

THE HIGASI METHOD OF MEASURING DIPOLE MOMENTS AND ITS CORRECTION

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The Higasi method of measuring dipole moments on 150 substances in benzene and dioxane solutions at the temperature of 25°C has been tested. Values of the dipole moments, obtained by the Higasi method, are compared with those achieved by means of the Halverstadt and Kumler method and a systematic deviation is found. On the basis of this comparison a semiempiric correction of the Higasi relation has been suggested. Furthermore, some Higasi presumptions have been verified.

For calculations of the dipole moments from experimental data, the experimentally found value of the molar polarization of a polar substance in the Debye equation¹ is employed. If we use for dipole moment measurements the method of dilute solutions of a polar substance in a nonpolar solvent, the value of the molar polarization extrapolated for an infinite dilution of the solution must be inserted into the Debye equation. For calculation of this extrapolated value a number of methods are published in the literature, which are from the experimental point of view based on the measurements of concentration dependences of two properties of the solution (permittivity and density or specific volume²⁻⁵, or permittivity and index of refraction⁶⁻⁹). In order to speed up and simplify the measurements and calculation of the dipole moments, Higasi suggested¹⁰ a simple relationship which requires measurement of the concentration dependence of the permittivity of the solution only. A quite adequate relationship in a somewhat other shape has been suggested by Srivastava and Charandas¹¹.

All the assumptions generally made to derive relations for a calculation of the dipole moment from experimental data may be summarized in the following equations:

$$p_{12} = \omega_1 p_1 + \omega_2 p_2, \quad (1)$$

$$\epsilon_{12} = \epsilon_1 + \alpha \omega_2; \quad \omega_2 < 0.01, \quad (2)$$

$$v_{12} = v_1 + \beta \omega_2; \quad \omega_2 < 0.01, \quad (3)$$

$$\beta = 0, \quad (4)$$

$$p_{2e} + p_{2a} = p_1, \quad (5)$$

where p is the specific polarization, ϵ permittivity, v specific volume, α and β denote tangents of concentration dependences, ω the mass fraction, indexes 12, 1, 2 relate to the solution, solvent, and polar substance, respectively, indexes e and a denote the electronic and atomic polarizations. Assumptions (1)–(3) are experimentally verified and are usually approximately fulfilled for the great majority of substances^{3,12}; the realization of assumptions (4) and (5), however, is greatly problematic, particularly assumption (5) can obviously be met only exceptionally.

Assuming validity of relations (1)–(3), the Halverstadt–Kumler relationship³ can be obtained to calculate the extrapolated value of the molar polarization; the latter relationship yields in connection with the Debye equation¹ relation

$$\mu_{\text{HK}} = \left(\frac{9kT}{4\pi N} \right)^{1/2} \left\{ \left[\frac{3v_1}{(\epsilon_1 + 2)^2} \alpha + \frac{p_1}{v_1} \beta + p_1 - (1 + \varphi) r_2^{\text{D}} \right] M_2 \right\}^{1/2}; \quad (6)$$

If we assume validity of all five assumptions, we obtain the Higasi equation¹⁰

$$\mu_{\text{H}} = \left(\frac{9kT}{4\pi N} \right)^{1/2} \left[\frac{3v_1}{(\epsilon_1 + 2)^2} M_2 \alpha \right]^{1/2} = \gamma [M_2 \alpha]^{1/2}, \quad (7)$$

where $r_2^{\text{D}} = (n_2^2 - 1) \cdot v_2 / (n_2^2 + 2)$ and φ is the correction factor for the atomic polarization of a polar substance ($\varphi = p_{2a} / p_{2e} = p_{2a} / r_2^{\text{D}}$).

To verify validity of the Higasi assumptions (4) and (5) we adapt equation (6) to shape

$$\mu_{\text{HK}} = \left(\frac{9kT}{4\pi N} \right)^{1/2} \left\{ \left[\frac{3v_1}{(\epsilon_1 + 2)^2} \alpha + L_1 + L_2 \right] M_2 \right\}^{1/2}, \quad (8)$$

where $L_1 = p_1 \beta / v_1$ and $L_2 = p_1 - (1 + \varphi) r_2^{\text{D}}$. Deviation $\Delta\mu_{\text{H}} = \mu_{\text{H}} - \mu_{\text{HK}}$ depends on the magnitude of term $(L_1 + L_2) M_2$. According to (4) $L_1 = 0$ and according to (5) likewise $L_2 = 0$. Validity of both assumptions has been examined on a limited sort of material^{10,13} and it has been found that these assumptions are for some substances fulfilled and that in other cases at least $L_1 + L_2 = 0$ holds.

