Journal of materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 1, Page 356-363

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Membrane Potential Studies of Parchment Supported Silver Oxalate membrane

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Received 29Aug2016,
Revised 29Sept 2016,
Accepted 03 Oct 2016

Keywords

- ✓ Membrane potential;
- ✓ Fixed charge density,
- ✓ Parchment supported membrane

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ABSTRACT

Parchment-supported silver oxalate membrane has been prepared by the interaction method. The membrane potential across the membrane in contact with different 1:1 electrolytes has been measured. The experimentally measured membrane potential values were used to evaluate the thermodynamically effective fixed charge density of the membrane-electrolyte systems using Teorell, Meyer, and Sievers (T. M. S.) [1, 2] and Kobatake et. al. [3] theories. The values of effective charge densities were quite low (they were in the order of 10^{-2} – 10^{-3} eq/l) and hence very difficult to determine by usual exchange methods. The values of effective charge densities by two theories were the same order of magnitude for each membrane-electrolyte system. Membrane potential across silver oxalate membrane for a wide interval of concentrations at different concentration ratios (γ = 2, 5, 10, 15, and 20) have been studied. The results have been analyzed by means of the Kobatake equation for membrane potential.

1. Introduction

A large number of interesting works have been published for developing new membranes with desired properties, on account of their utilization for the economic separation processes. In this regard, ion-exchange membranes have emerged as the most advanced and economical separation membranes. These membranes are being widely used for the processes like electrodialysis of sea water or brackish water, separation of inorganic toxic metal ions, pharmaceutical products, sugar processing and beverages industries [4–8]. A variety of membranes can be constructed whose structure is well defined and whose permeation mechanisms and particular parameters can be varied in a controlled manner. By correlating structure and ion permeation in such membranes, it should be possible to develop experimental criteria for determining the structure, and hence the mechanism of ion permeation through an unknown membrane. In an attempt to develop these criteria, a number of inorganic precipitated membranes [9–12] have been prepared with ion exchange sites and have studied the extent to which their chemical and transport properties depend on various external forces such as different chemical environments, temperature etc. The ionic selectivity of a membrane and the concentration range of the external salt solution in which its cationic behavior is shown both depend strongly on the fixed charge concentration of the membrane. The membrane fixed charge density can be determined using several methods: analytical titration [13], streaming potential measurements [14], and membrane potential measurements [15, 16]. In previous works, we have studied different parchment-supported membranes in order to evaluate the fixed charge density and to study the permeation of different electrolytes [17–23]. In this paper, we describe the preparation of silver oxalate parchment supported membrane. The effective charge density which is considered as the most effective parameter controlling the membrane phenomena has been determined by the different methods using membrane potential measurements.

2. Experimental

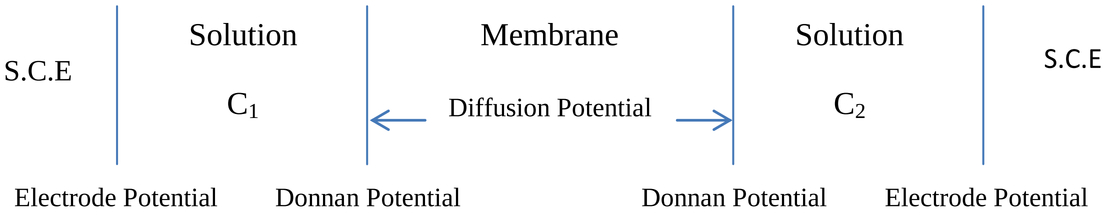
2.1. *Preparation of Membrane*

All the reagents used were of analytical reagent (AR) grade (BDH) without further purification and their solutions were prepared in deionized water.

Parchment supported silver oxalate membrane was prepared by the method of interaction described by Siddiqi et al. [24–27]. First parchment (Supplied by M/s Baird and Tatlock London Ltd.) was soaked in distilled water for about two hours and then tied to the flat mouth of a beaker containing 0.2 M silver nitrate solution. This was suspended for 72 h in a 0.2 M sodium oxalate solution at room temperature. The two solutions were interchanged and kept for another 72 h. In this way, a fine deposition of silver oxalate was obtained on the surface of parchment paper. The membrane thus obtained was well washed with deionized water for the removal of free electrolytes. The membrane was clamped between two half cells of an electrochemical cell. The membrane prior to the measurements had been aged by about 24 h immersion in 1 M in the testing electrolyte.

