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by data on the effect of cations on the electrochemical reduction of anions². However, later analogous maxima on $C-\varphi$ curves, although not so distinct, were obtained by Grahame^{3,4} in dilute solutions of electrolytes without the ability to undergo specific adsorption, in particular NaF solutions. Thus the reality of the specific adsorption of La^{3+} cations became doubtful. However, Grahame's technique⁵ differed considerably from that employed by Vorsina and Frumkin⁶. The former made measurements at a dropping electrode using an impedance bridge at frequencies above 240 c/s, whereas Vorsina and Frumkin^{1,2} used a stationary mercury electrode of large area, the measurements being made by comparing the double-layer capacitance against a standard capacitance, using a half-wave rectified current⁶. The aim of the present work was to explain the reasons for the discrepancies in the double-layer capacitance data, obtained in different conditions, and to establish to what extent the shape of $C-\varphi$ curves can serve as evidence of the occurrence of the specific adsorption of cations.

EXPERIMENTAL

The shape of the electrode. As shown by Grahame⁵, one of the reasons for the dispersion of the measured capacitance with the frequency consists in the unsymmetrical disposition of the electrodes, especially in the case of a stationary mercury electrode of large surface. To estimate approximately this effect, we shall represent the equivalent circuit of the cell with unsymmetrical disposition of the electrodes by the simplified scheme shown in Fig. 1a. If the impedance is measured by a bridge method, it should be equal to the impedance of the series-connected capacitance C_2 and the resistance R_2 . Simple calculation shows that

$$C_2 = C_1 \frac{(n+1)^2 R_1^2 C_1^2 \omega^2 + 16}{2(n^2+1) R_1^2 C_1^2 \omega^2 + 16} \quad (1)$$

where ω is the angular frequency. It follows from Eqn. (1) that when $n = 3$ and $R_1 = 60 \Omega \text{ cm}^2$, increase in frequency

THE SHAPE OF DIFFERENTIAL CAPACITANCE CURVES FOR DILUTE SOLUTIONS

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Differential capacitance curves ($C-\varphi$ curves) in dilute solutions containing univalent and multivalent cations were first obtained by Vorsina and Frumkin^{1,2}, who showed that addition of small amounts of lanthanum salts to 10^{-3} N HCl may make the minimum on the $C-\varphi$ curves near the zero-charge point less pronounced, and that at less negative potentials a maximum capacitance appeared, whose magnitude increased with the concentration of the La^{3+} ions. Since in the absence of LaCl_3 , KCl and HCl solutions do not exhibit capacitance maxima, Vorsina and Frumkin ascribed the latter to specific adsorption of the La^{3+} cations, whose occurrence had already been indicated by the electrocapillary measurements available at that time and also

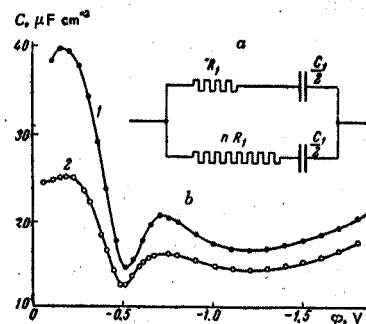


Fig. 1. a) Simplified equivalent circuit for a cell with asymmetrical disposition of the electrodes; b) differential capacitance curves for 0.01 N Na_2SO_4 at 400 c/s (bridge method): 1) pendant mercury drop electrode; 2) stationary mercury electrode with a large surface.

from 20 to 400 c/s leads to a dispersion of capacitance $\Delta C_2 = 2.75 \mu\text{F cm}^{-2}$ for $C_1 = 16 \mu\text{F cm}^{-2}$ and $\Delta C_2 = 6.4 \mu\text{F cm}^{-2}$ for $C_1 = 36 \mu\text{F cm}^{-2}$. In other words, the absolute decrease in capacitance is greater, the higher the double-layer capacitance, resulting in a smoother $C-\phi$ curve. This result is confirmed experimentally when comparison is made of $C-\phi$ curves measured at a frequency of 400 c/s for a pendant mercury drop electrode and for a stationary mercury electrode with a relatively large surface ($S = 5.69 \text{ cm}^2$)† (Fig. 1b). Eqn. (1) shows that the same result, *i.e.* a smoother $C-\phi$ curve, should be obtained on increasing R_1 , which corresponds to a lower solution concentration. Thus unsymmetrical disposition of electrodes in dilute solutions can result in a smoothed out $C-\phi$ curve even at low frequencies.

