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Permeation Studies on Binary Liquid Mixtures of Acetone with Benzene & Chloroform

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An experimental investigation on the electrokinetic transport of the binary mixtures of benzene-acetone and acetone-chloroform through a pyrex membrane is described. The linear phenomenological equations between the thermodynamic fluxes and forces hold good in both the cases. Dependence of the phenomenological coefficients on composition of the mixtures has been investigated. Onsager reciprocity relationship has also been tested. The experimental results indicate that permation is non-ideal in character. Characterization of membrane-permeant interface in terms of zeta-potential has also been carried out.

Membrane permeation under the action of gradients of pressure and/or electric potnetial difference is studied with the twin object of dimensional and electrochemical characterization of membranes[1-4], and examination of applicability of the transport equations deduced on the basis of non-equilibrium thermodynamic principles[5-10]. To obviate complications arising on account of membrane and electrode polarization, non-aqueous permeants are preferably used in such studies. In very few investigations mixtures have been used[11-13]. In this paper we report studies on hydrodynamic and electro-osmotic permeation of the binary mixtures of benzene and acetone, and acetone and chloroform through a pyrex membrane to investigate the dependence of transport coefficients on composition and nature of the permeating mixtures. Streaming potential and membrane conductance measurements have also been carried out. The results have been analysed to investigate alteration in the electrical character of the membrane-permeant interface with change in permeant composition. An attempt has also been made to express non-ideality in permeation in terms of excess phenomenological coefficients.

Materials and Methods

Benzene, acetone, and chloroform were BDH, (India) reagents and were used without further purification. Pyrex sinter of porosity grade G-4 obtained from M/s Corning, India, was used as the membrane.

An experimental cell similar to that described earlier[14] was used for the measurement of electro-osmotic and hydrodynamic permeabilities. The membrane was cleaned by boiling it with 50% conc. nitric acid (AR). It was washed with distilled water and dried at 120° for ~ 3 hr. The membrane was then equilibrated with the experimental liquid. The cell was filled with fresh permeant to ensure that concentration of the experimental solution remained the same as that compounded before equilibration. An electronically operated power supply (Toshniwal, India) was used to apply potential gradients. The platinum electrodes were cleaned with nitric acid and washed before use and kept in direct contact with the membrane. The volumetric flux was measured by following the rate of movement of the permeant in a horizontal fixed capillary tube having cross-sectional area equal to 1.0×10^{-2} cm^2. The electroosmotic flow in all instances was found to be from positive to negative electrode.

Hydrodynamic permeability was measured with the same cell. A known hydrodynamic pressure was applied across the membrane and volumetric flux was measured as already described. The electrodes were kept short-circuited throughout the hydrodynamic permeability measurements.

Streaming potnetials at different pressures were recorded using a digital multimeter, HIL 2142.

Results and Discussion

According to the theory of non-equilibrium thermodynamics, the volumetric flux, J_v, and the flow of electric current, I, under the simultaneous action of pressure difference, ΔP, and electrical potential difference, $\Delta \phi$, across the membrane may be expressed as[15,16],

$$J_v = \frac{L_{11}}{T} \Delta P + \frac{L_{12}}{T} \Delta \phi \qquad \ldots (1)$$

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Table 1—Phenomenological Coefficients L_{11}/T and L_{12}/T for Benzene-Acetone and Acetone-Chloroform/Pyrex Systems ($T = 30 \pm 0.5$°C)

Benzene-acetone			Acetone-chloroform		
x_{benzene}	$(L_{11}/T)\times 10^{12}$ ($m^5s^{-1}N^{-1}$)	$(L_{12}/T)\times 10^{11}$ ($m^3s^{-1}V^{-1}$)	$x_{\text{chloroform}}$	$(L_{11}/T)\times 10^{12}$ ($m^5s^{-1}N^{-1}$)	$(L_{12}/T)\times 10^{11}$ ($m^3s^{-1}V^{-1}$)
0.00	9.44	20.08	0.00	9.00	20.57
0.20	6.87	8.48	0.17	8.43	10.60
0.40	5.27	3.59	0.40	7.19	5.38
0.60	3.91	1.00	0.60	6.16	1.94
0.73	3.49	0.37	0.80	5.83	0.53
1.00	4.14	—	1.00	5.00	0.25

