ACTIVATION ENTHALPY AND ENTROPY FOR HYDRODYNAMIC FLOW THROUGH SOME ALKALINE BATTERY SEPARATORS

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The hydrodynamic flow of water and potassium hydroxide through some alkaline battery separators have been analysed in term of activation energy parameters viz., enthalpy of activation, ΔH^* and entropy of activation, ΔS^*. The very large negative ΔS^* for the flow through some separators is indicative of an extensive ordering process and of an interaction between the liquid with the separator material during flow. These interactions depend on the chemical nature of the separator surface.

During operation of many electrochemical devices, the electrolyte components move from one electrode compartment to another through battery separators. The performance requirement of a battery is that it does not fail after repeated cycles of charging and discharging of the battery. In alkaline battery, especially Ni-H_2 battery, it has been found that the battery fails after a certain number of cycles and one of the reasons for the failure is the drying of the separators. It could also be due to blocking of separators due to suspended impurities in the electrolyte or disintegeration of the electrode plate or the separator. The examination of the battery after its opening does reveal some particles on the membrane surface which may be due to one of the reasons mentioned above. However the membrane looked completely dry as if it was not soaked in the alkaline solution. In order to find out the reason for dryness, the hydrodynamic flow of potassium hydroxide and water was studied through different separators at different temperatures.

EXPERIMENTAL

Deionised water having conductivity of the order of 10^{-6} Ohm^{-1} cm^{-1} and 45% potassium hydroxide solution made from Fischer ACS certified reagent was used.

Ion Exchange separators ZAMM-0 and P-2193-40/60 supplied by RAI - millipore Co., New York; polysulphone HT-100 and HT-200 supplied by Gelman Sciences Inc., Ann Arbor, Michigan; K 168SP on PP-S49024 and WR Grace inter-separator supplied by Grace Company, New York, and Fuel Cell grade asbestos + 5% EBL(ethyl butyl latex as binder) supplied by Quinn-T Company, New York were used in the present study.

The permeation cell (Figure-1) consisted of two hollow bocks A, B of plexiglass with the separator between the two blocks. The area of separator exposed to solution is a circle of 2 dm. Each block had a capacity of 10.0 dm^3 solution and had 1/4" stainless steel fittings, S_1, S_2 at the top for connecting a pressure head, and a glass capillary, C of 0.1 dm internal diameter. Pressure was applied by adjusting the pressure head in case of porous separators, while in other cases flow was affected by applying a pressure of nitrogen through one of the stainless steel fittings. The pressure was regulated with a valve and was measured with a pressure gauge having a accuracy of 2% at 3.0 psi reading. The studies with potassium hydroxide were carried out in a nitrogen atmosphere and the contact to atmosphere was avoided by using intermediate chambers of potassium hydroxide pellets.

Neoprene rubber gaskets were used on both sides of the separator to overcome leakage. GE-RTV-102 silicone cement was used for sealing the two half cells. All experiments were carried out in a water bath maintained to $\pm$ 0.05 °C. In the case of separators having low permeation rate, flow was followed by following the level in tube 'C' with a travelling microscope of least count $\pm$ 0.001 dm. In case of separators with faster flow, rise/drop (x) in liquid level in the tube attached to the half-cell was recorded with a stop-watch having least count of 0.02 sec. The rate dx/dt was estimated as the rate of flow at the specified pressure difference.

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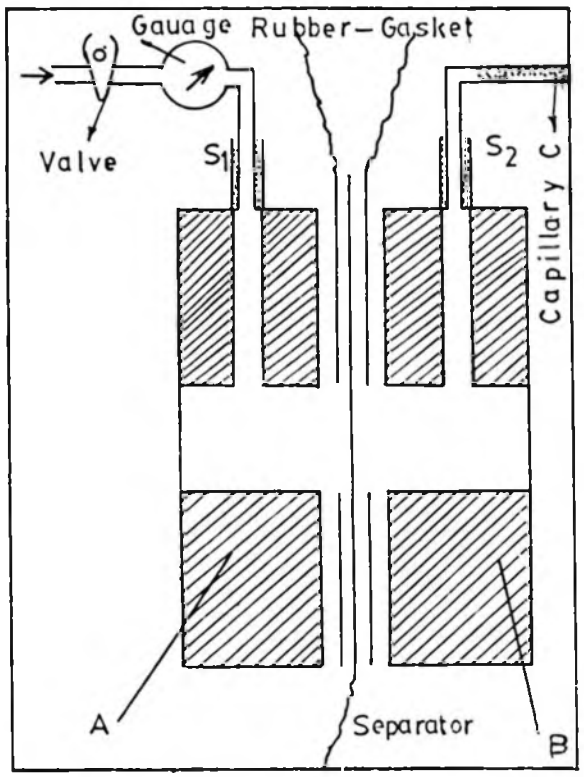


