

## Estimation of Water–Organic Interfacial Tensions. A Linear Free Energy Relationship Analysis of Interfacial Adhesion

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The work of adhesion between water and a series of immiscible organic liquids has been found to obey a linear solvation free energy relationship (LSER) on the basis of solute parameters for the organic compound. This relationship, together with the surface tensions of water and of the pure organic liquids, allows reasonably accurate estimation of the corresponding interfacial tensions and provides insight into the nature of intermolecular forces at the water–organic interface. Furthermore, the similarity of this multiparametric LSER to that for partitioning of organic solutes between water and the gas phase ( $\log L_W$ ) leads to a much simpler two-parameter relationship. Estimation of the interfacial tension with this latter relationship requires a knowledge of only two parameters,  $\log L_W$  and the surface tension of the pure organic liquid. Since reasonably accurate group contribution methods are available for estimating both  $\log L_W$  and surface tensions from molecular structure, this result provides a novel approach for a priori estimation of the water–organic interfacial tension directly from the chemical structure of the organic compound itself.

### Introduction

Interfacial tension is the fundamental parameter of surface chemistry that characterizes the free energy per unit area required for formation of an interface between two phases at constant temperature, pressure, and chemical composition. The interfacial tension governs the strength of adhesion between two surfaces, the stability of emulsions, the mobility of a liquid through orifices, wettability, miscibility, contact angles between phases in contact with one another, and the dynamics of phase separation after mixing in extraction processes.<sup>1–3</sup> Furthermore, the interfacial tension between organic liquids and water is an important determinant of the paths and transport mechanisms of organic liquids in the environment.<sup>4</sup>

Theoretical and empirical methods for calculating interfacial tensions are of interest because experimental interfacial tension data are available for only a rather limited set of organic liquids. (The largest compilations typically contain just over a hundred compounds, many of which are simple homologs.) In addition, it would be desirable to predict the interfacial tension between water and an organic liquid under conditions where accurate measurement of the equilibrium interfacial tension is difficult or impossible (e.g., for compounds that react with water at an appreciable rate or for water–organic interfaces in microheterogeneous environments).

Although there is an extensive literature on the prediction of the surface tensions of pure organic liquids on the basis of their molecular structure, recent reviews<sup>3,4</sup> have concluded there are no really reliable methods for predicting interfacial tensions between organic liquids and water. In particular, there are no

suitable methods for predicting organic–water interfacial tensions based solely on a knowledge of the molecular structure of the organic liquid.

The principal methods available for estimating interfacial tensions have been reviewed by Lyman et al.<sup>3</sup> and by Demond and Lindner.<sup>4</sup> On the basis of a comprehensive comparison of the accuracy of these methods, the latter authors concluded that the most reliable approaches are the mutual solubility method of Donahue and Bartell<sup>5</sup> and the method of Fu et al.<sup>6</sup> In the method of Donahue and Bartell,<sup>5</sup> the interfacial tension ( $\gamma_{12}$ ) between two liquid phases is estimated from the empirical relationship:

$$\gamma_{12} = a + b \log(S_{1/2} + S_{2/1}) \quad (1)$$

where  $a$  and  $b$  are empirically determined constants and  $S_{1/2}$  and  $S_{2/1}$  are, respectively, the mole fraction saturation solubilities of liquid 1 in liquid 2 and of liquid 2 in liquid 1.<sup>7</sup> In the approach developed by Fu et al.,<sup>6</sup> the interfacial tension is estimated on the basis of interfacial activity coefficients calculated from regular solution theory and pure component parameters derived from vapor–liquid and/or liquid–liquid equilibria. Demond and Lindner concluded that the Donahue and Bartell method provides reasonably good predictions of the interfacial tension when experimentally measured mutual solubilities are available, but it is much less accurate when the solubilities are unknown and must be estimated from other parameters. In the latter case, the Fu approach performed somewhat better, in addition to permitting one to treat more complex ternary or quaternary mixtures within the same conceptual framework.<sup>4</sup>

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Conceptually related to interfacial tension is the work of adhesion of one liquid to the other,  $W_{12}$ , defined<sup>8</sup> as

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \quad (2)$$

Early work by Girifalco and Good<sup>9</sup> and by Fowkes<sup>10</sup> emphasized the importance of general dispersion interactions between the two liquid phases in determining  $W_{12}$ . Subsequent work, particularly by Fowkes, has shown that the interfacial adhesion can be factored into a sum of contributions from dispersion ( $W_d$ ), polar ( $W_p$ ) and hydrogen bonding ( $W_h$ ) interactions:<sup>8,10,11</sup>

$$W_{12} = W_d + W_p + W_h \quad (3)$$

Many types of solvent–solute interactions, which in general depend on these same factors, have been successfully treated by using linear solvation free energy relationships (LSER) of the type:<sup>12–15</sup>

$$\Delta G = c + a \Sigma\alpha_2 + b \Sigma\beta_2 + s\pi_2 + rR_2 + v(V_x/100) \quad (4)$$

where  $\Delta G$  refers to the free energy change associated with the solvent–solute interaction (measured for a series of solutes in a single solvent medium),  $c$  is a constant, and  $\Sigma\alpha_2$ ,  $\Sigma\beta_2$ ,  $\pi_2$ ,  $R_2$ , and  $V_x$  are medium-insensitive parameters representing, respectively, the hydrogen bond acidity, hydrogen bond basicity, dipolarity, excess molar refraction, and molar volume of the organic solute molecule. This suggested to us that, if interfacial adhesion were indeed related to the larger problem of solvent–solute interactions, an linear solvation free energy relationship (LSER) of this type might permit quantitative estimation of  $W_{12}$  for compounds with known solute parameters. In this paper, we show that this is indeed the case. The resultant LSER for  $W_{12}$  based on solute parameters is chemically reasonable and leads to the perception of a much simpler relationship that requires only two parameters for the estimation of the organic–water interfacial tension, these being the surface tension of the pure organic liquid and the Henry's law constant for partitioning of the organic solute between the gas phase and water. Since both of these parameters can be estimated with reasonable accuracy by group contribution methods, the present work provides a framework for a priori estimation of the water–organic interfacial tension directly from the chemical structure of the organic compound itself.

