STUDIES OF ASSOCIATION IN SOLUTION FROM PERMITTIVITY MEASUREMENTS: STATISTICAL PROBLEMS

Otto EXNER

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6

Association of a solute can be followed by permittivity measurement which allows us in principle to calculate the equilibrium constant K and dipole moments of the monomer μ_M and dimer μ_D. However, the procedures used in the literature are unsatisfactory from the statistical point of view and the published values are mostly completely wrong. In all known examples their errors were badly underestimated. Using a correct statistical approach several examples have been now reevaluated. It is practically impossible to calculate reliably all three parameters from permittivity data of common accuracy. Better results are obtained if either μ_M or K can be determined in an independent way. A symmetrical structure of the dimer is preferable in several cases (acetic acid, 2-pyrrolidinenone) contrary to the previous claims.

Common procedures of determining dipole moments in solution[1−3] are based on a plot of relative permittivities ε vs the weight fraction w_2, which is complemented either by a plot of specific volumes d^{-1} — method of Halverstadt–Kumler[4], or of squared refractive indices n_D^2 — method of Guggenheim–Smith[5]. At sufficiently low concentrations, the plots are reasonably linear and the dipole moment of the solute is obtained from their slopes, called α, β and γ, respectively. If the solute associates in solution, it is usually the plot ε vs w_2 which deviates significantly from linearity (most often downwards), while the other plots are not affected. In such cases a quadratic interpolation was suggested[5−7], Eq. (1), to obtain μ_M from the coefficient α_0.

$$\varepsilon = \varepsilon_1 + \alpha_0 w_2 + \alpha' w_2^2 \tag{1}$$

On the other hand the curved plot may be exploited to calculate the equilibrium constants (which may be often obtained from other experiments) and the dipole moments of the polymeric species (not accessible by another way). If we take only the dimeric form into consideration, the experimental permittivity will depend on the dipole moments* of the monomer, μ_M, and dimer, μ_D, and on the equilibrium

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* The subscripts M and D refer to the monomer and dimer, respectively, the subscript 1 to the solvent, 2 to the total amount of the solute in either form. Symbols without subscript concern the solution (a three-component system).

constant, K:

$$\varepsilon = f(\mu_M, \mu_D, K, w_2) \, . \tag{2}$$

According to the method used[4,5], the function in Eq. (2) may still contain either the densities d, or refractive indices n_D of the solution, in addition to the constants of the solvent $(\varepsilon_1, d_1, n_1)$.

If a theoretical form of Eq. (2) is given, the three unknowns are determined by three measured values of ε. In practice, however, the experimental errors may be considerable with respect to the narrow range of ε values. In such a case the results become sensitive to both the quality of data and the statistical treatment. A correct statistical procedure meets particularly the following requirements: 1. It exploits evenly all measured values, either with equal weights or with different, a priori defined weights. 2. It yields a characteristic, evaluating the adherence of the model to the data. 3. It gives any idea about the reliability of the estimated parameters, also about their mutual dependence. The latter term means that the optimum estimate of one parameter of Eq. (2) depends also on the simultaneous estimation of the remaining ones. When the value of one parameter (say K) is shifted out of its optimum value, the fit is worsened much more if the remaining parameters (μ_M, μ_D) retain their values, but much less if they are also shifted properly. In the extreme case many sets of parameters, controlled by a functional dependence, may yield a satisfactory fit. Most objectively this feature is demonstrated on a contour diagram, see later Figs 2, 7, 9, 10. The statistical procedures used in the literature[7-18] were criticised in our previous paper[19] and found unsatisfactory with respect to the above conditions. The most serious mistake is a transformation of original variables, ε and w_2 in Eq. (2), to obtain a linear equation with both variables on either side[10,11]. In this way biased, sometimes quite bad estimates are obtained. This defect was demonstrated[19] by calculating back the experimental values of ε as they should be to correspond exactly to the suggested values of μ_M, μ_D, and K, see also later Figs 1, 3, 4, 5. Less effective is also approximating Eq. (2) by a quadratic function,[7,17] Eq. (1), since the fit can be rather poor. Most of the methods described give no quantitative evaluation of the fit and either no, or too optimistic estimates of the uncertainty in the parameter values. The last objection applies even to the otherwise correct procedure of Walmsley, Jacob and Thompson[14,15].

In the preliminary communication[19] the mistakes of the literature were demonstrated and a statistically unobjectionable procedure was suggested. In this paper the procedure is examined more closely as regards its premises and consequences, several sets of literature data are recalculated with its aid, and some chemical implications are discussed.
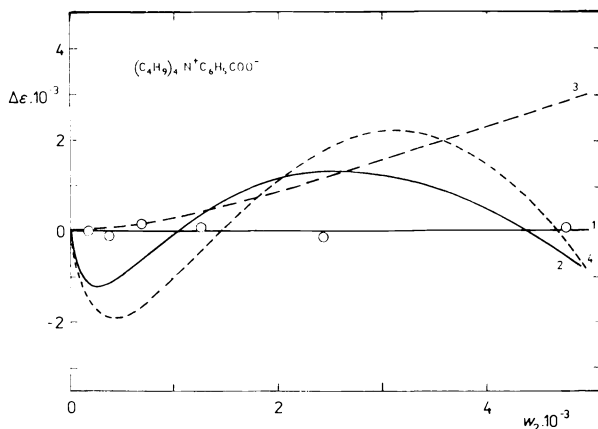
FIG. 1

Comparison of experimental and calculated relative permittivities: 1 best fit according to Eq. (10) (reference line), 2 with the constraint $\mu_D = 0$, 3 with the parameters calculated in ref.[10], 4 quadratic interpolation; points — experimental data from ref.[10]
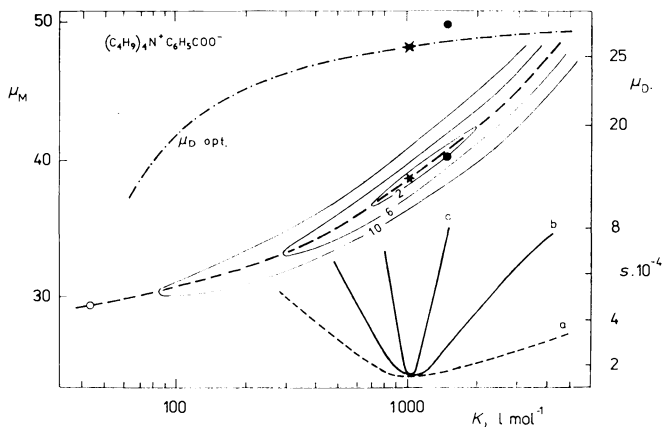

