

## A COMMENT ON EVALUATION OF EFFECTS OF MIXED SOLVENTS BY MEANS OF THE BORN AND KIRKWOOD METHOD

Vojtěch BEKÁREK

*Institute of Analytical and Organic Chemistry, Palacký University, 771 46 Olomouc*

Received August 8, 1988

Accepted April 6, 1989

The evaluation of the mixed solvent effect by means of the Kirkwood and Born functions of the relative permittivity of the mixed solvent has been criticized as a thermodynamically inconsistent procedure. A procedure has been suggested to estimate the composition of solvation sphere around dipolar molecules or transition states in binary mixtures of a polar and a nonpolar solvents.

Since 1941, when Glasstone, Laidler, and Eyring<sup>1</sup> used the Kirkwood and Born methods also for evaluation of mixed solvent effects on reaction rates, this procedure working with relative permittivity of mixed solvents has become quite common and is recommended by authorities (see e.g.<sup>2-5</sup>) as a method for obtaining quantitative information about the nature of dipolar particles (the Kirkwood<sup>6</sup>-Bell<sup>7</sup> method) and ions (the Born method<sup>8</sup>) in solution. The aim of this present communication is to show that the application of relative permittivity of mixed solvent in the Kirkwood-Bell and Born methods is thermodynamically inconsistent and, furthermore, to show how a study of effects of solvent mixtures upon spectra and reaction rates can be used for evaluation of solvation of dipolar molecules and/or transition states in mixed solvents.

### RESULTS AND DISCUSSION

The change in Gibbs energy connected with the transition of the particle studied from vacuum into the solvent ( $\Delta G$ ) is a consequence of the interactions between this particle and the solvent molecules in solvation layers. The following relations (1) and (2) were derived by Kirkwood<sup>6</sup> and Born<sup>8</sup>, respectively, for the magnitude of this change in the case of a dipolar particle and ion, respectively.

$$\Delta G = -(\bar{\mu}/2\pi\epsilon_0 r^3) [(\epsilon_r - 1)/(2\epsilon_r + 1)] \quad (1)$$

The Kirkwood (-Bell) equation

$$\Delta G = -(z^2 e^2 / 8\pi \epsilon_0 r) [(\epsilon_r - 1) / \epsilon_r]. \quad (2)$$

### The Born equation

In these equations  $z$  means the ion valence,  $r$  means the ion radius or the radius of the cavity around the dipolar molecule,  $\epsilon_r$  stands for relative permittivity of solvent,  $\epsilon_0$  is the permittivity of vacuum, and  $\bar{\mu}$  is the dipole moment of dipolar molecule. Both the equations are used for the purposes of correlation and evaluation of the depth of influence of medium upon the property studied as well as for estimation of properties of the dissolved particles, such as e.g. the ion radii in solution or the dipole moment of transition state or of excited molecules.

In the case of a mixed solvent the Gibbs energy of solvation can be expressed as a sum of contributions of the Gibbs energy changes of the dissolved particle caused by interactions with the individual solvents of the mixture in the solvation layer. Thus for a binary mixed solvent (the effects of binary mixed solvents have been studied most frequently) composed of solvents A and B the solvation Gibbs energy reads as follows:

$$\Delta G = \varphi_A \Delta G_A + \varphi_B \Delta G_B. \quad (3)$$

In Eq. (3)  $\varphi_A$  and  $\varphi_B$  mean the volume fractions of these solvents in the solvation layer, and  $\Delta G_A$  and  $\Delta G_B$  stand for the solvation Gibbs energy of the dissolved particle in the pure solvents A and B, respectively.

In real systems,  $\varphi_A$  and  $\varphi_B$  in solvation layer are different from the corresponding values in the binary solvent used (the solvent sorting), and  $\Delta G_A$  and  $\Delta G_B$  are not constant but depend on the composition of binary solvent. However, for the purpose of analysis of the problem of applicability of relative permittivity of mixtures in the Kirkwood or Born method, let us introduce the following simplifying presumptions: 1) The ratio  $\varphi_A/\varphi_B$  in the solvation layer is identical with that in the mixed solvent, i.e. no specific solvation of solute (preferent solvation by one of the solvents) takes place in the solution. 2) The solvents A and B form mutually ideal solution within the whole concentration region, hence for the relative permittivity of this mixture it is  $\epsilon_{rAB} = \varphi_A \epsilon_{rA} + \varphi_B \epsilon_{rB}$ . 3) Only nonspecific interactions (i.e. those whose effect on the properties of solute is evaluated by the Kirkwood or Born equation) are possible between the particle dissolved and both solvents.

