Notes

On the Estimation of Zeta-Potential from Electroosmotic Flux Data

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Electroosmotic flux data are often used for characterization of electrified interfaces. Our analysis of the recently reported experimental results [*J. phys. Chem.*, 79 (1975), 2574] shows that the estimated zeta-potentials are likely to be suspect if the influence of externally applied electrical potential is not taken care of.

STUDIES on electroosmotic phenomenon with charged and uncharged membranes convincingly demonstrate that volumetric flux depends non-linearly on electrical potential difference[1-5]. Ravina and Zaslvaski[6] earlier inferred on the basis of available experimental data that deviation from strict non-linearity in weak field was typical of the results of many authors. Precise reasons for the occurrence of non-linearity are far from being clearly understood[7-10].

The electrochemical double layer responsible for the occurrence of the electrokinetic phenomenon may arise due to either preferential adsorption of ions by the matrix of the membrane or unequal distribution of ions in solution contained within the pores of the membrane. Direct determination of the nature of electrical double layer has been accomplished only in a few cases using spectroscopic techniques[11-13]. Electrokinetic properties are generally used to ascertain the character of electrical double layer. The double layer is endowed with an electrical potential called electrokinetic or zeta-potential. This zeta-potential which is characteristic of the membrane material and permeating species is normally regarded to be independent of the applied electrical potential. Experimentally observed non-linear electroosmotic effects, however, indicate that zeta-potential may depend on the applied electrical potential. Our analysis of the recently obtained experimental results[14-15] on electroosmosis of alcohol-water mixtures through ion-exchange membranes shows that zeta-potential increases with increase of potential and this dependence is linear in character. The results of such an analysis of the data are reported in this note.

The data on electroosmosis with Zeokarb 226 (H^+ form)/alcohal-water system recently reported by Rastogi *et al.*[14] clearly shows a non-linear relationship. In the case of Zeokarb 226 (H^+ form), for 10% alcohal-water mixture the direction of electroosmotic flux undergoes reversal beyond a certain value of applied potential difference. They have used the following non-linear phenomenological equation:

$$J_v = L_{12}(\Delta\phi/T) + \tfrac{1}{2}L_{122}(\Delta\phi/T)^2 \qquad \ldots(1)$$

for description of their data. J_v is the volumetric flux; $\Delta\phi$ the potential difference and L_{12} and L_{122} are first and second order phenomenological coefficients respectively. The phenomenological description of the phenomenon under discussion is not based on any atomistic model. It, however, assumes that during electroosmosis the electrical character of the interface involved remains unchanged. In the absence of any evidence to the contrary one may start with the assumption that electrical character of the interface is influenced by the operating electrical potential. If one further assumes that when the electrical potential is applied the electrified interface acquires an altered character which subsequently remains unchanged during electroosmosis, the linear relationship (2),

$$J_v = A\zeta\epsilon/4\pi\eta l\ (\Delta\phi) \qquad \ldots(2)$$

based on atomistic interpretation of the electrified interface may be considered to be applicable. In Eq. (2) A is the effective cross-sectional area and l is the thickness of the membrane; ϵ and η are dielectric constant, and coefficient of viscosity of the permeating liquid respectively and ζ is the electrokinetic potential. The electroosmotic flux data may consequently be used for the estimation of zeta-potential for different applied electrical potentials. In the absence of a precise knowledge of A and l one may write Eq. (2) as

$$J_v = \Psi\epsilon/4\pi\eta\ (\Delta\phi) \qquad \ldots(3)$$

where $\Psi = K\zeta$; $K = A/l$ and may be called the membrane constant. We have used Eq. (3) to evaluate Ψ. Evaluation of zeta-potential itself is difficult since precise estimation of effective cross-sectional area is not possible. The values of dielectric constants and viscosity used (obtained from literature[16,17]) are given in Table 1. The dependence of Ψ on potential difference has been depicted in Figs. 1-4. In all the cases computed Ψ values satisfy relationship (4)

$$\Psi = \Psi^\circ + B(\Delta\phi) \qquad \ldots(4)$$

where $\Psi^\circ = K\zeta^\circ$, ζ° being the electrical potential of the double layer in the absence of any externally applied electrical field. Ψ_0 values for different systems under considerations are included in Table 2.

It may be noted that K, unlike zeta-potential, is characteristic of the membrane equilibrated with the permeant and is independent of the applied electrical potential. It, however, does depend on the composition of the permeating liquid. This is particularly the case with membranes composed of ion-exchanger materials, since these materials undergo swelling upon equilibration. The extent of swelling depends on the nature and composition of permeating liquid[18].