FIG. 2

Mutual dependence of parameters: in the middle contour diagram of μ_M vs K (in log scale), when μ_D has always its optimum value (the latter shown separately at the top), * optimum values, ● ref.[10] ○ best values with the constraint $\mu_D = 0$. At the bottom dependence of the standard deviation on K for both μ_M and μ_D optimized (a), for μ_D kept constant (b), and for μ_M constant (c)
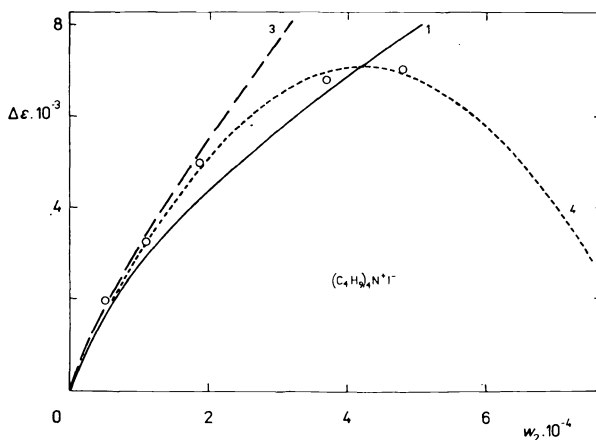
FIG. 3

Comparison of experimental and calculated permittivities: 1 according to Eq. *(10)* with $K = 10^5$, 3 with the parameters calculated in ref.[10], 4 quadratic interpolation. Experimental data from ref.[10]
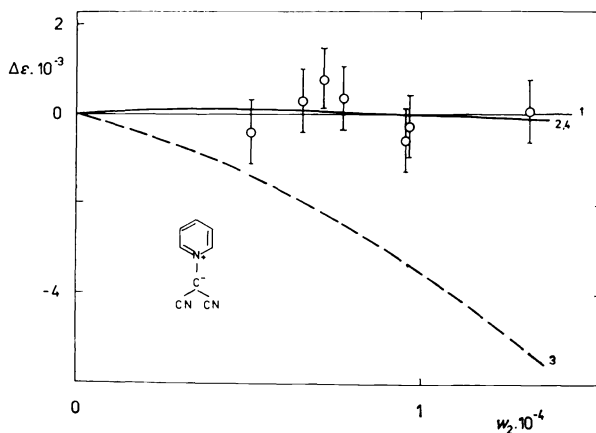

FIG. 4

Comparison of experimental and calculated relative permittivities: 1 linear interpolation, 2 Eq. *(10)* with $\mu_D = 0$, 3 with the parameters calculated in ref.[11], 4 quadratic interpolation (indistinguishable from 2). Experimental points — ref.[11]

FIG. 5

Comparison of experimental and calculated relative permittivities: **1, 2,** and **4** see Fig. 1, **3** with the parameters calculted in ref.[18], **5** with the constraint $\mu_M = 4 \cdot 63$. Experimental points — ref.[18]
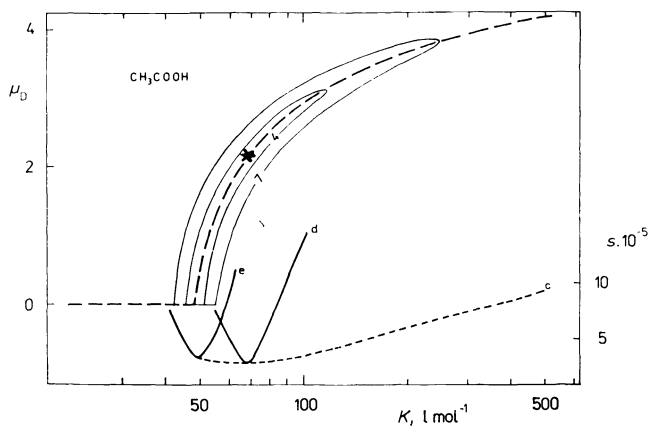
FIG. 6

Mutual dependence of the parameters μ_D and K for μ_M fixed to $4 \cdot 63$; at the bottom dependence of the standard deviation on K for μ_D optimized (c), for μ_D constant (d), and for $\mu_D = 0$ (e)
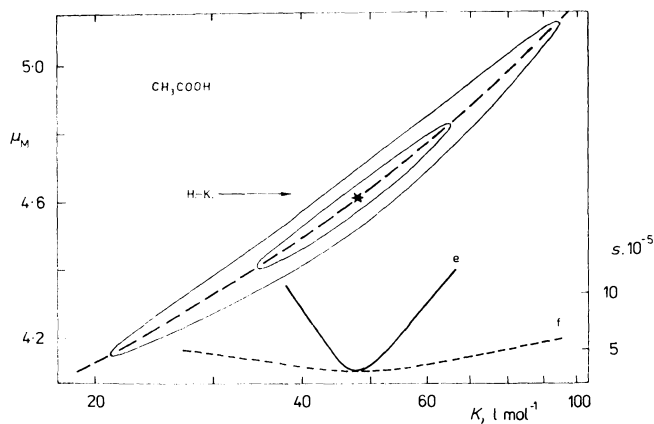
FIG. 7