Introducing Eq. (1) into Eq. (3) we obtain Eq. (4) for the Gibbs energy change connected with the transition of dipolar molecule from vacuum into this mixed solvent.

$$\Delta G = -\frac{\bar{\mu}}{2\pi\epsilon_0 r^3} \left( \varphi_A \frac{\epsilon_{rA} - 1}{2\epsilon_{rA} + 1} + \varphi_B \frac{\epsilon_{rB} - 1}{2\epsilon_{rB} + 1} \right). \quad (4)$$

An analogous equation can be obtained, on introducing Eq. (2) into Eq. (3), for the transition of the ion from vacuum into the mixed solvent.

In terms of Eq. (4), the accepted presumptions (1)–(3) being fulfilled, thus the solvation Gibbs energy of a dipolar molecule in a mixed solvent should be proportional to the sum of the Kirkwood functions of relative functions of relative permittivities of the pure solvents in such a ratio in which these solvents are present in the mixture. Since, in addition, it is  $\varphi_A + \varphi_B = 1$ ,  $\Delta G$  and, hence, also the property studied should exhibit a linear dependence on the solvent composition. In this sense, the deviations from this linear dependence were also used for evaluation of specific solvation of solutes in binary mixed solvents<sup>3</sup>.

However, the procedure currently used for evaluation of mixed solvent effects adopts Eqs (1) and (2) in such a way that the relative permittivities of mixed solvents are introduced thereinto, hence the Kirkwood equation is used in the form:

$$\Delta G = -(\bar{\mu}/2\pi\epsilon_0 r^3)((\epsilon_{rAB} - 1)/(2\epsilon_{rAB} + 1)). \quad (5)$$

The presumptions (1)–(3) being fulfilled, this Eq. (5) can be rewritten in terms of composition and relative permittivities of the pure components in the following form:

$$\Delta G = -\frac{\bar{\mu}}{2\pi\epsilon_0 r^3} \cdot \frac{\varphi_A \epsilon_{rA} + \varphi_B \epsilon_{rB} - 1}{2\varphi_A \epsilon_{rA} + 2\varphi_B \epsilon_{rB} + 1}. \quad (6)$$

If Eq. (5) were thermodynamically consistent and, hence, if it were possible to use the relative permittivity of mixed solvent in the Kirkwood equation, then the Eq. (6), and hence also Eq. (5), should be transferable into the consistent form of Eq. (3). Using the above-mentioned presumptions (1)–(3) and the condition  $\varphi_A + \varphi_B = 1$ , however, we can transform Eq. (6) gradually into Eq. (9):

$$\Delta G = -\frac{\bar{\mu}}{2\pi\epsilon_0 r^3} \left( \varphi_A \frac{\epsilon_{rA} - 1}{2\varphi_A \epsilon_{rA} + 2\varphi_B \epsilon_{rB} + 1} + \varphi_B \frac{\epsilon_{rB} - 1}{2\varphi_A \epsilon_{rA} + 2\varphi_B \epsilon_{rB} + 1} \right) \quad (7)$$

$$\Delta G = \varphi_A \Delta G_A \frac{1}{\varphi_A \left( 1 + \frac{2\varphi_B \epsilon_{rB} + \varphi_B}{2\varphi_A \epsilon_{rA} + \varphi_A} \right)} + \varphi_B \Delta G_B \frac{1}{\varphi_B \left( 1 + \frac{2\varphi_A \epsilon_{rA} + \varphi_A}{2\varphi_B \epsilon_{rB} + \varphi_B} \right)} \quad (8)$$

$$\Delta G = \varphi_A \Delta G_A \frac{2\epsilon_{rA} + 1}{2\epsilon_{rAB} + 1} + \varphi_B \Delta G_B \frac{2\epsilon_{rB} + 1}{2\epsilon_{rAB} + 1}. \quad (9)$$