Measuring circuit. The bridge method for the measurement of double-layer capacitance is the most accurate, since it permits the impedance due to capacitance and resistance to be balanced out separately, which is particularly important in dilute solutions when the phase-shift angle is much less than 90° . In the comparison method the cell can be replaced by a standard capacitance and the potential drop across either can be determined for the same current. If the resistance R_1 cannot be neglected, it can be readily shown that the measured capacitance will be

$$C_s = \frac{C_1}{\sqrt{R_1^2 C_1^2 \omega^2 + 1}} \quad (2)$$

It is evident from Eqn. (2) that the error in the determination of the capacitance ($\Delta C = C_1 - C_2$) depends on the magnitude of C_1 . Thus for $R_1 = 60 \Omega \text{ cm}^2$ and $\omega = 2\pi \times 50$, $\Delta C = 0.7 \mu\text{F cm}^{-2}$ for $C_1 = 16 \mu\text{F cm}^{-2}$ and $\Delta C = 6.2 \mu\text{F cm}^{-2}$ for $C_1 = 36 \mu\text{F cm}^{-2}$. Hence the use of the comparison method in dilute solutions can also result in distorted, *i.e.* smoother, $C-\phi$ curves.

Capacitance measurements at frequencies below 10 c/s. According to our experimental data, $C-\phi$ curves determined by the bridge method for a drop electrode in 0.01 N Na_2SO_4 solution remain practically unchanged in the frequency range between 10 and 10000 c/s. However, at frequencies less than 10 c/s and an alternating current amplitude $\geq 10 \text{ mV}$ † it is impossible to balance out the bridge completely, *i.e.* to obtain a straight line on the screen of the oscilloscope used as a null instrument. Experiment shows that, to reduce the potential across the measuring diagonal under these conditions, it is necessary to increase the resistance of the bridge arm adjacent to the cell. However, the sinusoid on the oscilloscope screen is then distorted, indicating the appearance of new harmonics in the circuit. Thus at frequencies less than 10 c/s and an alternating current amplitude $\geq 10 \text{ mV}$ the electrical double layer in our circuit is practically non-equivalent to the usual plane condenser. The reason for this is not so far understood; the use of capillaries covered with silicone grease and of mercury drop electrodes suspended from amalgamated wires has shown that the phenomenon is not connected with the effect of penetration of the electrolyte

into the capillary. Fig. 2 (curve 2) shows our $C-\phi$ curve determined for 0.01 N Na_2SO_4 by the bridge method using a half-wave rectified current. Since complete balance of the bridge under these conditions could not be obtained, we determined, for a constant resistance, the values of capacitance (using a capacitance box) for which the potential across the measuring diagonal of the bridge was a minimum. Such capacitance values are somewhat too high. Fig. 2 shows that high capacitance values are also obtained in measurements by the comparison method using a half-wave rectified current, the $C-\phi$ curve in the latter case being smoother. Fig. 3 shows that the distortion of the $C-\phi$ curves obtained by the comparison method at low frequencies decreases, when the frequency is raised from 0.5 to 5 c/s, but at 1 c/s it is still relatively high.

Finally, we must note that when a stationary mercury electrode of large surface is employed, there is a possibility that it may be contaminated with traces of organic substances. Thus, when the double-layer capacitance in dilute solutions is measured for a stationary mercury electrode of large surface by the comparison method at frequencies below 10 c/s, a large number of factors lead to distortion of the $C-\phi$ curves. Obviously, $C-\phi$ curves of the correct shape are obtained by means of the impedance bridge for a pendant mercury drop electrode with a symmetrically placed auxiliary electrode. This is confirmed by the good agreement between the experimental and calculated $C-\phi$ curves when specific adsorption of ions is absent⁴. In our study of the effect of cations on the shape of $C-\phi$ curves in dilute solutions we therefore measured the capacitance at a dropping mercury electrode by the impedance bridge method. The principle of this method was described by Grahame⁵; one of the present authors has described certain special features of the circuit used in experiments on dilute solutions⁷. The potentials obtained in the present work are given in volts with respect to the normal calomel electrode.