## Results

**Experimental Data Compilation.** Literature data for the interfacial tension at the organic liquid–water interface ( $\gamma_{12}$ ) and for the corresponding surface tension of the organic liquid ( $\gamma_2$ ) are collected in Table 1. This table is based on a rather thorough search of the literature for compounds with known Abraham solute parameters whose surface and interfacial tensions have been measured at or near 20°. (The experimental temperatures are listed in the table.) The corresponding experimental work of adhesion  $W_{12}(\text{exp})$ , was calculated from eq 2 as the difference between the surface tensions of the individual pure liquids ( $\gamma_1$  and  $\gamma_2$ ) and the equilibrium interfacial tension at the interface between the mutually saturated liquids ( $\gamma_{12}$ ). The value of the surface tension of water at 20° ( $\gamma_1 = 72.75 \text{ dyn/cm}^{16}$ ) was used throughout. Although some of the data refer to slightly higher or lower temperatures, the variation in  $\gamma_1$  with temperature (ca. 1 dyn/cm over the range of the data<sup>16</sup>) is small relative to the standard error in the linear free energy relationships derived from the data analysis (ca. 3 dyn/cm, vide infra). Also listed in Table 1 are the literature values of  $\log L_W$ , where  $L_W$  is the dimensionless Ostwald coefficient

for solubility of the gaseous organic compound in water, defined as<sup>14</sup>

$$L_W = [\text{solute in water}]/[\text{solute in the gas phase}] = 1/H \quad (5)$$

where  $H$  is the dimensionless Henry's law constant (expressed as the concentration ratio rather than in units of pressure).

**Multiple Regression Analysis.** The values of the solute parameters  $\Sigma\alpha_2$ ,  $\Sigma\beta_2$ ,  $\pi_2$ , and  $R_2$  were taken from the compilations of Abraham;<sup>12–14</sup> the alternative  $\Sigma\beta_2^0$  value was employed for aniline, the only compound in the data set with a medium-sensitive hydrogen bond basicity. The solute molar volumes,  $V_x$ , were either taken from the same compilations or calculated as described by Abraham and McGowan.<sup>17</sup> Standard techniques of multiple regression analysis<sup>18</sup> were employed to correlate the interfacial work of adhesion  $W_{12}$  with these five solute parameters. The resultant best-fit equation for the 103 organic compounds of Table 1, retaining all five solute parameters, was found to be the following:

$$W_{12} = 50.4 + 38.6\Sigma\alpha_2 + 48.6\Sigma\beta_2 + 31.5\pi_2 - 3.0R_2 - 6.22V_x \quad (6)$$

with a multiple regression correlation coefficient of  $r = 0.984$ , a standard error of 3.5 and an  $F$  value of 600. Examination of the partial  $F$  values indicated that only the  $R_2$  term was of borderline statistical significance.

With this five-parameter equation, clear systematic deviations between the experimental and calculated values of  $W_{12}$  were observed for longer chain  $n$ -alkanes. The existence of an additional anisotropic dispersion contribution to the interfacial work of adhesion between water and higher  $n$ -alkanes was first pointed out by Fowkes.<sup>10</sup> This additional contribution becomes significant for  $n$ -alkanes higher than  $n$ -hexane and is roughly proportional to the number of carbon atoms in the alkyl chain above six. This suggested to us the inclusion of an additional parameter,  $N_C$ , specific to the  $n$ -alkanes higher than  $n$ -hexane.  $N_C$  is equal to the total number of carbon atoms in the  $n$ -alkane minus six (i.e.,  $N_C = 0$  for all  $n$ -alkanes up through  $n$ -hexane and is 1 for  $n$ -heptane, 2 for  $n$ -octane, etc.). Multiple regression analysis for the first 103 compounds of Table 1 provided the following six-parameter equation:

$$W_{12} = 52.9 + 39.3 \Sigma\alpha_2 + 51.0 \Sigma\beta_2 + 31.2\pi_2 - 2.38R_2 - 9.92V_x + 1.77N_C \quad (7)$$

with a multiple regression correlation coefficient of  $r = 0.987$ , a standard error of 3.2 and an  $F$  value of 614. The slightly improved statistical quality of this equation over the five-parameter equation is, of course, due entirely to the much better fit of the data for the  $n$ -alkanes. Examination of the cross-correlation matrix indicated that there were no significant colinearities between the six solute parameters. The standard errors and partial  $F$  values of the coefficients and the range of parameter values covered by the data set are given in Table 2. Table 1 lists the values of  $W_{12}$  calculated from eq 7 and values of  $\gamma_{12}$  calculated from the equation  $\gamma_{12} = \gamma_1 + \gamma_2 - W_{12}$  (see eq 2) for each compound. Also listed are the differences between the experimental and calculated values of  $W_{12}$  ( $\Delta W$ ), which are equal in magnitude, but opposite in sign, to the differences between the experimental and calculated values of  $\gamma_{12}$ . The experimental and calculated values of  $W_{12}$  are compared in Figure 1.

## Discussion

The standard error associated with the estimation of  $\gamma_{12}$  from calculated values of  $W_{12}$  and experimental surface tensions ( $\gamma_2$ )

