0.603	
3-methylhexane	6.04		5.89	6.29	0.474	0.439	0.535	2.39	4-methyl-2-pentanone	5.76	5.67	6.05	0.479	0.456	0.554	
2,3-dimethylpentane	6.04		5.87	6.29	0.479	0.439	0.541	2.36	formic acid	3.64	3.59	4.19	0.401	0.385	0.612	5.25
2,4-dimethylpentane	6.04		5.86	6.29	0.464	0.423	0.524	2.19	acetic acid	4.26	4.09	4.73	0.424	0.375	0.581	4.00
ethylcyclohexane	6.14		6.06	6.38	0.510	0.490	0.572	2.83	propionic acid	4.76	4.60	5.17	0.455	0.409	0.582	7.32
2,2,3-trimethylpentane	6.34		6.17	6.55	0.501	0.462	0.553	2.30	butyric acid	5.19	5.05	5.55	0.478	0.438	0.583	6.55
2,2,4-trimethylpentane	6.34		6.17	6.55	0.484	0.446	0.534	2.12	isobutyric acid	5.19	5.04	5.55	0.473	0.433	0.577	6.11
nonane	6.62		6.57	6.80	0.509	0.497	0.551	2.59	valeric acid	5.57	5.45	5.88	0.499	0.467	0.587	6.34
2,2,5-trimethylhexane	6.62		6.49	6.80	0.501	0.473	0.543	2.20	isovaleric acids	5.57	5.42	5.88	0.492	0.453	0.579	
cis-decahydro-naphthalene	6.53		6.44	6.72	0.566	0.544	0.617	3.32	hexanoic acid	5.91	5.81	6.18	0.518	0.491	0.591	
trans-decahydro-naphthalene	6.53		6.47	6.72	0.549	0.535	0.598	3.12	octanoic acid	6.51	6.44	6.70	0.546	0.529	0.596	
decane	6.88		6.85	7.02	0.523	0.517	0.558	2.62	oleic acid	8.56		8.50	0.621		0.607	
bicyclohexyl	7.04		6.99	7.17	0.583	0.571	0.615		propionic anhydride	5.93	5.94	6.19	0.508	0.510	0.579	
dodecane	7.35		7.35	7.44	0.548	0.548	0.567	2.68	butyric anhydride	6.52	6.52	6.71	0.532	0.532	0.580	
o-xylene	5.75		5.77	6.04	0.495	0.499	0.572	3.58	methyl formate	4.21	4.14	4.69	0.379	0.361	0.524	
p-xylene	5.75		5.78	6.04	0.484	0.491	0.560	3.42	ethyl formate	4.72	4.65	5.14	0.411	0.392	0.529	
ethylbenzene	5.74		5.78	6.03	0.485	0.495	0.562	3.43	propyl formate	5.16	5.18	5.52	0.442	0.448	0.541	
isopropylbenzene	6.07		6.08	6.31	0.502	0.506	0.566	3.22	methyl acetate	4.72	4.66	5.14	0.416	0.400	0.536	
mesitylene	6.08		6.09	6.33	0.508	0.510	0.572	3.40	propyl acetate	5.54	5.48	5.85	0.464	0.449	0.547	3.38
tetralin	6.17		6.20	6.41	0.542	0.550	0.606	3.96	isopropyl acetate	5.54		5.85	0.455		0.537	3.16
butylbenzene	6.36		6.41	6.57	0.518	0.528	0.572	3.26	butyl acetate	5.88	5.85	6.15	0.484	0.475	0.554	3.29
sec-butylbenzene	6.36			6.57	0.520		0.573	3.16	isobutyl acetate	5.88	5.81	6.15	0.481	0.464	0.550	2.94
tert-butylbenzene	6.36			6.57	0.522		0.576	3.15	pentyl acetate	6.20	6.18	6.43	0.502	0.497	0.560	
p-cymene	6.37		6.38	6.58	0.518	0.522	0.571	3.20	isopentyl acetate	6.20	6.15	6.43	0.499	0.489	0.557	