Table 2—Examination of Validity of Onsager's Reciprocity Relationship for Acetone-chloroform/Pyrex System ($T = 30 \pm 0.5$ °C)

Mol fr. of chloroform	$(\Delta\phi/\Delta P)\times 10^4$ $I=0$ ($N^{-1}m^2V$)	$(L_{22}/T)\times 10^6$ (Ohm^{-1})	$(L_{21}/T)\times 10^{11}$ ($m^3s^{-1}V^{-1}$)	$(L_{12}/T)\times 10^{11}$ ($m^3s^{-1}V^{-1}$)
0.00	1.02	2.00	20.4	20.57
0.17	1.33	0.74	9.8	10.6
0.40	1.74	0.31	5.4	5.38
0.60	1.40	0.15	2.10	1.94
0.80	0.71	0.07	0.50	0.58
1.00	0.08	—	—	—

J-ccs 86
19-11-91

$$I = \frac{L_{21}}{T}\Delta P + \frac{L_{22}}{T}\Delta\phi \qquad \ldots (2)$$

L_{ij} (i, j = 1, 2) are the phenomenological coefficients. From Eq. (1) it easily follows that,

$$(J_v)_{\Delta\phi=0} = \frac{L_{11}}{T}\Delta P \qquad \ldots (3)$$

and

$$(J_v)_{\Delta P=0} = \frac{L_{12}}{T}\Delta\phi \qquad \ldots (4)$$

According to Eqs (3) and (4), $(J_v)_{\Delta\phi=0}$ and $(J_v)_{\Delta P=0}$ are linearly related to ΔP and $\Delta\phi$ respectively. The experimental results show that Eqs (3) and (4) are valid for the benzene-acetone and the acetone-chloroform systems within the domain of investigation. The values of L_{11}/T and L_{12}/T obtained from the plots of $(J_v)_{\Delta\phi=0}$ versus ΔP and $(J_v)_{\Delta P=0}$ versus $\Delta\phi$ are recorded in Table 1.

The streaming potential, $(\Delta\phi)_{I=0}$, according to eq. (2), is given by,

$$(\Delta\phi)_{I=0} = -\frac{L_{21}}{L_{22}}\Delta P \qquad \ldots (5)$$

and

$$\left(\frac{I}{\Delta\phi}\right)_{\Delta P=0} = \frac{L_{22}}{T} \qquad \ldots (6)$$

So that the membrane conductance, K_m may be expressed as

$$(I/\Delta\phi)_{\Delta P=0} = \frac{L_{22}}{T} = K_m \qquad \ldots (7)$$

According to Onsager's reciprocity relationship[15,16],

$$\frac{L_{12}}{T} = \frac{L_{21}}{T} \qquad \ldots (8)$$

The validity of Eq. (5) has been tested and it is found that $(\Delta\phi)_{I=0}$ varies linearly with the applied pressure difference on the two sides of the membrane. The values of (L_{22}/T) and $(\Delta\phi/\Delta P)_{I=0}$ have been recorded in Table 2. Using Eqs (5) and (7), we have calculated values of L_{21}/T for chloroform-acetone system to test the validity of Eq. (8). The values of L_{12}/T and L_{21}/T recorded in Table 2 are in reasonable agreement. It may be noted that uncertainty in the values of the cross phenomenological coefficients does not exceed ± 5%.

Following the treatment of Overbeek[17], it can be shown that in the case of flow through membrane

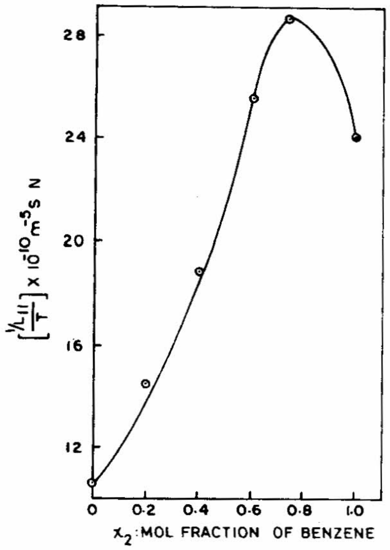

Fig. 1—Test of the validity of Eq. (13) for acetone-benzene/pyrex system.