**TABLE 1: Compilation of Experimental Data for Organic Liquid–Water Interfacial Tensions, Organic Liquid Surface Tensions, and the Logarithm of the Water–Gas Phase Partitioning Coefficient (Log  $L_W$ ) for Each Organic Compound, together with Experimental and Calculated Works of Adhesion at the Organic Liquid–Water Interface ( $W_{12}$  and the Corresponding Residuals  $\Delta W_{12}$ ) and Calculated Interfacial Tensions ( $\gamma_{12}$ )**

no.	compound	$\gamma_{12}$ (exptl) <sup>a</sup>	$T(^{\circ}\text{C})^b$ reference	$\gamma_2$ (exptl) <sup>a</sup>	$T(^{\circ}\text{C})^c$ reference	Log $L_W^d$	$W_{12}$ (exptl) <sup>a</sup>	$W_{12}$ (calcd) <sup>a</sup> eq 7	$\Delta W^{a,e}$ (exptl – calcd)	$\gamma_{12}$ (calcd) <sup>a,f</sup>	$W_{12}$ (calcd) <sup>a</sup> eq 9	$\Delta W^{a,g}$ (exptl – calcd)
Aliphatic Hydrocarbons												
1	pentane	49.0	20 <sup>h</sup>	15.80	25 <sup>h</sup>	−1.70	39.6	44.8	−5.2	43.8	43.4	−3.8
2	2-methylbutane	49.6	20 <sup>h</sup>	14.99	20 <sup>h</sup>	−1.75	38.1	44.8	−6.7	42.9	42.9	−4.8
3	<i>n</i> -hexane	51.1	20 <sup>h</sup>	18.41	20 <sup>h</sup>	−1.82	40.1	43.4	−3.3	47.8	42.2	−2.1
4	2-methylpentane	48.9	25 <sup>i</sup>	18.41	20 <sup>j</sup>	−1.84	42.3	43.4	−1.1	47.8	42.0	0.3
5	3-methylpentane	49.9	25 <sup>i</sup>	18.12	20 <sup>j</sup>	−1.84	41.0	43.4	−2.4	47.5	42.0	−1.0
6	2,2-dimethylbutane	49.7	25 <sup>i</sup>	16.18	20 <sup>j</sup>	−1.84	39.2	43.4	−4.2	45.5	42.0	−2.8
7	2,3-dimethylbutane	49.8	25 <sup>i</sup>	17.43	20 <sup>j</sup>	−1.72	40.4	43.4	−3.0	46.8	43.2	−2.8
8	<i>n</i> -heptane	50.2	25 <sup>h</sup>	19.66	25 <sup>h</sup>	−1.96	42.2	43.8	−1.6	48.6	42.8	−0.6
9	3-methylhexane	50.4	25 <sup>i</sup>	19.56	20 <sup>j</sup>	−1.99	41.9	42.0	−0.1	50.3	40.4	1.5
10	2,3-dimethylpentane	49.6	25 <sup>d</sup>	18.30	25 <sup>k</sup>	−1.85	41.5	42.0	−0.5	49.1	41.9	−0.4
11	2,4-dimethylpentane	50.0	25 <sup>i</sup>	17.66	20 <sup>j</sup>	−2.08	40.4	42.0	−1.6	48.4	39.4	1.0
12	<i>n</i> -octane	50.8	20 <sup>h</sup>	21.62	20 <sup>h</sup>	−2.11	43.6	44.2	−0.6	50.2	43.4	0.2
13	isooctane	50.1	25 <sup>h</sup>	18.33	25 <sup>h</sup>	−2.12	41.0	40.6	0.4	50.5	39.0	2.0
14	2,3,4-trimethylpentane	49.0	25 <sup>k</sup>	21.20	25 <sup>k</sup>	−1.88	45.0	40.6	4.4	53.4	41.5	3.5
15	<i>n</i> -decane	51.2	24.5 <sup>h</sup>	23.89	20 <sup>h</sup>	−2.32	45.4	44.9	0.5	51.7	45.4	0.0
16	<i>n</i> -dodecane	52.8	24.5 <sup>h</sup>	24.91	25 <sup>h</sup>		44.9	45.7	−0.8	52.0		
17	tetradecane	52.2	20 <sup>h</sup>	26.56	20 <sup>h</sup>		47.1	46.4	0.7	52.9		
18	cyclohexane	50.2	25 <sup>h</sup>	24.65	25 <sup>h</sup>	−0.90	47.2	46.9	0.3	50.5	51.9	−4.7
19	methylcyclohexane	41.9	25 <sup>l</sup>	23.68	20 <sup>j</sup>	−1.25	54.5	45.6	8.9	50.8	48.2	6.3
20	2-methyl-2-butene	36.7	20 <sup>h</sup>	17.64	20 <sup>h</sup>	−0.96	53.7	50.9	2.8	39.5	51.3	2.4
21	1-heptyne	28.2	20 <sup>h</sup>	22.68	20 <sup>h</sup>	−0.44	67.3	59.9	7.4	35.5	56.8	10.5
Aliphatic Halocarbons												
22	dichloromethane	28.3	20 <sup>h</sup>	27.84	20 <sup>h</sup>	0.96	72.3	71.4	0.9	29.2	71.7	0.6
23	trichloromethane	32.8	20 <sup>h</sup>	27.32	20 <sup>h</sup>	0.79	67.3	68.0	−0.7	32.1	69.9	−2.6
24	carbon tetrachloride	45.0	20 <sup>h</sup>	27.04	20 <sup>h</sup>	−0.06	54.8	56.3	−1.5	43.5	60.8	−6.0
25	1,2-dichloroethane	28.4	25 <sup>l</sup>	32.23	20 <sup>j</sup>	0.62	76.6	75.1	1.5	29.9	68.1	8.5
26	1,1,1-trichloroethane	36.6	25 <sup>l</sup>	25.18	20 <sup>j</sup>	0.14	61.3	61.9	−0.6	36.0	63.0	−1.7
27	1,1,2-trichloroethane	29.6	25 <sup>h</sup>	34.02	25 <sup>h</sup>	1.43	77.2	74.6	2.6	32.1	76.6	0.6