In this paper 120 substances measured in benzene and 30 substances measured in dioxane (see Experimental) have been employed. Average value of quantity L_1 and L_2 was in benzene equal to -0.101 and $+0.072 \text{ cm}^3$, in dioxane to -0.037 and -0.019 cm^3 , respectively (all at the temperature of 25°C). Assumptions (4) and (5) are then with the examined substances met only very approximately, but it can be demonstrated that errors produced by introducing them are for benzene solutions compensated between one another, in case of the dioxane solutions the errors are mostly added. Sum $L_1 + L_2$, however, has in most cases a negative value and the Higasi method yields therefore mostly higher values of the dipole moments than the method of Halverstadt and Kumler (Figs 1, 3a).

Figs 1 and 3a likewise show that the Higasi method yields for smaller dipole moments less accurate values than for the larger ones. Reasons for that may be given very easily, if we realize that the $(L_1 + L_2)(\epsilon_1 + 2)^2 / 3v_1 \alpha$ ratio defines magnitude of deviation $\Delta\mu_{\text{H}}$. This ratio is for smaller dipole moments greater than for the larger ones.

The shape of equation (8) led us to the idea to introduce correction

$$\mu_{\text{K}} = \gamma (M_2 \alpha - K)^{1/2} \quad (9)$$

into the Higasi equation (7), our requirement being that the distribution of deviations of corrected values, $\Delta\mu_K = \mu_K - \mu_{HK}$, should be symmetric with respect to axis $\Delta\mu = 0$. We found empirically for correction K that it depends linearly on the magnitude of the dipole moment ($K = k_1\mu + k_2$). By introducing into equation (9) and solving quadratic equation for μ , thus produced, we obtained relationship

$$\mu_K = \gamma \left[M_2\alpha - \left(k_2 - \frac{k_1^2\gamma^2}{4} \right) \right]^{1/2} - \frac{k_1\gamma^2}{2}. \quad (10)$$

By introducing numeric values γ , k_1 , and k_2 , we obtained in the Debye units

$$\mu_K = 9.62 \cdot 10^{-2} (M_2\alpha - 40)^{1/2} - 0.05 (\text{benzene } 25^\circ\text{C}),$$

$$\mu_K = 8.98 \cdot 10^{-2} (M_2\alpha - 40)^{1/2} - 0.03 (\text{dioxane } 25^\circ\text{C}).$$

It follows from Figs 2 and 3b that these equations meet our requirement. The introduced correction of the Higasi equation merely diminishes absolute value of the probable deviation, but it does not diminish dispersion of these deviations. Distribution of the deviations of corrected values of the dipole moments (Figs 2, 3b) justifies to a certain extent the statement that for the corrected values of the dipole moments greater than 3D or equal to 2–3D, errors smaller than 5% or 10%, respectively, may be expected. Neither the Higasi equation nor the corrected equation suggested, can therefore substitute the widely used Halverstadt and Kumler method. The Higasi equation may find application, where lower requirements of accuracy are needed, especially for rapid informative determination of the dipole moments values.

It must be stressed in the conclusion that in terms of the reference method the Halverstadt and Kumler method, which was tacitly taken as giving accurate values of the dipole moments, has been employed in this paper. This assumption is not quite

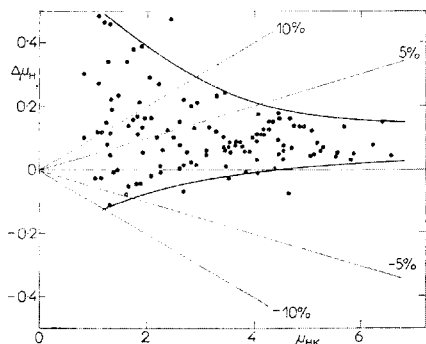


FIG. 1

Dependence of Deviation $\Delta\mu_H = \mu_H - \mu_{HK}$ on the Magnitude of Dipole Moment μ_{HK} for Measurements in Benzene at 25°C