consisting of n capillaries of equivalent pore radius, r, we have,

$$\frac{L_{11}}{T} = \frac{n \pi r^4}{8 \eta l} \qquad \dots (9)$$

and

$$\frac{L_{12}}{T} = \frac{n \varepsilon r^2 \zeta}{4 \eta l} \qquad \dots (10)$$

wherein η is viscosity coefficient, ε, is the dielectric constant of the permeant and l is the thickness of the membrane. ζ denotes electrokinetic potential at the membrane-permeant interfacial region.

$$\frac{L_{11}}{T} = \frac{n \pi r^4}{8 \eta_i^m l} \qquad \dots (11)$$

η_i^m, the coefficient of viscosity for the ideal mixture may be expressed as[18],

$$\eta_i^m = x_1 \eta_1 + x_2 \eta_2 \qquad \dots (12)$$

where x_1 and x_2 are mole fractions of components 1 and 2 respectively. Using Eqs (11) and (12), it is possible to write,

$$\left(\frac{L_{11}}{T}\right)_i^m = \frac{(L_{11}/T)_1 (L_{11}/T)_2}{(L_{11}/T)_2 + x_2[(L_{11}/T)_1 - (L_{11}/T)_2]} \qquad \dots (13)$$

The difference between the observed and ideal phenomenological coefficients, called excess phenomenological coefficients, may be expressed as[14,19],

$$\left(\frac{L_{11}}{T}\right)^E = \left(\frac{L_{11}}{T}\right) - \left(\frac{L_{11}}{T}\right)_i^m \qquad \dots (14)$$

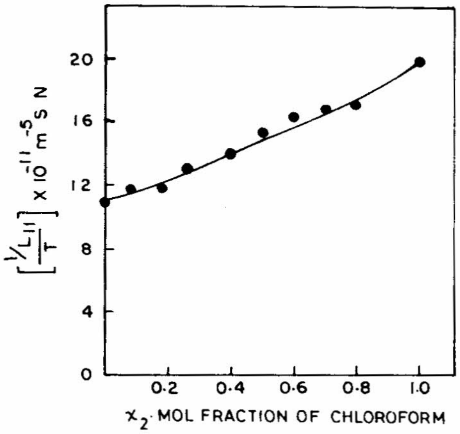

Fig. 2—Test of the validity of Eq. (13) for acetone-chloroform/pyrex system

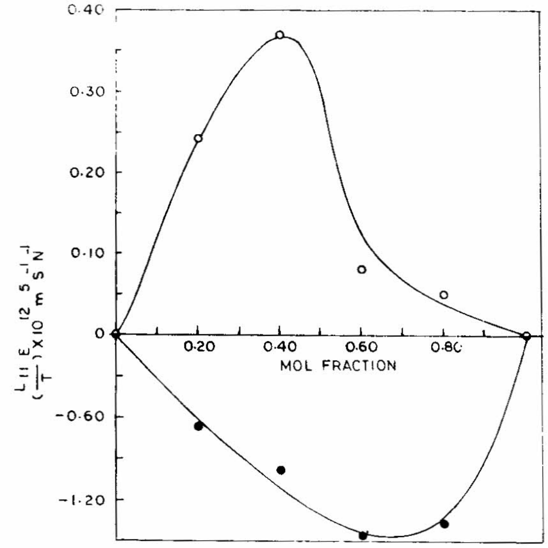

Fig. 3—Dependence of $(L_{11}/T)^E$ on composition [–○–, mole fraction of benzene in acetone-benzene mixture; –●–, mole fraction of chloroform in acetone-chloroform mixture]

For ideal permeation $(L_{11}/T)^E = 0$ and the total permeation is such that permeation of one component is not influenced by that of the other. Non-ideality in permeation arises on account of interaction amongst the components of the mixture and their interactions with the membrane matrix. If hydrodynamic permeation were ideal, Eq. (13) should hold good. Validity of this equation for acetone-benzene and acetone-chloroform mixtures were examined by plotting $1/(L_{11}/T)$ against x_2. The experimental results (Figs 1 and 2) are not consistent with Eq. (13). The permeation is thus non-ideal in both the cases.

