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Electrokinetic phenomena at the α-Al_2O_3 mixture of polar liquids interface

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The general parameters of the electrokinetic systems porous Al_2O_3/polar liquids: acetone, acetonitrile, nitromethane and their binary mixtures have been investigated.

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1. Introduction

Electrokinetic phenomena have hitherto found many applications both in industry and in measurement techniques. An example is the application of streaming potential phenomenon in constructing the electrokinetic transducer [1].

As is well-known, the flow of a polar liquid, a dilute electrolyte solution through a porous dielectric diaphragm, a capillary, gives rise to a potential difference at both sides of the diaphragm [2]. This effect is a result of perturbing the double layer equilibrium at the solid–electrolyte solution interface by the liquid flow [3]. This phenomenon makes it possible to convert a mechanical signal which provokes the liquid flow through the porous diaphragm into an electric signal. If the diaphragm material and porosity, the solvent and the electrolyte are chosen properly, a constant ratio of the electric signal to the volume flow rate of liquid can be attained [4].

The electrokinetic sensing device, we have constructed, is shown in Fig. 1. It has so far been applied, for example, in the manometers measuring the ventilation parameters of the human respiratory system; measured pressures of several centimetres water column; the feeding system parameters of internal combustion engines; pressures from − 0·6 to + 1·0 atm; and the parameters of sea waves acting on harbour breakwaters.

The transducer consists of a porous dielectric diaphragm (7) with electrodes deposited on both its sides (8, 9) mounted in a housing (3). The housing (3) is connected on both sides with Kovar rings (1, 2) having electrical contacts with the electrodes (8, 9). Elastic, hermetically closed bellows (5, 6) are connected to the rings (1, 2). The bellows and the diaphragm pores are filled with the working liquid, a pure solvent or an electrolyte solution.

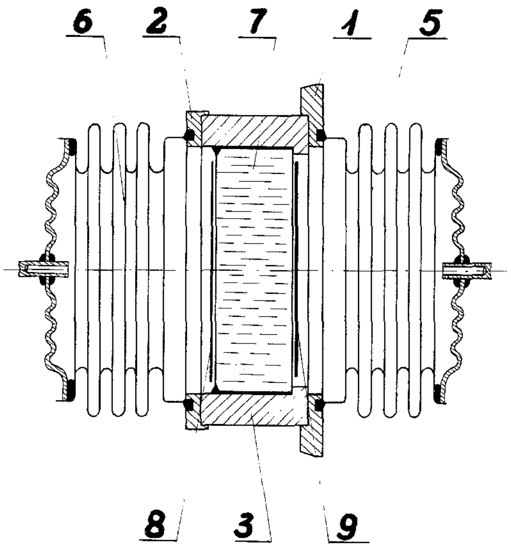

Fig. 1. The cross-section of the electrokinetic transducer.

A difference in external pressures applied to the bellows provokes a flow of liquid through the porous diaphragm and the appearance of a voltage between the transducer electrodes. Since the amount of liquid flowing through the diaphragm is limited by the elastic bellows, the transducer can be used for measuring the pressure variation or variable pressures.

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Electrokinetic manometers working on the electrokinetic transducer principle as presented in Fig. 1 are characterized by a high sensitivity [4, 5] (1–3 V atm^{-1}), a large working frequency range (0·01–10 000 Hz), and a good temperature stability [6]. Both the sensitivity and the stability depend on the double layer properties at the porous diaphragm–liquid interface.

The following relationship can be deduced from known phenomenological equations used in the thermodynamics of irreversible processes [5]:

$$\alpha = \frac{U_1}{P} = \frac{L_e R}{1 + L_{11} R} \qquad (1)$$

where α = mechano-electric transmittance of the transducer,
U_1 = voltage across the output terminals of the transducer loaded with a resistance R,
P = applied pressure difference,
L_e = phenomenological cross-coefficient,
L_{11} = electrical conductance of the transducer.
The magnitude L_e in (1) is determined by the double layer structure at the diaphragm–liquid interface.

As the electro-mechanical parameters of the transducer are determined by the L_e parameter, by the sensitivity α, and by the streaming potential E_p, it is necessary to study the double layer in many systems to find one with optimum properties. The work carried out up to now has dealt with pure liquids [7] and with binary systems composed of water, methanol, and acetone [8]. In this work, streaming potential measurements are described for transducers with an α-Al_2O_3 diaphragm filled with acetone, acetonitrile, nitromethane, and with their binary mixtures.

2. Experimental

2.1. *General aspects*

Transducers with a sintered α-Al_2O_3 diaphragm and with aluminium electrodes have been used in order to attain the good purity and tightness which are important for very pure solvents and for very dilute electrolyte solutions [1] (Fig. 1) where the equilibrium at the interface is established after hundreds of hours. The transducers have been preliminarily tested by measuring their hydrodynamical permeability and specimens with similar permeabilities have been selected for use.

The transducers have been filled with acetone, acetonitrile, nitromethane, and with binary mixtures of these substances. The mixture compositions have been determined refractometrically. The liquids have been distilled twice before preparing the mixtures and filling the transducers. Essential parameters of the studied liquids are shown in Table 1.

2.2. *Apparatus and measurement method*

The internal conductance, L_{11}, the streaming potential, E_p, at $R = \infty$, the sensitivity, α, i.e. the streaming potential at the load resistance R = 1 MΩ, and the streaming current I_0, (at $R = 0\Omega$) have been measured.

The internal conductance L_{11} has been measured by the bridge method by means of an ML-27 bridge from Unitra.