The Eq. (9) obtained, of course, differs from Eq. (3), namely by the presence of the terms  $(2\epsilon_{rA} + 1)/(2\epsilon_{rAB} + 1)$  and  $(2\epsilon_{rB} + 1)/(2\epsilon_{rAB} + 1)$ . Hence the application of

relative permittivity of mixed solvent in the Kirkwood equation leads to a different and thus thermodynamically inconsistent dependence of the solvation Gibbs energy of the dissolved dipolar particle on the solvation Gibbs energies of this particle in the pure solvents. The difference consists in the presence of the terms  $(2\varepsilon_{rA} + 1)/(2\varepsilon_{rAB} + 1)$  and  $(2\varepsilon_{rB} + 1)/(2\varepsilon_{rAB} + 1)$  in Eq. (9). On the other hand, however, the presence of these terms in Eq. (9) explains the well-known fact (which also makes mixed solvents so popular for studies of medium effects) of mostly linear dependences of  $\Delta G$  on the Kirkwood (or Born) function of relative permittivity. It is possible to consider the terms  $(2\varepsilon_{rA} + 1)/(2\varepsilon_{rAB} + 1)$  and  $(2\varepsilon_{rB} + 1)/(2\varepsilon_{rAB} + 1)$  to represent reasonable characteristics of specific solvation of the particle dissolved in a mixed solvent, i.e. of the weight of the contribution of  $\Delta G_A$  and  $\Delta G_B$  to the overall solvation Gibbs energy. An analogous analysis of the Born equation again gives an equation different from Eq. (3); in this case the terms causing the inconsistency have the form of  $\varepsilon_{rA}/\varepsilon_{rAB}$  and  $\varepsilon_{rB}/\varepsilon_{rAB}$ .

In real systems, however, the general presumptions (1)–(3), which were used to prove thermodynamic inconsistency of application of relative permittivity of mixtures in the Kirkwood and/or Born methods, are no more valid. As far as the first two presumptions are concerned, not only  $\varphi_A$  and  $\varphi_B$  are different in the surroundings of the particle dissolved and in the mixed solvent as a consequence of specific solvation (the so-called solvent sorting) but also the relative permittivity of the individual solvents in the mixture depends on its composition. The third presumption concerning nonspecific interactions between solute and solvent can be fulfilled experimentally, however, this presumption deserves an analysis with respect to the concept of so-called collision complexes<sup>9–11</sup>, and it will be dealt with in the last section of this present communication.

The problem of dependence of relative permittivity on composition, can be quantitatively evaluated for mixtures of a polar solvent ( $\mu \neq 0$ ) with a nonpolar one ( $\bar{\mu} = 0$ ): the relative permittivity of nonpolar solvent is equal to the square of its refractive index  $n$ ,  $\varepsilon_r = n^2$ .

In the overall polarizability of polar solvents usually predominant is the contribution of their orientational polarizability which is greater than their deformation polarizability. The differences between refractive indexes or their squares of polar and nonpolar solvents are much smaller than those between their relative permittivities. Moreover, it is possible, from the standpoint of the Kirkwood or Born function, to presume a linear dependence of refractive index on composition for many mixtures, particularly those composed of solvents with close refractive indexes. Hence the orientational polarizability of these molecules is predominantly responsible for the dependence of relative permittivity of a polar solvent on the composition of mixed solvent. Figure 1 shows the dependence of relative permittivity and refractive index of the mixture cyclohexane–1,2-dichloroethane on the composition of this mixture over the entire concentration region. This is a mixture of solvents whose

refractive indexes are very close, viz. 1.426 and 1.441. Hence, if the deviations from the relation  $\epsilon_{rAB} = \varphi_A \epsilon_{rA} + \varphi_B \epsilon_{rB}$  are due to the orientational polarizability of the polar solvent in a mixture, then it is possible, on the other hand, to calculate the relative permittivity of this more polar solvent from this relation – directly from the experimental value  $\epsilon_{rAB}$  and relative permittivity of the nonpolar component which is equal to the square of refractive index in the whole concentration range. Table I presents the values thus obtained for relative permittivity of 1,2-dichloroethane in its mixtures with cyclohexane, and Fig. 1 shows the dependence of the relative permittivity of 1,2-dichloroethane on the composition of the mixture (curve 3). Hence for evaluations of effects of real mixtures composed of a polar and a nonpolar solvents we should use, in the Kirkwood or Born method, the relative permittivity of the polar solvent in the sense of Eqs (3) and (4).

