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Non-equilibrium Thermodynamic Studies of Electrokinetic Effect: Part IX—Streaming Potentials During Flow of Acetonitrile & Acetonitrile-Methanol Mixtures Through Sintered Pyrex Glass

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Streaming potential developed during the flow of acetonitrile and methanol-acetonitrile mixtures (25% and 75%) through a sintered pyrex glass disc at 25° have been measured. The Onsager's reciprocity relation equating cross-phenomenological coefficient (L_{12}) with phenomenological coefficient (L_{21}) has been found to hold good for the electrokinetic effect across sintered pyrex disc.

THE theory[1,2] of thermodynamics of irreversible processes has been extensively applied by various workers[3-11] for studying the phenomenon of electrokinetics. The theory of irreversible thermodynamics implies the validity of Onsager's reciprocity relations (ORR) and its verification in diverse systems has not been attempted, specially in the case of non-aqueous solvents. The purpose of the present paper is to report the data on streaming potential and to test the ORR relations in non-aqueous solvents bathing a pyrex sintered disc of porosity 10^{-2}-10^{-3} cm at 25°.

Materials and Methods

Acetonitrile and methanol used here were purified as described earlier[12]. The cross-phenomenological coefficient L_{21} was evaluated earlier[12,13] and the coefficient L_{12} was evaluated by streaming potential measurements.

The apparatus used for measuring streaming potential consisted essentially of a pyrex glass tube A (length 28 cm, int. diam. 2·5 cm) fitted with sintered glass disc of porosity G_3 in the middle (Fig. 1). The platinum electrodes ending in perforated platinum disc were introduced into the tube A such that the platinum discs were close (within 2 mm) to the sintered disc. The whole length of each platinum electrode except the perforated disc was insulated from the liquid medium by sealing it in a glass tube. The tube A had two side tubes H and K with standard joints D and E respectively. A graduated tube T (length 80 cm, diam. 1 cm) was fixed at the standard joint D. A reservoir R was used to introduce the liquid in tube T at any desired rate. There was an arrangement for attaching guard tubes both to the tube T and the reservoir R. A tube S of narrow bore (5-6 mm) having a horizontal tube X and a vertical tube Y joined through a stopcock V_2, was fixed at the standard joint E. The diameters of the tubes X and Y were about 5 mm. The lengths of the tubes X and Y were usually about 10 cm.

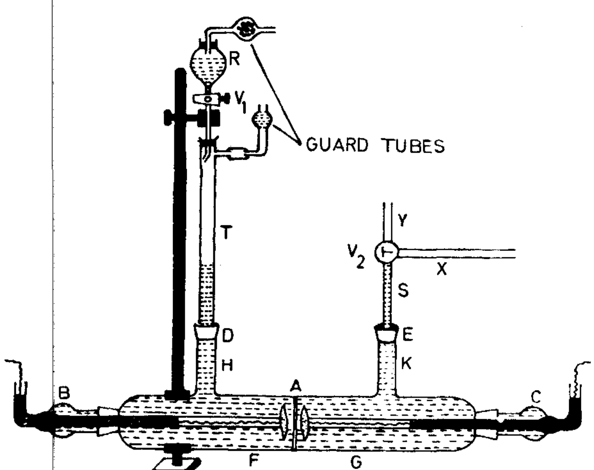

Fig. 1 — APPARATUS FOR MEASURING STREAMING POTENTIAL

Procedure — The apparatus was washed thoroughly with concentrated nitric acid. The cleaning of the disc and the apparatus required forcing nitric acid under pressure followed by forcing conductivity water to remove traces of nitric acid. The apparatus was dried in an oven at 200° for 1 hr.

In order to fill the liquid in the apparatus, the liquid was filled in one part of the tube A in its upright position. The other part was gradually evacuated and the liquid allowed to pass through the sintered disc such that the pores were wetted with the liquid and no trace of air was left entrapped in the pores of the sintered disc. The other part of the apparatus was also filled with the liquid. The tubes T and S were then introduced. Mercury was introduced into the electrode tubes to make electrical contacts. The apparatus was suitably mounted inside the air thermostat where it was allowed to attain a constant temperature.

