Equations Correlate Molar Dielectric Constants with Homolog Chain Length

Sir:

Dielectric constants (ε) are useful in evaluating polarities, estimating some solubilities, selecting plasticizers for polymers (1,2), and calculating molar polarizations and dipole moments (3,4).

Relative dielectric constants (or relative permittivities) of nonpolar materials, according to Maxwell's relationship (4), are related to refractive indexes (n): $\varepsilon = n^2$. The relationship is good for saturated hydrocarbons and fair for some olefins, but poor for nonhydrocarbons (Table 1).

Dielectric constants (ε) do not have a linear relationship with homolog chain length (HCL); hence, three-parameter expressions (Eqs. 1–3) have been used to correlate ε with homolog carbons, C:

$$\varepsilon = 2.0688 + 5.1869/(\mathrm{C} + 2.74) \qquad [1]$$

(n-FA, C_6–C_{18}, 71°C; $r^2 = 0.9997$; Ref. 5)

$$\varepsilon = 1.8582 + 58.959/(\mathrm{C} + 3.36) \qquad [2]$$

(TG, C_{15}–C_{33}, 40°C; $r^2 = 1.000$; Ref. 5)

$$\varepsilon = 2.1071 + 18.277/(\mathrm{C} + 1.02) \qquad [3]$$

(methyl n-alkanoates, C_7–C_{19}, 40°C; $r^2 = 0.9997$; Ref. 5)

Molar dielectric constants (M/ε and εM), however, are linear with HCL (except for some lower homologs). Equation 4 has been published for correlating M/ε with homolog carbons for 1-alkenes (6).

$$\mathrm{M}/\varepsilon = 2.384 + 6.34363\mathrm{C} \qquad [4]$$

(1-alkenes, C_6–C_{13}, 20°C; $r^2 = 0.9998$; Ref. 6)

In the present work, Equations 5 and 6 were developed for correlating molar dielectric constants with HCL (measured by homolog carbons, C) (Tables 2, 3). Equations 5 and 6 have the advantages of being simple, not requiring adjustable parameters, and having linear relationships with entities (e.g., molar volumes) that also are linear with HCL:

$$\mathrm{M}/\varepsilon = \mathrm{b} + \mathrm{mC} \qquad [5]$$

$$\varepsilon\mathrm{M} = \mathrm{b}' + \mathrm{m}'\mathrm{C} \qquad [6]$$

where b and b′ are the intercept and m and m′ are the slope.

Equations correlating ε with homolog carbons, C, can be developed by dividing M.W. equations (M = b + 14.027C) by Equation 8. This is illustrated with n-alkane data (Eqs. 7–9).

TABLE 1
Comparison of Dielectric Constants at 20°C and Squared Refractive Indexes $[(n^{20}_D)^2]^a$

Compound	ε^{20}	Δ^b	Compound	ε^{20}	Δ^b
Hexane	1.89	0.0004	Butyl acetate	5.07	3.127
Octane	1.948	0.0047	Triacetin	7.11	5.065
Decane	1.99	–0.0013	Acetone	21.01	19.16
Isopentane	1.85	–0.017	Butylmethyl ketone	14.56	12.60
Methylcyclopentane	1.19	–0.0027	Propanal	18.5	16.64
Cyclohexane	2.02	0.015	Benzaldehyde	17.85	15.46
Ethylcyclohexane	2.05	0.0035	Ethanol	25.3	23.45
cis-Decahydronaphthalene	2.22	0.0266	Acetic acid	6.20	4.32
trans-Decahydronaphthalene	2.18	–0.0206	Acetic anhydride	22.45	20.52
1-Heptene	2.09	0.131	Butylamine	4.71	2.741
1-Tridecene	2.14	–0.084	Dibutylamine	2.77	0.760
Cyclopentene	2.08	–0.056	Tributylamine	2.23	0.240
Cyclohexene	2.22	–0.128	Butanenitrile	24.83	22.91
Benzene	2.28	0.027	*N,N*-Dimethylformamide	38.25	36.20
Butylbenzene	2.36	0.141	*N*-Methylformamide	189.0	187.0
Styrene	2.47	0.098	1-Chlorobutane	7.28	5.314
1,2,3,4-Tetrahydronaphthalene	2.77	0.394	1-Bromopropane	8.09	6.033
1-Methylnaphthalene	2.92	0.305	1-Iodobutane	6.27	4.020
Diethyl ether	4.27	2.44	Carbon disulfide	2.63	0.033
Diisopentyl ether	2.82	0.296	Dimethyl sulfide	6.70	4.62

[a] Data from Reference 7.
[b] $\Delta = \varepsilon^{20}$ less $[(n^{20}_D)^2]$, where 20 is 20°C.