28	1-chloro-2-methylpropane	24.4	20 <sup>h</sup>	22.20	20 <sup>h</sup>		70.6	62.2	8.4	32.8		
29	2-chloro-2-methylpropane	23.8	20 <sup>h</sup>	18.91	20 <sup>h</sup>	−0.80	67.9	58.6	9.3	33.1	53.0	14.9
30	trichloroethylene	34.5	24 <sup>h</sup>	28.80	25 <sup>h</sup>	0.32	67.1	60.8	6.3	40.8	64.9	2.2
31	1,1,2,2-tetrachloroethylene	47.5	20 <sup>h</sup>	31.74	20 <sup>h</sup>	−0.07	57.0	56.2	0.8	48.3	60.7	−3.7
32	tribromomethane	40.9	20 <sup>h</sup>	45.53	20 <sup>h</sup>	1.56	77.4	74.6	2.8	43.7	78.0	−0.6
33	bromoethane	31.2	20 <sup>h</sup>	24.20	20 <sup>h</sup>	0.54	65.8	65.0	0.8	32.0	67.2	−1.4
34	1,2-dibromoethane	36.5	20 <sup>h</sup>	40.21	20 <sup>h</sup>	1.71	76.4	80.1	−3.7	32.8	79.6	−3.2
35	1-bromobutane	36.8	25 <sup>m</sup>	25.73	26.1 <sup>j</sup>	0.29	61.7	62.2	−0.5	36.3	64.6	−2.9
36	1-bromohexane	39.9	25 <sup>m</sup>	28.04	20 <sup>j</sup>	−0.13	60.9	59.5	1.4	41.3	60.1	0.8
37	diiodomethane	48.5	20 <sup>h</sup>	50.76	25 <sup>n</sup>		75.0	77.1	−2.1	46.4		
38	iodoethane	40.0	16 <sup>h</sup>	29.10	20 <sup>h</sup>	0.54	61.9	65.1	−3.2	36.8	67.2	−5.3
Aliphatic Ethers												
39	diethyl ether	10.7	20 <sup>h</sup>	17.11	20 <sup>h</sup>	1.17	79.2	76.3	2.9	13.6	73.9	5.3
40	diisopropyl ether	17.9	25 <sup>h</sup>	17.27	25 <sup>h</sup>	0.39	72.1	71.7	0.4	18.3	65.6	6.5
Aliphatic Aldehydes & Ketones												
41	heptanal	13.7	20 <sup>h</sup>	26.84	20 <sup>h</sup>	1.96	85.9	84.8	1.1	14.8	82.3	3.6
42	2-butanone	1.0	25 <sup>h</sup>	23.96	25 <sup>h</sup>	2.72	95.7	93.6	2.1	3.1	90.3	5.4
43	2-pentanone	6.3	20 <sup>h</sup>	24.15	20 <sup>h</sup>	2.58	90.6	91.6	−1.0	5.3	88.8	1.8
44	2-hexanone	9.7	20 <sup>h</sup>	25.49	20 <sup>h</sup>	2.41	88.5	90.2	−1.7	8.0	87.0	1.5
45	3-hexanone	13.6	20 <sup>h</sup>	25.39	20 <sup>h</sup>		84.6	89.6	−5.0	8.6		
46	4-methyl-2-pentanone	10.1	25 <sup>h</sup>	23.39	24 <sup>h</sup>	2.24	86.0	89.3	−3.3	6.8	85.2	0.8
47	3,3-dimethyl-2-butanone	10.8	20 <sup>h</sup>	23.43	20 <sup>h</sup>		85.4	88.4	−3.0	7.8		
48	2-heptanone	12.4	25 <sup>h</sup>	26.12	25 <sup>h</sup>	2.23	86.5	89.4	−2.9	9.5	85.1	1.4
49	2-octanone	14.1	20 <sup>h</sup>	26.79	20 <sup>h</sup>	2.11	85.5	87.5	−2.0	12.1	83.9	1.6
50	cyclohexanone	3.9	25 <sup>l</sup>	35.23	20.7 <sup>j</sup>	3.60	104.1	98.8	5.3	9.2	99.7	4.4
Esters and Nitriles												
51	methyl acetate	1.6	25 <sup>l</sup>	25.17	21 <sup>j</sup>	2.30	96.3	89.5	6.8	8.4	85.9	10.4
52	ethyl acetate	6.8	25 <sup>h</sup>	23.39	25 <sup>h</sup>	2.16	89.3	87.6	1.7	8.5	84.4	4.9
53	isopropyl acetate	10.0	25 <sup>l</sup>	22.14	21 <sup>j</sup>	1.94	84.9	85.7	−0.8	9.2	82.1	2.8
54	<i>n</i> -butyl acetate	14.5	25 <sup>h</sup>	24.88	25 <sup>h</sup>	1.94	83.1	84.2	−1.1	13.4	82.1	1.0
55	isobutyl acetate	13.2	25 <sup>l</sup>	23.06	25 <sup>o</sup>	1.73	82.6	84.4	−1.8	11.4	79.8	2.8
56	ethyl butyrate	15.7	20 <sup>h</sup>	24.46	20 <sup>h</sup>	1.83	81.5	83.6	−2.1	13.6	80.9	0.6
57	ethyl hexanoate	19.8	20 <sup>h</sup>	25.81	20 <sup>h</sup>	1.64	78.8	80.9	−2.1	17.7	78.9	−0.1
58	butyronitrile	10.4	20 <sup>h</sup>	27.44	20 <sup>h</sup>	2.67	89.8	92.1	−2.3	8.1	89.8	0.0
Aliphatic Amines and Nitro-compounds												
59	dipropylamine	1.7	20 <sup>h</sup>	22.82	20 <sup>h</sup>	2.68	93.9	89.9	4.0	5.7	89.9	4.0
60	di- <i>n</i> -butylamine	10.3	20 <sup>h</sup>	24.60	20 <sup>h</sup>	2.38	87.1	87.1	0.0	10.3	86.7	0.4
61	triethylamine	0.1	20 <sup>p</sup>	19.99	20 <sup>j</sup>	2.36	92.6	87.2	5.4	5.5	86.5	6.1
62	nitromethane	9.7	20 <sup>h</sup>	37.48	20 <sup>h</sup>	2.95	100.6	96.3	4.3	14.0	92.8	7.8

