

## A COMPARISON OF METHODS FOR DETERMINING DIPOLE MOMENTS IN SOLUTION

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The equations (1)–(6) serving to determine dipole moments in solution were statistically tested on selected experimental data. Two kinds of data sets were used, referring to compounds with zero and non-zero dipole moments, respectively. Essentially the same results were obtained with the methods of Guggenheim–Smith, Eq. (3), of Halverstadt–Kumler, Eq. (1), and with the complete Debye equation (2). The differences between them are less important than the error introduced by estimating the atomic polarization to 5–15% of the molecular refraction and/or by calculating the latter from increments. More sophisticated equations (4) and (5) based on the Onsager theory do not yield better results than the Debye theory, this means that the agreement with the gas phase values is not improved.

The methods of measuring dipole moments in solution have been reviewed in textbooks<sup>1,2</sup>. They are mostly based on the Debye theory and assume in addition the additive behaviour of the total polarizations of solvent and solute. Most conveniently the concentration is given<sup>3,4</sup> in the weight fraction of the solute ( $w_2$ ), relative permittivity and density of the solutions are expressed through the derivatives  $\alpha = \partial \epsilon_{12} / \partial w_2$  and  $\beta = \partial d_{12}^{-1} / \partial w_2$ ; the subscripts 1, 2, and 12 refer respectively to solvent, solute, and solution.\* In these terms the dipole moment  $\mu$  is mostly given by the equation:

$$\frac{N_A}{9kT\epsilon_0} \mu^2 = M_2 \left[ \frac{3\alpha}{d_1(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \left( \beta + \frac{1}{d_1} \right) \right] - R_D(1 + a) \quad (1)$$

Eq. (1) is usually connected with the names of Halverstadt and Kumler<sup>3</sup> but it has been here complemented by the correction for atomic polarization, estimated most frequently to  $a = 0.05$ , but even to 0.015. The molar refraction  $R_D$  can be measured in the liquid phase (in the case of liquid compounds), or calculated approximately from atomic increments<sup>5</sup>, or determined separately in solution. In the last case the coefficient  $\gamma = \partial n_{12}^2 / \partial w_2$ , expressing the refractive index of solutions,\* still

\* If the dependence of  $\epsilon$  on  $w_2$  is not strictly linear,  $\alpha$  means the limiting value for  $w_2 \rightarrow 0$ . Unfortunately, the symbols  $\alpha$ ,  $\beta$ , and  $\gamma$  have been used also with another meaning<sup>6–8</sup>, e.g.  $\beta = \partial d_{12} / \partial w_2$ ,  $\beta = d_1^{-1} \partial d_{12} / \partial w_2$ ,  $\beta = \partial d_{12} / \partial x_2$  (related to the mole fraction  $x_2$ ), similarly  $\gamma = n_1^{-1} \partial n_{12} / \partial w_2$ . In this paper the symbols used by different authors have been unified.

appears in the complete Debye equation:

$$\frac{N_A}{9kT\epsilon_0} \mu^2 = M_2 \left[ \frac{3\alpha}{d_1(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \left( \beta + \frac{1}{d_1} \right) - (1 + a) \frac{3\gamma}{d_1(n_1^2 + 2)^2} - (1 + a) \frac{n_1^2 - 1}{n_1^2 + 2} \left( \beta + \frac{1}{d_1} \right) \right] \quad (2)$$

Eq. (2) can be considerably simplified assuming that the atomic polarizations of solute and solvent are in the ratio of their molar volumes. Then the term with  $\beta$  drops and the equation of Guggenheim–Smith results<sup>4,9</sup>:

$$\frac{N_A}{9kT\epsilon_0} \mu^2 = \frac{M_2}{d_1} \left[ \frac{3\alpha}{(\epsilon_1 + 2)^2} - \frac{3\gamma}{(n_1^2 + 2)^2} \right]. \quad (3)$$

The relative merits of Eqs (1) and (3) have been discussed mostly with reference to experimental procedures of measuring either the densities or the refractive indices of solutions. Very few comparative studies were undertaken<sup>10,11</sup> to reveal inasmuch the two results differ or even which equation is better; of course, the correction for atomic polarization must be taken into account, which is involved in Eq. (1) but not in (3). If all three gradients —  $\alpha$ ,  $\beta$ , and  $\gamma$  — are available, Eq. (2) seems to be the only reasonable choice but one can doubt whether the accuracy is actually better and worth the greater experimental effort. Attempt was also made<sup>4,10</sup> to improve Eq. (3) by introducing still the coefficient  $\beta$ , but this improvement converts it effectively into Eq. (2). So it happened that the results of identical methods were compared<sup>10</sup>, differing in fact only by the computational error.