Fig. 1 Experimental set up

RESULTS AND DISCUSSION

The hydrodynamic permeability L_P, is estimated by using the relation [1,2]

$$J_V = L_P \cdot \Delta P \qquad ...(1)$$

where J_V is the volume flux per unit area of the membrane. ΔP is the applied pressure difference. If r is the radius of the capillary tube in which liquid flow is recorded and R is the radius of the separator, J_V is estimated from

$$J_V = (dx/dt)(r^2/R'^2) \qquad ...(2)$$

Since the pressure applied is small, linear relation between J_V and ΔP is expected to hold. The values of J_V at different pressures were determined, and the values of L_P for the various cases estimated from the linear plots of J_V vs ΔP are given in Table 1 for different separators. On comparing equation (1) with Poissuille's law for viscous flow through a bundle of capillaries, the variation of permeability with temperature can be witten as [3,4].

$$\ln L_p = \text{constant} - E_\eta/RT \qquad ..(3)$$

where E_η is the energy of activation for the flow process, R is the gas constant and T is temeprature in degrees Kalvin. The values of E_η were estimated from the plots of log L_P versus 1/T. These values are given in Table 2.

Since the flow of a liquid through a capillary or diaphragm or membrane is a rate process, it takes place with a definite velocity under given conditions of pressure and it seems reasonable to suppose that the theory of the absolute reaction rates [5,6] can be applied to the problem of hydrodynamic flow. Equating the energy of activation to enthalpy of activation ΔH^* for the flow, the entropy of activation ΔS^*, is estimated from the following Eyring's rate equation for the flow.

$$\eta = \frac{NR}{\bar{V}} \cdot e^{\Delta S^*/R} \cdot e^{\Delta H^*/RT} \qquad ...(4)$$

where η is the viscosity of the liquid, $\bar{V}$ is the molar volume, N is the Avogadro's number, h is Planck's constant. Using $N = 6.022 \times 10^{23}$ $h = 6.626 \times 10^{-34}$ Js, $\eta = 0.001002$ Nsm^{-2} for water and 0.00535 Nsm^{-2} for 45% potassium hydroxide at T=293°K R = 8.3144 J deg^{-1} M^{-1}, $\bar{V}$ = 18.0 dm^3/M for water and 12.5 dm^3/M for KOH solution, the values of ΔS^* were estimated and are given in Table 2.

The retention of a liquid in the separator may be considered to depend on the interactions between the liquid and porous material of the separator. Entropy being a measure of randomness, lower value of entropy can be taken to indicate the presence of ordered flow arising due to some interaction between the liquid and the material of the separator. It is proposed that lower entropy of activation of flow through separators is associated with attractive force between the liquid and the separator material and this reduces the possibility of drying of the separator. Looking at the values of ΔS^* for different separators in Table 2, it appears that the separator at Sr.No.6 is not suitable because it will be difficult to keep it wet or to retain alkali in it for a longer time. All other separators reported here show the tendency to remain wet even if the potassium hydroxide depletes because entropy of activation for water flow is also negative. The positive value of ΔS^* for water in case of WR Grace Interseparator points out that the separator will dry out if the concentration of potassium hydroxide decreases. This may happen sometimes in the course of cycling. The suitability of the separators on the basis of the concept of negative entropy of activation can be written in the following order:

TABLE 1

HYDRODYNAMIC PERMEABILITY (L_p) DATA (in m^3./S/N) AT DIFFERENT TEMPERATURES

Permeability (medium)	293	295	298	303	308	313	318	323 K
		1. Separator: RAI, Zamm -0						
$L_p \times 10^{12}$ (water)	-	-	1.16	1.33	-	1.48	1.79	1.93
$L_p \times 10^{13}$ (KOH)	-	-	2.48	-	3.02	-	3.32	3.80
		2. Separator: WR Grace Interseparator						
$L_p \times 10^{7}$ (water)	-	-	0.633	0.881	1.294	-	-	-
$L_p \times 10^{7}$ (KOH)	-	-	0.531	0.655	0.734	-	-	-
		3. Separator: Polysulphone, HT-200						
$L_p \times 10^{9}$ (water)	-	-	8.55	10.82	13.32	14.19	17.71	-
$L_p \times 10^{9}$ (KOH)	-	-	-	11.12	13.75	18.75	22.88	27.70
		4. Separator: Polysulphone HT-100						
$L_p \times 10^{9}$ (water)	-	-	3.84	4.13	4.58	4.86	-	-
$L_p \times 10^{9}$ (KOH)	-	-	2.48	3.53	4.38	4.85	-	7.00
		5. Separator FCGA + 5% EBL						
$L_p \times 10^{7}$ (water)	-	-	2.34	-	-	4.09	5.19	5.32
$L_p \times 10^{9}$ (KOH)	-	-	4.24	5.4	6.78	8.64	-	-
		6. Separator RAI P 2193-40/60						
$L_p \times 10^{13}$ (water)	-	0.160	-	0.399	0.537	0.923	-	1.375
$L_p \times 10^{13}$ (KOH)	0.124	-	-	0.214	-	0.625	-	1.247
		7. Separator: K 168 SP on PP-S49024						
$L_p \times 10^{9}$ (water)	-	-	2.499	4.550	6.330	10.065	-	-
$L_p \times 10^{9}$ (KOH)	-	-	3.19	3.73	4.74	6.60	7.05	8.18

TABLE 2

ACTIVATION ENTHALPY (J/M X 10^3) AND ENTROPY ($JK^{-1} M^{-1}$) FOR HYDRODYNAMIC FLOW THROUGH DIFFERENT SEPARATORS

Separator	Water ΔH^*	Water ΔS_1^*	45% KCM ΔH^*	45% KCM ΔS_1^*
1. RAI: Zammo	6.93	-39.90	5.58	-37.24
2. WR Grace	21.8	+10.75	10.7	-19.76
3. HT- 200	16.9	- 5.97	12.0	-15.33
4. HT-100	5.50	-44.88	13.8	- 9.05
5. FCGA + 5%EBL	12.08	-22.39	16.07	- 3.69
6. RAI P 2193-40/60.	27.05	+28.67	27.70	+38.26
7. K 168 SP on PP 349024	30.81	+41.50	13.94	- 8.71

Ion Exchange (RAI, ZAMM-0) > WR Grace Inter Separator > Polysulphone (HT 200) > polysulphone (HT 100) > K On PP > FCGA + 5% EBL. In view of the above rating, a combination of separators viz., RAI, ZAMM-0 and WR Grace interseparator in series or alone might improve the battery life.

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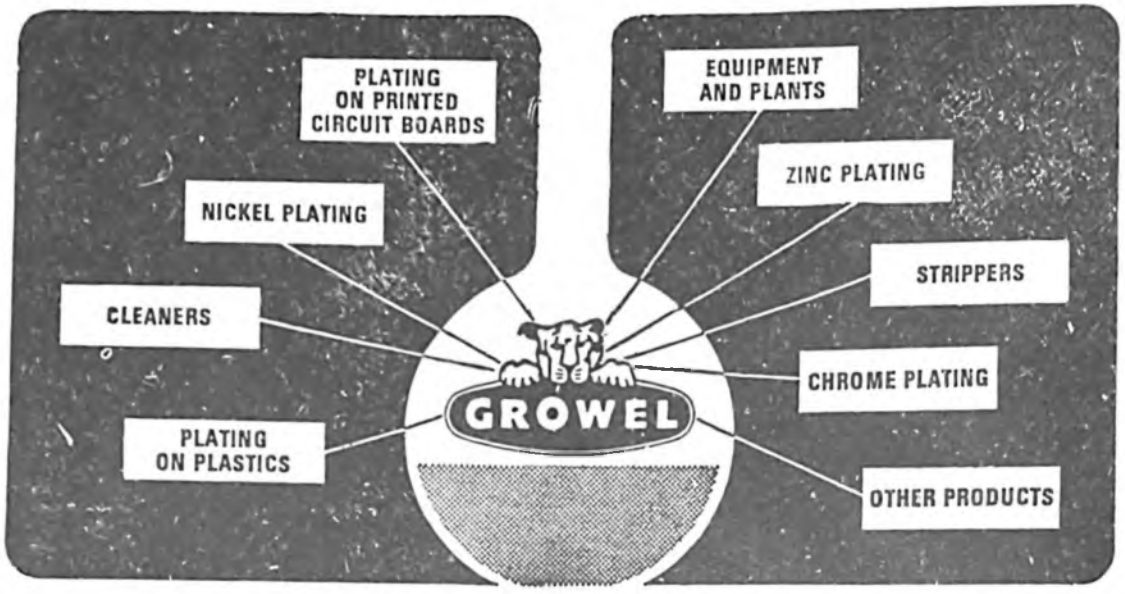
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