TABLE 1: (continued)

no.	compound	$\gamma_{12}$ (exptl) <sup>a</sup>	$T$ (°C) <sup>b</sup> reference	$\gamma_2$ (exptl) <sup>a</sup>	$T$ (°C) <sup>c</sup> reference	Log $L_w$ <sup>d</sup>	$W_{12}$ (exptl) <sup>a</sup>	$W_{12}$ (calcd) <sup>a</sup> eq 7	$\Delta W^{a,e}$ (exptl – calcd)	$\gamma_{12}$ (calcd) <sup>a,f</sup>	$W_{12}$ (calcd) <sup>a</sup> eq 9	$\Delta W^{a,g}$ (exptl – calcd)
Aliphatic Alcohols and Thiols												
63	1-butanol	1.8	25 <sup>h</sup>	24.95	25 <sup>h</sup>	3.46	95.9	97.3	–1.4	0.4	98.2	–2.3
64	isobutyl alcohol	2.1	18 <sup>h</sup>	22.94	20 <sup>h</sup>	3.30	93.6	96.3	–2.7	–0.6	96.5	–2.9
65	2-butanol	2.1	25 <sup>i</sup>	22.54	25 <sup>o</sup>	3.39	93.2	97.9	–4.7	–2.6	97.4	–4.2
66	1-pentanol	4.4	25 <sup>h</sup>	25.36	25 <sup>h</sup>	3.35	93.7	95.9	–2.2	2.2	97.0	–3.3
67	3-methyl-1-butanol	5.0	18 <sup>h</sup>	24.12	20 <sup>h</sup>	3.24	91.9	95.0	–3.1	1.9	95.8	–3.9
68	1-hexanol	6.8	25 <sup>h</sup>	25.81	25 <sup>h</sup>	3.23	91.8	94.5	–2.7	4.1	95.7	–3.9
69	1-heptanol	7.7	25 <sup>h</sup>	27.06	20 <sup>h</sup>	3.09	92.1	93.1	–1.0	6.7	94.3	–2.2
70	1-octanol	8.5	20 <sup>h</sup>	27.50	20 <sup>h</sup>	3.00	91.7	91.7	0.0	8.5	93.3	–1.6
71	2-octanol	9.4	20 <sup>h</sup>	26.32	20 <sup>h</sup>		89.7	92.5	–2.8	6.6		
72	1-nonanol	8.5	25 <sup>q</sup>	26.41	20 <sup>i</sup>	2.85	90.7	90.4	0.3	8.8	91.7	–1.0
73	1-decanol	8.3	25 <sup>q</sup>	27.32	20 <sup>i</sup>	2.67	91.7	89.0	2.7	11.0	89.8	1.9
74	1-undecanol	8.3	25 <sup>q</sup>	25.46	20 <sup>i</sup>		89.9	87.6	2.3	10.6		
75	1-dodecanol	7.7	25 <sup>q</sup>	26.06	20 <sup>i</sup>		91.2	86.2	5.0	12.7		
76	cyclohexanol	3.9	16.2 <sup>h</sup>	33.40	20 <sup>h</sup>	4.01	102.2	101.4	0.8	4.9	104.0	–1.8
77	ethyl mercaptan	26.1	20 <sup>h</sup>	23.47	20 <sup>h</sup>	0.84	70.1	69.6	0.5	26.6	70.4	–0.3
Benzene and Derivatives												
78	benzene	35.0	20 <sup>h</sup>	28.88	20 <sup>h</sup>	0.63	66.6	67.7	–1.1	33.9	68.2	–1.6
79	toluene	36.1	25 <sup>h</sup>	27.93	25 <sup>h</sup>	0.65	64.6	66.3	–1.7	34.4	68.4	–3.8
80	ethylbenzene	38.4	25 <sup>h</sup>	28.75	25 <sup>h</sup>	0.58	63.1	65.1	–2.0	36.4	67.6	–4.5
81	<i>o</i> -xylene	37.2	25 <sup>h</sup>	29.76	25 <sup>h</sup>	0.66	65.3	67.1	–1.8	35.4	68.5	–3.2
82	<i>m</i> -xylene	37.9	20 <sup>h</sup>	29.02	20 <sup>h</sup>	0.61	63.9	65.9	–2.0	35.9	67.9	–4.0
83	<i>p</i> -xylene	37.7	20 <sup>h</sup>	28.55	20 <sup>h</sup>	0.59	63.6	65.9	–2.3	35.4	67.7	–4.1
84	<i>n</i> -propylbenzene	38.5	20 <sup>h</sup>	28.98	20 <sup>h</sup>	0.39	63.2	63.9	–0.7	37.8	65.6	–2.4
85	mesitylene	38.7	20 <sup>h</sup>	28.00	20 <sup>h</sup>	0.66	62.1	66.0	–3.9	34.8	68.5	–6.4
86	<i>p</i> -cymene	34.6	20 <sup>h</sup>	29.44	20 <sup>h</sup>	0.70	67.6	63.7	3.9	38.5	68.9	–1.3
87	<i>n</i> -butylbenzene	39.6	20 <sup>h</sup>	29.23	20 <sup>h</sup>	0.29	62.4	62.3	0.1	39.7	64.6	–2.2
88	styrene	35.5	19 <sup>h</sup>	32.00	20 <sup>h</sup>	0.91	69.3	69.9	–0.6	34.9	71.1	–1.8
89	chlorobenzene	37.4	20 <sup>h</sup>	33.59	20 <sup>h</sup>	0.82	68.9	66.7	2.2	39.6	70.2	–1.3
90	bromobenzene	38.1	25 <sup>h</sup>	35.24	25 <sup>h</sup>	1.07	69.9	69.3	0.6	38.7	72.8	–2.9
91	iodobenzene	41.8	20 <sup>h</sup>	39.27	20 <sup>h</sup>	1.28	70.2	72.3	–2.1	39.7	75.1	–4.9
92	2-bromotoluene	41.2	20 <sup>h</sup>	34.63	20 <sup>h</sup>		66.2	67.5	–1.3	39.9		
93	anisole	25.8	20 <sup>h</sup>	35.70	20 <sup>h</sup>	1.80	82.6	80.3	2.3	28.1	80.6	2.0
94	ethyl phenyl ether	29.4	20 <sup>h</sup>	33.46	20 <sup>h</sup>	1.63	76.8	79.0	–2.2	27.2	78.8	–2.0
95	benzaldehyde	15.5	20 <sup>h</sup>	38.54	20 <sup>h</sup>	2.95	95.8	93.4	2.4	17.9	92.8	3.0
96	acetophenone	13.2	25 <sup>i</sup>	39.80	20 <sup>i</sup>	3.36	99.4	97.4	2.0	15.2	97.1	2.3
97	aniline	5.8	20 <sup>h</sup>	42.67	20 <sup>h</sup>		109.7	108.3	1.4	7.2		
98	nitrobenzene	25.6	20 <sup>h</sup>	43.38	20 <sup>h</sup>	3.02	90.5	90.9	–0.4	25.2	93.5	–3.0
99	2-nitrotoluene	27.2	20 <sup>h</sup>	41.46	20 <sup>h</sup>	2.63	87.0	89.0	–2.0	25.2	89.4	–2.4
100	3-nitrotoluene	27.7	20 <sup>h</sup>	40.99	20 <sup>h</sup>	2.53	86.1	87.7	–1.6	26.1	88.3	–2.2
101	phenol	0.8	20 <sup>p</sup>	40.90	20 <sup>i</sup>	4.85	112.9	110.5	2.4	3.2	112.9	0.0
102	benzyl alcohol	4.8	22.5 <sup>h</sup>	39.71	20 <sup>h</sup>	4.86	107.7	110.6	–2.9	1.9	113.0	–5.3
Others												
103	carbon disulfide	48.1	25 <sup>h</sup>	31.58	25 <sup>h</sup>		56.2	56.1	0.1	48.2		
Aliphatic Carboxylic Acids												
104	pentanoic acid	2.3	25 <sup>r</sup>	27.29	19.2 <sup>i</sup>		97.7	108.9	–11.2			
105	3-methylbutanoic acid	2.7	20 <sup>h</sup>	25.51	20 <sup>h</sup>	4.47	95.5	110.1	–14.6			
106	hexanoic acid	4.9	25 <sup>r</sup>	27.49	25 <sup>i</sup>		95.3	107.6	–12.3			
107	heptanoic acid	7.0	20 <sup>h</sup>	28.15	20 <sup>h</sup>		93.9	106.2	–12.3			
108	octanoic acid	8.5	20 <sup>h</sup>	28.82	20 <sup>h</sup>		93.1	104.8	–11.7			