Mutual dependence of parameters μ_M and K for $\mu_D = 0$, * optimum values, the arrow shows the Halverstadt–Kumler value. At the bottom dependence of the standard deviation on K for μ_M optimized (f) and μ_M constant (e)
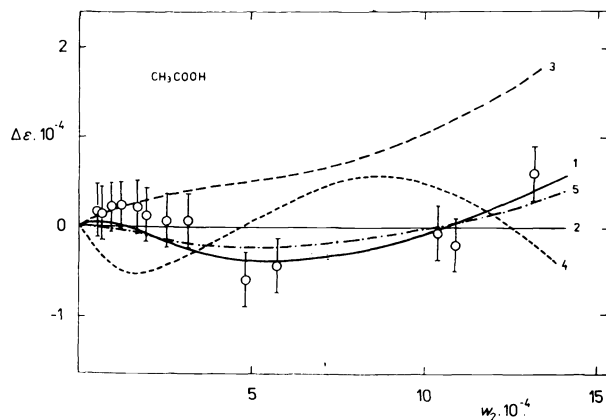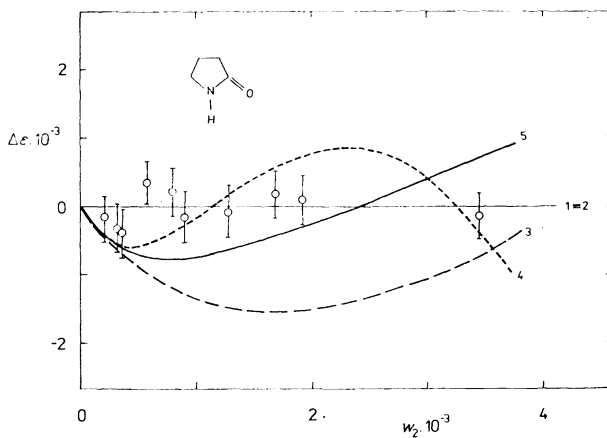

FIG. 8

Comparison of experimental and calculated relative permittivities: 1, 2, and 4 see Fig. 1, 3 with the parameters calculated in ref.[9], 5 with the constraint $\mu_M = 11·69$. Experimental points — ref.[9]
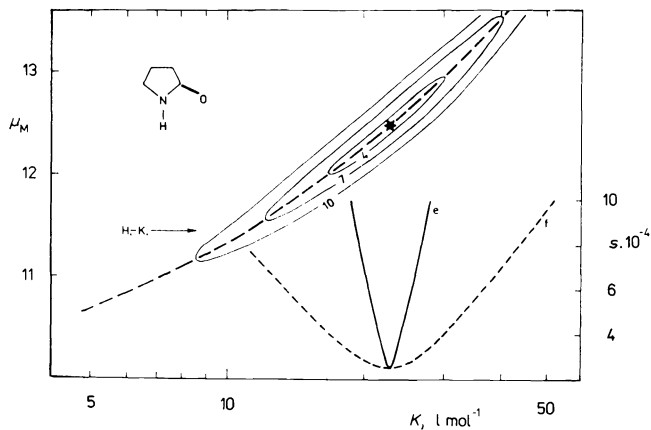
FIG. 9

Dependence of parameters μ_M and K for $\mu_D = 0$. See Fig. 7 for descriptive details
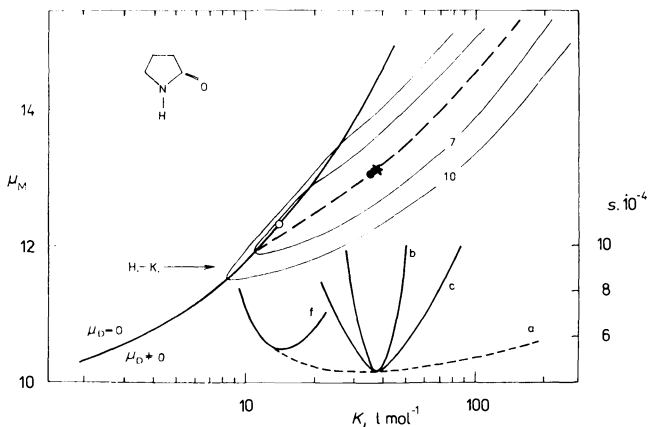
FIG. 10

Dependence of parameters: the contour map of μ_M vs K (when μ_D has always its optimum value) decomposes into two parts with $\mu_D = 0$ and $\mu_D \neq 0$, respectively; * optimum values, ● ref.[15], ○ best values with the constraint $\mu_D = 0$, the arrow shows the Halverstadt–Kumler value. At the bottom dependence of the standard deviation on K for both μ_M and μ_D optimized (a), μ_D kept constant (b), μ_M kept constant (c), and μ_D equal to zero (f)

THEORETICAL

A theoretical model of Eq. (2) is derived within the framework of the Halverstadt––Kumler method[4], i.e. based on the experimental permittivity and density. In a three-component system monomer–dimer–solvent an additive relationship in terms of specific polarizations is assumed, the concentrations being given as weight fractions w:

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{1}{d} = w_1 p_1 + w_M p_M + w_D p_D .\tag{3}$$

The specific polarizations p_M, p_D are expressed by molar polarizations P_M and P_D, and by the monomer molecular weight M. The polarizations are resolved into orientation polarizations P_M^O and P_D^O, and molar refractions R_M and R_D; p_1 is expressed through the experimental quantities ε_1 and d_1:

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{1}{d} = (1 - w_2)\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\frac{1}{d_1} + w_M\frac{P_M + aR_M}{M} + w_D\frac{P_D + aR_D}{2M} .\tag{4}$$

The constant a (> 1) involves the empirical correction for atomic polarization. Two plausible assumptions may now be made, Eqs (5) and (6).

$$R_D = 2R_M \tag{5}$$

$$\frac{1}{d} = \frac{1}{d_1} + \beta w_2 \tag{6}$$

Equation (5) follows from the additivity of molar refraction[7,11,12]. Equation (6) is commonly assumed in the Halverstadt–Kumler method[4], applied here it means that dimerization does not influence density[7,10,11]. Introducing R_D and d from Eqs (5) and (6) into Eq. (4) we get:

$$\frac{\varepsilon - 1}{\varepsilon + 2}\left(\frac{1}{d_1} + \beta w_2\right) = (1 - w_2)\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\frac{1}{d_1} + w_M\frac{P_M}{M} + w_D\frac{P_D}{2M} + w_2 aR_M .\tag{7}$$

