Equations Correlate Molar Surface Tensions with Homolog Chain Length

Sir:

Surface tensions (γ, expressed dyn/cm or N/m), which are important both in theory and in practice (1,2), are not linear with homolog chain length (HCL). Hence, a relatively complex expression (Eq. 1) has been used to correlate γ with HCL (3):

$$\gamma^e = b + m \log L \quad [1]$$

where e, b, m, and L are exponent, intercept, slope, and chain length (measured by number of carbons, C, or M.W., M); e usually is 0.5, 1, 2, or 3. Molar surface tensions (M/γ), however, increase linearly with HCL (except for some lower homologs); hence, the simple Equation 2 is adequate for the M/γ vs. HCL correlations:

$$M/\gamma = b + mC \quad [2]$$

where M is in g and slope (m) and intercept (b) are g·cm/dyn.

Equation 2 has the advantages of simplicity, freedom from the need for adjustable parameters, and linearity of M/γ with entities (such as molar volumes) that also are linear with HCL. Another advantage is that M.W. equations ($M = b + mC$) can be divided by molar surface tension equations ($M/\gamma = b + mC$) to get equations for calculating γ from carbons (as shown by Eqs. 3–5) (based on *n*-alkane data):

$$M = 2.016 + 14.027\ C \quad [3]$$

$$M/\gamma = 2.162 + 0.38023\ C \quad [4]$$

$$\gamma(C + 5.686) = 5.3021 + 36.891\ C \quad [5]$$

TABLE 1
Equations[a] Correlating Molar Surface Tensions (M/γ) with Total Homolog Carbons, C: Esters[b,c,d,e]

	Carbons (C)	Temperature (°C)	Intercept (b)	Slope (m)	Correlation coefficient (r)	I^b
Me *n*-alkanoates	5–17	20	2.02	0.411	3, 49	32
Me *n*-alkanoates	9–19	40[f]	2.74	0.398	3, 77	32
Me *n*-alkanoates	7–19	75[g]	3.23	0.431	3, 82	32
Et *n*-alkanoates	6–14	20	2.27	0.418	4, 81	32
Et *n*-alkanoates	6–20	75[g]	3.65	0.416	3, 68	32
Pr *n*-alkanoates	7–15	20	2.39	0.401	4, 55	32
Bu *n*-alkanoates	8–16	20	2.44	0.397	4, 66	32
Pn *n*-alkanoates	7–23	20	2.11	0.438	6, 00	32
R acetates	7–16	20[h]	2.41	0.378	5, 06	32
Di-R carbonates	5–13	20	2.14	0.470	3, 65	48
Di-R succinates	8–14	20	1.37	0.512	6, 60	62
Di-Et dialkanoates	7–12	20	2.26	0.398	3, 84	62
Di-Pr dialkanoates	8–16	20	2.73	0.383	3, 84	62
R Glycolates	5–9	20	1.06	0.543	3, 70	48
R 3-methoxypropionates	7–11	20	1.90	0.465	4, 32	48
R 3-butoxypropionates	11–14	20	3.39	0.378	3, 18	48
Triglycerides	15–33	40	2.02	0.546	4, 24	91.97
Triglycerides	33–57	80	6.77	0.456	5, 24	91.97
Triglycerides	15–27	80	2.18	0.563	4, 07	91.97
R 1-naphthoates	13–18	20	–2.12	0.537	3, 64	17.87

[a] $M/\gamma = b + mC$, where M, γ, b, m, and C are M.W., surface tension (dyn/cm), intercept, slope, and number of carbon atoms, respectively.
[b] I is the intercept in the equation $M = I + 14.027\ C$.
[c] Data are from Jasper (4) unless otherwise indicated.
[d] Correlation coefficient, r, of 0.99949, for example, is given as 3, 49.
[e] R is *n*-alkyl; Et, Pr, Bu, and Pn are ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl, respectively.
[f] Data from Reference 5.
[g] Data from References 6 and 7.
[h] Data from Reference 8.

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TABLE 2
Equations[a] Correlating Molar Surface Tensions (M/γ) with Homolog Carbons, *C*: Oxygen and Nitrogen Compounds[b,c,d]