The relative permittivities and refractive indexes of both components of a mixed solvent being known, it is of course possible to calculate the proportions of both solvents in the solvation layer of the solute from the experimental data on the effects of the pure solvents and the solvent mixture considered on some of the solute properties. Here the starting relation is Eq. (3), in which the volume fractions of components of the solvent mixture have the meaning of the volume fractions of these components in the solvation (cybotactic) layer around the solute and in the following text they will be denoted as  $\varphi_A^c$  and  $\varphi_B^c$ . The  $\Delta G_A$  and  $\Delta G_B$  values of this equation can then be expressed, in the sense of Eq. (4), by some of the so-called semi-empirical equations for evaluation of solvent effects, e.g. the Kirkwood or the Born equations. Thus it is possible by the iteration procedure to obtain informa-

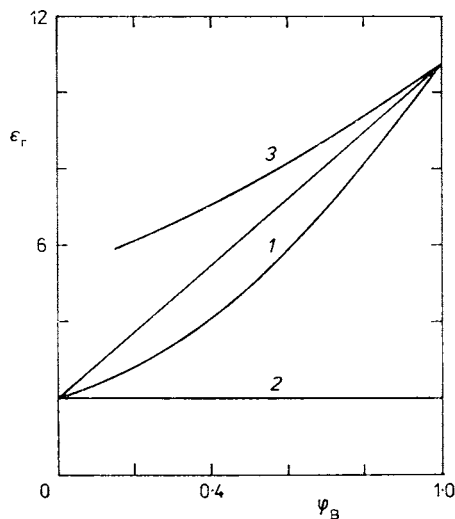


FIG. 1

The dependence of relative permittivity ( $\epsilon_r$ ) of the mixture cyclohexane (A)–1,2-dichloroethane (B) (1), that of the square of refractive index ( $n^2$ ) of this mixture (2), and that of relative permittivity of 1,2-dichloroethane (3) upon the composition ( $\varphi$ ) of this mixture

tion about average composition of the solvation layer around the dissolved molecule (e.g. from the data about the mixed solvent effects upon electronic spectra) or the transition state (from the data about the mixed solvent effects on rate constants).

Table I presents the results of calculation of the cybotactic layer around 1-nitro-2-(4'-dimethylaminophenyl)ethene and around the transition state of reaction of triethylamine with ethyl iodide in the solvent mixture of cyclohexane and 1,2-dichloroethane. For this calculation we have used the relative permittivity of 1,2-dichloroethane in its mixture with cyclohexane ( $\epsilon_{rB}$  in Table I) and the dependence of wavenumber of the absorption maximum of 1-nitro-2-(4'-dimethylaminophenyl)ethene and the rate constant of reaction of triethylamine with ethyl iodide on the relative permittivity and refractive index of the pure solvents and, finally, the data about the effect of the mixed solvent cyclohexane-1,2-dichloroethane on the properties mentioned<sup>13-15</sup>. The correlation equations used for the pure solvents have the form:

$$\tilde{\nu} \cdot 10^{-3} (\text{cm}^{-1}) = 28.22 - 11.90f(\epsilon_r)_B f(n^2)_B \quad R = 0.986 \quad n = 39 \quad (10)$$

$$\log k = -10.43 + 70.98f(\epsilon_r)_K f(n^2)_K \quad R = 0.987 \quad n = 10. \quad (11)$$

The subscripts B and K in Eqs (10) and (11) denote the Born and Kirkwood functions, respectively, of relative permittivity and refractive index of the pure solvents.

TABLE I

The relative permittivity<sup>12</sup> ( $\epsilon_{rAB}$ ) and the square of refractive index<sup>15</sup> ( $n_{AB}^2$ ) of cyclohexane-1,2-dichloroethane mixture, the relative permittivity of 1,2-dichloroethane ( $\epsilon_{rB}$ ) in this mixture, the wavenumber of absorption maximum of 1-nitro-2-(4'-dimethylaminophenyl)ethane ( $\tilde{\nu}$ ), and logarithm of rate constants of the reaction of triethylamine with ethyl iodide at 298 K ( $\log k$ ) in cyclohexane-1,2-dichloroethane mixture<sup>15</sup>, and the calculated volume fractions of 1,2-dichloroethane in the solvation layer of 1-nitro-2-(4'-dimethylaminophenyl)ethene  $\phi_B^e(\tilde{\nu})$  and of the transition state of the above-mentioned reaction  $\phi_B^e(\log k)$