The weight fractions w_M and w_D are determined by Eqs (8) and (9).

$$w_M + w_D = w_2 \tag{8}$$

$$K = \frac{c_D}{c_M^2} = \frac{w_D}{w_M^2}\frac{M}{2\,000d} = \frac{Mw_D}{2\,000w_M^2}\left(\frac{1}{d_1} + \beta w_2\right) \tag{9}$$

The equilibrium constant K refers to molar concentrations. Solving Eqs (8) and (9) for w_M and w_D, and introducing into Eq. (7) we get:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \frac{1 - w_2}{1 + d_1\beta w_2} + \frac{2P_M^O - P_D^O}{8\,000K}\left[\left(1 + \frac{8\,000Kd_1w_2}{M + Md_1\beta w_2}\right)^{1/2} - 1\right] +$$

$$+ \frac{P_D^O d_1 w_2}{2M(1 + d_1\beta w_2)} + \frac{aR_M d_1 w_2}{M + Md_1\beta w_2} . \tag{10}$$

This equation represents our theoretical model of Eq. (2). Starting from a set of experimental data w_2 and ε, we can optimize the parameters P_M, P_D, and K in Eq. (10). The simplest optimization procedure is based on the least-squares condition, Eq. (11), where f is the number of degrees of freedom.

$$s^2 f = \sum_i [\varepsilon_i - f(\mu_M, \mu_D, K, w_{2i})]^2 = \min \tag{11}$$

Finally, the dipole moments of the monomer and dimer, μ_M and μ_D, are obtained from P_M^O and P_D^O (in units C m):

$$\mu^2 = \frac{9kT\varepsilon_0}{N_A} P^O . \tag{12}$$

The experimental data are seldom so accurate and extensive to allow optimization of all three parameters simultaneously. One possible constraint is assuming a symmetrical structure of the dimer, i.e. $\mu_D = P_D^O = 0$. Then an economical optimization procedure consists in choosing an arbitrary value of K and determining the best P_M^O by regression with the fixed origin in the coordinates w_2 and $(\varepsilon - 1)/(\varepsilon + 2)$. The inaccuracy introduced by minimizing errors in $(\varepsilon - 1)/(\varepsilon + 2)$, instead of errors in ε, is immaterial since the two quantities are approximately linearly related within the narrow region of ε. In the next step, one calculates the standard deviation s for the given K and P_M^O. The two steps are then repeated, until the minimum value of s is obtained.

When the assumption $P_D^O = 0$ does not apply, a convenient procedure may begin with calculating P_M^O according to the Halverstadt–Kumler method[4] from the slope (α_0) of the linear part of the ε/w_2 plot at low concentrations. With this value of P_M^O fixed, one can choose an arbitrary value of K, calculate the corresponding best P_D^O by simple regression, and repeat the procedure to obtain the minimum s. In some cases it appeared necessary to optimize all three parameters, in particular when there was no linear part of the ε vs w_2 plot to determine P_M^O. Then the second of the mentioned procedures was repeated for variable values of P_M^O and the absolute minimum of the standard deviation was found.

The correction for atomic polarization, included in the value of a in Eq. (10), was taken as 5%, as recommended recently[20]. The remaining values: d_1, ε_1, β, R_M, w_2, and ε were from experiments. The general adherence of the model is evaluated first according to the standard deviation s as compared to the assumed experimental error. As a secondary criterion the random distribution of deviations may be considered, when observed in the direction of increasing w_2 values. Last but not least, all parameters (K, P_M^O, P_D^O) must acquire physically possible and chemically acceptable values: all values positive, P_M^O in agreement with the Halverstadt–Kumler value if available, P_D^O giving μ_D possible for a certain structure. The accuracy of individual parameters may be estimated by mapping the values of s for various combinations of the parameters. The necessary calculations are lengthy but they reveal best the mutual dependence of parameters.

RESULTS

Equation (10) was applied to several sets of literature data, particularly to those processed formerly by statistically incorrect procedures. Three examples were already presented in the graphical form[19] and the deficiency of former statistical methods[9-11,14,15,18] was proved in a convincing manner[19]. In this·paper we focus attention to numerical values and to further examples. Tables I − V list all the values of μ_M, μ_D, and K obtained, sometimes also the estimates of their errors with respect to their dependence. In addition to the best solution also some alternatives are given, for comparison also the solutions claimed in the literature.

Tetrabutylammonium Benzoate in Benzene (ref.[10])

In this example most significant results were obtained since the permittivity values are rather precise and their plot vs w_2 is markedly curved, without any linear part. For this reason all the values μ_M, μ_D, and K were optimized (Table I). In Fig. 1 our best solution was taken as reference and compared to various alternatives and to experimental points. Their scatter suggests a larger experimental error than it would correspond to ε given to 5 decimals. Fig. 1 also allows to reject with certainty the hypothesis $\mu_D = 0$. The quadratic interpolation, Eq. (1), yields still a worse fit. Worst of all is the biased estimate of the original literature[10], obtained from a statistically incorrect transformation: this theory has actually little relation to the experimental facts.

The mutual dependence of parameters is shown in Fig. 2. In the plane μ_M vs K the couples of parameters giving the same final standard deviation are connected by a curve, yielding a contour diagram. The condition is that the third parameter μ_D acquires always its optimum value for the given couple μ_M and K. The absolute minimum is marked by an asterisk, the dashed line represents the bottom of a valley

and gives approximately the optimum values of μ_M for a given K and vice versa. The optimum values of μ_D corresponding to this line are shown on the dot-and-

TABLE I

Dimerization of tetrabutylammonium benzoate in benzene from permittivity data[10]

Method	$\mu_M{}^a$	$\mu_D{}^a$	K^a	s	n^b	Fig.^{c}
	10^{-30} Cm		dm^3 mol^{-1}	10^{-5}		
Best fit, Eq. (10)	38·67	25·80	1 060	15	6	1; 1
	(35·0—48·3)	(25·0—26·7)	(500—4 000)			
Eq. (10) with $\mu_D = 0$		[0]	43	114	6	1; 2
According to ref.[10]	40·20	27·33	1 510	180	6	1; 3
Quadratic interpolation^d	—	—	—	177	6	1; 4
Experimental error^e				10	6	
Range of ε values				7 211	6	