It is clear from the preceding discussion that values of zeta-potential obtained from electroosmotic data are suspect if the effect of electrical potential applied is ignored. It can accurately be estimated

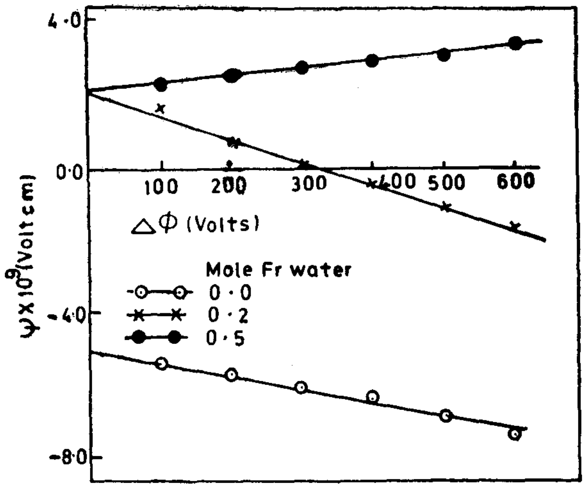

Fig. 1 — Dependence of Ψ' on applied potential difference, $\Delta\phi$, for Zeokarb 226 (H^+ form)/methanol-water mixture system

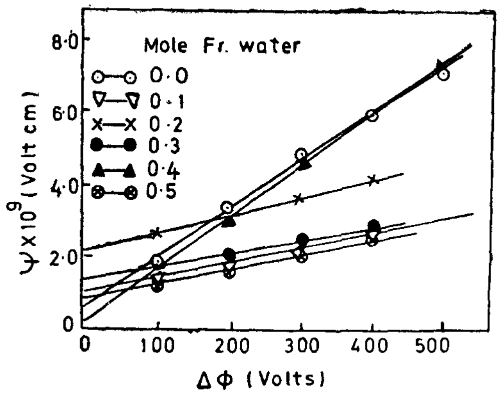

Fig. 2 — Dependence of Ψ' on applied potential difference, ($\Delta\phi$), for Zeokarb 225 (H^+ form)/methanol-water mixture system

TABLE 1 — DIELECTRIC CONSTANTS AND VISCOSITY FOR METHANOL-WATER MIXTURES[16,17]

Mole fr. of water	Viscosity (millipoise)	Dielectric constant
0·0	5·44	32·7
0·1	5·67	35·7
0·2	6·67	38·0
0·3	7·44	40·5
0·4	8·74	43·5
0·5	9·84	47·3

TABLE 2 — Ψ'_0 VALUES FOR DIFFERENT MEMBRANES

Mole fr. of water	Ψ' (volt cm)			
	Zeokarb 226 (H^+ form) $\times 10^9$	Zeokarb 225 (H^+ form) $\times 10^9$	Zeokarb 225 (Ba^{2+} form) $\times 10^9$	Zeokarb 225 (Al^{3+} form) $\times 10^9$
0·0	−4·90	0·60	9·40	12·50
0·1	—	0·25	6·65	11·60
0·2	2·10	2·10	10·05	9·30
0·3	—	1·40	12·60	7·65
0·4	—	1·00	12·80	5·40
0·5	2·00	0·85	10·60	—

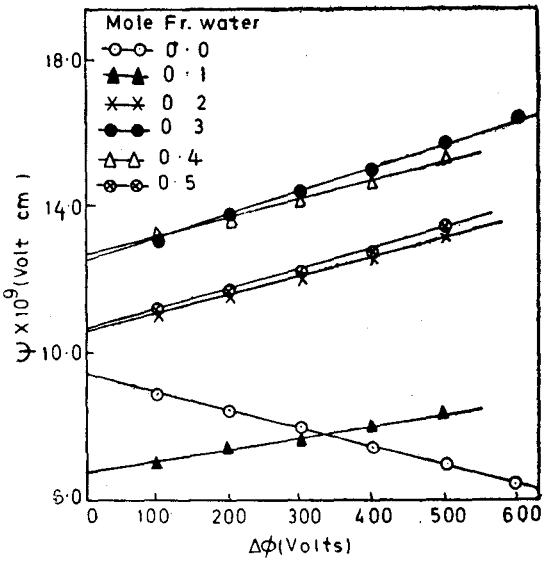

Fig. 3 — Dependence of Ψ' on applied potential difference, $\Delta\phi$, for Zeokarb 225 (Ba^{2+} form)/methanol-water mixture system

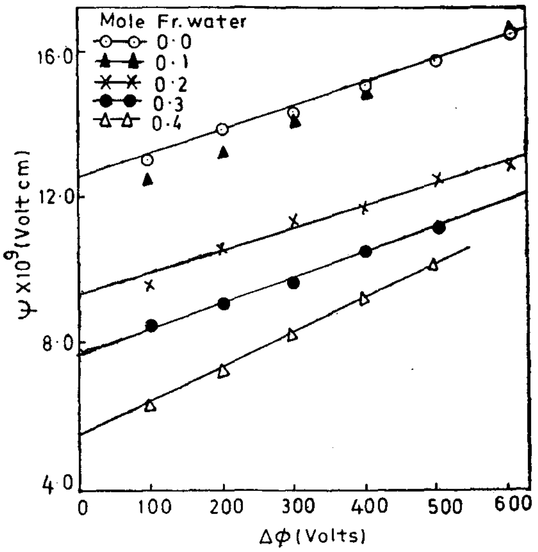

Fig. 4 — Dependence of Ψ' on applied potential difference, $\Delta\phi$, for Zeokarb 225 (Al^{3+} form)/methanol-water mixture system

from electroosmotic flux data only if the mode of dependence of zeta-potential on the externally applied potential difference is properly ascertained.