2.2. *Membrane Potential Measurements*

The potential developed by setting up a concentration cell of the type in scheme 1 described by Siddiqi et al. [28]. The membrane potential was obtained by taking the same electrolyte at different concentrations on the two sides of the membrane, such that the concentration ratio $\gamma = 10$. The potentials were monitored by means of Knick Digital Potentiometer (No. 646). All measurements were carried out using a water thermostat at 30 ± 0.1^{o}C. The solutions were vigorously stirred by a pair of magnetic stirrer in order to be maintained uniform in both the half cells. The 1:1 electrolytes examined were sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH_4Cl), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), ammonium nitrate (NH_4NO_3), sodium nitrite ($NaNO_2$), potassium nitrite (KNO_2), sodium bromide (NaBr), potassium bromide (KBr), ammonium bromide (NH_4Br), sodium acetate (CH_3COONa), potassium acetate (CH_3COOK), and ammonium acetate (CH_3COONH_4).



Scheme 1 [28]

3. **Results and discussion**

3.1. *Evaluation of Thermodynamically Effective Fixed Charge Density*

Effective fixed charge density of parchment-supported silver oxalate membrane has been estimated from membrane potential data. The potentiometric methods used for estimation were: Teorell-Meyer-Sievers method [1, 2] and Kobatake et al. method [3]. The experimentally determined membrane potentials which were generated between both sides of the parchment-supported silver oxalate membrane for various 1:1 electrolytes at different concentrations C_1 and C_2 such that $C_2/C_1 = 10$ are given in Table 1.

Table 1. Values of experimentally measured membrane potential E_m (mV) at 30^{o}C through silver oxalate membrane for various uni-univalent electrolytes of different concentrations at $\gamma = 10$.

(C_2/C_1) M	Electrolytes													
	NaCl	KCl	NH_4Cl	$NaNO_3$	KNO_3	NH_4NO_3	$NaNO_2$	KNO_2	NaBr	KBr	NH_4Br	CH_3O_2Na	CH_3O_2K	$CH_3O_2NH_4$
1/0.1	0.8	1	1.8	4.3	4.3	4.8	2	2.2	0.1	0.6	1.9	7.5	11.2	14.2
0.5/0.05	2	3	3.4	6.4	6.2	6.5	4.9	4.2	1.4	1.8	3.3	9.8	13.5	17.6
0.2/0.02	5.2	6.7	7	9.3	8.4	8.1	8.2	8.8	7.4	6.6	6.3	14	16.3	21.9
0.1/0.01	10.2	10	11.1	12.1	11.1	11.1	14.5	13.2	13.6	14.3	11.2	20.4	22.2	29.5
0.05/0.005	15.6	14.2	16.3	19.1	18.4	15.2	23.8	22.1	20.8	23.7	18.1	29.6	31	34.3
0.02/0.002	20.1	21.6	21.9	22.7	24.5	26	27.1	27.3	27.1	31.2	28.7	38.3	38.6	40.7
0.01/0.001	26.3	29	28.9	30.7	31.1	30.8	32.7	32.2	31.1	34.2	41.3	41.1	41.3	45.1
0.005/0.0005	27.7	31.1	29.2	31.7	34.3	33.6	34.1	36.2	34.2	36.2	42.8	43.6	44	48.3

The values of membrane potentials are low when the membrane is used to separate concentrated solutions whereas they increase with dilution and reach a maximum limit. The signs of membrane potentials with different electrolytes are positive. This means that the membrane is negatively charged and cation selective. The selectivity increases when the concentrations of electrolyte are decreased. The negative charge on the membrane surface may be attributed to adsorption of anions.

3.1.1. *Teorell, Meyer, and Sievers (T. M. S.) Method*

The graphical method of Teorell, Meyer, and Sievers determines the fixed charge density X in equivalent per litter and the cation-to-anion mobility ratio (u_+/u_-) in the membrane phase. Theoretical concentration potentials (E_m) existing across the membrane carrying a net negative charge of unity (X = 1) and different mobility ratios are calculated according to equation (1) [1, 2] as a function of C_2, the concentration ratio (C_1/C_2) being kept at a constant value for different mobility ratios.

$$E_m = 59.16\left[\log\frac{C_2\sqrt{4C_1^2+X^2}+X}{C_1\sqrt{4C_2^2+X^2}+X}+U\log\frac{\sqrt{4C_2^2+X^2}+UX}{\sqrt{4C_1^2+X^2}+UX}\right] \qquad (1)$$

where:

$$U = \frac{u_+ - u_-}{u_+ + u_-} \qquad (2)$$

E_m: membrane potential in millivolts
u_- and u_+: Mobilities of cation and anion respectively in the membrane
C_1 and C_2: Concentrations of the electrolyte solutions on either side of the membrane
X: Charge density expressed in equivalents per liter