$\phi_B^a$	0.00	0.20	0.40	0.60	0.80	1.00
$\epsilon_{rAB}$	2.02	2.80	4.00	5.70	7.80	10.65
$n^2$	2.03	2.04	2.05	2.06	2.07	2.08
$\epsilon_{rB}$		5.92	6.97	8.15	9.25	10.65
$\tilde{\nu} \cdot 10^{-3}, \text{cm}^{-1}$	25.22	24.10	23.64	23.20	22.88	22.67
$\phi_B^e$		0.465	0.64	0.80	0.915	1.00
$\log k$	-7.52	-6.10	-5.37	-4.76	-4.27	-3.92
$\phi_B^e(\log k)$		0.44	0.64	0.79	0.91	1.00

<sup>a</sup> The volume fraction of 1,2-dichloroethane in the mixed solvent.

For a mixed solvent composed of a nonpolar solvent A and a polar solvent B we can rewrite Eqs (10) and (11) to the forms from which the composition of cybotactic layer,  $\varphi_A^c$  and  $\varphi_B^c$ , is calculated.

$$\tilde{\nu} \cdot 10^{-3} (\text{cm}^{-1}) = 28.22 - 11.9f(\epsilon_{rA})_B f(n_A^c)_B \varphi_A^c - \quad (12)$$

$$- 11.9f(\epsilon_{rB})_B f(n_B^c)_B \varphi_B^c$$

$$\log k = -10.43 + 70.98f(\epsilon_{rA})_K f(n_A^c)_K \varphi_A^c + \quad (13)$$

$$+ 70.98f(\epsilon_{rB})_K f(n_B^c)_K \varphi_B^c.$$

The composition of cybotactic layer will depend, for a certain property, on the nature of the solvents used, particularly of the polar solvent and will exhibit various deviations from the composition of mixed solvent. Thus e.g. in the case of the above-mentioned reaction studied in the mixture cyclohexane–acetone<sup>16</sup> the volume fraction of acetone in the cybotactic layer of the transition state has the following values (in parenthesis given is the volume fraction of acetone in the mixed solvent): 0.55 (0.20), 0.70 (0.40), 0.81 (0.60), 0.92 (0.80). The greater differences  $\varphi_B^c - \varphi_B$  in the case of the cyclohexane–acetone mixtures as compared with the effects of cyclohexane–1,2-dichloroethane mixtures are in accordance with the higher polarity of acetone as compared with 1,2-dichloroethane.

Applications of the Born or Kirkwood methods or other methods from the field of the so-called semi-empirical methods for evaluation of medium effects appear to be incorrect from the standpoint of the concept of the so-called collision complexes in solution<sup>9–11</sup>. This concept was developed with the aim of interpreting the manifestations of effects of media of both mixed and pure solvents upon infrared spectra of phenols predominantly. Allerhand and Schleyer<sup>17</sup>, studying the effects of perfluorooctane–hexane and perfluorooctane–tetrachloromethane mixtures upon the valence vibrations of phenol, found that  $\nu_{O-H}$  exhibits two absorption bands in these mixtures. Allerhand and Schleyer interpreted this finding by the existence of clusters in these solvent mixtures – hence the phenol molecules exist in two different media in these mixed solvents. Horák et al.<sup>9–11</sup> measured the IR spectra of a number of substituted phenols in various solvent mixtures and ascribed the observed dual manifestations of OH group in the region of its valence vibrations to the existence of weak complexes (they differentiate them from possible strong complexes based on hydrogen bonding between the phenolic group and electron-donor solvents) between the phenol and solvents even so “inert” as e.g. perfluorooctane, aliphatic hydrocarbons, and tetrachloromethane. This interpretation of the medium effects upon IR spectra was then generalized by the authors also to the effect of pure solvents and to effects on other properties (beside IR spectra) in solution. In terms of this concept, solute and solvent molecules form collision complexes at first (most

often 1 : 1) — a specific interaction — and these complexes are subsequently solvated by further solvent molecules. Hence in a mixed solvent there exist two different collision complexes which are further solvated by the solvent mixture. Therefrom it follows, however, that interpretations of properties of solutes also in pure solvents by means of e.g. the Born or the Kirkwood method are in principle inadmissible (unless, of course, we are studying the medium effect upon a complex already formed in the solution), because the effect studied here is not a medium effect on the solute but that on various complexes formed from the solute and the pure solvent used, which contradicts the presumptions of both the Born and the Kirkwood method.