TABLE 1 (Continued)

solvent	a_β	a_σ	a_w	y_β	y_σ	y_w	ced × 10^{-8}	solvent	a_β	a_σ	a_w	y_β	y_σ	y_w	ced × 10^{-8}
cyclohexylbenzene	6.73		6.89	0.562		0.605		benzyl acetate	6.22		6.45	0.531		0.592	4.22
1-pentene	5.21	4.96	5.56	0.403	0.349	0.491	2.31	ethyl butyrate	5.88	5.83	6.15	0.483	0.470	0.553	3.16
cis-2-pentene	5.21	4.99	5.56	0.413	0.364	0.503	2.49	isopentyl isovalerate	7.00		7.13	0.537		0.567	2.32
trans-2-pentene	5.21	5.00	5.56	0.408	0.361	0.497	2.45	methyl acrylate	5.00		5.38	0.436		0.543	
1-hexene	5.58	5.43	5.89	0.436	0.401	0.512	2.43	methyl methacrylate	5.40		5.73	0.465		0.556	3.81
1-heptene	5.92	5.82	6.19	0.462	0.438	0.527	2.52	methyl oleate	8.71	8.81	8.63	0.612	0.633	0.595	
1-octene	6.23	6.17	6.46	0.483	0.469	0.538	2.57	methyl benzoate	5.91	6.03	6.18	0.518	0.550	0.592	4.54
1-nonene	6.52	6.49	6.71	0.501	0.494	0.547	2.62	ethyl benzoate	6.22	6.32	6.45	0.526	0.553	0.587	-
1-decene	6.78	6.77	6.94	0.517	0.515	0.554	2.65	propyl benzoate	6.51	6.68	6.70	0.539	0.584	0.588	3.22
cyclohexene	5.33	5.26	5.67	0.470	0.449	0.565		benzyl benzoate	7.04		7.17	0.577		0.608	
styrene	5.61	5.71	5.92	0.482	0.508	0.565	3.80	ethyl cinnamate	6.67	6.77	6.85	0.557	0.581	0.601	
β-pinene	6.42		6.62	0.531		0.583		γ-butyrolactone	4.87		5.27	0.477		0.603	
2-butanol	5.14	4.94	5.50	0.463	0.412	0.568	5.38	ethyl carbonate	5.67	5.68	5.97	0.471	0.475	0.549	
2-methyl-1-propanol	5.14	4.93	5.50	0.460	0.407	0.565	5.51	ethyl oxalate	6.04	6.11	6.29	0.511	0.529	0.577	
2-methyl-2-propanol	5.14	4.87	5.50	0.450	0.385	0.553	4.94	ethyl malonate	6.34	6.39	6.56	0.528	0.539	0.583	
1-pentanol	5.52	5.38	5.84	0.489	0.453	0.577	5.24	methyl maleate	5.93	6.09	6.19	0.522	0.567	0.595	
2-pentanol	5.52	5.34	5.84	0.485	0.439	0.573	4.86	ethyl maleate	6.52	6.67	6.71	0.540	0.577	0.589	
3-pentanol	5.52	5.34	5.84	0.491	0.443	0.580	4.92	butyl phthalate	8.00		8.00	0.604		0.605	
2-methyl-1-butanol	5.52	5.37	5.84	0.491	0.452	0.580	5.03	bis(2-ethylhexyl) phthalate	9.33		9.18	0.643		0.610	
butyl sebacate	8.69		8.61	0.614		0.597		*sec*-butylamine	5.24	5.08	5.59	0.446	0.406	0.541	3.21
fluorobenzene	5.09	5.12	5.46	0.440	0.449	0.543		*tert*-butylamine	5.24		5.59	0.428		0.519	2.81
p-fluorotoluene	5.49	5.50	5.80	0.469	0.473	0.556		cyclohexylamine	5.72	5.68	6.01	0.514	0.502	0.596	3.98
hexafluorobenzene	5.60		5.91	0.479		0.562	3.08	*o*-toluidine	5.65	5.70	5.95	0.527	0.541	0.615	5.27
1,1,2,2-tetrachloro-difluoroethane	5.44	5.27	5.76	0.423	0.385	0.504		allylamine	4.64	4.54	5.06	0.417	0.392	0.542	
1,2-dibromo-tetra-fluoroethane	5.43	5.33	5.76	0.420	0.397	0.500		ethylenediamine	4.67	4.70	5.09	0.475	0.484	0.616	
1-chloropropane	4.87	4.78	5.27	0.411	0.387	0.519	3.21	ethylenimide	3.95		4.46	0.375		0.540	
2-chloropropane	4.87	4.68	5.27	0.397	0.351	0.502	2.93	diethylamine	5.25	5.06	5.60	0.437	0.391	0.530	
1-chlorobutane	5.29	5.24	5.63	0.443	0.432	0.536	3.17	dipropylamine	5.96	5.86	6.22	0.482	0.460	0.549	2.96
1-chloro-2-methyl-propane	5.29	5.19	5.63	0.439	0.415	0.530		diisopropylamine	5.96	5.81	6.22	0.467	0.435	0.532	
2-chloro-2-methyl-propane	5.29	5.18	5.63	0.421	0.395	0.509	2.66	dibutylamine	6.54	6.49	6.73	0.518	0.505	0.564	2.96
1-chloropentane	5.66	5.63	5.95	0.469	0.463	0.547	3.15	pyrrole	4.63	4.70	5.05	0.450	0.471	0.586	6.50
1-chloronaphthalene	6.18	6.31	6.41	0.544	0.579	0.608		piperidine	5.38	5.30	5.71	0.493	0.473	0.590	4.32
dichloromethane	4.30	4.33	4.76	0.388	0.397	0.528	4.43	triethylamine	5.97	5.81	6.23	0.478	0.442	0.543	