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Influence of Temperature on Ultracentrifugal Stability of Emulsion of Benzene in Ethylene Glycol

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The ultracentrifugal stability of benzene in ethylene glycol nonaqueous emulsion stabilized with sodium dioctylsulphosuccinate has been determined over the temperature range 10° to 35° in an ultracentrifuge at 25980 rpm. The emulsion is found to be less stable at higher temperatures.

EMULSIONS may be unstable with respect to temperature. The temperature dependence of stability of emulsions is of great practical importance, since commercial emulsions may have to be stored for varying periods of time in warehouses, where they may be exposed to high as well as low temperatures. In view of this, it is surprising that very little attention[1,2] has been devoted to this aspect of emulsion stability.

In continuation of our earlier work[3,4], the present communication reports the effect of temperature on the ultracentrifugal stability of oil-in-oil emulsion (nonaqueous system) prepared with benzene and ethylene glycol as two nonaqueous phases and sodium dioctylsulphosuccinate as emulsifying agent.

The nonaqueous emulsion of benzene (BDH) in ethylene glycol (BDH) was prepared with 1:1 phase ratio by volume and 1·0% concentration of sodium dioctylsulphosuccinate (BDH; w/v % of ethylene glycol). The heterogeneous mixture of benzene and ethylene glycol containing anionic surfactant was homogenized with a Braun emulsator, for final making of the emulsion.

A Beckman Spinco model E analytical ultracentrifuge was used in this work with a 12 mm light path and a 4-degree sector angle standard cell having a capacity of about 0·8 ml. After preparation of the 0/0 emulsion, 0·7 ml of the emulsion was injected into the ultracentrifuge cell with a hypodermic needle. The cell was then placed in an analytical rotor and subsequently centrifuged at 25980 rpm. The time required for acceleration to this constant speed was 2 min and 45 sec (±15 sec). Zero time in the experiments was taken as the time at which constant speed was reached. Samples of the emulsion were ultracentrifuged at controlled temperatures between 10° and 35° (±0·2°) at the constant speed.

During centrifugation three layers develop in the cell : transparent layer of benzene, the remaining opaque, concentrated stable emulsion and the transparent layer of ethylene glycol. Photographic records were made of the cell at regular time intervals during the experiment at each temperature. The layers give sharp boundaries on a photographic plate which change position with time as more benzene is separated from the emulsion. Determination of the positions of the boundaries on a series of such plates taken at successive time intervals permits calculation of the rate of separation of benzene from the emulsion at all temperatures. Measurements were made with a travelling microscope determining the distance from the top of the cell to the benzene-emulsion and emulsion-ethylene glycol interfaces, and to the bottom of the cell.

The volume, V, corresponding to a length, l, in the cell is given by

$$V = 4\pi t[(d+l)^2 - d^2]/360$$
$$= \pi t l(2d+l)/90$$

where d is the distance from the centre of rotation to the top of the cell, and t is the thickness of the cell. A graph was plotted of the volume as a function of the measured value of l from the top of the cell using an optical enlargement of 2·03. The plot was then used to determine the volume from the differences between the measured distances to the different interfaces.

The per cent of the initially emulsified benzene which separated at any given time was determined by dividing the volume of the benzene layer by the

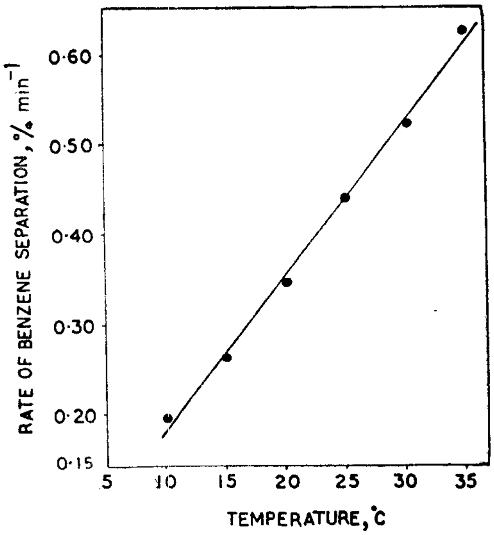

Fig. 1 — Effect of temperature on the ultracentrifugal stability of a 50% benzene-50% ethylene glycol-1·0% sodium dioctylsulphosuccinate nonaqueous emulsion