^{a} A priori fixed parameters are given in brackets. In important cases confidence limits are given in parentheses, their estimation see text. ^{b} Number of experimental points in the ε vs w_2 plane. ^{c} First number denotes the figure, the second the respective curve. ^{d} The method of ref.^{7} allows calculation of K only if μ_M and μ_D are known. The standard deviation is that of the quadratic interpolation (independent of subsequent calculations). ^{e} The estimate of the experimental error is based on the accuracy to which the permittivity values are given in the original literature, but corrected with respect to the fit to the theoretical curves, particularly to the deviations of subsequent points. Some subjectivity cannot be avoided.

TABLE II

Dimerization of tetrabutylammonium iodide in benzene from permittivity data[10]

Method	$\mu_M{}^a$	$\mu_D{}^a$	K^a	s	n^b	Fig.^{c}
	10^{-30} Cm		dm^3 mol^{-1}	10^{-5}		
According to Eq. (10)	96·33	[0]	10^{5f}	46	5	3; 1
According to ref.[10]	42·33	0	1 560	332	5	3; 3
Quadratic interpolation^d	—	—	—	20	5	3; 4
Experimental error^e		·		1	5	
Range of ε values				703	5	

$^{a-e}$ See Table I. ^{f} No convergence, the values of K arbitrary chosen.

TABLE III

Apparent dimerization of pyridiniodicyanomethylide in dioxan from permittivity data[11]

| Method | $\mu_M{}^a$ | $\mu_D{}^a$ | K^a | s | n^b | Fig.^{c} |
| | | | | | | |
	10^{-30} C m		dm^3 mol^{-1}	10^{-5}		
Best fit, Eq. (*10*) with $\mu_D = 0$	31·10 (30·8—31·9)	·[0]	1·6 (0—5)	51	7	4; 2
Halverstadt–Kumler[4]	31·20	—	[0]	47	7	4; 1
According to ref.[11]	30·67	[0]	3	341	7	4; 3
Quadratic interpolation^d	[31·20]	[0]	3·1	51	7	4; 4
Experimental error^e				70	7	
Range of ε values				10 000	7	

$^{a-e}$ See Table I.

TABLE IV

Dimerization of acetic acid in benzene from permittivity data[18]

| Method | $\mu_M{}^a$ | $\mu_D{}^a$ | K^a | s | n^b | Fig.^{c} |
| | | | | | | |
	10^{-30} C m		dm^3 mol^{-1}	10^{-5}		
Best fit, Eq. (*10*)	5·57 (4·6-?)	3·27 (1·9-?)	405 (60-?)	2	13	5; 1
Eq. (*10*) with the H.–K. value	[4·63]	2·20 (0—3·7)	68 (43—190)	3	13	5; 5
Eq. (*10*) with $\mu_D = 0$	4·63 (4·2—5·2)	[0]	48 (21—96)	3	13	5; 2
Halverstadt–Kumler^{4,g}	4·63	—	[0]	—	3	—
According to ref.[18]	5·00	2·77	0·14	8	13	5; 3
Quadratic interpolation^d	[4·63]	[0]	7·2	7	13	5; 4
Experimental error^e				3	13	
Range of ε values				186	13	

$^{a-e}$ See Table I. ^{g} Calculated from the linear part of the curve (3 points), a reliable estimate of s not possible.

-dashed line at the top of the figure. Evidently, the dependence of parameters is strong. The three curves at the bottom show how the standard deviation increases if the value of K is shifted from its optimum position. The increase is greatest if μ_M is kept constant and μ_D optimized, much lower if μ_D is kept constant, and lowest if both μ_M and μ_D are optimized. The last curve allows to delimit the admissible range of parameter values, provided an acceptable standard deviation is chosen.

TABLE V

Dimerization of 2-pyrrolidinone in benzene from permittivity data[9,15]

Method	$\mu_M{}^a$	$\mu_D{}^a$	K^a	s	n^b	Fig.^{c}
	10^{-30} Cm		dm^3 mol^{-1}	10^{-5}		
Best fit, Eq. (*10*)	12·73 (12·1—13·5)	0	22·5 (15—33)	26	10	8; 1
Eq. (*10*) with the H.-K. value	[11·70]	0	11·7	81	10	8; 5
Halverstadt–Kumler^{4,g}	11·70	—	[0]	—	4	—
According to ref.^{9}	11·83	7·33	25·4	139	10	8; 3
Quadratic interpolation^d	[11·70]	[0]	4·9	50	10	8; 4
Experimental error^e, ref.^{9}				20	10	
Range of ε values, ref.^{9}				3 490	10	
Best fit, Eq. (*10*)	13·13 (11·6—?)	7·17 (0—10)	36·5 (9—?)	45	15	—
Eq. (*10*) with the H.-K. value	[11·67]	0	9·5	78	15	—
Eq. (*10*) with $\mu_D = 0$	12·33	[0]	14·5	49	15	—
Halverstadt–Kumler^{4,g}	11·67	—	[0]	—	5	—
According to ref.^{15}	13·03 (12·3—13·7)	6·87 (6·0—7·7)	33 (28—38)	45	15	—
Quadratic interpolation^d	[11·67]	[0]	3·2	97	15	—
Experimental error^e, ref.^{15}				40	15	
Range of ε values, ref.^{15}				4 880	15	
Best fit, Eq. (*10*)	12·53 (11·7—13·6)	0	19·5 (10—36)	25	9	—
Eq. (*10*) with the H.-K. value	[11·67]	0	9·6	57	9	—
Experimental error^e, ref.^{9}				20	9	
Range of ε values, ref.^{9}				2 310	9	

$^{a-e}$ See Table I. ^{g} Calculated from the linear parts of the curves (4 and 5 points, respectively), reliable estimates of s not possible.