<sup>a</sup> In units of dyn/cm (or erg/cm<sup>2</sup>). <sup>b</sup> Temperature and reference for the interfacial tension. <sup>c</sup> Temperature and reference for the surface tension. <sup>d</sup> Reference 14. <sup>e</sup> Residuals expressed as  $\Delta W = W_{12}(\text{exptl}) - W_{12}(\text{calcd})$  where  $W_{12}(\text{calcd})$  are the values predicted by eq 7. <sup>f</sup> Interfacial tension calculated as  $\gamma_{12}(\text{calcd}) = \gamma_1 + \gamma_2 - W_{12}(\text{calcd})$ ; see eq 2. <sup>g</sup> Residuals expressed as  $\Delta W = W_{12}(\text{exptl}) - W_{12}(\text{calcd})$  where  $W_{12}(\text{calcd})$  are the values predicted by eq 9. <sup>h</sup> Reference 4. <sup>i</sup> Li, B.; Fu, J. *Fluid Phase Equilib.* **1991**, *64*, 129. <sup>j</sup> Reference 22. <sup>k</sup> Abramzon, A. A. *J. Appl. Chem. (Leningrad)* **1991**, *64*, 2369. <sup>l</sup> Backes, H. M.; Ma, J. J.; Bender, E.; Maurer, G. *Chem. Eng. Sci.* **1990**, *45*, 275. <sup>m</sup> Turkevich, L. A.; Mann, J. A. *Langmuir* **1990**, *6*, 445. <sup>n</sup> Reference 9. <sup>o</sup> Reference 16. <sup>p</sup> Chavepey, G.; Platten, J. K.; Quazzani, M. T.; Glinski, J.; Cornu, D. *J. Colloid Interface Sci.* **1993**, *157*, 278. <sup>q</sup> Chavepey, G.; De Saedeleer, C.; Platten, J. K. *J. Colloid Interface Sci.* **1994**, *167*, 464. <sup>r</sup> Villers, D.; Platten, J. K. *J. Phys. Chem.* **1988**, *92*, 4023.

is 3.2 dyn/cm for the first 103 compounds in Table 1. This error is smaller than those found by Demond and Lindner<sup>4</sup> for the estimation of  $\gamma_{12}$  for 67 compounds using the methods of Donahue and Bartell<sup>5</sup> (3.8 dyn/cm) and of Fu et al.<sup>6</sup> (3.7 dyn/cm). Goodness of fit is only one criterion for judging whether a multiparametric regression equation is a valid LSER; the coefficients of the regression equation must also conform to reasonable chemical principles. In the present case,  $W_{12}$  exhibits an excellent correlation with a relationship (eq 7) based on six medium-insensitive solute parameters in which the principal contributors are the constant term and the coefficients of the

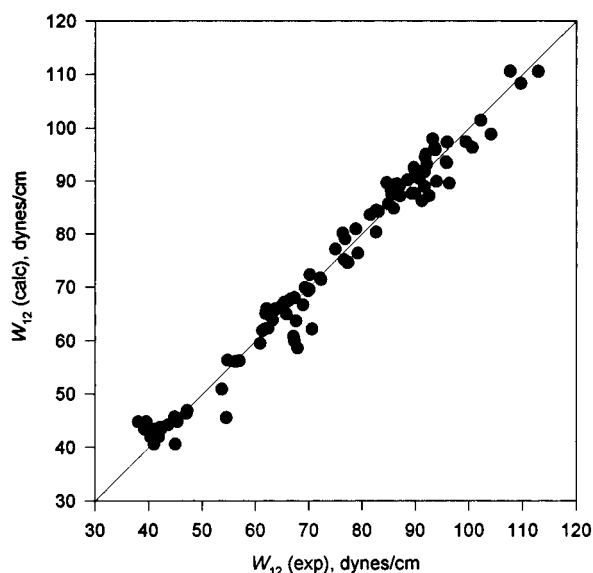
$\pi_2$ ,  $\Sigma\alpha_2$ , and  $\Sigma\beta_2$  terms. The latter three, which reflect the dipolarity and the hydrogen bond acidity and basicity of the organic component, clearly correspond to the polar ( $W_p$ ) and hydrogen bonding ( $W_h$ ) contributions to the interfacial adhesion postulated by Fowkes (eq 3).<sup>10</sup> Thus, eqs 6 and 7 provide a quantitative confirmation, based on independent, medium-insensitive, solute-specific parameters, of the sum-of-interactions approach exemplified conceptually in eq 3. For *n*-alkanes, correction for the known secondary contribution of chain alignment to  $W_d$  is accomplished via the inclusion of the  $N_C$  term. The constant  $c$  and the  $V_x$  term in eqs 6 and 7 incorporate

