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Differences of the order $\langle(\Delta \log \alpha)^4\rangle_{av}$ or higher are neglected.

For many emulsions the function $N(\alpha)$ is known and permits the calculation of $\langle(\Delta \log \alpha)^2\rangle_{av}$. For most commercial emulsions this quantity turns out to be ~ 0.4 . Inspection of r.l.f. curves shows that the error caused by neglecting this second order correction is negligible. In the worst cases at the most curved parts of the r.l.f. curve it amounts to less than 5 percent of exposure. Although the correction is insignificant for the shape of the r.l.f. curve it becomes important for the intermittency effect (see paper III) when small differences in r.l.f. are the object of the theory.

Summarizing we have found that the two main causes for deviations from the o.p., namely inhomogeneous light intensity and grain size, cause the real r.l.f. curve to be practically identical with the ideal r.l.f. curve that would be obtained if the light intensity would be homogeneous and equal to the value at the center of the plate,

and if the plate contained only grains of size a_0 , defined above.

Finally we wish to point out that it is not consistent with the observed behaviour of characteristic curves for various intensities, to explain the slope $0 < x < 1$ of the r.l.f. curves as the result of two groups of grains, the first group having a slope 0 (no r.l.f.) and the second group having a slope = 1 (one trap depth only), in the intensity region studied. If the o.p. would hold within each one of these two groups the resulting slope would lie indeed between 0 and 1 according to (22), but the characteristic curves for low intensities behave experimentally in a way that contradicts such an assumption. For this reason the scheme with many trap depths had to be introduced.

Note added in proof: The author is greatly indebted to Dr. J. H. Webb for bringing to his attention a series of recent studies by P. C. Burton and W. F. Berg (Phot. J. **86B**, 2, 62 (1946) and **88B**, 13, 84, 123 (1948)) which provide strong support for the assumptions made in Sections 6 and 11.

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Dielectric Behavior of Solutions of Electrolytes in Solvents of Low Dielectric Constant. V. The Influence of Temperature and Concentration on Dielectric Properties*

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Dielectric loss and conductance data for octadecyltributylammonium thiocyanate in benzene show large changes in the significant frequency region of absorption and in the magnitude of conductance when the temperature is lowered from 25° to 6°C, but their variation with concentration is very similar at the two temperatures. The broad frequency range of absorption observed at concentrations in the range 0.008–0.02 molal and the failure of the change in macroscopic viscosity to account for the temperature effect suggest that a better understanding of similar systems requires more detailed examination of the interaction of the ionic and dipolar aggregates with the solvent.

OF the several approaches employed in this laboratory in the investigation of the behavior of electrolytes in solvents of low dielectric constant, the measurement of dielectric absorption by a calorimetric method has been among the most revealing. In the earlier papers of this series the information obtained from such measurements has been used, in conjunction with conductance, cryoscopic, and polarization data, to demonstrate the strong dependence of the nature and extent of ion association on the constitution and type of electrolyte.^{1,2}

An investigation of the temperature dependence of

the dielectric absorption of such systems in the 5–25°C range has formed the basis of the present work. The study was prompted principally by the continued need for new approaches to the complex picture presented by the known results. The available data have been used as well, insofar as seemed justified, in examining the role of concentration as an influence on association. A further result of the work has been the possibility of direct intercomparison of cryoscopic and absorption data.

For the study, octadecyltributylammonium thiocyanate, a fairly strong electrolyte representative of the quaternary ammonium salts already examined³ was selected. Benzene solutions of that salt have now been investigated at several concentrations both at 25° and at about 6°. Audiofrequency conductance determina-

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¹ (a) Sharbaugh, Schmelzer, Eckstrom, and Kraus, J. Chem. Phys. **15**, 47 (1947); (b) Sharbaugh, Eckstrom, and Kraus, J. Chem. Phys. **15**, 54 (1947).

² H. A. Strobel and H. C. Eckstrom, J. Chem. Phys. **16**, 817 (1948).

³ With the exception of the picrates, all of the strong quaternary ammonium electrolyte already examined at 25° have behaved similarly.