In this paper Eqs (1) and (3) are compared by using two approaches. On the set of compounds with zero dipole moment, a direct examination of the fundamental assumptions is possible since the atomic polarization is in principle known. On the broader set of compounds with non-zero dipole moment, the results of the two equations can be compared but the actual value of the dipole moment remains unknown. In the latter case we extended the comparison to two more sophisticated equations based on the Onsager theory instead of the Debye theory:

$$\frac{N_A}{9kT\epsilon_0} \mu^2 = M_2 \left( \frac{2\epsilon_1 + n_1^2 + \gamma}{n_1^2 + \gamma + 2} \right)^2 \left[ \frac{\alpha(2\epsilon_1^2 + n_1^4)}{d_1\epsilon_1^2(2\epsilon_1 + n_1^2)^2} + \frac{\epsilon_1 - n_1^2 - \gamma}{\epsilon_1(2\epsilon_1 + n_1^2 + \gamma)} \cdot \left( \beta + \frac{1}{d_1} \right) - \frac{(n_1^2 + 2)^2}{(2\epsilon_1 + n_1^2)^2} \cdot \frac{\partial p_1}{\partial w_2} \right] \quad (4)$$

$$\frac{N_A}{9kT\varepsilon_0} \mu^2 = \left[ \frac{M_2 \alpha (2\varepsilon_1 + 1)^2}{27d_1 \varepsilon_1^2} + \frac{M_2 (\varepsilon_1 - 1) (2\varepsilon_1 + 1)}{9\varepsilon_1} \left( \beta + \frac{1}{d_1} \right) - (1 + a) R_D \right] \cdot \left[ \frac{2\varepsilon_1 + 1}{2\varepsilon_1 + 1 + (2\varepsilon_1 - 2)(1 + a) R_D / M_2 (\beta + d_1^{-1})} \right]^2 \quad (5)$$

Eq. (4) was derived by Cumper and Langley<sup>12</sup>. It requires measurement of both the densities and the refractive indices but the empirical correction for the atomic polarization is dropped; the derivative  $\partial p_1 / \partial w_2$  can be taken as zero. The equation of Sagnes and Casadevall<sup>13</sup> (5) was rearranged<sup>14</sup> in order to introduce the symbols  $\alpha$  and  $\beta$ , it requires then the same input data as Eq. (1). A mere comparison of Eqs (2), (4) and (5) does not imply which is better; to this purpose a reference to gas phase measurements was designed.

Still another equation was derived by Franchini<sup>6</sup> from the Cohen-Henriquez theory. In the form

$$\frac{N_A}{9kT\varepsilon_0} \mu^2 = \frac{M_2}{d_1} \left[ \frac{3\alpha}{(\varepsilon_1 + 2)^2} - \frac{3\gamma}{(n_1^2 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right] - aR_D \quad (6)$$

it represents just an amendment of the Guggenheim-Smith equation (3) by a more or less empirical term. Note still that an attempt was made to determine dipole moments in solution solely from permittivity measurements<sup>15</sup>. In spite of some limited success<sup>16</sup>, this approach has been ultimately disproved on a broad experimental material<sup>17</sup>.

## EXPERIMENTAL DATA

The values of dipole moments and relevant primary quantities were searched for using McClellan's Tables<sup>18</sup>, and always checked in the original literature. As diverse structures as possible were included; of a series of similar compounds only some representatives were taken. More recent literature sources were generally preferred, the related data being always from one laboratory. In the case of a serious disagreement in the literature the respective compound was omitted. Four sets of compounds were investigated:

*Set A:* Compounds with zero dipole moments measured in tetrachloromethane solution. Of 33 compounds were 10 hydrocarbons (7 molecules with a symmetry centre, in addition mesitylene, adamantane, and cyclopentane), the remaining mostly halogen compounds (18) with a symmetry centre (12) or with the  $D_{3h}$  symmetry. Omitted were quinones and bisarylmercury compounds the anomalous atomic polarization of which is not yet explained<sup>19,20</sup>. Further compounds with an unexpectedly high atomic polarization were retained (tetranitromethane, carbon disulphide). The values of the total polarization originated mostly from Le Fèvre and his colleagues, see review<sup>7</sup>. The values of molar refractions were taken from liquid phase measurements (mostly ref.<sup>21</sup>) as far as available, otherwise they were calculated using atomic increments<sup>5</sup> and referring to the most similar compounds. The error of the latter procedure should in no case

exceed 1%, which is reflected in the value of  $P_A/R_D$  (Fig. 1) as 0.01. The values of refractive indices  $n_2$  were taken preferably from liquid state measurements<sup>21</sup>, otherwise from solution in tetrachloromethane (as investigated in connection with dipole moments), or were only estimated. The error of this quantity is irrelevant (Fig. 1,  $x$ -axis).

*Set B:* Compounds with zero dipole moments measured in benzene. Of 34 compounds were 19 hydrocarbons (15 molecules with a symmetry centre, in addition mesitylene, triphenylene, hexane, and 2-methylbutane), further mostly halogen compounds (13) with a symmetry centre (10); 14 compounds were common with the set A. Omitted were all compounds giving donor-acceptor complexes with benzene, in particular nitro compounds. The experimental values were selected like in the set A.

*Set C:* Compounds with non-zero dipole moments measured in tetrachloromethane. From the original set of 100 compounds, those with  $\mu < 3.3 \cdot 10^{-30}$  C m were excluded on the basis of a preliminary statistical treatment. Of the remaining 92 compounds, 44 had  $\mu$  between 3.3 and 6.7, 27 between 6.7 and 10, 14 between 10 and 13.3, and 7 between 13.3 and 15 ( $10^{-30}$  C m). Mostly represented were halogen compounds (29), further aldehydes and ketones (8), esters of various acids (8), alcohols and ethers (7), nitriles (5), nitro compounds (3), various sulfur compounds (11), the rest were bifunctional derivatives; 47 compounds belonged to the aromatic series. The experimental values of  $\alpha$ ,  $\beta$ , and  $\gamma$  were taken almost exclusively from the papers of LeFèvre's school<sup>7,22</sup>, the values of  $R_D$  were calculated from the increments<sup>5</sup>. The calculation according to Eqs (1)–(6) was programmed for the HP 9820 A calculator. The program included recalculation of the molecular weight the changes of which are not without influence<sup>18</sup>. When our calculated values of  $\mu$  and/or  $P_2^0$  were in serious disagreement with the original literature, the respective compound was omitted.

*Set D:* Compounds with non-zero dipole moments measured in the gas phase and in tetrachloromethane solution as well. The set of 30 compounds consisted almost exclusively of those contained already in the set C, even two compounds with rather low  $\mu$  were included. The distribution of  $\mu$  values is seen in Fig. 3. The representation of structures was also similar as in the set C, with prevailing halogen compounds (16) and somewhat less represented aromatic derivatives (9). The gas phase data were taken from the tables<sup>18</sup> preferring those from microwave spectroscopy whenever possible. However, some values derived from the optical Stark effect and from the temperature dependence of permittivity were also included. Hence the accuracy varied from 0.003 to  $0.15 \cdot 10^{-30}$  C m.

## RESULTS AND DISCUSSION

Our first objective was to compare the equations of Halverstadt-Kumlet, Eq. (1), and of Guggenheim-Smith, Eq. (3), with regard to their use in routine work. This can be done conveniently in terms of the atomic polarization  $P_A$ . In Eq. (1),  $P_A$  is expressed as a given fraction of the molar refraction of the solute, the proportionality constant  $a$  being arbitrary but invariable for any solute and any solvent:

$$P_A = a \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \frac{M_2}{d_2} \quad (7)$$

Eq. (3) implies that  $P_A$  is related to the solute molar volume and the proportionality

constant is given by the properties of the solvent  $\epsilon_1$  and  $n_1$ . By eliminating  $\mu$  from Eqs (2) and (3) we get

$$P_A = \left( \frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) \left( \beta + \frac{1}{d_1} \right) M_2, \quad (8)$$