In my opinion neither the concept of clusters in solvent mixtures nor the concept of collision complexes are necessary for explanation of dual manifestation of O—H valence vibrations (or other vibrations) in IR spectrum. The IR spectroscopy consists in rapid processes (the excitation takes place within  $10^{-13}$  to  $10^{-14}$  s) as compared with translational motions of molecules in solutions ( $10^{-10}$  s) and reflects manifestations of local parts of molecules<sup>18</sup> (e.g. the OH group of phenols). Therefore, we can very easily imagine that in a mixed solvent there is a molecule of one or the other solvent of the mixture near the group studied (e.g. OH group of phenol). These molecules then solvate the phenol near its OH group for at least  $10^{-10}$  s, which is a time  $10^3$  times longer than that necessary for a vibrational excitation. This applies in particular to such mixtures as perfluorooctane-hexane, where the relative permittivities of both solvents are very close (hence also the probability of solvation of e.g. phenol at the OH group is close for these solvents) and different effects of these solvents upon  $\nu_{\text{O-H}}$  are dictated by different refractive indexes of these solvents.

Studies of medium effects of mixed solvents upon electronic spectra — from experimental standpoint — throw doubt on the interpretation of medium effects upon IR spectra. With respect to the rate of excitation this method is still faster (by one order of magnitude) than the vibrational spectroscopy. In contrast to the vibrational spectroscopy (and particularly  $\nu_{\text{O-H}}$ ) the manifestations of molecules in electronic spectra are most often a matter of the whole molecule<sup>18</sup> and not only of one its part. Therefore, electron spectroscopy reflects the solvation changes of the whole molecule and not only of some of its part. In accordance therewith, these phenomena were not observed in the electronic spectra measured in mixed solvents (see e.g. refs<sup>3,19</sup>).

#### REFERENCES

1. Glasstone S., Laidler K. J., Eyring H.: *The Theory of Rate Processes*. McGraw Hill, New York 1941.
2. Jungers J. C.: *Cinétique chimique appliquée*. Société des Editions Technip, Paris 1958.
3. Reichardt Ch.: *Solvents and Solvent Effects in Organic Chemistry*. Verlag Chemie, Weinheim 1988.



4. Entelis S. G., Tiger R. P.: *Reaction Kinetics in the Liquid Phase*. Keter Publishing House, Jerusalem 1976.
5. Abraham M. H.: *Prog. Phys. Org. Chem.* 11, 1 (1974).
6. Kirkwood J. G.: *J. Chem. Phys.* 2, 351 (1934).
7. Bell R. P.: *Trans. Faraday Soc.* 27, 797 (1931).
8. Born M.: *Z. Phys.* 1, 45 (1920).
9. Horák M., Plíva J.: *Spectrochim. Acta* 21, 911 (1965).
10. Horák M., Moravec J., Plíva J.: *Spectrochim. Acta* 21, 919 (1945).
11. Horák M., Poláková J., Jakoubková M., Moravec J., Plíva J.: *Collect. Czech. Chem. Commun.* 31, 622 (1966).
12. Jungers J. C., Sajes L., De Aguirre D.: *L'analyse cinétique de la transformation chimique*, Vol. II. Editions Technip, Paris 1968.
13. Bekárek V., Nevěčná T.: *Chem. Listy* 81, 443 (1987).
14. Nevěčná T., Vymětalová J., Bekárek V.: *Acta Univ. Palacki. Olomuc.* 85, 55 (1986).
15. Bekárek V.: *Acta Univ. Palacki. Olomuc.*, in press.
16. Bekárek V., Nevěčná T.: *Collect. Czech. Chem. Commun.* 50, 1928 (1985).
17. Allerhand A., Schleyer P. R.: *J. Am. Chem. Soc.* 85, 371 (1963).
18. Exner O.: *Struktura a fyzikální vlastnosti organických sloučenin*. SNTL, Prague 1985.
19. Dimroth K., Reichardt C.: *Z. Anal. Chem.* 215, 344 (1966).

Translated by J. Panchartek.