1,1-dichloroethane	4.79	4.79	5.20	0.410	0.409	0.523	3.66	pyridine	4.85	5.00	5.25	0.444	0.487	0.563	5.00
1,1,1-trichloroethane	5.15	5.19	5.51	0.429	0.439	0.526	3.22	quinoline	5.82	6.01	6.10	0.524	0.577	0.603	
pentachloroethane	5.76	5.87	6.05	0.499	0.528	0.577		formamide	3.81	3.95	4.34	0.437	0.487	0.645	16.29
o-dichlorobenzene	5.63	5.64	5.93	0.498	0.501	0.583	4.44	*N*-methylformamide	4.41		4.86	0.457		0.613	
m-dichlorobenzene	5.63	5.77	5.93	0.492	0.529	0.575	4.24	*N*,*N*-dimethylformamide	4.90	4.89	5.29	0.480	0.476	0.604	6.14
3-chloropropene	4.70		5.12	0.398		0.514	3.44	*N*,*N*-dimethylacetamide	5.31		5.66	0.509		0.613	5.71
1,1-dichloroethylene	4.62		5.04	0.376		0.490	3.21	*N*-methylpropionamide	5.30		5.65	0.502		0.606	
cis-1,2-dichloroethylene	4.62		5.04	0.408		0.533		1,1,3,3-tetramethylurea	5.93		6.20	0.547		0.624	
trans-1,2-dichloro-ethylene	4.62		5.04	0.399		0.520		1-methyl-2-pyrroli-dinone	5.44		5.76	0.526		0.626	
trichloroethylene	4.99	5.07	5.37	0.436	0.455	0.544	3.81	1-butanethiol	5.63	5.37	5.94	0.523	0.452	0.612	3.39
tetrachloroethylene	5.33	5.44	5.67	0.465	0.493	0.559	3.86	benzenethiol	5.66	5.57	5.96	0.558	0.531	0.650	4.42
1-bromopropane	4.99	4.99	5.37	0.429	0.429	0.535	3.50	methyl sulfide	4.50	4.48	4.94	0.390	0.385	0.517	3.75
2-bromopropane	4.99	4.95	5.37	0.416	0.407	0.519	3.20	ethyl sulfide	5.37	5.36	5.71	0.451	0.448	0.540	3.30
1-bromonaphthalene	6.26	6.41	6.48	0.552	0.593	0.613		thiophene	4.78	4.87	5.19	0.434	0.459	0.554	4.36
bromoform	5.08	5.32	5.45	0.471	0.540	0.581		teterahydrothiophene	5.11	5.18	5.47	0.474	0.493	0.583	4.35
1,2-dibromoethane	5.04	5.18	5.41	0.465	0.507	0.577	5.34	2-methoxyethanol	4.87	4.84	5.26	0.458	0.451	0.580	
1,1,2,2-tetrabromoethane	5.86	6.02	6.13	0.541	0.589	0.620	5.98	2-ethoxyethanol	5.28	5.23	5.63	0.477	0.462	0.577	4.85
iodomethane	4.26	4.33	4.73	0.389	0.408	0.533	4.39	2-butoxyethanol	5.98	5.92	6.24	0.512	0.497	0.581	
1-iodopropane	5.19	5.26	5.55	0.452	0.468	0.551		furfuryl alcohol	5.11		5.48	0.484		0.595	5.76
2-iodopropane	5.19	5.25	5.55	0.440	0.455	0.537		triethylene glycol	6.23		6.46	0.570		0.634	
diiodomethane	5.03		5.40	0.495		0.614	6.32	2-(2-methoxyethoxy)-ethanol	5.78	5.83	6.06	0.514	0.529	0.594	
nitromethane	4.10	4.20	4.59	0.402	0.433	0.565	7.09	salicylaldehyde	5.61		5.91	0.525		0.615	
nitroethane	4.63	4.67	5.05	0.435	0.446	0.567	5.79	4-hydroxy-4-methyl-2-pentanone	5.91		6.18	0.524		0.598	
1-nitropropane	5.08	5.09	5.45	0.461	0.464	0.570	4.85	2-chloroethanol	4.62		5.04	0.461		0.601	
2-nitropropane	5.08	5.09	5.45	0.455	0.459	0.562	4.56	2-cyanoethanol	4.75		5.16	0.493		0.633	
acetonitrile	3.97	3.82	4.48	0.374	0.332	0.537	6.29	2-aminoethanol	4.55	4.59	4.99	0.493	0.506	0.648	
propionitrile	4.53	4.50	4.97	0.413	0.405	0.544		triethanolamine	6.37		6.58	0.613		0.675	
butyronitrile	4.99	4.95	5.37	0.446	0.436	0.556	4.21	2,2′-thiodiethanol	5.70		5.99	0.564		0.655	
isobutyronitrile	4.99	4.93	5.37	0.434	0.420	0.541	3.96	2-furaldehyde	4.98		5.36	0.468		0.585	
valeronitrile	5.39	5.35	5.72	0.472	0.461	0.565	4.25	bis(2-chloroethyl) ether	5.72	5.87	6.01	0.501	0.540	0.581	
hexanenitrile	5.75	5.72	6.04	0.494	0.485	0.572	3.97	epichlorohydrin	4.73	4.95	5.14	0.424	0.484	0.545	
4-methylvaleronitrile	5.75	5.68	6.04	0.493	0.475	0.570		*o*-nitroanisole	5.97	6.11	6.23	0.544	0.584	0.618	
octanenitrile	6.37	6.47	6.58	0.527	0.552	0.581	3.59	morpholine	5.12	5.18	5.49	0.485	0.502	0.596	5.02