TABLE I. Data measured and calculated for all the solutions investigated.*

Molality $m \times 10^2$	Dielectric constant ϵ_0	Loss factor maximum $\Delta\epsilon''_{\max}$	α_{expt}	Critical frequency $\nu_c(\text{Mc})$	"Average particle radius" $a(\text{\AA})$	Dipole moment $\mu(D)$
Data for Octadecyltributylammonium thiocyanate						
0.850	2.300	0.0053	0.40	120	9	3.8
	2.325**	0.0039	0.32	45	11	2.8
1.261	2.326	0.0094	0.45	27	15	4.4
	2.342**	0.0081	0.32	10.7	18	3.3
1.59	2.370	0.0162	0.45	12.0	19	5.0
	2.386	0.0144	0.40	5.2	22	4.6
1.73	2.376	0.0204	0.41	9.6	20	5.1
2.04	2.454	0.0368	0.39	4.8	25	6.2
	2.473	0.0345	0.40	2.0	30	5.8
Data for Tri-isoamylammonium picrate						
11.08	3.93	—	0.0	490	4.8	10.4
10.85	4.03	—	0.0	275	5.3	8.9

* All data taken at 25° except those in italics which were taken at 6°.
 ** Estimated quantities.

tion at 5.3° have provided further information. In addition a 0.1 molal solution of a weak electrolyte, tri-isoamylammonium picrate, was studied at low temperatures.

EXPERIMENTAL

Materials

The benzene used was obtained thiophene-free and purified as described in previous papers of this series.¹ Some of the tri-isoamylammonium picrate prepared by Copenhafer⁴ was still on hand and was used after a further recrystallization from ethyl alcohol; M.P., 127.5–128.5° (corr.). Octadecyltri-*n*-butylammonium thiocyanate was made and recrystallized according to the method outlined in an earlier paper.²

Method and Equipment

The calorimetric dielectric absorption apparatus used in these determinations has already been described. As indicated in Part III of this series, RCA 9005 diodes now serve in place of the original custom-made volt-meter tubes.⁵

In order to work at temperatures as low as 6° several changes were made in the temperature-controlling system. As before, the temperature of the air bath, containing the calorimetric cell bulb and associated components, was maintained by a flow of constant temperature water supplied by a large reservoir. The flow was increased for this and succeeding work, and the lines between the air-bath jacket and reservoir were reinsulated and shortened. To maintain the water reservoir at temperatures below 15°, ice water was

⁴ D. T. Copenhafer, thesis, Brown University (1942).

⁵ It was not mentioned in that paper, but the change in tubes made possible a considerable shortening of the leads between the electrodes of the calorimetric cell and the diode plates. The inductance of the measuring circuit was thus decreased and the accuracy of the determination of the voltage across the cell at high frequencies increased.

TABLE II. Conductance of octadecyltributylammonium thiocyanate in benzene at 25.00±0.01°C.*

Molality $m \times 10^2$	χ_0 ohm ⁻¹ cm ⁻¹	Molarity $c \times 10^2$	$\Lambda \times 10^3$
40.18	2.498×10 ⁻⁵	29.41	84.9
25.03	1.258×10 ⁻⁵	19.51	64.5
13.04	5.219×10 ⁻⁶	10.72	48.7
9.57	3.352×10 ⁻⁶	7.99	41.97
6.21	1.591×10 ⁻⁶	5.27	30.21
3.800	4.89 ×10 ⁻⁷	3.259	15.01
2.249	9.28 ×10 ⁻⁸	1.943	4.78
2.045**	7.00 ×10 ⁻⁸	1.769	3.953
1.733**	4.103×10 ⁻⁸	1.500	2.738
1.604	3.462×10 ⁻⁸	1.390	2.491
1.259**	1.865×10 ⁻⁸	1.093	1.706
0.934	9.74 ×10 ⁻⁹	0.812	1.200
0.853**	8.12 ×10 ⁻⁹	0.742	1.094
0.726	5.90 ×10 ⁻⁹	0.631	0.934
0.442	2.437×10 ⁻⁹	0.3848	0.633
0.2033	7.17 ×10 ⁻¹⁰	0.1772	0.4046

* The data for this table are taken from H. S. Young, thesis, Brown University (1948) with the exception of those for the asterisked (**) concentrations, which are from the work of the present authors. χ_0 and Λ are the specific conductance and the equivalent conductance respectively.

forced from an auxiliary, well-insulated bath through the cooling coils of the thermostating system; no difficulty was experienced in holding the water reservoir constant to within 0.002° for 10–15 hours at a time. With this arrangement the air bath could be held as low as 6° with a variation of no more than 0.02° during a period of several hours, depending on changes in room temperature, etc.

