

LETTER TO THE EDITOR

Semi-empirical expression for the dielectric constant of polar, polarisable liquids

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Abstract. A new formula is compared with that of Onsager, Kirkwood and Fröhlich (OKF) for 39 associated and non-associated liquids. The new expression is found to be generally superior to the older one and often yields excellent estimates of the static dielectric constant with no disposable parameters such as the uncertain Kirkwood correlation factor g needed in the OKF equation.

In the course of work on a finite-length dipole treatment of the double layer in aqueous electrolytes (Macdonald and Kenkel 1983), we stumbled across a simple dielectric constant formula which has proved to have high accuracy and predictive value. The formula is semi-empirical and has no adequate theoretical background because it was later found that it arose from a defective theoretical analysis. Nevertheless, its wide applicability to real liquids makes it useful for obtaining good estimates, over a broad range of temperature and density, of the vapour-phase dipole moment μ_v , given a value of the bulk static dielectric constant ϵ , or vice versa.

The new formula may be written

$$\epsilon = \epsilon_\infty \cosh[r_N(9y/\epsilon_\infty)^{1/2}] \quad (1)$$

where the conventional quantity y is

$$y \equiv 4\pi N_v \mu_v^2 / 9kT \quad (2)$$

and

$$r_N \equiv \mu / \mu_v \quad (3)$$

$$N_v \equiv N_A \rho / M_0. \quad (4)$$

Thus r_N is the factor by which the dipole moment in the liquid, μ , differs from that in the vapour. Here N_A is Avogadro's number, ρ is the density at absolute temperature T and M_0 is the molecular weight. As usual, the quantity ϵ_∞ is the dielectric constant at sufficiently high frequencies that permanent dipole effects no longer contribute to ϵ . For comparison, the more complicated, conventional Onsager–Kirkwood–Fröhlich (OKF) formula (Böttcher 1973), written in terms of

$$r_0 \equiv \mu_{\text{Onsager}} / \mu_v$$

is

$$\epsilon = \epsilon_{\infty} + [\epsilon/(2\epsilon + \epsilon_{\infty})][r_0^2(9y)]. \quad (5)$$

Here, $r_0^2 \equiv g$, the factor usually introduced to account for possible association in the liquid. In Onsager's original treatment, $g = 1$, induced polarisation was neglected, and ϵ_{∞} was thus taken unity. When such polarisation is not neglected, it is customary (Böttcher 1973) to take $\epsilon_{\infty} = n^2$ or sometimes 1.05 or 1.1 times n^2 , where n is the index of refraction.

Although the OKF equation has a definite theoretical basis, there is uncertainty in the proper calculation (Hasted 1972, Böttcher 1973, Sceats *et al* 1979[†], Stillinger 1982) of g , and modern work has even called in question the entire theoretical justification of the OKF formula. As R H Cole (1980) has recently written:

'... the problem of evaluation to obtain ϵ for even moderate polar substances is at present in a less well defined and satisfactory state than it seemed to be 10 years ago. Then it appeared that Onsager's equation was a reasonably good relation between molecular dipole moments and static permittivities, with substantial deviations only for strong dipole interactions or specific short range effects such as association and hydrogen bonding. Since then, several statistical many-body dipole interaction theories have been developed, all of which predict static permittivities much larger than the Onsager value for even relatively small values of the dipole interaction strength as expressed by the variable y ... The extent of the deviations can be suggested by the fact that the value of y appropriate to liquid water gives permittivities larger than the experimental one, ordinarily accounted for by a Kirkwood g factor of order 2.5 as a result of intermolecular hydrogen bonding... The moral seems to be that the point dipole interaction models used are a poor representation of real molecular charge interactions and orientation-dependent intermolecular forces in such systems...'

Thus, the OKF formula should probably be considered as semi-empirical as well. Unfortunately, modern complicated statistical treatments still lack adequate predictive value to be of general practical use (Wertheim 1979, Cole 1980, Stillinger 1982). It is therefore the object of this note to compare the applicability of the new formula and the OKF expression for a wide variety of dipolar liquids at many temperatures. In order to do so most simply with only one disposable constant, r , we shall employ experimental values of ϵ and μ_v and shall take $\epsilon_{\infty} = n^2$. When necessary, we use the Clausius–Mossotti relation to obtain n^2 at various densities, given its value at one density.

Tables 1 and 2 shows our results for r_N and r_0 . If we wished to use either equation (1) or (5) to obtain μ_v or ϵ , given the other, without any disposable constants, we would set $r = 1$ and thus take $\mu = \mu_v$. Therefore the closer the values of r_N and r_0 are to unity, the better this possibility is satisfied. A solid dot has been placed in the tables by each row where r_N is closer to unity than r_0 or where they are equally close. The results indicate for non-associated liquids that the two formulae are roughly equivalent in their predictive value, although for some materials one is better and for other materials the other is superior. Most of the data used here were obtained from Böttcher (1973) and Weast (1981–2), but we also used results from Malmberg and Maryott (1956), Gray (1972), Fine and Millero (1973), Hasted and Schahidi (1976) and Stillinger (1982) for water and

[†] The equation for ϵ quoted in this paper is not that actually used, and two of the calculated μ values in table 9 have misprints.

Table 1. Values of r_N and r_0 for some non-associated liquids. An asterisk after a temperature value indicates the boiling point.