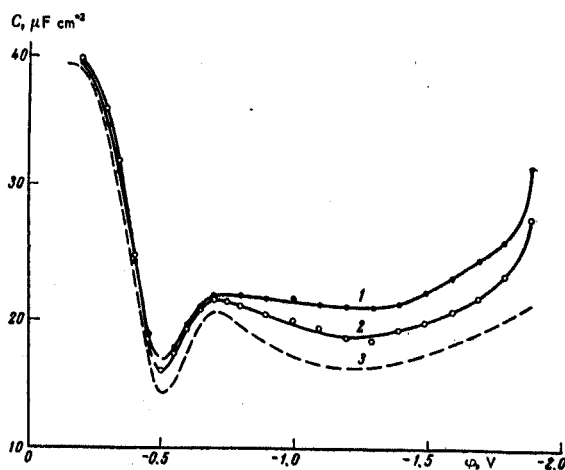


Fig. 2. Differential capacitance curves for 0.01 N Na_2SO_4 : 1) comparison method, 1 c/s; 2) bridge method, 1 c/s; 3) bridge method, 400 c/s; pendant mercury drop electrode.

† S was determined as half the surface area of a strongly compressed ellipsoid of revolution.

‡ The relatively high alternating potential difference ($\geq 10 \text{ mV}$) applied to the cell is due to technical difficulties associated with the amplification of low frequencies.

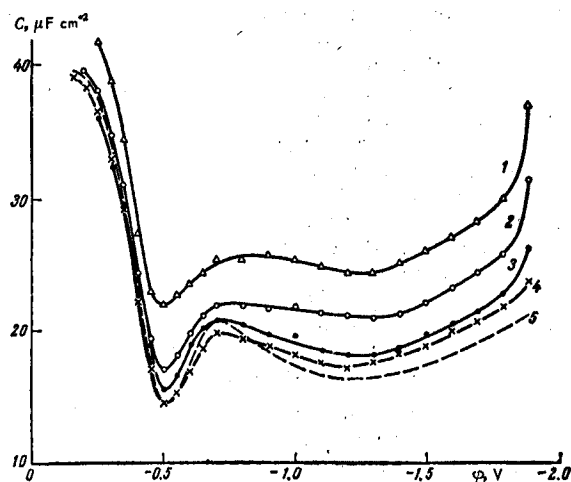


Fig. 3. Differential capacitance curves in 0.01 N Na_2SO_4 for a pendant mercury drop electrode determined by the comparison method at different frequencies: 1) 0.5 c/s; 2) 1 c/s; 3) 2 c/s; 4) 5 c/s; 5) (broken curve) bridge method at 400 c/s.

The $\text{La}_2(\text{SO}_4)_3$ employed was prepared from "Kahlbaum" $\text{La}(\text{NO}_3)_3$ recrystallised from twice distilled water, using twice distilled H_2SO_4 , as described in Brauer⁸. The Na_2SO_4 was twice recrystallised from twice distilled water and ignited.

Results

The continuous lines in Fig. 4 represent $C-\phi$ curves obtained in Na_2SO_4 solutions and in Fig. 5 the $C-\phi$ curves for $\text{La}_2(\text{SO}_4)_3$ solutions. It is seen that in both cases the minimum near the zero-charge point is followed by a maximum. However, in the presence of La^{3+} ions the maximum is appreciably higher than in the presence of Na^+ . The increase in capacitance on going from Na^+ to La^{3+} over the potential range -0.6 to -0.7 V is consistent with the data of Vorsina and Frumkin^{1,2}. There are two possible reasons for this phenomenon: either the increase in the maximum on the $C-\phi$ curves below the zero-charge potential on transition from Na^+ to La^{3+} is connected with the specific adsorption of the La^{3+} cations, or it is due to a decrease in diffuseness of the double layer as a result of attraction of multivalent cations into it when the surface becomes negatively charged.

DISCUSSION

To solve the above problems, we calculated $C-\phi$ curves for 0.1, 0.01, and 0.001 N Na_2SO_4 solutions and for 0.1, 0.01, and 0.003 N $\text{La}_2(\text{SO}_4)_3$ solutions using the data for 1 N Na_2SO_4 and 0.3 N $\text{La}_2(\text{SO}_4)_3$. The calculation was based on Grahame's method^{3,4}, which assumes the absence of specific adsorption of ions. In this case, according to Grahame's assumption, the capacitance of the dense layer C_g at constant temperature depends only on the surface charge and is independent of the electrolyte concentration,