Straight lines denoted by 10, 5, -5, -10% express the course of dependences of 10, 5, -5, -10% relative deviation $\Delta\mu/\mu$ on the magnitude of the dipole moment (the same for Figs 2 and 3).

justified (even though quite convenient for purposes of the present paper), for the dipole moment values (achieved by means of an arbitrary extrapolation method) are known to be charged with an error whose magnitude cannot be determined exactly¹⁴. All the conclusions presented in this paper must be then interpreted on the basis of the comparison between the Higasi method and that of Halverstadt and Kumler.

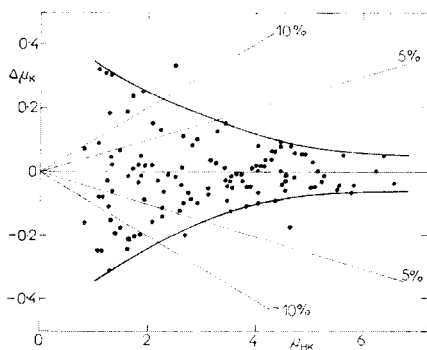


FIG. 2

Dependence of Deviation of Corrected Values $\Delta\mu_K = \mu_K - \mu_{HK}$ on the Magnitude of Dipole Moment μ_{HK} for Measurements in Benzene at 25°C

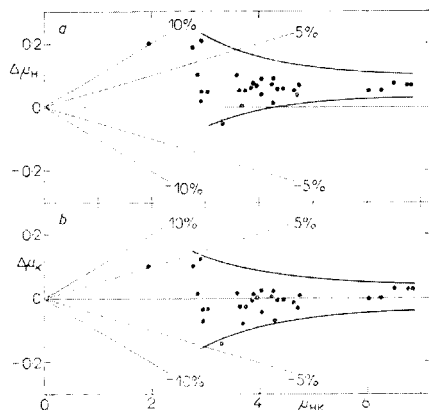


FIG. 3

Dependences of a) Deviation $\Delta\mu_H = \mu_H - \mu_{HK}$ and of b) Deviation of Corrected Values $\Delta\mu_K = \mu_K - \mu_{HK}$ on the Magnitude of Dipole Moment for Measurements in Dioxane at 25°C

EXPERIMENTAL

The substances, on which the Higasi method was tested, were chosen from published measurements made in our laboratory in the last years, so that the values of the dipole moments might cover as greatest range as possible. In a set of the substances examined, various organic compounds were represented, such as halogenated derivatives, nitro derivatives of aromatic hydrocarbons, ethers, alcohols, aldehydes, esters, amides and nitriles of carboxylic acids, oximes, heterocyclic compounds, organic compounds of boron, phosphorus, sulphur, selenium, tellurium *etc.*

As solvents, benzene and dioxane purified by conventional methods^{15,16} were employed. The measurements were made at the temperature of 25°C. Permittivity of the solutions was measured by means of a heterodyne apparatus at a frequency of 1.2 Mc with a precision within $\pm 1 \cdot 10^{-4}$. The specific volume of the solutions was measured with an Ostwald-Sprengel pycnometer with a precision of $\pm 1 \cdot 10^{-5} \text{ cm}^3 \text{ g}^{-1}$. Usually five measurements over a concentration range of $1 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ were made.

To calculate the dipole moments by the Halverstadt-Kumler method, the values of tangents α and β were obtained graphically, since the least squares method does not yield reliable results, if few values are available. Molar refractivity ($R_2^D = r_2^D \cdot M_2$) was obtained as a sum of the Vogel contributions¹⁷, in some cases it was calculated from measured values of the refractive index and density. For correction factor φ (equation (6)), value 0.05 (ref.¹⁴) was selected. For calculations involving the Higasi method, the calculated values $9.62 \cdot 10^{-2}$ D (benzene 25°C) and $8.98 \cdot 10^{-2}$ D (dioxane 25°C) were used in equation (7) for coefficient γ .

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