

DIPOLE MOMENTS OF SOME HETEROCYCLIC COMPOUNDS

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ABSTRACT

Dielectric constants, densities and refractive indices of six heterocyclic polar liquids of the pyran and furan groups have been measured and the moment values calculated using the equations of Onsager-Böttcher, Syrkin and Buckingham. A comparison of the moment values thus obtained with those measured in benzene shows that better agreement with benzene values is obtained by the use of Buckingham's equation especially in the case of furfuryl and tetrahydrofurfuryl alcohols where the equations of Onsager-Böttcher and Syrkin fail. The relative merits of the three equations have also been discussed critically.

1. INTRODUCTION

In recent years the theory of the dielectric constant of polar liquids has attracted much attention and consequently several formulæ are now available for the computation of the dipole moments of substances from pure liquid data. In this paper the results of the measurements of the dielectric constants, densities and refractive indices of a few pyran and furan liquid compounds are presented. Calculations of the moments of these substances from the above data have been made by the use of three formulæ due respectively to Onsager-Böttcher (1936), Syrkin (1942) and Buckingham (1953). The Onsager-Böttcher equation has been known to give consistent values for the dipole moment in several cases and has a theoretical basis. Syrkin's equation is of interest on account of its semi-empirical character. Buckingham's equation is more recent and is not only based on the Onsager model but contains several of the feasible modifications discussed by Wilson (1939), Jaffe (1940), Fröhlich and Sack (1944) and Scholte (1949). A comparison of the moment values calculated by using the three formulæ mentioned above with the moment values obtained from benzene solutions shows certain interesting features regarding the relative merits of these theories especially when applied to "associated" liquids. The heterocyclic liquids studied here are dihydropyran, tetrahydropyran, sylvan, furfural, furfuryl alcohol and tetrahydro furfuryl alcohol.

2. EXPERIMENTAL

Dihydropyran.—I.C.I. product was fractionated and dried over KOH. B.P. = 88° (uncorrected).

Tetrahydropyran.—I.C.I. sample was fractionally distilled and the fraction boiling between 87.5° and 88° (uncorrected) was collected and used.

Sylvan (2-methyl furan).—The material used was also from I.C.I. The fractionated liquid was used. B.P. = 64° (uncorrected).

Furfural (2-furfuraldehyde).—B.D.H. pure material was used after fractionation. B.P. = 162° (uncorrected).

Furfuryl alcohol.—I.C.I. sample was purified by fractional distillation. B.P. = 172° (uncorrected).

Tetrahydro furfuryl alcohol.—I.C.I. product was used after fractionation B.P. = 178° (uncorrected).

The apparatus used for the measurement of dielectric constants has been already described by the author in an earlier publication (Narasimhan, 1953). A constant voltage transformer was used to supply A.C. voltage for the measuring unit. The dielectric cell used was of the Sayce-Briscoe type with an electrical capacity of about 8 mmfd. and liquid capacity of about 15 c.c. The small electrical capacity of the test cell was necessitated by the large values of the dielectric constant of the liquids.

Densities were measured by means of an Ostwald-Sprengel pycnometer. Refractive indices were measured with a Pulfrich refractometer provided with water circulation from a thermostat. All measurements have been made at a temperature of 35° C.

3. RESULTS

Table I shows the results obtained for the six heterocyclic liquids, namely, dihydropyran, tetrahydropyran, sylvan, furfural, furfuryl alcohol and tetrahydro furfuryl alcohol. Refractive indices have been measured for three wave-lengths for extrapolation to infinite wave-length. However, we have used in the present calculations the value for the sodium D line only in order to arrive at the value of " $n_{\text{effective}}$ " by using the relation

$$1.05 MR_D = \frac{n_{\text{eff.}}^2 - 1}{n_{\text{eff.}}^2 + 2} \cdot \frac{M}{d}$$

The values of n_{eff} thus obtained are given in the last column of Table I. The use of n_{eff} instead of n_D thus allows for the atom polarisation, the neglect of which in the original Onsager-Böttcher equation was criticised by Wilson (1939).

TABLE I
Temperature 35° C.

No.	Substance	Dielectric constant ϵ	Density d	Refractive index			
				n_{5893}	n_{5460}	n_{4358}	$n_{eff.}$
	Dihydropyran ..	5.1364	0.91324	1.42304	1.43627	1.44617	1.44741
	Tetrahydropyran ..	5.7517	0.86867	1.41040	1.41211	1.43715	1.43391
	Sylvan ..	2.5676	0.90029	1.42599	1.42863	1.45440	1.45057
	Furfural ..	6.7690	1.14550	1.51879	1.52481	1.55385	1.55004
	Furfuryl alcohol ..	5.4914	1.12009	1.48054	1.48370	1.49727	1.50896
	Tetrahydro furfuryl alcohol	5.3610	1.04307	1.44746	1.44915	1.45681	1.47353