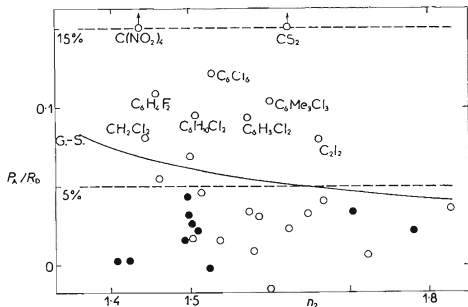


FIG. 1

Atomic Polarization of Compounds with Zero Dipole Moment (in tetrachloromethane)

Full line — required by the Guggenheim-Smith equation (3) in dependence on the refractive index, broken lines — estimates in use in connection with the Halverstadt-Kumler equation (1), full points — hydrocarbons, empty points — other compounds (set A).

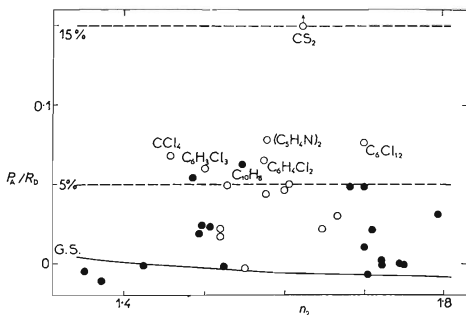


FIG. 2

Atomic Polarization of Compounds with Zero Dipole Moment (in benzene)

The same symbols are used as in Fig. 1 (set B).

where the molar volume  $V_2$  is represented by the two last terms. Eqs (7) and (8) will yield different estimates if either the solvent or the refractive index of the solute ( $n_2$ ) are varied. In Figs 1 and 2 are plotted the calculated values of  $P_A/R_D$  as functions of  $n_2$ . In tetrachloromethane (Fig. 1) an estimate according to Eq. (8) is not far from Eq. (7) with  $a = 0.05$ , while in benzene (Fig. 2) it is considerably lower, corresponding rather to  $a = 0.02$ . An experimental decision was attempted referring to symmetrical compounds with zero dipole moments the atomic polarization of which is known (sets *A* and *B*). Figs 1 and 2 reveal that the expected  $P_A$  is often far from reality whether Eq. (7) or (8) is used. Although the experimental error may be considerable, some values of  $P_A$  exceed 10% of  $R_D$  with certainty, while some others are almost negligible. Any regularity cannot be traced except that hydrocarbons show lower values than compounds containing polar substituents. In practice the value  $a = 0.05$  can be recommended in the Halverstadt-Kumler method; deviations can then be encountered mostly with strongly polar molecules and are not so consequential since the latter used to have high dipole moments. The results obtained should be comparable to those from the Guggenheim-Smith method if tetrachloromethane was used as solvent, with a reasonable approximation it holds also for dioxan. In benzene solutions the atomic polarization according to Guggenheim-Smith is definitely too low.

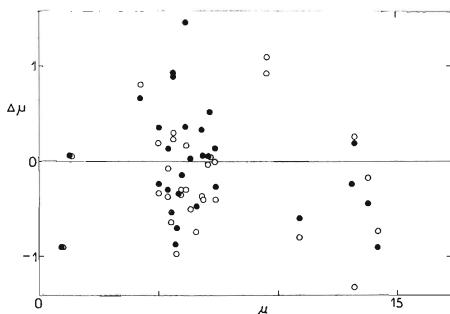


FIG. 3

Differences of Dipole Moments Measured in the Gas Phase and in Tetrachloromethane Solution

Full points — calculated on the basis of Onsager theory, Eq. (4), empty points — calculated using the Debye equation (2), set *D*;  $\mu$  in  $10^{-30}$  C m.