[a] The a_β values inside the brackets are obtained from Eq 1.

TABLE 1 (Continued)

solvent	a_β	a_σ	a_w	y_β	y_σ	y_w	ced × 10^{-8}	solvent	a_β	a_σ	a_w	y_β	y_σ	y_w	ced × 10^{-8}
α-tolunitrile	5.78	5.89	6.06	0.525	0.556	0.606		ethyl lactate	5.70	5.61	5.99	0.508	0.483	0.590	4.29
benzonitrile	5.42	5.58	5.75	0.488	0.530	0.581	5.38	methyl salicylate	6.06		6.31	0.544		0.613	
acrylonitrile	4.33	4.38	4.79	0.387	0.400	0.524		methyl acetoacetate	5.59		5.90	0.509		0.597	
methacrylonitrile	4.82		5.23	0.419		0.533		ethyl acetoacetate	5.93	5.94	6.19	0.516	0.519	0.588	
propylamine	4.81	4.66	5.22	0.423	0.383	0.539	3.78	methyl cyanoacetate	5.20	5.28	5.55	0.502	0.526	0.612	6.99
isopropylamine	4.81	4.62	5.22	0.406	0.359	0.516	3.29	ethyl cyanoacetate	5.58	5.62	5.88	0.511	0.523	0.600	
butylamine	5.24	5.12	5.59	0.455	0.425	0.552	3.52	trifluoroacetic acid	4.64		5.07	0.409		0.532	
isobutylamine	5.24	5.07	5.59	0.452	0.410	0.549	3.34	*o*-chloroaniline	5.59	5.71	5.89	0.521	0.555	0.611	5.37

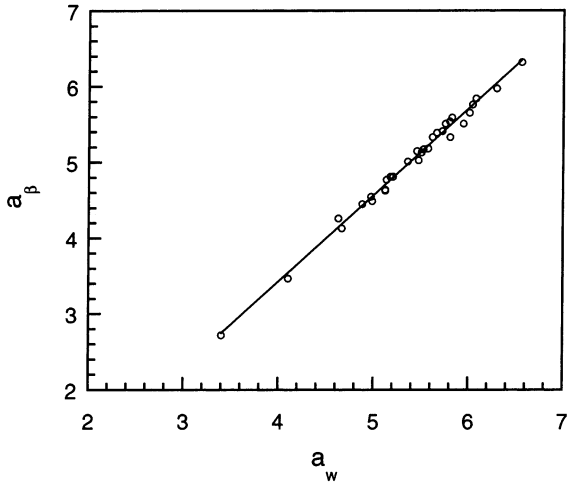

Figure 1. Relation between a_β and a_w. Regression line: $a_\beta = 1.140a_w - 1.143$ ($r = 0.9959$).