4. CALCULATION OF MOMENT VALUES

Following Böttcher (1936) we can calculate the dipole moment, μ , from the expression

$$\mu = \left[\frac{9kT}{4\pi N} \cdot \frac{M}{d} \cdot \frac{(\epsilon - n^2)(2\epsilon + n^2)}{t(n^2 + 2)^2} \right]^{\frac{1}{2}} \quad (1)$$

where ϵ , d and n refer as usual to the dielectric constant, density and refractive index of the liquid. The moment values shown in Table II under the heading "Onsager-Böttcher" have been obtained in this way using the values of $n = n_{eff.}$ Similarly, the values under the heading "Syrkin" have been calculated using the equation of Syrkin, namely,

$$\mu = \left[\frac{9kT}{4\pi N} \cdot \frac{\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} \cdot {}_vP}{1 - \left(\frac{\epsilon - 1}{\epsilon + 2}\right)^2} \right]^{\frac{1}{2}} \quad (2)$$

where ${}_vP = 1.05 MR_v$. In calculating the moment values by the use of Buckingham's equation, namely,

$$\mu = \left[\frac{9kT(\epsilon - n^2)[\epsilon + (n^2 - \epsilon)A]^2 M}{4\pi N \cdot \epsilon(2\epsilon + n^2)[1 + (n^2 - 1)A]^2 d} \right]^{\frac{1}{2}} \quad (3)$$

the A values have been obtained from the appropriate molecular diagrams. (Angyal, Barclay and Le Fevre, 1950) and by the use of Osborn's (1945) graphs. The A values are given in Table II and the moment values calculated by using

equation (3) are entered under the heading "Buckingham". The last column of Table II gives the dipole moment values of the substances measured in benzene (Soundararajan, 1950; Hassel and Naeshagen, 1930; Shott-L'vova and Syrkin, 1938).

TABLE II
Dipole Moments of Six Heterocyclics from Liquid Data

No.	Substance	A (Osborn)	μ Onsager- Böttcher	μ Syrkin	μ Buckingham	$\mu_{\text{obsd.}}$ (benzene)
1	Dihdropyran	0.16	1.43 D	1.48 D	1.87 D	1.38 D
2	Tetrahydropyran	0.16	1.63 D	1.68 D	2.15 D	1.63 D
3	Sylvan	0.08	0.60 D	0.62 D	0.68 D	0.72 D
4	Furfural	0.14	1.50 D	1.59 D	2.13 D	3.57 D
5	Furfuryl alcohol	0.13	1.37 D	1.44 D	1.92 D	2.00 D
6	Tetrahydro furfuryl alcohol	0.11	1.48 D	1.54 D	2.12 D	2.34 D

5. DISCUSSION

The moment values calculated from the equations of Onsager-Böttcher and Syrkin are in satisfactory agreement with the moment values observed in benzene in the cases of dihydropyran, tetrahydropyran and sylvan while in the cases of furfural and the two alcohols the calculated values are too low. The failure of these equations in the cases of the two alcohols is not altogether unexpected since several other alcohols give similar results. The moment values calculated by the use of the Onsager-Böttcher equation and the Syrkin equation are indeed very close, the latter equation giving slightly higher values. Since we are comparing the calculated moment values with those obtained from benzene solutions and not μ_{gas} values the agreement for the first three liquids (Table II) is quite good as regards equations (1) and (2). On the other hand, equation (3) of Buckingham gives much higher moment values than equations (1) and (2) for dihydropyran and tetrahydropyran and it seems unlikely that the μ_{gas} values will be so large for these substances.

The moment values for sylvan as obtained from the three equations are closer to one another and to the benzene value. Thus in the case of non-polar and very slightly polar molecules the three equations show the required convergence. Equation (3) fails in the case of furfural and a probable reason for the failure of all the three equations might be "association" of the molecular dipoles.

A word of caution seems to be necessary before we ascribe the failure of the polar liquid theories, in general, to association effects. In the case of furfuryl and tetrahydro furfuryl alcohols using equations (1) and (2) alone one is apt to conclude that the lower moment values are due to association. However, Buckingham's equation gives in these cases moment values which are very close to the benzene values and thus we find that an indiscriminate attribution of failure of polar liquid theories to association effects might lead to erroneous conclusions. The results obtained by equation (3) in the cases of the two alcohols mentioned above is extremely interesting in that polar liquid theories, in general, fail in the case of alcohols. It may also be noted here that the benzene solutions of the two heterocyclic alcohols do not show abnormal polarisation effects (Soundararajan, 1950).

From the above comparative study of the three equations as applied to the heterocyclic compounds under consideration it is clear that the equations of Onsager-Böttcher and Syrkin are quite satisfactory in the case of such of those molecules which do not have associating groups. The failure of these equations in the case of the alcohols points to the fact that the neglect of the shape factor of the molecule is a serious drawback in these equations. This is illustrated well by the success of Buckingham's equation in the very same cases. As mentioned earlier the moment values for furfural calculated from the three equations do not agree with the benzene value. In conclusion, it may be remarked that although Buckingham's equation promises to be more reliable in the case of several liquids yet it is not altogether completely satisfactory, as will be seen from the results obtained with dihydropyran and tetrahydropyran.

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