For work below 25° the air bath was always flushed with dry air for a few minutes before and during the cooling process to avoid any condensation of moisture. The possible introduction of moist air during a run was minimized by the tight fit of the air bath and cover. In order to have the upper solution level visible within the capillary of the calorimetric cell during low temperature determinations, small amounts of solution were added to the cell during the cooling period to offset the normal contraction. Additional solution was introduced into the flared open end of the capillary by means of a transfer pipet of small diameter. While the meniscus remained in the capillary stem, the "vapor" bulb attached to the open end of the stem kept evaporation to a minimum.^{1a} On low temperature runs re-

TABLE III. Conductance of octadecyltributylammonium thiocyanate in benzene at 5.25±0.07°C.

Molality $m \times 10^2$	χ_0 ohm ⁻¹ cm ⁻¹	Molarity $c \times 10^2$	$\Lambda \times 10^3$
13.48	2.88 ×10 ⁻⁶	11.32	25.5
8.39	1.475×10 ⁻⁶	7.21	20.46
5.77	7.62 ×10 ⁻⁷	5.02	15.18
3.63	1.837×10 ⁻⁷	2.96	6.21
2.50	6.51 ×10 ⁻⁸	2.210	2.95
1.171	6.94 ×10 ⁻⁹	1.040	0.667
0.769	2.77 ×10 ⁻⁹	0.685	0.405
0.339	6.32 ×10 ⁻¹⁰	0.303	0.2098
0.1065	1.100×10 ⁻¹⁰	0.0951	0.1156
0.0468	3.84 ×10 ⁻¹¹	0.0418	0.0918
0.0223	1.12 ×10 ⁻¹¹	0.0199	0.0561

quiring two days, however, a little solvent was lost overnight as the bath warmed. The resulting change in concentration (estimated to be ≤ 1.0 percent) was found to have a negligible effect on the results as long as the change in conductance was taken into account. It was

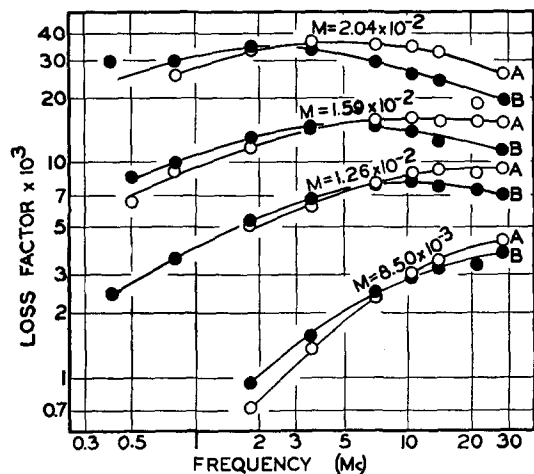


FIG. 1. Loss factor as a function of concentration, frequency, and temperature. Curves: A, $t = 25^\circ$; B, $t = 6^\circ$ (at molalities given above).

possible to find the new conductance by restandardization of the cell for that solution by calorimetric measurements at 60 cycles per second.^{1,2}

In practice, a given solution was run first at 25° and then at the lower temperature to avoid unnecessary handling. In the calorimetric method of loss measurement, the rate of rise of fluid in the cell capillary is compared at radio frequency and at an audio frequency for which the solution conductance is known. Ideally this comparison should be made under otherwise identical conditions, but in the present work it was found most convenient to make all of the audiofrequency calibrations at 25° . The principal error in this procedure should be proportional to the variation in the product cd/γ (where c is the specific heat, d the density, and γ the thermal expansion coefficient of the solutions^{1a}) and is estimated to be of negligible importance in the present work. With the approximation, the specific conductivity χ_ω at any radian frequency ω can be computed from the relation $\chi_\omega = \chi_0(V_0^2 t_0 / V_\omega^2 t_\omega) = A/V_\omega^2 t_\omega$. In this expression, V is the voltage across the cell, t the time of rise through a standard capillary interval, and the subscripts 0 and ω refer to audio and radio frequency, respectively. The heating constant A and its determination have been discussed elsewhere,² as have calculations based on Debye's relaxation theory and empirical modifications of it.