We used the doubled minimum value and obtained the confidence limits of μ_M, μ_D, and K as given in Table I. Due to the dependence of parameters, these limiting values must be combined with each other only in one sense, either the upper limits together, or the lower limits. While the broad confidence interval makes the values of μ_M and K almost worthless, remarkably enough μ_D is obtained with a reasonable precision. The literature values[10] do not seem so bad at first sight since both μ_M and K fall within our estimated limits. However, they are markedly shifted from the best values (see the full points in Fig. 2) and this is sufficient to break completely the fit in Fig. 1.

Tetrabutylammonium Iodide in Benzene (ref.[10])

The permittivity data are given with more precision than in the preceding example, but the range of concentrations is narrower and the number of points too small. The result is quite different: no theory fits the data even approximately. With the assumption $\mu_D = 0$ no convergence was obtained (Table II). For $\mu_D \neq 0$ no convergence was obtained either, although there were only two degrees of freedom. In Fig. 3 the theoretical values have been plotted arbitrarily with the value $K = 10^5$ but already for this value μ_M is inacceptably large. (Since the discrepancies between calculated and experimental alues are very large in this case, Fig. 3 was plotted in actual values, not in differences as Fig. 1.) When both μ_M and K are taken from the literature[10], the fit is still worse, the theoretical curve passing far from the experimental points. The quadratic interpolation may appear still the best but it requires an impossible function ε vs w_2 which has a maximum within the measured region and returns to ε_1 of the pure solvent within the interval of experimentally accessible concentrations. We may conclude that the method of Bauge and Smith[10] is completely fallacious: it yields biased estimates and cannot differentiate cases with a good fit from those giving no fit at all. Concerning the last example, the state of tetrabutyl-ammonium iodide in benzene solution cannot evidently be described in terms of a monomer–dimer equilibrium.

Pyridiniodicyanomethylide in Dioxan (ref.[11])

The experimental permittivities are given only to three decimals but the range of ε values is broad. As we showed previously[19], the data can be treated by the conventional Halverstadt–Kumler[4] method and no deviation from linearity is apparent outside the experimental error (Fig. 4). Treating according to Eq. (10) with $\mu_D = 0$ yields a small apparent value of K (Table III) with a confidence interval between zero and 5. By a quadratic interpolation an insignificant term in w_2^2 is obtained in Eq. (1). If the value of α' is used to calculate[7] K, a small value of K is obtained, too, but its unreability is not immediately evident. To conclude, the method of

Trainer, Skinner and Fuoss[11] is as bad as that of Bauge and Smith[10] for the same reason. In this case it yielded a dimerization constant for the system where there is no observable association at all.

Acetic Acid in Benzene (ref.[18])

The permittivity data are given to five decimals but our preliminary treatment revealed large deviations of certain points, always in the same directon irrespective of any theoretical curve. Hence four points at highest concentrations were deleted with a significant improvement of accuracy (Table IV). In Fig. 5 note the change of scaling on the y-axis with respect to Figs 1 and 4 which corresponds to the accuracy improved by an order of magnitude. As expected, the treatment of data[18] in terms of the Bauge and Smith[10] theory gives again quite false results, the quadratic interpolation is not better. The treatment according to our Eq. (*10*) reproduces the measured permittivity practically within experimental errors, however, it is difficult to decide between the calculations with $\mu_D = 0$ and with μ_D freely fitted. Figure 5 does not convince that the latter possibility (curve 1) is superior: although it yields a lower standard deviation, it deviates for the eight lowest concentrations in the same direction. For a decision two further sources of information may be referred to. The first three points of the ε vs w_2 curve served to determine the dipole moment according to Halverstadt–Kumler[4] which is attributable to the monomer. The second possibility is to adopt the value of K from other than dielectric measurements but the agreement between these measurements[21−25] is very bad. For this reason we focussed attention on the Halverstadt–Kumler dipole moment (4·63 − all dipole moments in 10^{-30} C m) and restricted the set of hypotheses to those which agree with this value. Figure 6 shows the dependence of μ_D on K with this restriction. Since μ_D cannot be negative, the graph decomposes into two parts: one with μ_D optimized and different from zero, the other with $\mu_D = 0$. It is not possible to give any more definite value to K but still less to μ_D due to the steep curve in the critical region. The hypothesis $\mu_D = 0$ cannot be rejected and is particularly attractive since symmetrical dimers occur in the crystals of many carboxylic acids and are claimed also in the liquid phase and in solutions[16,17,26]. Note that in Fig. 5 the curve 5 is not superior to the curve 2 from which it differs by a non-zero value of μ_D. If we reverse the assumption and keep the constraint $\mu_D = 0$, we obtain the dependence of μ_M on K as shown in Fig. 7. Again the range of acceptable values would be too broad, but the agreement of the optimum value of μ_M with the Halverstadt–Kumler limit is remarkable. Hence we consider the values $\mu_M = 4·63$ and $\mu_D = 0$ as the most probable solution conforming with the available permittivity measurements. However, the resulting value of $K = 49$ would be the lowest reported, less than one half of the lowest ones from more recent cryoscopic[25] and calorimetric[22] determinations.

2-Pyrrolidinone in Benzene

In addition to a study at higher concentrations[27], two sets of permittivity data are available: one in connection with densities[9], the other with refractivity indices[15]. We have processed the two sets separately according to Eq. (*10*), the necessary value of β was calculated from the first paper[9] and used in both sets: its effect on the resulting accuracy is negligible. The data were restricted to concentrations with $w_2 < 0{\cdot}005$. The results from the two sets differ, demonstrating the instability of the calculations with respect to the experimental errors. In the first set[9] good fit was obtained with $\mu_D = 0$ (Fig. 8); even when μ_D was optimized, zero value always was obtained (Table V). The quadratic interpolation is distinctly worse, and the parameters calculated in the original literature by a statistically not satisfying method[9] are evidently biased. The mutual dependences of parameters (Fig. 9) reveal a well developed minimum. The only reason why our solution cannot be simply accepted is the disagreement with the Halverstadt–Kumler value. The plot ε vs w_2 is linear up to $w_2 = 0{\cdot}0006$, determining the value $\mu_M = 11{\cdot}70$ with a relative realiability. If we accept this value as fixed, optimum value of μ_D is again zero but the overall fit is worsened considerably (Table V). At the same time also the value of K is shifted to still lower values and differs more from literature data[28,29] which, however, show serious diasagreement between each other.