**TABLE 2: Summary of Standard Errors and Partial  $F$  Values of the Coefficients of Equations 7 and 9 and the Corresponding Range of Solute Parameters for the Data Set of Table 1**

Parameters and Coefficients of Equation 7							
	const	$\Sigma\alpha_2$	$\Sigma\beta_2$	$\pi_2$	$R_2$	$V_x$	$N_C$
coefficient	52.9	39.3	51.0	31.2	-2.38	-9.92	1.77
std. error	1.5	2.6	2.3	2.0	1.6	1.4	0.4
partial $F$		226	493	253	2.2 <sup>a</sup>	48	22
parameter range							
min		0	0	0	0	0.424	0
max		0.60	0.79	1.11	1.45	2.08	8
mean		0.07	0.26	0.46	0.35	0.98	0.20

Parameters and Coefficients of Equation 9			
	const	$\log L_W$	$N_C$
coefficient	61.5	10.6	2.1
std error	0.5	0.24	0.9
partial $F$		1929	5.3
parameter range			
min		-2.32	0
max		4.86	4
mean		1.07	0.08

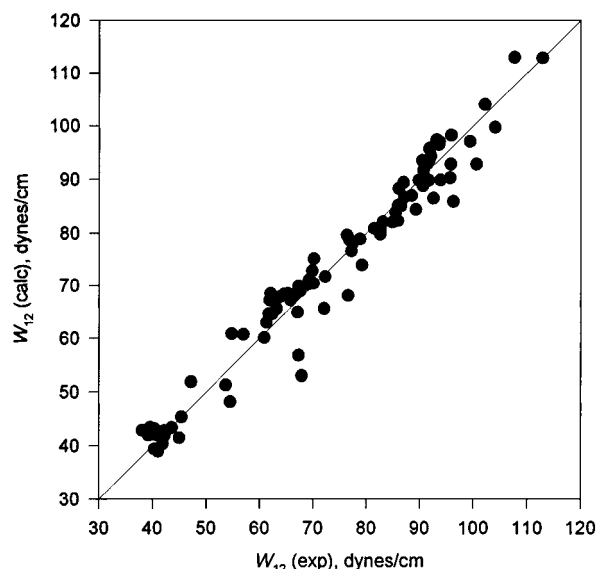
<sup>a</sup> Indicates value of borderline statistical significance. (See ref 18.)**Figure 1.** Correlation of  $W_{12}$  calculated from eq 7 with experimental  $W_{12}$  for compounds 1–103 in Table 1.

the contribution of general dispersion interactions to interfacial adhesion. The weak inverse dependence on  $V_x$  may reflect a small molecular-size-dependent correction to the general dispersion interactions and/or compensation for differences in molecular contact areas at the interface (cavitation-like interactions).

A particularly noteworthy feature of eqs 6 and 7 is the strong dependence of the work of interfacial adhesion on solute dipolarity and hydrogen bonding propensities. Comparison with other known LSERs based on solute parameters<sup>12–15</sup> revealed only one other example of a similar pronounced dependence on  $\pi_2$ ,  $\Sigma\alpha_2$ , and  $\Sigma\beta_2$ , coupled with a small inverse dependence on  $V_x$ , viz., the partitioning of organic solutes between water and the gas phase ( $\log L_W$ ), for which the LSER is<sup>14</sup>

$$\log L_W = -0.994 + 3.813\Sigma\alpha_2 + 4.841\Sigma\beta_2 + 2.549\pi_2 + 0.577R_2 - 0.869V_x \quad (8)$$

Furthermore, the relative contributions of the terms of eq 8 are almost identical to those in eqs 6 and 7. (Except for the  $R_2$

**Figure 2.** Correlation of  $W_{12}$  calculated from eq 9 with experimental  $W_{12}$  for 91 compounds having experimental  $\log L_W$  data in Table 1.

term, the corresponding coefficients of eq 8 are all numerically a factor of ca. 10 larger than those of eqs 6 and 7.) Clearly, then, one should expect to find a rather good correlation of  $W_{12}$  with  $\log L_W$ . Indeed, multiple regression analysis for the 91 compounds of Table 1 with known values of  $\log L_W$  (excluding compound 105) leads to the simple two-parameter equation:

$$W_{12} = 61.5 + 10.6 \log L_W + 2.13 N_C \quad (9)$$

with a multiple regression correlation coefficient of  $r = 0.979$ , a standard error of 4.0, and an  $F$  value of 1025. The standard errors and partial  $F$  values of the coefficients and the range of parameter values covered by the data set are given in Table 2. Table 1 lists the values of  $W_{12}$  calculated from eq 9 for each compound and the corresponding residuals ( $\Delta W$ ); the experimental and calculated values of  $W_{12}$  are compared in Figure 2.

A physically reasonable rationale for eq 9 is that the relative contributions of dipolar and specific solute–water interactions to the free energy of transfer of an organic molecule from the gas phase to bulk water (i.e., to  $\log L_W$ ) closely parallel those that come into play when the molecules at the surface of water and the organic liquid (i.e., that part of them exposed to the gas phase) are brought into molecular contact with each other to create the interface.