	Carbons (C)	Temperature (°C)	Intercept (b)	Slope (m)	Correlation coefficient (r)	I^b
Ethers, ROR	6–16	25	2.79	0.378	3, 49	18.016
$CH_2(OR)_2$	5–13	20	3.32	0.358	3, 79	34.02
2-Alkanones	3–7	20	1.14	0.450	4, 59	16
3-Alkanones	5–8	25	1.16	0.469	3, 35	16
Ketones, RCOR	5–11	25	1.19	0.466	3, 50	16
n-Alkanals	2–7	20	1.19	0.434	3, 36	16
n-Alkanols, ROH[e]	3–10	25	1.29	0.431	3, 24	18.016
2-ROH	3–8	20	1.55	0.426	4, 84	18.016
Poly(ethylene glycol)[f]	6–776	80	0.350	0.560	7, 00	—[f]
Acids, RCOOH	3–10	20	1.29	0.422	3, 85	32
Acids, RCOOH	6–18	75[g]	2.50	0.432	3, 83	32
Amines, RNH_2	3–6	20	1.43	0.404	4, 68	17.031
R_2NH	4–12	20	2.14	0.386	3, 85	17.031
R_3N	9–15	20	2.69	0.398	6, 50	17.031
Hydrazines, R_2NNH_2	6–10	20	1.96	0.444	5, 10	32.05
Nitriles, RCN	8–19	20	1.31	0.396	4, 24	13.00
$(CH_2)_n(CN)_2$	5–9	20	0.031	0.386	4, 23	23.97
3-R Pyridines	6–11	20	–0.450	0.518	4, 21	8.96

[a]$M/\gamma = b + mC$, where M, γ, b, m, and C are M.W., surface tension (dyn/cm), intercept, slope, and number of carbon atoms, respectively.
[b]Data from Jasper (4) unless otherwise indicated.
[c]I is the intercept in the equation $M = I + 14.027\ C$.
[d]Correlation coefficient, r, of 0.99949, for example, is given as 3, 49.
[e]Data from Reference 9.
[f]M.W. are calculated as $M = 18.02 + 22.025\ C$; carbons are calculated as $C = (M - 18.02)/22.025$; data are from References 4 and 10.
[g]Data from References 6 and 7.

TABLE 3
Equations[a] Correlating Molar Surface Tensions (M/γ) with Homolog Carbons, *C*: Hydrocarbons and Halogen, Sulfur, Phosphorus, and Boron Compounds[b,c,d,e]

	Carbons (C)	Temperature (°C)	Intercept (b)	Slope (m)	Correlation coefficient (r)	I^b
n-Alkanes	9–20	20	2.16	0.380	4, 39	2.016
Branched alkanes[f]	30–78	80	3.85	0.454	4, 02	2.016
Branched alkanes[g]	59–103	80	3.90	0.456	4, 85	2.016
R Cyclopentanes	6–15	20	1.47	0.380	4, 24	0.0
R Cyclohexanes	7–16	20	1.60	0.358	4, 21	0.0
1-Alkenes	9–20	20	2.05	0.378	4, 22	0.0
1-Alkynes	7–12	20	1.64	0.371	3, 86	–2.016
R Benzenes	9–16	20	0.464	0.412	3, 79	–6.048
R Fluorides	6–8	20	2.99	0.313	5, 71	20
R Chlorides[h]	6–18	20	2.31	0.382	4, 88	36.46
$(CH_2)_nCl_2$	4–9	20	2.13	0.364	4, 18	70.9
R Bromides[h]	3–18	20	3.64	0.376	3, 76	80.92
$(CH_2)_nBr_2$	4–9	20	3.72	0.389	4, 61	159.8
R Iodides	6–16	20	4.86	0.369	4, 83	127.92
$(CH_2)_nI_2$	3–9	20	4.82	0.457	3, 84	253.81
Thiols, RSH	3–8	20	1.73	0.443	4, 25	34.08
Sulfides, RSR	4–12	20	1.84	0.442	4, 48	34.08
RSSR	2–10	20	1.79	0.521	3, 38	66.145
Tri-R phosphites	6–24	20	4.38	0.432	3, 89	82
Tri-R borates	9–30	20	4.85	0.386	4, 39	61.83

[a]$M/\gamma = b + mC$, where M, γ, b, m, and C are M.W., surface tension (dyn/cm), intercept, slope, and number of carbon atoms, respectively.
[b]I is the intercept in the equation $M = I + 14.027\ C$.
[c]Correlation coefficient, r, of 0.999939, for example, is given as 4, 39.
[d]R is *n*-alkyl.
[e]Data from Jasper (4) unless otherwise indicated.
[f]Data from Reference 10; structure: $R_2CH(CH_2)_4CHR_2$.
[g]Data from Reference 10; structure: $R_2CH(CH_2)_4C(Et)_2(CH_2)_4CHR_2$.
[h]Data from References 4 and 10.

Reported in Tables 1–3 are (M/γ) vs. HCL expressions (Eq. 2) for 51 members of homologous series. As indicated by the correlation coefficients (r), agreement of calculated with experimental or literature values is good or excellent.

Values for the parameters in Equation 2, as listed in Tables 1–3, can be used to calculate M/γ in 51 homologous series; surface tensions, of course, can be easily calculated from M/γ. The M.W. needed for the calculations can be obtained from Equation 6 (intercepts, I, are listed in Tables 1–3):

$$M = I + 14.27\ C \qquad [6]$$

The values for the parameters in Equation 2, as listed in Tables 1–3, were used to calculate many new or additional surface tensions by interpolation. Upward extrapolation to the next homolog would give 51 additional surface tensions.

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