We shall next examine inasmuch the difference in estimating  $P_A$  becomes evident in practice, *i.e.* in the final values of dipole moments. For this purpose a set of compounds was selected with non-zero dipole moments and for which the measurements of  $\epsilon_{12}$ ,  $d_{12}$ , and  $n_{12}$  are available (in tetrachloromethane). After a preliminary treatment it was necessary to eliminate compounds with  $\mu < 3.3$  since the deviation between individual methods were too large and irregular. This was only a confirmation of the old experience that low dipole moments are not reliable. The statistical results are assembled in Table I. Lines 2 and 3 reveal no significant difference between the treatment by Eqs (1), (2), or (3). The differences are even smaller than within the framework of one method if different corrections for  $P_A$  are used, *viz.* 5% or 15%, respectively, (line 1). Note that the values less than 10 ( $10^{-32}$  C m) are completely insignificant throughout the Table, values less than 20 might be still comparable to experimental errors. Most relevant is the result of line 3 which can be worded: If measurements of both densities and refractive indices are available, simpler Eq. (3) yields as good results as the complete Eq. (2) — the measurement of densities is of no use. On the other hand, if only the measurement of densities can be exploited, even Eq. (1) gives results of the same value but it requires still a complementary information, the value of  $R_D$ . An important exception are in this case coloured compounds,

TABLE I

Statistical Comparison of Equations (1)–(6) in Use to Calculate the Dipole Moment in Solution  
Solvent tetrachloromethane, units  $10^{-32}$  C m,  $n = 92$  (set C with  $\mu > 3.3$ ) unless otherwise noted.

| No             | Equations compared<br>(correction for $P_A$ ) |           | Mean<br>difference <sup>a</sup><br>$\Delta$ | Mean square<br>difference <sup>b</sup><br>$\delta$ | Standard<br>deviation <sup>c</sup><br>$s$ |
|----------------|---|-----------|---|--|---|
| 1              | (1) (5%)                                      | (1) (15%) | +15   | 18   | 10  |
| 2 <sup>d</sup> | (1) (5%)                                      | (2) (5%)  | + 2   | 4  | 4   |
| 3              | (3)   | (2) (5%)  | — 1   | 2  | 2   |
| 4 <sup>e</sup> | (4)   | (2) (5%)  | +11   | 39   | 37  |
| 5 <sup>e</sup> | (5) (5%)                                      | (1) (5%)  | +28   | 30   | 12  |
| 6              | (6) (5%)                                      | (3)       | + 3   | 4  | 3   |
| 7 <sup>f</sup> | (2) (5%)                                      | gas phase | —25   | 56   | 51  |
| 8 <sup>f</sup> | (4)   | gas phase | + 2   | 59   | 59  |
| 9 <sup>f</sup> | (5) (5%)                                      | gas phase | +10   | 53   | 52  |

<sup>a</sup>  $\Delta = (\sum \mu_i - \sum \mu_j)/n$ ; <sup>b</sup>  $\delta^2 = \sum (\mu_i - \mu_j)^2/n$ ; <sup>c</sup>  $s^2 = \delta^2 - \Delta^2$ ; <sup>d</sup> not including coloured compounds and two compounds eliminated *ex post* (4-bromobiphenyl and 4-iodobiphenyl),  $n = 87$ ; <sup>e</sup> not including coloured compounds (even slightly coloured like nitro compounds),  $n = 85$ ; <sup>f</sup>  $n = 30$  (set D).

eliminated *ex post* from the statistical treatment (line 2). With such compounds the values of  $n_{12}$  in solution are enhanced and the apparent dipole moment is too low, *e.g.* for 1,2-diphenylethanedione the difference amounts to  $0.62 \cdot 10^{-30}$  C m, *i.e.* 15 times the mean square difference  $\delta$ . For such compounds the Halverstadt–Kumler method gives better results.