The audiofrequency conductances reported were measured by the substitution method on a special bridge built around the Campbell-Shackelton shielded ratio box by Leeds and Northrup. The conductance cells used were periodically cleaned with fuming nitric

acid, baked at 140° overnight, and cooled while being flushed with dry air. Both conductance series were initiated with the most concentrated solution, and successively less concentrated solutions were obtained by a dilution method.⁶ For the measurements at 25° the conductance cells were placed in an air bath, and observations were made when temperature equilibrium was established.

For the work at about 5° the regular conductance cell cap was replaced by one that was open to the atmosphere through a stopcock and a drying tube. A fairly constant ($\pm 0.07^\circ$) temperature was secured for those measurements by immersing the cell directly in a benzene-benzene ice bath that was stirred vigorously. Before each dilution and the accompanying weighings, the cell was removed and allowed to come to room temperature.

RESULTS

In Table I are collected the results determined experimentally and the constants calculated for these solutions at 25° and at 6° . For convenience the dielectric constants previously determined at 25° for two of these solutions have been included with the new measurements. Benzene was the solvent in all cases.

The frequency dependence of the dielectric loss factors $\Delta\epsilon''$ has, in this work as before, been found in disagreement with the assumption of a single relaxation process. The results are fitted quite accurately however, by the relation of Cole and Cole⁷

$$\Delta\epsilon'' = \frac{1}{2}(\epsilon_0 - \epsilon_\infty) \cos \frac{1}{2} \alpha \pi / [\cosh(1 - \alpha)x + \sin \frac{1}{2} \alpha \pi] \quad (1)$$

based on an empirical relaxation function. In this equation α is an additional parameter to which suitable

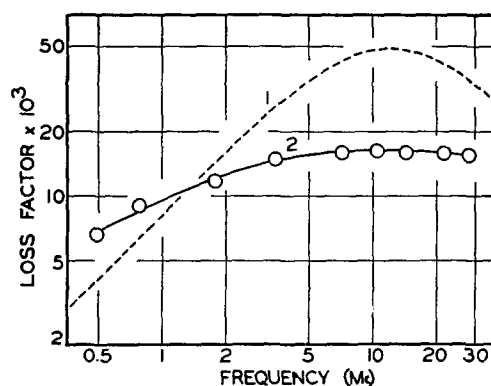


FIG. 2. Loss factor as a function of frequency for $1.6/10^{-2}$ molar benzene solution at 25° . Curves: 1. Loss factor calculated for this system if a single relaxation time assumed. 2. Experimental loss factor.

values must be given, $\Delta\epsilon''$ is the imaginary part of the complex dielectric constant, ϵ_0 and ϵ_∞ are the limiting

⁶ The method used is essentially that outlined in Mead, Fuoss, and Kraus, *Trans. Faraday Soc.* **32**, 594 (1936).

⁷ K. S. and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

dielectric constants at low and high frequency, and $x = \ln(\nu/\nu_c)$ where ν is the frequency of measurement and ν_c the critical frequency for which $\Delta\epsilon''$ has a maximum value $\Delta\epsilon''_{\max}$. The values of α quoted in Table I are based on the best fit of Eq. (1) to the data. It should be observed that the values of α calculated from the observed values of $\Delta\epsilon''_{\max}$ alone are somewhat greater. Work in progress should reveal the reason for this lack of agreement.