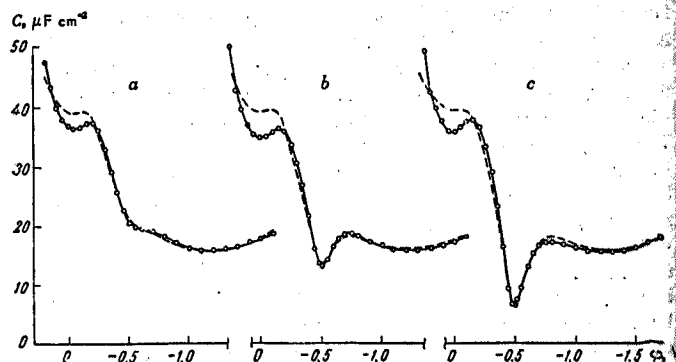


Fig. 4. Differential capacitance curves in Na_2SO_4 solutions at 400 c/s and 25°C; a) 0.1 N; b) 0.01 N; c) 0.001 N. Continuous curves — experimental data; broken curves — calculated data.

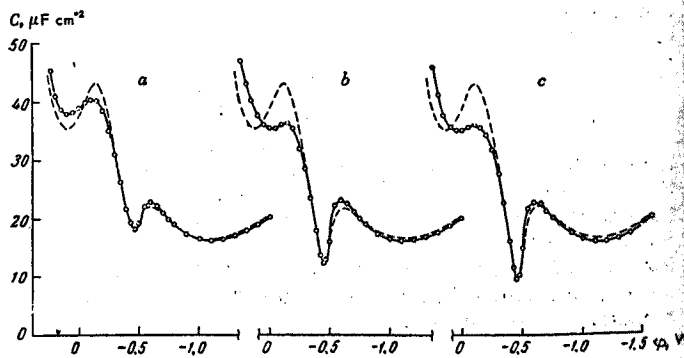


Fig. 5. Differential capacitance curves in $\text{La}_2(\text{SO}_4)_3$ solutions at 400 c/s and 25°C; a) 0.1 N; b) 0.01 N; c) 0.003 N. Continuous curves — experimental data; broken curves — calculated data.

the measured double-layer capacitance C being equivalent to two condensers connected in series: C_g and C_d , where C_d is the differential capacity of the diffuse layer. Thus

$$\frac{1}{C} = \frac{1}{C_g} + \frac{1}{C_d} \quad (3)$$

The calculation has been described in detail by Boguslavskii and Damaskin⁹. The formulae for the ionic charge ($\epsilon_2 = -\epsilon$) and for the diffuse layer capacitance C_d can be readily found from the fundamental equation of the classical double-layer theory¹⁰. For electrolytes of the type of Na_2SO_4 and $\text{La}_2(\text{SO}_4)_3$ they are given in Table 1, where $A = [(DRT/2\pi)c]^{\frac{1}{2}}$, $y = \psi_1 F/RT$, D is the dielectric constant, R the gas constant, T the absolute temperature, c the concentration, F the Faraday, ψ_1 the potential at a distance of the mean ionic radius from the electrode surface, and $y_{\min}$ the value of y at which C_d passes through a

TABLE 1.

Quantity	Na ₂ SO ₄	La ₂ (SO ₄) ₃
ϵ_2	$-A(e^{2v} + 2e^{-v} - 3)^{1/2}$	$-A(3e^{2v} + 2e^{-3v} - 5)^{1/2}$
C_d	$\frac{AF}{RT} \frac{e^v + e^{-v} + 1}{(1 + 2e^{-v})^{1/2}}$	$\frac{3AF}{RT} \frac{e^{2v} - e^{-3v}}{(3e^{2v} + 2e^{-3v} - 5)^{1/2}}$
$\gamma_{\min}$	-0.631	+0.218

minimum. The electrode potential φ_a , measured relative to the zero-charge point, is

$$\varphi_a = \psi_1 + \frac{e}{K_g} \quad (4)$$

where K_g is the integral capacitance of the dense layer, which, according to our experimental data is $29 \mu\text{F cm}^{-2}$ in the vicinity of the zero-charge point. Thus the potential of the minimum on the $C-\varphi$ curve in $0.01 N$ Na₂SO₄ is $\varphi_{a,\min} = -16.2 + (-0.425/29) \times 1000 = -31 \text{ mV}$, i.e. it is 31 mV more negative than the zero-charge point, in good agreement with experimental findings. Thus in $0.01 N$ Na₂SO₄ $\varphi_{z.c.} = -0.473 \text{ V}$ and $\varphi_{\min} = -0.505 \text{ V}$. This effect, due to the asymmetry of the valence type of the electrolyte, must be taken into account in determining the zero-charge point from the minimum on $C-\varphi$ curves in dilute Na₂SO₄ or H₂SO₄ solutions.