For the measurement of streaming potentials, the liquid was allowed to flow under a constant pressure gradient. Depending on the rate of flow of the liquid from reservoir R (controlled by stopcock V_1) into the limb T, it was possible to adjust a desirable pressure gradient. The streaming potential developed was measured with the help of an electrometer (Electronics Corporation of India), capable of reading up to 0·01 mV. The resistance of the system (electro-osmotic cell) with the liquid contained in the apparatus, was measured with the help of a conductivity bridge (Toshniwal Instruments, Bombay).

At the time of filling the apparatus and taking the observations guard tubes with silica gel were used. All the experiments on streaming potential measurements were carried out at 25°.

Results and Discussion

Streaming potential is defined as the potential difference per unit pressure difference in the stationary state with zero electric current and mathematically it can be written in the form of Eq. (1):

$$\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = \left(\frac{L_{12}}{L_{11}}\right) \quad ...(1)$$

where $\Delta\phi$ is the streaming potential, ΔP is the pressure difference across the diaphragm, L_{12} is the cross-phenomenological coefficient and L_{11} is the phenomenological coefficient related to the resistance of the electro-osmotic cell.

According to the theory of irreversible processes, the phenomenological relation[2] for the current flow across the diaphragm at $\Delta P = 0$, can be written in the form of Eq. (2).

$$I = \left(\frac{L_{11}}{T}\right)\cdot \Delta\phi \quad ...(2)$$

On comparing Eq. (2) with Ohm's law, we find that

$$L_{11} = \frac{T}{R} \quad ...(3)$$

where R is the resistance of the electro-osmotic cell and T is the absolute temperature.

On substituting (3) into (1), we obtain Eq. (4).

$$\left(\frac{\Delta\phi}{\Delta P}\right)_{I=0} = \frac{L_{12}R}{T} \quad ...(4)$$

Values of $\Delta\phi$, corresponding to different values of ΔP, across the disc were measured with an electrometer. The pressure difference ΔP was measured with the help of cathetometer capable of reading upto 0·001 cm. The values of $\Delta\phi$ so obtained for different systems are given in Table 1.

The plot of $\Delta\phi$ versus ΔP is found to be linear for each system. The right hand side of Eq. (4) was estimated from the slope of such linear plots for different systems and on substituting the value of R, L_{12} was estimated.

The phenomenological coefficient L_{21} estimated earlier[12,13] and L_{12} estimated above for different systems are given in Table 2.

TABLE 1 — DATA OF THE STREAMING POTENTIAL ACROSS PYREX SINTERED DISC AT 25°C

ΔP (cm)	$\Delta\phi$ (mV)	ΔP (cm)	$\Delta\phi$ (mV)	ΔP (cm)	$\Delta\phi$ (mV)
ACETONITRILE; $R=0·92\times10^4$ ohm		25% MeOH-MeCN; $R=0·66\times10^4$ ohm		75% MeOH-MeCN; $R=0·44\times10^4$ ohm	
10·0	6·02	10·0	10·32	10·0	4·17
20·0	12·20	20·0	21·86	20·0	8·06
30·0	19·04	30·0	35·38	30·0	13·20
40·0	24·98	40·0	42·24	40·0	16·35
50·0	32·16	50·0	54·92	50·0	20·10

TABLE 2 — VALUES OF THE CROSS-PHENOMENOLOGICAL COEFFICIENTS L_{12} AND L_{21} FOR DIFFERENT SYSTEMS AT 25°

System	L_{12} (cm^3 °K A J^{-1})	L_{21} (cm^3 °K A J^{-1})
Acetonitrile	0·27	0·26
25% MeOH-MeCN	0·71	0·69
75% MeOH-MeCN	0·35	0·36

The data in Table 2 show that magnitude of L_{12} is in excellent agreement with L_{21} for various systems reported here. This proves that Onsager's reciprocity relation holds good for electrokinetic effects across pyrex sintered disc involving the flow of MeCN and MeCN-MeOH mixtures.

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