Concerning the more sophisticated methods of calculating dipole moments, which are not based on the Debye theory, we shall first mention the Franchini equation (6). According to Table I, line 6, it behaves as a minor modification of the Guggenheim–Smith equation yielding essentially the same results. More important are the two equations (4) and (5), based on the Onsager theory. According to the values of  $\Delta$  (Table I) their results are significantly different from the preceding methods. In the case of the Sagnes–Casadevall equation (5), they are systematically higher by an almost constant difference (positive  $\Delta$  and small  $s$  in line 5), while in the case of Eq. (4) they are scattered ( $s$  almost equal to  $\delta$  in line 4). The immediate comparison was made always to that equation which is based on the same input data; in this way the effect of experimental error is minimized. The question arises which approach is better, *i.e.* whether the acknowledged superiority of the Onsager theory, proven mostly on pure liquids<sup>23</sup>, applies even for solutions. As a reference only the gas phase measurements come into consideration. In particular if determined by advanced microwave spectroscopy, they are more accurate than any solution values and free of any specific effects. The statistical comparison must be restricted to a smaller set but even so the result is surprising (Table I, lines 7–9): Both the Debye equation (2) and the equations (4), (5) based on the Onsager theory reproduce the gas phase values with an almost equal error. Eq. (2) yields somewhat lower values Eq. (5) a little bit higher, but the scatter is the same. The statistical results are demonstrated in Fig. 3 which reveals that the scatter is larger than the possible experimental errors and is not caused by big errors of some particular compounds. There is simply no evidence in favour of the Onsager theory. Eqs (4) and (5) are thus of no advantage in relation to their complex form. In addition Eq. (4) requires measurement of three experimental quantities:  $\epsilon$ ,  $d$  and  $n$ .

In virtue of the above results we can recommend the Guggenheim–Smith method as the most economical with respect to the experimental effort. The results are practically equal as in the Halverstadt–Kumler method with a 5% correction for  $P_A$ . Only in the case of coloured compounds the latter is the method of choice and molar refraction  $R_D$  must be approximately calculated from increments.

#### REFERENCES

1. Minkin V. I., Osipov O. A., Zhdanov Yu. A.: *Dipole Moments in Organic Chemistry* (English translation). Chapter II, Plenum Press, New York 1970.
2. Exner O.: *Dipole Moments in Organic Chemistry*, Chapter 2. Thieme, Stuttgart 1975.
3. Halverstadt I. F., Kumler W. D.: *J. Amer. Chem. Soc.* 64, 2988 (1942).



4. Smith J. W.: *Trans. Faraday Soc.* **46**, 394 (1950).
5. Vogel A. I.: *J. Chem. Soc.* **1948**, 1833.
6. Franchini P. F.: *Trans. Faraday Soc.* **63**, 2610 (1967).
7. Le Fèvre R. J. W.: *Advan. Phys. Org. Chem.* **3**, 1 (1965).
8. Hedestrand G.: *Z. Phys. Chem. (Leipzig) B* **2**, 428 (1929).
9. Guggenheim E. A.: *Trans. Faraday Soc.* **45**, 714 (1949); **47**, 573 (1951).
10. Cumper C. W. N., Vogel A. I., Walker S.: *J. Chem. Soc.* **1956**, 3621.
11. Béguin C., Gäumann T.: *Helv. Chim. Acta* **41**, 1376 (1958).
12. Cumper C. W. N., Langley P. G.: *Trans. Faraday Soc.* **67**, 35 (1971).
13. Sagnes R., Casadevall A.: *Bull. Soc. Chim. Fr.* **1971**, 1990, 3924.
14. Exner O., Jehlička V., Vodička L., Jakoubek P.: *This Journal* **45**, 2400 (1980).
15. Higasi K.: *Bull. Inst. Phys. Chem. Res. (Tokyo)* **22**, 805 (1943).
16. van Woerden H. F., Havinga E.: *Rec. Trav. Chim. Pay-Bas* **86**, 341 (1967).
17. Jehlička V., Cibulka I.: *This Journal* **40**, 3095 (1975).
18. McClellan A. L.: *Tables of Experimental Dipole Moments*, Vol. 1/2. Freeman, San Francisco 1963 and Ralara Enterprises, El Cerrito 1974.
19. Vulfson S. G., Vereshchagin A. N., Arbusov B. A.: *Dokl. Akad. Nauk SSSR* **209**, 885 (1973).
20. Horning W. C., Lautenschlaeger F., Wright G. F.: *Can. J. Chem.* **41**, 1441 (1962).
21. Rossini F. D., Pitzer K. S., Arnett R. L., Braun R. M., Pimentel G. C.: *Selected Values of Physical and Thermodynamical Properties of Hydrocarbons and Related Compounds*. Carnegie Press, Pittsburgh 1953.
22. Bonham J. S., Cheng C. L., La Fèvre R. J. W., Ritchie G. L. D.: *Aust. J. Chem.* **26**, 421 (1973).
23. Smyth C. P.: *Dielectric Behaviour and Structure*, Chapter I., 16. McGraw-Hill, New York 1955.

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