For quantitative description of non-ideality in hydrodynamic permeation, excess phenomenological coefficients defined by Eq. (14) were estimated.

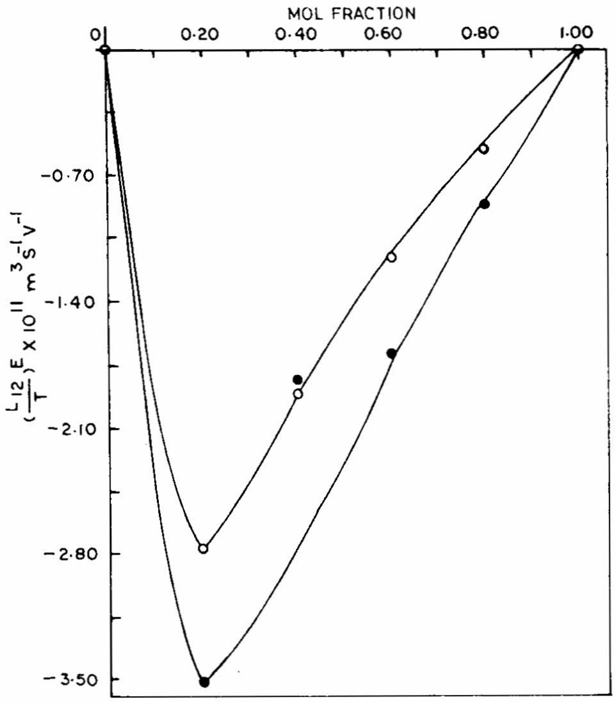

Fig. 4—Dependence of $(L_{12}/\mathrm{T})^{\mathrm{E}}$ on composition [−○−, mole fraction of benzene in acetone-benzene mixture; −●−, mole fraction of chloroform in acetone-chloroform mixture]

Their dependence on composition is depicted in Fig. 3. In the case of acetone-benzene mixture, benzene acts as a Π-electron donor and may form a complex[20]. In case of acetone-chloroform system the non-ideal permeation may also be attributed to the formation of a complex[21,22] between acetone and chloroform.

The permeation behaviour of mixtures through a membrane under the action of electrical potential gradient can also be analysed by studying electro-osmotically driven flux which is attributed to the existence of an electrical double layer. Using Eq. (10), we may write

$$\left(\frac{L_{12}}{\mathrm{T}}\Big/\zeta\right) = \frac{(\mathrm{A/l})\,\varepsilon}{4\,\pi\,\eta} \qquad \ldots (15)$$

where $(\mathrm{A/l}) = \dfrac{n\,\pi\,r^2}{\mathrm{l}}$

For ideal mixtrue, ε_i^m, the dielectric constant may be expressed as[23],

$$\varepsilon_i^m = x_1\,\varepsilon_1 + x_2\,\varepsilon_2 \qquad \ldots (16)$$

From Eqs (15) and (16), for ideal permeation, one may write,

$$\left(\frac{L_{12}}{\mathrm{T}}\right)_i^m = [x_1(L_{12}/\zeta\mathrm{T})_1\,\eta_1 + x_2(L_{12}/\mathrm{T}\zeta)_2]\,\frac{\zeta_i^m}{\eta_i^m} \qquad \ldots (17)$$

Table 3—Zeta-Potential for Different Compositions of Acetone-Benzene, and Acetone-Chloroform/Pyrex Systems (T = 30 ± 0.5°C)

Acetone-benzene system		Acetone-chloroform system	
Mol. fr. of benzene	ζ (mV)	Mol fr. of chloroform	ζ (mV)
0.00	50.5	0.00	55.5
0.20	24.2	0.20	34.8
0.40	14.1	0.40	25.3
0.60	4.7	0.60	12.3
0.73	5.3	0.80	5.5
1.00	—	1.00	4.8

Eq. (17) can be used to compute $(L_{12}/\mathrm{T})_i^m$ values and the excess electroosmotic phenomenological coefficient, $(L_{12}/\mathrm{T})^{\mathrm{E}}$, defined as[14,19],

$$\left(\frac{L_{12}}{\mathrm{T}}\right)^{\mathrm{E}} = \left(\frac{L_{12}}{\mathrm{T}}\right) - \left(\frac{L_{12}}{\mathrm{T}}\right)_i^m \qquad \ldots (18)$$

If one of the permeants is such that it shows no electroosmotic permeability, e.g., benzene, Eq. (17) reduces to,

$$(L_{12}/\mathrm{T})_i^m = x_1\,(L_{12}/\mathrm{T}\zeta)_1\,\frac{\eta_1\,\zeta_i^m}{\eta_i^m} \qquad \ldots (19)$$

since $(L_{12}/\mathrm{T})_2 = 0$.