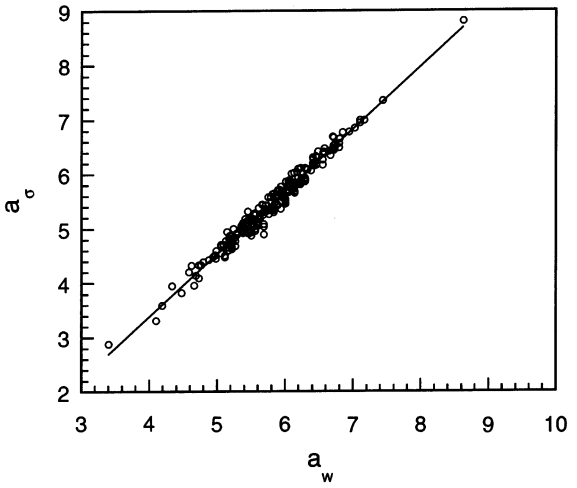

Figure 2. Relation between a_σ and a_w. Regression line: $a_\sigma = 1.147a_w - 1.211$ ($r = 0.9866$).

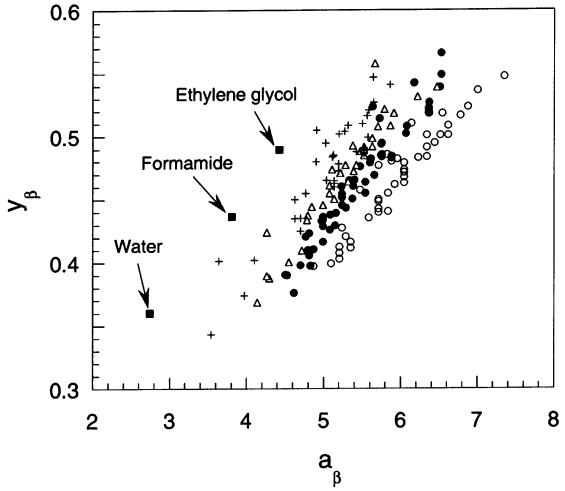

Figure 3. Relation between y_β and a_β. The data points are categorized according to the magnitude of cohesive energy density (ced): The value of ced ($\times 10^{-8}$) is 1.7−3 (○), 3−4 (●), 4−5 (△), 5−10 (+), >10 (■).

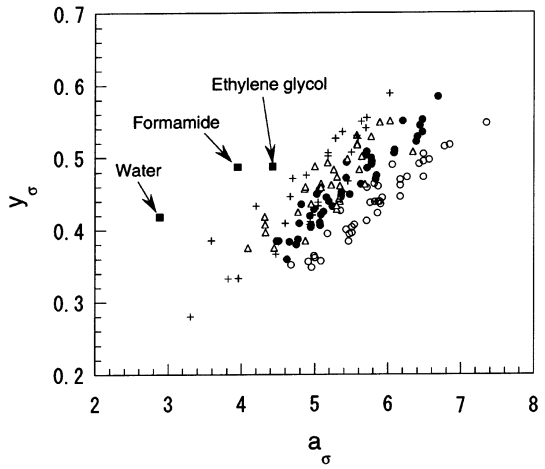

Figure 4. Relation between y_σ and a_σ. The data points are categorized according to the magnitude of cohesive energy density (ced): The value of ced ($\times 10^{-8}$) is 1.7−3 (○), 3−4 (●), 4−5 (△), 5−10 (+), >10 (■).

equal to $\pi a_w^3/6$. The good linearity between a_β and a_w (Figure 1) and between a_σ and a_w (Figure 2) suggests that SPT might be one of reliable theories for estimating solvent sizes.