There are also included in Table I values of apparent average dipole moments and molecular radii a . These

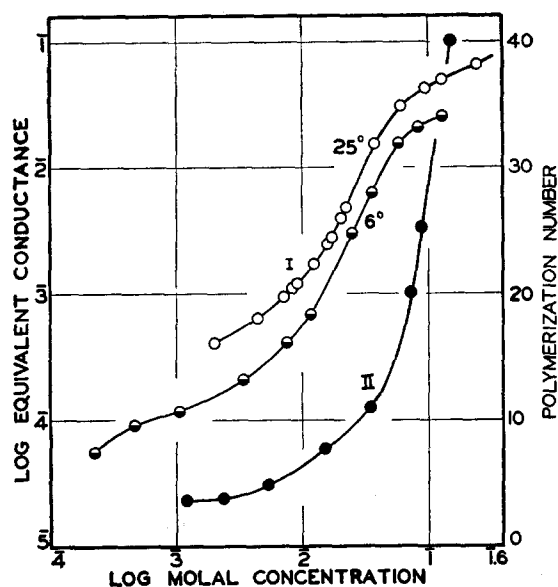


FIG. 3. Equivalent conductance and polymerization number as a function of concentration. Curves I: Equivalent conductance at 25° and at 6°; curve II: Polymerization number.

were calculated by the method previously described² and are subject to the same criticism that they have a simple significance only for the case of a single relaxation process. The physical constants necessary for the calculations at 25° and at 6°C are based on previous data;² those at 6° were obtained with sufficient accuracy by adding to the solvent values at 6°C (from the *International Critical Tables*) the solution-solvent difference found at 25°.

In Tables II and III are presented conductance data for octadecyltributylammonium thiocyanate in benzene at $25 \pm 0.01^\circ$ and $5.25 \pm 0.070^\circ$. The specific conductance of the solvent was of the order of $10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ for both runs so that the solvent correction was never greater than one percent.

DISCUSSION

The major factors in selecting lower, rather than higher, temperatures in extending the dielectric absorption and conductance studies on quaternary ammonium salts in benzene were the more convenient ranges of concentration and frequency usable and the possibility

of comparing the results with the data available from freezing point measurements. Octadecyltributylammonium thiocyanate was chosen for the study because it is relatively soluble, and both cryoscopic and 25° conductance data have been obtained in other work.

The dielectric properties and conductance were found to change smoothly with temperature over the range 6°–25° and only a comparison of the results at the two extreme temperatures will be made here. The measured loss factors $\Delta\epsilon''$ are plotted in Fig. 1 as a function of frequency for concentrations in the range 0.0085–0.020 molal at both 25° and 6°. From these curves it is evident that the general form is similar at both temperatures for a given concentration, and that the frequency range of absorption changes greatly with both temperature and concentration.

At no concentration in the range is the frequency dependence at all similar to that required for a system having a single characteristic relaxation time. This is shown by the comparison in Fig. 2 of the observed data at 0.016 molal and 25° with the Debye-type curve required to give the same critical frequency of maximum absorption and total dispersion of the dielectric constant. The difference can be expressed by the value of the empirical parameter α necessary to fit the data, and values so obtained are given in Table I. The values at 6° are a little smaller at all but the highest concentration, but show no remarkable behavior apart from the fact that, as in other systems, they represent such great departures from simple behavior.

The effect of temperature on the frequency ν_c of maximum absorption is seen from Table I to be a large one, as the decrease of 20° in temperature reduces ν_c by a factor of about 2.5. This is comparable with the decrease by a factor of roughly two in equivalent conductance at a given molality as shown in Fig. 3.

Neither factor varies appreciably with concentration, and both represent changes very much greater than the 35 percent increase of solution viscosity for the same temperature drop. If the picture of a mixture of ionic and polar aggregates with mobilities determined by hydrodynamic viscous flow is assumed, it is clear that a considerable change in constitution of these aggregates with temperature must be postulated. Further, the remarkable similarity in the effect of concentration on absorption and conductance at the two temperatures, except for the scale factors, also makes this viscous flow model seem less plausible than for data at a single temperature and suggests rather that the mechanism of solute-solvent interaction must be examined more explicitly in these systems.

The very broad range of frequencies in which absorption is significant makes highly uncertain the calculation of dipole moments μ or molecular radii a from the Debye viscosity model of the relaxation process or the extension of it represented by Eq. (1). The calculated values of a in Table I do, to the extent that they mean anything, indicate very large increases in apparent

size of polar aggregates, for the calculated radii increase by a factor of almost three, from 10A at 0.0085 *m* to nearly 30A at 0.020 *m*.

The calculated dipole moments are consistently smaller at the lower temperature and increase with formal concentration. The values are of reasonable magnitude for ionic association, but more quantitative inferences seem unjustified in view of the difficulties already mentioned.