For electrolytes of asymmetric valence types, C_d cannot be expressed directly in terms of ϵ_2 as was done for uni-univalent electrolytes⁹. For this reason, in order to find the dependence of C_d on ϵ_2 for Na₂SO₄ and La₂(SO₄)₃ solutions, it is necessary to calculate these quantities for various values of y by the equations listed in Table 1.

Fig. 5 shows that in La₂(SO₄)₃ solutions $C-\varphi$ curves have a minimum near the zero-charge point, even at relatively high concentrations of the salt. This appears to be due to the very low activity coefficient f_a for 3:2 electrolytes (see Table 2). Another reason for the apparently low concentration of La₂(SO₄)₃ may be the formation of the complex anions $[\text{La}(\text{SO}_4)_2]^-$ in strong La₂(SO₄)₃ solutions by the reaction $2\text{La}_2(\text{SO}_4)_3 \rightarrow \text{La}[\text{La}(\text{SO}_4)_2]_2$, as in scandium sulphate solutions¹¹. The sharp increase in the "hump" on the positive branch of the $C-\varphi$ curve on increase in the concentration of La₂(SO₄)₃ confirms the formation of such complex ions, since it does not occur in Na₂SO₄ solutions (Figs. 4 and 5).

In view of the indeterminacy of the activity coefficients within the double layer and the possibility of complex formation in La₂(SO₄)₃, C_d and ϵ_2 were calculated using values of the concentration c_1 in the formula for A such that the experimental and calculated double-layer differential capacities at the minimum on the $C-\varphi$ curve near the zero-charge point coincided. Table 2 lists the values of certain coefficients determined for La₂(SO₄)₃ solutions of different concentrations (λ and λ_∞ are the equivalent conductances in the given solutions and at infinite dilution). The close agreement between c_1/c and λ/λ_∞ is striking, but cannot be interpreted at present.

The calculated $C-\varphi$ curves for Na₂SO₄ and La₂(SO₄)₃ solutions are represented by broken lines in Figs. 4 and 5.

TABLE 2.

$c_{\text{La}_2(\text{SO}_4)_3} N$	f_a^*	λ/λ_∞ (expt.)	c_1/c
0.3	0.054	0.12	0.12
0.1	0.10	0.17	0.16
0.01	0.38	0.30	0.31
0.003	0.57	0.42	0.49

* The values of f_a for $c < 0.06 N$ were calculated from Eqn. (5-61) in Ref. 12 for $a = 3 \times 10^{-8} \text{ cm}$; for $c > 0.06 N$, f_a was assumed to be equal to the activity coefficient of $\text{In}_2(\text{SO}_4)_3$ ¹³. The two sets of values agree satisfactorily at $c = 0.06 N$, f_a being 0.140 (calc.) and 0.142.

It is evident that the calculated double-layer capacitance curves closely follow the experimental curves in the presence of both Na⁺ and La³⁺ ions, with the exception of the anodic branches, where the discrepancy between the calculation and experiment is due to specific adsorption of the SO₄²⁻ ions¹⁴. The much greater discrepancies at positive surface charges in the case of lanthanum sulphate appear to be due to the formation of complex ions in concentrated solutions of the former. Calculation and experimental findings show that the large maximum on the $C-\varphi$ curves at potentials more negative than the zero-charge point in solutions containing La³⁺ ions is mainly caused by the smaller diffuseness of the double layer, compared with solutions containing Na⁺ ions. This conclusion did not follow from Vorsina and Frumkin's calculations², since they were based on the unjustified assumption that the integral capacitance of the compact part of the double layer at negative surface charges is constant ($K_g = 19 \mu\text{F cm}^{-2}$). In view of the assumptions made in the calculation, due to the strong deviation of La₂(SO₄)₃ solutions from ideality, the observed differences between the calculated and experimental $C-\varphi$ curves at negative surface charges (Fig. 5) cannot be ascribed to specific adsorption of La³⁺ ions, in particular since these discrepancies are partly due to the small specific adsorption of SO₄²⁻ ions, as in the case of Na₂SO₄ solutions. The calculations therefore cannot demonstrate the specific adsorption of La³⁺ ions. However, we showed earlier¹⁵ that adsorption, to a small extent, of La³⁺ cations on a mercury electrode, in excess of the amount equivalent to the anions, can be reliably demonstrated by differential capacitance and electrocapillary measurements on a negatively charged mercury surface in the presence of I⁻ anions, whose adsorption in the surface layer has an appreciable effect on the capacitance and the interfacial tension. The data obtained showed that at negative surface charges in the presence of La³⁺ cations the I⁻ anions are drawn into the electrical double layer, which is evidence of some adsorption of the lanthanum cations in excess of the equivalent amount, in agreement with the scheme proposed by Vorsina and Frumkin². Obviously, these conclusions do not prejudice the results of the present work.