Material	$T(^{\circ}\text{C})$	ε	y	r_N	r_0
Triethylamine	25	2.42	0.064	1.25	1.15
Dimethylamine	0	2.57	0.092	1.27	1.19
Bromoform	20	4.39	0.233	1.25	0.98
Chloroform	20	4.78	0.264	1.38	1.22
Chloroform	61*	4.23	0.220	1.38	1.24
Aniline	20	6.89	0.534	1.21	0.98
Aniline	185*	4.54	0.291	1.23	1.05
Iodobenzene	20	4.48	0.539	0.84	0.65●
Bromobenzene	25	5.40	0.559	1.00	0.82●
Chlorobenzene	20	5.64	0.584	1.02	0.86●
Chlorobenzene	132*	4.20	0.374	1.04	0.91●
Dibromomethane	15	7.41	0.624	1.17	0.99
1,1,1-trichloroethane	20	5.66	0.636	1.00	0.90●
2-chloro-2-methylpropane	20	9.90	0.656	1.32	1.32●
Ethanethiol	25	6.67	0.684	1.07	0.98
1-iodobutane	20	6.22	0.819	0.93	0.80●
1-chlorobutane	20	7.39	0.837	1.02	0.97●
1-bromobutane	20	7.07	0.837	1.00	0.91●
Dichloromethane	15	9.28	0.850	1.13	1.08
Iodomethane	20	7.10	0.875	0.98	0.82●
Iodomethane	42*	6.48	0.790	0.97	0.82●
Quinoline	25	9.00	0.904	1.08	0.87●
Quinoline	238*	5.05	0.445	1.07	0.90●
Iodoethane	25	7.64	0.920	0.99	0.86●
2,2-dichloropropane	20	11.37	1.034	1.12	1.11
<i>o</i> -nitrotoluene	222*	11.82	1.116	1.10	1.06
Bromomethane	0	9.82	1.331	0.93	0.88●
Bromomethane	20	9.39	1.148	0.98	0.94●
Bromomethane	38*	8.81	1.044	1.00	0.96●
Pyridine	25	12.2	1.211	1.08	0.99
Pyridine	116*	9.38	0.835	1.15	1.07
Butanone	80*	14.48	1.369	1.06	1.16●
Acetophenone	25	17.39	1.588	1.09	1.04
Acetophenone	202*	8.64	0.827	1.11	1.04
Chloromethane	-20	12.6	1.675	0.92	0.96
Ammonia	-34	22.0	2.206	0.96	1.15●
Propanone	25	20.7	2.290	0.93	1.08●
Propanone	56*	17.68	1.982	0.94	1.09●
Ethanal	21	21.1	2.775	0.86	0.95
Nitrobenzene	25	34.89	3.542	0.93	0.99
Nitrobenzene	211*	15.61	1.838	0.96	0.96
Cyanobenzene	15	26.0	3.613	0.83	0.86
Nitromethane	30	35.9	4.433	0.79	1.02
Nitromethane	101*	27.75	3.288	0.85	1.06
Cyanoethane	20	27.2	4.766	0.70	0.86
Cyanomethane	25	34.58	5.941	0.67	0.89
Cyanomethane	82*	26.2	4.622	0.70	0.88

Table 2. Values of r_N and r_0 for some associated liquids.

Material	$T(^{\circ}\text{C})$	ϵ	y	r_N	r_0
Propanoic acid	20	3.34	0.211	1.16	1.06
Heptanol-4	-30	17.5	0.483	1.95	2.02●
Heptanol-4	30	5.7	0.368	1.33	1.21
3-ethylpentanol-3	25	3.24	0.381	0.800	0.713●
Methanol	-113	64.0	3.17	1.09	1.61●
Methanol	80	54.0	2.52	1.17	1.67●
Methanol	25	32.63	1.45	1.33	1.76●
Water	-35	107.7	4.76	0.974	1.79●
Water	20	80.1	3.96	1.01	1.67●
Water	100	55.7	2.99	1.06	1.62●
Water	300	20.4	1.45	1.12	1.48●
Hydrogen cyanide	0	158.0	5.16	0.983	2.16●
Hydrogen cyanide	20	114.9	4.69	0.965	1.94●
Formamide	25	109.3	7.13	0.839	1.35●

from Middlehoec and Böttcher (1966) for heptanol-4 data. Because of uncertainties in the estimates of ϵ_x , n^2 , and ρ , the calculated y and r values are at best accurate to a few per cent. Incidentally, increasing ϵ_x within the experimental range always decreases r_0 but usually increases r_N . Thus for associated materials the OKF equation can be made (Hill 1963, 1970) to fit the data with an ϵ_x considerably larger than n^2 and with $\mu = \mu_v$, while the new equation usually requires $\mu > \mu_v$ when $\epsilon_x > n^2$, more physically reasonable behaviour.

In general it appears for non-associated liquids that while neither formula with $\epsilon_x = n^2$ is very good at the extremes of y , the OKF equation is somewhat better there while the new formula is better in the middle region of y where the majority of liquids fall. But the great virtue of equation (1) is that it yields r values reasonably near unity for many associating liquids as well, while the OKF equation requires the introduction of large $g = r_0^2$ factors. Surprisingly, the results of equation (1) are generally better for associating liquids at low temperatures, where one would expect maximum association, than at higher ones. It appears that the new equation with $r_N = 1$ can often account quite well for association effects, when present, through its form alone, without the need for the introduction of a $r_N \neq 1$ or g factor at all. It is particularly remarkable and possibly significant that an equation employing only the non-disposable parameters n^2 and y can provide such a good account of the static dielectric constant of many liquids, both associated and unassociated. In view of the simplicity of equation (1) compared to equation (5) and its often good applicability for both associated and unassociated liquids with $r_N = 1$, and thus the use of μ_v alone, it seems preferable. of the two semi-empirical equations, to the OKF.

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