From the plot of the cryoscopically determined polymerization number in Fig. 3, it may be seen that the apparent molecular weights increase from about five to fifteen times the formal weight over the range of the absorption measurements. This increase is proportionately smaller than the changes in conductance and in magnitude and frequency of absorption.

Some correlation can be made between the conductance and dielectric absorption data with regard to concentration effects. At concentrations below 10^{-4} molal in low dielectric constant solvents, the departures of the conductance from its limiting behavior have been attributed by Fuoss and Kraus¹⁰ to ion association, first into neutral dipoles and at somewhat higher concentrations into charged, linear triple ions. These postulates permitted a quantitative analysis of the minimum and subsequent rise characteristic of the equivalent conductance of such systems. At the higher concentrations—above 0.001 molal—for which cryoscopic and dielectric loss information are available, the situation is from any point of view much more complicated. The equivalent conductance, though small, rises rapidly, often with multiple inflections, and the apparent molecular weight increases markedly. These effects in the present system are well shown in Fig. 3.

It is interesting to note that at about 10^{-3} molal a fairly stable situation has developed both in the conductance and apparent molecular weight, the latter not quite four times the formal weight. This suggests that neutral octupoles may be a dominant type of stable aggregations. Absorption data were not taken at this low a concentration in the present work, but results for the closely similar salts with the same ammonium ion but nitrate and iodide cations gave simple absorption curves fitted by Debye equations ($\alpha=0.0$) to within experimental error at about 0.002 *m*. The accuracy of these data was not high,¹¹ but the simple frequency dependence and the high calculated critical frequencies (500 and 300 Mc) do support the presump-

tion that a single species of small polar aggregates is predominant at concentrations of about 10^{-3} *m*.

At higher concentrations the rapidly increasing conductance and molecular weight indicate a greater complexity of polar clusters, and the absorption curves at concentrations in this range are spread over a much broader frequency band. Any literal correspondence between this breadth and a distribution of aggregate sizes and shapes is too much to expect in view of the difficulties in accounting for the form of the absorption curves by such a picture.

The decreased rate of rise of conductance at greater concentrations (above 0.02 *m* in this case) is apparently accompanied by an increasingly less broad absorption curve. This effect, as measured by decreasing values of the parameter α , just begins to appear in the data of Table I. Measurements on the closely similar octadecyltributylammonium chloride¹² indicate that α drops from a maximum of 0.5 at 0.013 *m*. to 0.03 in the range 0.05–0.07 *m*. Cryoscopic data on sufficiently soluble quaternary salts⁴ show maxima in the apparent molecular weight at about 0.1 *m*, followed by quite rapid drops. No adequate absorption data have been obtained in this range because the present apparatus does not give results of sufficient accuracy in the frequency range below 1 Mc, which is of significance at these concentrations, but it would be of great interest to explore the higher concentration region more extensively in suitable systems.

As an example of a salt for which the absorption behavior is much simpler, data are also given in Table I for tri-*iso*amylammonium picrate at 0.11 *m* in benzene. The loss factor $\Delta\epsilon''$ was found to increase linearly with frequency at both 25° and 6° over the range 0.5–30 Mc, and the data are consistent with a single Debye-type dispersion region with critical frequency much greater than 30 Mc. Here the Debye viscosity picture would seem more reasonable. Again, however, the change in the calculated critical frequency from 490 to 275 Mc accompanying the temperature drop is considerably more than can be attributed to increased viscosity alone and the need for a more detailed picture of salt-solvent interaction is once more suggested.

Although the discussion here has been primarily in terms of a particular ammonium salt, the available conductance, cryoscopic and loss data indicate similar behavior for benzene solutions of all quaternary ammonium salts which have three or four short chain alkyl groups (e.g., butyl) and any not too large anion (e.g., the very large picrate ion is excluded). The presence of two or more long chains can from conductance data be expected to give very complex behavior.

¹² Unpublished data in this laboratory.

¹⁰ R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 476, 1019, 2387, 3614 (1933).

¹¹ The uncertainty arises principally from the large corrections necessary to account for losses in the cell walls, and to a lesser extent from residual errors in the calibration method (see reference 2).