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TABLE 2
Equations Correlating Molar Dielectric Constants (M/ε or εM) with Homolog Carbons (C): Oxygen Compounds

Compound	Carbons, C	Temp. (°C)		Intercept, b or b′	Slope, m or m′	Corr. Coeff., r^2	Ref.	I[a]
DiR ethers	6–20	20	M/ε	–5.078	5.901	1.000	7,8	18.02
Methyl *n*-alkanoates	8–16	20	M/ε	–12.07	5.604	0.9998	9	32
Methyl *n*-alkanoates	5–9	40	M/ε	–5.503	5.057	0.9990	9	32
Methyl *n*-alkanoates	10–20	40	M/ε	–14.12	5.929	0.9997	9	32
Ethyl *n*-alkanoates	7–16	20	M/ε	–8.11	5.097	0.9998	8	32
R acetates	6–16	20	M/ε	–8.708	5.190	0.9992	10	32
Phenyl *n*-alkanoates	8–18	20	M/ε	–21.99	5.902	0.9999	8	23.94
Di-R phthalates	16–24	20	M/ε	–22.07	4.051	0.9988	8	53.92
Di-R phthalates	12–26	45	εM	1319	22.07	0.9989	11	53.92
Di-R sebacates	12–54	25	M/ε	–45.04	7.316	1.000	8	61.95
R benzoates	9–13	20	M/ε	–17.79	4.662	0.9996	8	23.98
TG[b]	21–57	20	M/ε	–30.55	5.567	1.000	8	91.97
TG	21–39	40	M/ε	–32.34	5.815	0.9998	11	91.97
TG	15–27	40	M/ε	–21.15	5.354	0.9993	11	91.97
2-Alkanones	6–11	20	M/ε	–9.192	2.681	0.9999	12	16.00
1-Alkanols	6–10	20	M/ε	–11.21	3.069	0.9866	7,8	18.02
1-Alkanols	12–22	75	M/ε	–34.34	6.593	0.9991	13	18.02
2-Alkanols	5–10	25	εM	1484	–57.21	0.9933	7,8	18.02
$ROCH_2CH_2OH$	16–22	65	M/ε	–25.11	5.911	0.9993	14	34.02
n-Alkanoic acids	5–9	20	M/ε	6.174	6.485	0.9970	3,7,12	32
n-Alkanoic acids	6–18	71	M/ε	3.959	6.590	1.000	9	32

[a] I is the intercept in the M.W.: $M = I + 14.027C$.
[b] The ε value for triolein is used to estimate the ε value for tristearin.

$$M = 2.016 + 14.027C \qquad [7]$$

$$M/\varepsilon = 6.886 + 6.4760C \qquad [8]$$
(*n*-alkanes, 20°C; C_5–C_{19}; $r^2 = 1.000$; Ref. 7)

$$\varepsilon(C + 1.063) = 0.31130 + 2.1660C \qquad [9]$$

Equations correlating ε with homolog carbons can be obtained also by dividing Equation 10 by Equation 7:

$$\varepsilon M = -19.004 + 30.185C \qquad [10]$$
(*n*-alkanes, 20°C; C_5–C_{19}; $r^2 = 1.000$)

$$\varepsilon(C + 0.1437) = -1.3548 + 2.1519C \qquad [11]$$

M/ε vs. C equations and εM vs. C equations are presented in Tables 2 (oxygen-containing compounds) and 3 (hydrocarbons; nitrogen-, halogen-, and sulfur-containing compounds). As indicated by the correlation coefficients, r^2, the agreement of calculated ε values with literature values is fair to excellent.

Because of data scarcity, some equations in Tables 2 and 3 are based on only a few homologs. Such equations are particularly valuable because they can be used to estimate many additional or new dielectric constants by interpolation or prudent upward extrapolation.

TABLE 3
Equations Correlating Molar Dielectric Constants (M/ε or εM) with Homolog Carbons (C): Hydrocarbons, Nitrogen, Halogen, and Sulfur Compounds

Compound	Carbons, C	Temp. (°C)		Intercept, b or b′	Slope, m or m′	Corr. coeff., r^2	Ref.	I[a]
n-Alkanes	5–22	20	M/ε	6.980	6.467	1.000	8	2.02
2-Methyl alkanes	5–10	20	M/ε	6.880	6.473	1.000	15	2.02
1-Alkenes	6–13	20	M/ε	2.384	6.346	0.9998	6	0.0
R Cyclopentanes[b,c]	5–40	20	M/ε	3.666	6.436	1.000	16	0.0
R Cyclohexanes[b,c]	8–40	20	M/ε	3.235	6.435	1.000	16	0.0
R Benzenes	8–14	20	M/ε	–11.61	6.860	0.9997	7	–6.05
Amines, RNH_2	6–11	20	M/ε	–8.870	5.612	0.9997	8	17.03
Amines, R_2NH	4–8	20	M/ε	–7.022	6.698	0.9998	7	17.03
Amines, R_3N	6–12	20	M/ε	4.380	6.227	0.9999	8	17.03
Nitriles, RCN	4–8	20	M/ε	–3.590	1.571	0.9990	8	13.00
Alkyl chlorides	6–12	20	M/ε	–9.331	4.819	0.9996	8	36.46
Alkyl bromides	7–18	25	M/ε	–5.863	5.577	0.9988	8	80.91
Alkyl iodides	6–16	20	M/ε	2.741	6.099	0.9998	8	127.9
Thiols, RSH	5–8	20	M/ε	–4.298	5.151	0.9995	8	34.08
Sulfides, RSR	4–10	25	εM	41.63	25.54	0.9940	8	34.08

[a] I is intercept in $M = I + 14.027C$.
[b] R is *n*-alkyl.
[c] The R cyclopentane and R cyclohexane equations are based on the assumption that $\varepsilon = n^2$ (Refs. 15 and 16).

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Charles H. Fisher*
Chemistry Department
Roanoke College
Salem, Virginia 24153

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*E-mail: fisher@roanoke.edu