Correlation between Packing Density and Diameter. Figure 3 shows the relation between a_β and y_β. Here, part of the a_β values was obtained from a_w using eq 4, since the experimentally available a_β data are not so numerous. Relatively good correlation is observed for the individual group of solvents categorized by ced values. Namely, y_β increases with a_β for solvents having analogous magnitude of ced, which means that larger solvents tend to have less fractional free volume and thus less available volume. Notably, these correlations hold for both polar and nonpolar solvents. Similarly to Figure 3, Figures 4 and 5 illustrate the correlation between a_σ and y_σ and between a_w and y_w, respectively. Clearly, this relationship between the packing density and the solvent diameter is generally valid despite using the molecular diameters determined by the three different methods. In all the above three cases, the three solvents with large ced (water, formamide, ethylene glycol) give the packing densities (y) higher than ordinary typical solvents possessing the same diameter and less ced, regardless of the application of SPT. Corresponding to this high-packing density, these three solvents actually exhibit hydrophobicity or solvophobicity against nonpolar solutes. Actually, formamide and ethylene glycol show solvophobicity in micelle formation,[3] solubility of nonelectrolytes,[8] and organic reactions such as Diels−Alder reaction and 1,3-dipolar cycloaddition.[9,10] Since y is equal to $\pi a_1^3\rho/6$, the large packing density (y) of these three solvents is obviously attributable to their number density (ρ)

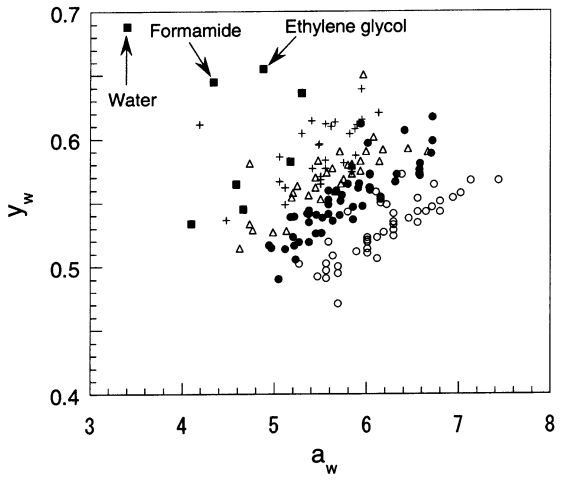

Figure 5. Relation between y_w and a_w. The data points are categorized according to the magnitude of cohesive energy density (ced): The value of ced ($\times 10^{-8}$) is 1.7−3 (○), 3−4 (●), 4−5 (△), 5−7 (+), >7 (■).

greater than that of ordinary solvents with the same size. Evidently, the greater ρ values are caused by the larger ced because of intermolecular hydrogen bonding of the solvents. According to Pohorille and Pratt, the free volume of water is distributed into small packets and consequently the free energy of cavity formation in water is inevitably larger than that of the organic solvent.[11] In view of their results, we can understand the meaning of the conclusion of the present study. As is clear from Figures 3−5, when we consider hypothetical water with the same size and less ced, its fractional free volume and available volume is larger (viz., packing density (y) is smaller) than that of real water and thus the effect of the smaller packets is decreased, leading to disappearance of hydrophobicity. The difference in the packing density (y) between real water and hypothetical water is due to hydrogen bonding. The novel point of the present method is that hydrophobicity and solvophobicity are characterized by considering the positions of water and the other polar solvents on the a_1-y map.

Conclusion

Hydrophobicity or solvophobicity is caused by the large deviation of packing density (y) from the value of a hypothetical solvent with the same size and less cohesive energy density (ced) induced by the structural difference, that is, hydrogen bonding.

References and Notes

(1) Reiss, H. *Adv. Chem. Phys.* **1966**, *9*, 1.
(2) Kodaka M. *J. Phys. Chem. B* **2001**, *105*, 5592.
(3) Akhter, M. S.; Alawi, S. M. *Colloids Surf.* **2003**, *219*, 281.
(4) Zhao, D.; Moore, J. S. *Macromolecules* **2003**, *36*, 2712.
(5) Riddick, J. A.; Bunger, W. B. In *Organic Solvents*, 3rd ed.; Weissberger, A., Ed.; Wiley-Interface: New York, 1970; Chapter 3.
(6) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261.
(7) Dack, M. R. J. *Chem. Soc. Rev.* **1975**, *4*, 211.
(8) Ruelle, P.; Kesselring, U. W. *J. Pharm. Sci.* **1998**, *87*, 987.
(9) Jenner, G.; Gacem, B. *J. Phys. Org. Chem.* **2003**, *16*, 265.
(10) Gholami, M. R.; Yangjeh, A. H. *Int. J. Chem. Kinet.* **2000**, *32*, 431.
(11) Pohorille, A.; Pratt, L. R. *J. Am. Chem. Soc.* **1990**, *112*, 5066.