We should like to express our deep gratitude to Academician A. N. Frumkin for his exceptional interest in this work and discussion of the experimental data. We should also like to thank A. I. Froiman (Engineer), and A. Glebov (Master Mechanic) for the design and construction of the low-frequency (0.5–20 c/s) sinusoidal count generator which was used in this work.

SUMMARY

1. The plateau on the $C-\varphi$ curves obtained for a stationary mercury electrode of large area in dilute solutions by comparison against a standard capacitance is due to the characteristics of the method of measurements. $C-\varphi$ curves of the correct shape are obtained from measurements by the bridge method for symmetrically disposed electrodes.
2. The much higher maximum on $C-\varphi$ curves at potentials more negative than the zero-chargepoint in solutions containing La^{3+} ions, compared with the analogous maximum for solutions of sodium salts, is mainly due to the reduced diffuseness of the double layer caused by multivalent cations being drawn into the latter when the surface becomes negatively charged.

TRANSFORMATION METHODS FOR DIFFUSIONAL EXTRACTION PROCESSES IN SOLIDS

G. A. Aksel'rud

The present paper deals with the following problem. Suppose that the kinetics of extraction of a solid consisting of a polydisperse mixture of porous particles are known under given experimental conditions, and it is desired to calculate the kinetics of extraction from a layer consisting of the same particles. The method used for this, based on the idea of process transformation, is general: the sequence of mathematical operations is always the same regardless of whether the mixture is polydisperse or monodisperse, whether the layer contains porous particles with the soluble material or homogeneous soluble inclusions (this determines the nature of the mass transfer — molecular or convective diffusion). The dissolution is of the usual type, *i.e.* it obeys first-order kinetics.

We shall start from the following two equations:

$$\begin{cases} m \frac{\partial c_1}{\partial t_1} + u \frac{\partial c_1}{\partial z} = \frac{\partial G}{\partial t}, \\ \frac{\partial G}{\partial t} = k\Omega(c_s - c_1), \end{cases} \quad (1)$$

$$(2)$$

the first of which defines the conservation of the mass of the soluble material^{1,3} and the second the dissolution kinetics; $c_1(z, t_1)$ is the concentration of the liquid filtering through the layer, m the porosity, z the direction of the filtration (cm), t_1 the time from the start of the filtration (sec), t the time from the start of dissolution (sec), u the rate of filtration (cm sec⁻¹), $G(z, t)$ the weight of the material which has dissolved from unit volume of the layer (g cm⁻³), Ω the dissolution surface in a unit volume of the layer, which changes in the course of the dissolution and therefore can be regarded as a function of the weight loss of the material, $\Omega = \Omega(G)$ (cm² cm⁻³), c_s the concentration at saturation (g cm⁻³), and k the mass-transfer coefficient (cm sec⁻¹).

The mass-transfer coefficient is determined by the hydrodynamic and diffusion conditions of the process. In the case of convective mass transfer k depends on the rate of filtration, the dimensions of the soluble inclusions, viscosity, and the diffusion coefficient^{1,3}. The rate of filtration can be eliminated from consideration, if the extraction kinetics are determined by molecular diffusion in the porous particles. In all cases the coefficient k changes in the course of dissolution and hence depends on G .

Let us analyse Eqns. (1) and (2). The presence of two time variables, t_1 and t , constitutes a certain disadvantage. They are related by the equation

$$t_1 = t + \frac{z}{u} m, \quad (3)$$

which can be used to express Eqn. (1) in terms of a single time variable; Eqn. (1) then simplifies. We have

$$u \frac{\partial c_1}{\partial z} = \frac{\partial G}{\partial t}. \quad (4)$$

Under the experimental conditions it often happens that the liquid reaches the point where the coordinate is z long before the dissolution time, so that we can put $t_1 \approx t$. The

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