It is important to emphasize that our eq 9 is distinct from the relationship proposed by Donahue and Bartell (eq 1) in a very fundamental physical sense. Equation 1 relates  $\gamma_{12}$  to the mutual saturation solubilities of the organic and aqueous bulk phases. In contrast, our eq 9 makes a clear separation between terms that undoubtedly are influenced by the cohesive intermolecular interactions present in the bulk liquid phases (the pure-liquid surface tensions) and terms that are not (the work of adhesion). The choice of the gas phase rather than the mutually-saturated bulk phases as the reference state for the requisite partitioning equilibrium ( $\log L_W$ ) conveniently factors out most the bulk phase solute–solute interactions from this latter term.<sup>19</sup>

In some cases, however, the use of parameters based solely on the properties of the isolated, monomeric solute may be inappropriate or inadequate and may require solute-specific correction terms. One example of this is our inclusion of the  $N_C$  term in the LSERs to correct for the known additional dispersion interaction to adhesion for the higher  $n$ -alkanes. A second example is provided by the five aliphatic carboxylic acids

in Table 1 (compounds 104–108) for which eq 7 systematically overestimates  $W_{12}$  by ca. 10–15 dyn/cm.<sup>20</sup> Equation 9 also overestimates  $W_{12}$  by a similar amount in the one case (compound 105) where the value of  $\log L_W$  is known. Multiple regression analysis with these five acids included (all 108 compounds of Table 1) leads to a large decrease in the coefficient of the  $\Sigma\alpha_2$  term (as well as an overall decrease in the quality of the correlation) but to only minor changes in the values of the other coefficients. This suggests that the effective hydrogen bond acidity of these acids at the air–liquid and/or organic–water interface is only about half that of the isolated, monomeric acid molecule, although other factors such as partial ionization at the organic–water interface may also play a role.

## Conclusions

The work of adhesion per unit area between water and a series of immiscible organic liquids has been found to correlate well with a six-parameter LSER, eq 7. This relationship, together with the surface tensions of water and of the pure organic liquid, allows reasonably accurate estimation of the corresponding interfacial tension for organic molecules for which the requisite solute parameters are currently available. Furthermore, the marked similarity of this multiparametric LSER to that for partitioning of organic solutes between water and the gas phase ( $\log L_W$ ) leads to the much simpler two-parameter relationship, eq 9. With this latter relationship, estimation of the interfacial tension requires a knowledge of only two parameters,  $\log L_W$  and the surface tension of the pure organic liquid. Since reasonably accurate group contribution methods are available for estimating both  $\log L_W$ <sup>21</sup> and surface tensions<sup>3,22</sup> of pure liquids from molecular structure, this provides a novel approach for a priori estimation of the water–organic interfacial tension directly from the chemical structure of the organic liquid itself.

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## References and Notes

- (1) Adamson, A. W. *Physical Chemistry of Surfaces*; 5th ed.; Wiley-Interscience: New York, 1990.
- (2) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; Wiley-Interscience: New York, 1988; Chapter IIA.
- (3) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods*; McGraw-Hill: New York, 1982.
- (4) Demond, A. H.; Lindner, A. S. *Environ. Sci. Technol.* **1993**, 27, 2318.
- (5) Donahue, D. J.; Bartell, F. E. *J. Phys. Chem.* **1952**, 56, 480.
- (6) Fu, J.; Li, B.; Wang, Z. *Chem. Eng. Sci.* **1986**, 41, 2673.
- (7) More recently, Apostoluk, W.; Szymanowski, J. *Solvent Extr. Ion Exch.* **1996**, 14, 635 suggested the alternative relationship
 
$$\gamma_{12} = a + b \log S_{1/2} + c \log S_{2/1}$$
 which gave reasonable estimates of  $\gamma_{12}$  for a set of 26 compounds. LSERs based on solvent properties of the organic phase were employed to correlate mutual solubilities and interfacial tensions for subsets of the data. In the preliminary stages of the work reported here, we investigated the use of both solvent and solute parameters for estimating  $W_{12}$ ; in all cases solute parameters were found to give better correlation than solvent parameters.
- (8) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; Wiley-Interscience: New York, 1988; p 75.
- (9) Girifalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, 61, 904.
- (10) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, 56, 40; *J. Phys. Chem.* **1980**, 84, 510.
- (11) Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed.; CRC Press: Boca Raton, 1991.
- (12) Abraham, M. H. *Chem. Soc. Rev.* **1993**, 22, 73.
- (13) Abraham, M. H.; Chadha, H. S.; Whiting, G. S.; Mitchell, R. C. *J. Pharm. Sci.* **1994**, 83, 1085.
- (14) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. S. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1777.
- (15) Quina, F. H.; Alonso, E. O.; Farah, J. P. S. *J. Phys. Chem.* **1995**, 99, 11708.
- (16) *(16) CRC Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boca Raton, 1990.
- (17) Abraham, M. H.; McGowan, J. C. *Chromatographia* **1987**, 23, 243.
- (18) Draper, N. R.; Smith, H. *Applied Regression Analysis*; J. Wiley & Sons: New York, 1981. Wittink, D. R. *The Application of Regression Analysis*; Allyn and Bacon: Boston, 1988.
- (19) Abraham<sup>14</sup> has discussed this point in the context of  $\log L_W$ .
- (20) It should be noted that the methods of Donahue and Bartell<sup>5</sup> and of Fu et al.<sup>6</sup> also give large errors and that they overestimate rather than underestimate the interfacial tensions of these same acids.<sup>4</sup>
- (21) (a) Hine, J.; Mookerjee, P. K. *J. Org. Chem.* **1975**, 40, 292. (b) Suzuki, T.; Ohtaguchi, K.; Koide, K. *Comput. Chem.* **1992**, 16, 41. (c) Meylan, W. M.; Howard, P. H. *Environ. Toxicol. Chem.* **1991**, 10, 1283. (d) Russell, C. J.; Dixon, S. L.; Jurs, P. C. *Anal. Chem.* **1992**, 64, 1350. (e) Drefahl, A.; Reinhard, M. *J. Chem. Inf. Comput. Sci.* **1993**, 33, 886. (f) Li, A.; Doucette, W. J.; Andren, A. W. *Chemosphere* **1994**, 29, 657. (g) Coe, D. A. *J. Chem. Inf. Comput. Sci.* **1995**, 35, 168.
- (22) Quayle, O. R. *Chem. Soc. Rev.* **1953**, 53, 439.