Values of $(L_{12}/\mathrm{T})_i^m$ for acetone-chloroform and acetone-benzene mixtures computed using Eqs (17) and (19) respectively have been used to estimate $(L_{12}/\mathrm{T})^{\mathrm{E}}$ values given in Fig. 4. It is seen that is both the cases electro-osmotic permeation is non-ideal.

Using Eq. (9) and definition of (A/l), the cell constant, average pore radius of the membrane may be expressed as,

$$r = \left[\frac{8\,\eta\,(L_{11}/\mathrm{T})}{(\mathrm{A/l})}\right]^{1/2} \qquad \ldots (20)$$

where (A/l) is given by[26],

$$\left(\frac{\mathrm{A}}{\mathrm{l}}\right) = \frac{K_m}{k} \qquad \ldots (21)$$

K_m is conductance of the membrane equilibrated with permeant of specific conductance k. The average pore radius of the membrane has been found to be of the order of 10^{-4} cm.

For the characterization of membrane-permeant interface in terms of zeta-potential, Eqs (10) and (21) may be used to obtain[18],

$$\zeta = \frac{4\,\pi\,\eta\,k}{K_m}\left(\frac{J_v}{\Delta\phi}\right)_{\Delta P=0} \times 9 \times 10^4\ \text{Volt}$$

Table 4—Coefficient of Viscostity, Dielectric Constant, Specific Conductance and Membrane Conductance (T = 30 ± 0.5°C; x_2 = Mole fraction of the second component in the mixture)

x_2	Viscosity coefficient × 10^4 N m^{-2} S		Dielectric constant		Specific conductance K × 10^3 ohm^{-1} m^{-1} (experimental)	Membrane conductance K_m × 10^5 ohm^{-1} (experimental)
	η	η_i^m (eq. 12)	ε	ε_i^m (eq. 16)		
			Acetone-benzene system			
0.00	2.95	2.95	19.3	19.3	0.320	0.220
0.20	3.02	3.67	14.1	15.9	0.112	0.095
0.40	3.22	4.43	10.4	12.5	0.056	0.050
0.60	3.34	5.16	6.4	9.1	0.004	0.005
0.73	3.42	5.64	4.3	6.8	0.0008	0.0005
1.00	6.64	6.64	2.2	2.2	—	—
			Acetone-chloroform system			
0.00	3.32	3.32	20.9	20.9	0.30	0.20
0.20	3.92	3.74	17.3	17.7	0.088	0.047
0.40	4.40	4.16	15.4	14.5	0.045	0.031
0.60	4.83	4.57	12.6	11.2	0.022	0.015
0.80	5.29	4.99	9.1	7.1	—	—
1.00	5.41	5.41	4.8	4.8	0.001	—

Values for the acetone-benzene system are from ref. 24, while those for the acetone-chloroform system are from ref. 25; η values for acetone-benzene system are experimental, and those for the acetone-chloroform system are from ref. 25.

The zeta-potentials for different compositions of acetone-benzene and acetone-chloroform mixtures have been recorded in Table 3. The values of coefficient of viscosity, η, dielectric constant, ε, specific conductance of the permeant, k, and the membrane conductance, K_m, used for the purpose of calculation are given in Table 4. It is noticed that zeta-potential always decreases by the addition of the other solvent and passes through a minimum in all cases at some concentration. η_i^m and ε_i^m values estimated using Eqs (12) and (16) respectively are also included in Table 4. Their comparison with η and ε values clearly shows that both the systems exhibit non-ideality. This supports the conclusion earlier derived on the basis of permeability measurements.

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