When the calculations were repeated with the second set[15], a similar picture was obtained as Fig. 8 but with a larger scatter. Differences between neighbouring points suggest a lower accuracy of this more recent set which is sufficient to obtain a different result: the optimum solution requires μ_D different from zero (Table V). Figure 10 shows the dependences of the parameters μ_M and K with μ_D taking always its optimum value. Since μ_D cannot be negative, the figure decomposes into two parts separated by the heavy line: on the left from this line the optimum values of μ_D are zero. The best solution agrees remarkably well with that given by Walmsley[15] within the framework of the Guggenheim–Smith method but there is a striking difference in the confidence intervals (Table V). Those given by Walmsley[15] are too narrow since the mutual dependence of parameters was not taken into account. Figure 10 reveals that even the value of $\mu_D = 0$ cannot be rejected, and the values of K and μ_M cannot be limited at all by any upper limit. The great uncertainty of parameters is connected also with the relative high standard deviation of the fit. Disagreement with the Halverstadt–Kumler dipole moment is similar as in the preceding set.

In the intention to improve the above results we tried to restrict the data sets to still lower concentrations. The third set in Table V, obtained from the first one by dropping the last point, yielded somewhat improved but essentially similar results. The Halverstadt–Kumler value falls now in the confidence interval, but this interval is also broader. To conclude, there are good grounds to believe that the dimer of

2-pyrrolidinone is symmetrical with $\mu_D = 0$, also the value $\mu_M = 11.70$ seems rather reliable. The dielectrometric measurements in the allowed concentration interval are, however, not quite satisfactorily reproduced by the theory.

DISCUSSION

Validity of the Theoretical Model

The validity of Eq. (10) depends on its premises, Eqs (3), (5), (6), (8) and (9). The fundamental assumption is that only a dimer and no higher polymers are formed, Eq. (8). Equation (9) is a thermodynamic expression for equilibrium, valid in dilute solutions. Equations (5) and (6) were assumed — more or less explicitly — in previous theoretical treatments[7–12,16], small deviations from them would not be observable in the final results. A convincing experimental proof of Eq. (6) can be obtained from density measurements[9] on benzene solutions of 2-pyrrolidinone up to $w_2 = 0.03$. Hence it is Eq. (3) which lies at the heart of the analysis. It is a logical extension of the well-known additive relationship, Eq. (13), on which the determinations of dipole moments in solution according to Halverstadt and Kumler[4], or Le Fèvre and Vine[8] are based.

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{1}{d} = w_1 p_1 + w_2 p_2 \qquad (13)$$

Sufficient accuracy of Eq. (13) has been proven in thousands of examples and the accuracy of Eq. (3) should not be lower. However, there is a difference in the concentration range in which the two equations are applied. The above methods[4,8] use Eq. (13) only as a limiting law and do not require a strictly linear dependence ε vs w_2, they need only its slope at the point $w_2 = 0$. Actually substituting $\left(d_1^{-1} + \beta w_2\right)$ for d^{-1} and $(1 - w_2)$ for w_1 into Eq. (13) yields a non-linear dependence of ε on w_2 but the curvature would be practically irrecognizable. On the contrary, in our treatment it is just this curvature from which K and μ_D are determined. At the same time low concentration is inevitable to maintain the validity of several fundamental assumptions: formation only of dimers, use of concentrations instead of activities, additivity of specific polarizations, most important is probably the assumption of a constant nonpolar solvent. An exact validity of Eq. (3) would require a non-linear ε vs w_2 plot even for $K = 0$, according to Eq. (10). On the other hand, a strictly linear plot would imply a finite value of K which, however, will be mostly statistically insignificant, compare similar problems with the quadratic interpolation[7]. In accordance with the common practice we consider a linear ε vs w_2 plot as a proof that any association is not observable. The validity of Eq. (3) and hence also of Eq. (10) thus requires a concentration neither too high nor too low. According to

the results of the preceding part we believe that Eq. (10) is experimentally verified in concentrations up to $w_2 = 0.005$ or 0.01 if dimerization actually takes place, see particularly Tables I and IV.

Comparison with Previous Treatments

Equations more or less similar to Eq. (10) have been derived several times in the literature. In addition to the treatments based on density measurements[7,11,13,16] there are also those using refractive indices[12,14,15] within the framework of the Guggenheim–Smith method[5], or even using[17] both d and n. Some of them are either a priori constrained[8,11], or at least practically restricted[7,12] to symmetrical dimers with $\mu_D = 0$. The main difference in derivation of these equations is in the additivity relationship corresponding to our Eq. (3). The additivity can be expressed in different concentration units; either in molar concentrations[11,12,14] or in molar fractions[7,9,13,16] instead of in weight fractions as in our Eq. (3) and in refs[8,17]. Alternatively, an additive relationship may be assumed in terms of the slopes α of the ε vs w_2 plots[10]. All these modifications do not differ too much in the region of low concentrations, only expressing in molar fractions deserves a comment. It is based on the Hedestrand theory[30] which uses instead of Eq. (13) an additivity relationships in terms of molar polarizations P_1 and P_2, and molar fractions x_1 and x_2:

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{1}{d} \left(x_1 M_1 + x_2 M_2 \right) = x_1 P_1 + x_2 P_2 . \tag{14}$$

The whole procedure is obsolete since Eq. (14) is exactly identical with Eq. (13) as can be shown by substituting $M_i p_i$ for P_i and $\left(w_i/M_i \right)/\left(w_1/M_1 + w_2/M_2 \right)$ for x_i. It means that for calculations according to Eq. (14) it is necessary to introduce the molecular weight of the solvent, M_1, which is in fact eliminated in the final result. If this unfortunate equation is extended to a three-component system including the monomer and dimer, it takes the form:

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{1}{d} \left(x_1 M_1 + x_M M + 2 x_D M \right) = x_1 P_1 + x_M P_M + x_D P_D \tag{15}$$

which is in fact identical with Eq. (3). However, the molar fractions x_M, x_D, and even x_1 are unknown unless the extent of dimerization is determined. For this reason some authors have introduced — in addition to the actual values x_1, x_M, x_D — still the fictive values x_1^*, x_2^* (denoted by us with an asterisk) which are calculated with the molecular weight of the monomer, i.e. without knowing anything about the

dimerization. The equation

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{1}{d}\left(x_1^* M_1 + x_2^* M\right) = x_1^* P_1 + x_2^* P_2^* \tag{16}$$

is then to be considered as a definition of the fictive value P_2^* from the known x_1^*, x_2^*, P_1 and the measured ε and d. An equation equivalent to our Eq. (3) can be written in these term as

$$P_2^*\left(x_M + 2x_D\right) = x_M P_M + x_D P_D \tag{17}$$

which is a slightly rewritten form of equation (2c) of ref.[16], or follows by comparing the fourth and fifth equations on p. 281 of ref.[7]. The whole theory in terms of molar fractions is equivalent to that in weight fractions but the latter is much simpler, compare the symbols x_1, x_1^*, etc. to the unambiguous symbols w_1 and w_2. The complex symbolism may be reason for several misprintes and mistakes in the literature[7] we have already corrected[19].

Statistical Problems

The statistical procedure is much more important for the results than differences in defining the additivity principle. From the examples given it is evident that particularly those methods must be rejected which transform the theoretical equation into a linear form with both variables on either side[10,11]. On the one hand the estimation of parameters are strongly biased, so that in the extreme case these theories have predicted values completely at variance with the experiments (Figs 1, 3, 4, 5). On the other hand there is no possibility to estimate the fit and to decide whether the theory is in accord with the experiments or not (compare Figs 1 and 3). In the age of computers all such procedures should be removed from the literature. This statement applies conditionally even for methods based on the expansion as power series[7,17], it means at least in cases when a physically better grounded solution can be suggested. The power series (in our cases restricted to the quadratic term) fits usually the data worse than a meaningful theoretical function, so that part of the information is lost (see Figs 1, 5, 8). Three parameters cannot be calculated from two coefficients of the quadratic expansion, even the two obtained may be displaced from the optimum values (Tables IV, V). The fit estimated in these cases is the fit of the quadratic interpolation and not of any theory. The confidence intervals of the parameters and their dependence remain usually unknown.

The statistical procedure presented in this paper is unobjectionable from the above points of view and meets the requirements formulated in the introduction. The inaccuracy of minimizing the sum of squares in $(\varepsilon - 1)/(\varepsilon + 2)$ instead of in ε itself

is quite negligible. An essential feature is the regression through a fixed origin which is also recommended[3] in simple determination of dipole moment. The main reason is the evidently greater accuracy in determining ε_1 of the pure solvent (no weighing, repeated measurements). This regression gives more wieght to the more remote points, this may be reasonable with respect to the lowered precision in preparing the most dilute solutions. However, restriction of the concentration range is necessary since one remote point, not obeying the theory, can spoil the results markedly. In any case the least-squares method should be complemented by an analysis of deviations (randomness of deviations, elimination of gross errors) and by consideration of the parameter values (particularly the agreement of μ_M with the Halverstadt––Kumler value if obtainable).

The main merit of our approach, even as compared to other correct procedures[14], is in the proper attention given to the mutual dependence of estimated parameters. In most cases just this dependence is critical for the significance of the results obtained (Figs 7, 9, 10), compare the overestimated accuracy in refs[9,14,15]. In all practical examples the results were limited by the precision in measuring ε and by the narrow interval of its values.

It follows that one series of measurements seems hardly sufficient to estimate all three parameters μ_M, μ_D, and K, according to Eq. (10). Merely exceptionally one of them may be obtained with an acceptable accuracy, e.g. μ_D in Fig. 2. Favourable are cases when the ε vs w_2 plot is linear through a given range of concentrations: then one can determine μ_M separately by the conventional approach. On the other hand, there is a rather bad experience with substituting the equilibrium constant K as obtained from independent non-dielectric measurements. We conclude that the statistical treatment outlined here is sufficient for the data obtainable by contemporary methods.

Structure of the Dimers

The dipole moment of the dimer allows some conclusions about its structure, at least whether it is centrosymmetrical or not. Previous erroneous or incomplete methods sometimes yielded non-zero dipoles for dimers which were otherwise believed to be symmetrical, eg. for acetic acid[16−18], or 2-pyrrolidinone[9,15]. These values were interpreted either in terms of an abnormally high atomic polarization — it means lose binding of the two molecules[15−17,31], or by an inherently asymmetrical structure at least of a part of dimeric species[9,16,17,31], this means also open-chain dimers[9,26] or higher polymers[24,26,27]. Our recalculation does not yield any proof for finite values of μ_D in the above cases, it means that the hypothesis $\mu_D = 0$ cannot be rejected. This, of course, would remove some difficulties with the interpretation. Considering the uncertainty in the parameters of dimers, the attempts to calculate them even for trimers[14] or tetramers[27] are clearly unrealistic.

CONCLUSIONS

The preceding examples and discussion have shown conclusively that the literature methods are either in principle wrong[10,11], or little efficient[7,17], or at least over-estimaing the precision of determined parameters[14]. One can say that all values of K and μ_D reported to date are wrong. The simple theory outlined in this paper, together with the appropriate statistical treatment, may be considered experimentally verified. As far as some more definite results could be obtained, they were easier to interpret than those reported previously. It is the accuracy of data which prevents to obtain more definite results; critical is particularly the condition of working in rather dilute solutions. Hence it seems hardly possible to get the values of μ_M, μ_D, and K with an acceptable accuracy by fitting one data set to the theoretical curve. More dependable results are obtained if the ε vs w_2 curve has a reasonably linear part, allowing to determine μ_M by the classical approach.

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