The streaming current, I_0, i.e. the maximum short-circuit current at the moment where the

Table 1. The physicochemical parameters of the liquids which have been used, all at the temperature, $t = 25°$ C

	Melting point (° C)	*Boiling point (° C)*	*Density ρ (gm cm^{-3})*	*Conductivity (ohm^{-1} cm^{-1})*	*Dielectric constant ϵ*	*Dipole moment (D)*	*Viscosity η (cp)*
Acetone $(CH_3)_2O$	−94·3	56·13	0·7886	$6{\cdot}0 \times 10^{-8}$	20·74	2·85	0·296
Acetonitrile CH_3CN	−44·9	81·6	0·7768	$1{\cdot}9 \times 10^{-7}$	36·2	3·94	0·325
Nitromethane CH_3NO_2	−28·5	101·3	1·1312	$5{\cdot}3 \times 10^{-8}$	35·9	3·54	0·596

Table 2. The basic parameters (sensitivity, α, and streaming potential, E_p) of the liquids which have been measured.

	$\alpha \times 10^6$ ($V\,m^2\,N^{-1}$)	$E_p \times 10^6$ ($V\,m^2\,N^{-1}$)
Acetone	11·7	19·0
Acetone–nitromethane 1:1	3·41	10·6
Nitromethane	1·71	2·34
Nitromethane–acetonitrile 1:1	1·23	1·30
Acetonitrile	1·90	2·12
Acetonitrile–acetone 1:1	1·36	1·51
Acetone	11·7	19·0

elastic bellows reaction is zero, has been determined by means of a BD-2 recorder from Kipp and Zonen.

The streaming potential, E_p, or the maximum open-circuit voltage (at $R = \infty$) and the sensitivity, α, for the transducer loaded by a resistance $R = 1\ M\Omega$, have been measured by means of a V 529 digital voltmeter from Elpo.

The streaming current, I_0, the streaming potential, E_p, and the sensitivity, α, have been determined by applying a unit pressure jump to the diaphragm of the transducer.

3. Results and discussion

The measured parameters are interrelated by the following equations [9]:

$$L_e = \left(\frac{I}{P}\right)_{E=0} = \left(\frac{I_0}{P}\right)_{E=0} \tag{2}$$

$$E_p = \left(\frac{E}{P}\right)_{I=0} = \left(\frac{U}{P}\right)_{R=\infty} = -\frac{L_e}{L_{11}} \tag{3}$$

$$\alpha = \left(\frac{U_1}{P}\right)_{R=1M\Omega} = -\frac{L_e R}{1+L_{11}R}. \tag{4}$$

The internal conductance and streaming current parameters are subjected to a systematic error since the electrode impedance affects the conductance measurements and the streaming current measurements are affected by the inertia of the mechanical parts of the recorder. The accuracy of the streaming potential, E_p, and of the sensitivity, α, amounted to 2–3% and hence the further analysis is based on these parameters. They are collected in Table 2.

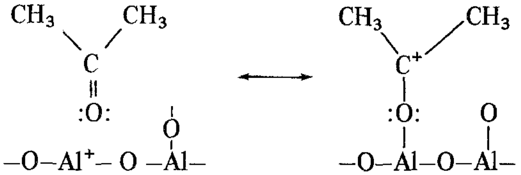
The sensitivity, α, is highest for the transducers filled with acetone and lowest for nitromethane and for the nitromethane–acetonitrile mixtures. The sensitivity variation is monotonic for the acetone–nitromethane systems and shows minima for the acetone–acetonitrile and acetonitrile–nitromethane systems.

Similar variations have been observed for the streaming potential, E_p, measurements: it is monotonic in the acetone–nitromethane system and minima are observed for the acetone–acetonitrile and acetonitrile–nitromethane systems.

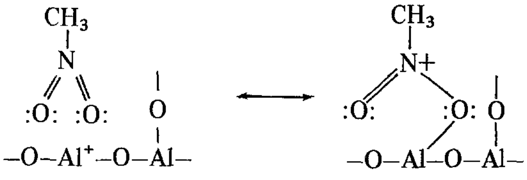
According to the classical streaming potential theory expressed by the Helmholtz–Smoluchowski equation [2], the experimental results show that the double layers formed by acetone and nitromethane have similar structures while the double layer at the α-Al_2O_3–acetonitrile interface should be different.

According to the findings of numerous authors cited in Tanabe's monograph [10], the α-Al_2O_3 surface in contact with a polar liquid has acid properties and hence it is a lone electron pair acceptor. The liquids studied in this work have functional groups with lone electron pairs either at the oxygen atom (acetone and nitromethane) or at the nitrogen atom (acetonitrile). In such cases the probable structures of the α-Al_2O_3 porous diaphragm–polar liquid interface can be presented as follows:

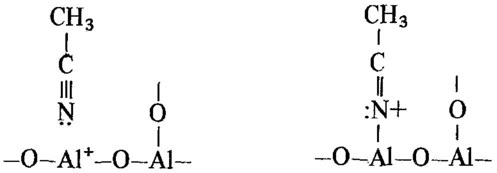
for acetone



for nitromethane



and for acetonitrile



The acetone, $(CH_3)_2CO$, and nitromethane, CH_3NO_2, molecules are bonded with the α-Al_2O_3 surface through their oxygen atoms while the acetonitrile molecules, CH_3CN are bonded through the nitrogen atoms. It suggests that the binding energy should be similar for acetone and nitromethane interacting with the α-Al_2O_3 surface. The binding energy of acetonitrile should be different in this case; this has been confirmed by experiment (Table 2).

This work has shown that the use of acetone–nitromethane mixtures leads to the construction of electrokinetic transducers with exploitation parameters (stability in time) similar to those of transducers filled with acetone but with an extended working temperature range (up to 40° C for acetone and up to 80° C for acetone–nitromethane mixtures).

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