The values thus calculated are plotted as a function of log ($1/C_2$) as illustrated in Figure 1. The observed membrane potential values given in Table 1 for each electrolyte solutions are also plotted in the same graph as a function of log ($1/C_2$). The experimental curve is shifted horizontally until it coincides with the theoretical curve. The extent of this shift gives (log X) and coinciding theoretical curve, the value for (u_+/u_-). The values derived in this way are given in Table 2. Some experimental curves do not coincide exactly as demanded by the theoretical method of T.M.S. and very rough approximation has been made. The reason for these discrepancy is low charge density of the membrane. This method gave a satisfactory result for the fixed charge density evaluation, the values of which are found to be low and hence very difficult to determine by the usual exchange reaction.

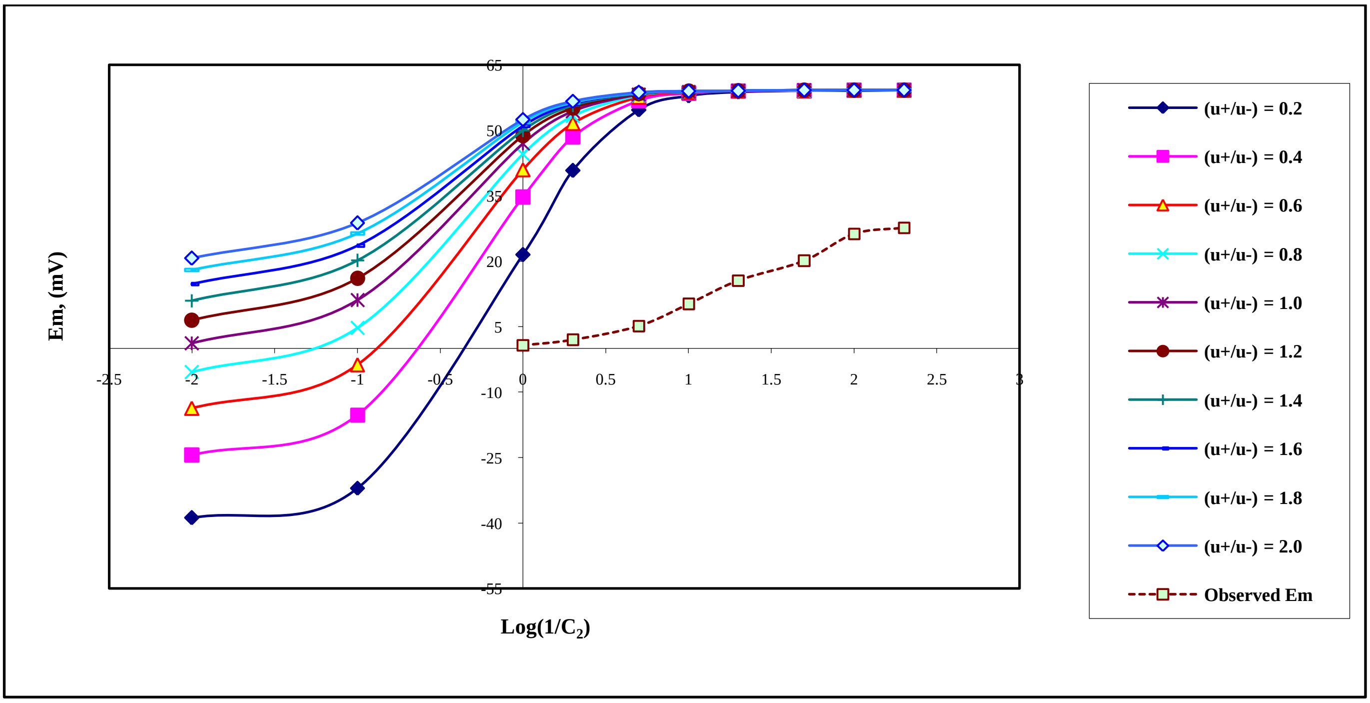


Figure 1. Membrane Potential vs. log ($1/C_2$) in contact with different concentrations of NaCl (TMS method).

Table 2. Comparison of Charge density values X (eq/l) by different methods for various electrolytes for silver oxalate membrane.

Electrolytes	T M S method	Kobatake et. al. method
NaCl	0.014	0.011
KCl	0.013	0.010
NH_4Cl	0.016	0.011
$NaNO_3$	0.007	0.009
KNO_3	0.005	0.007
NH_4NO_3	0.004	0.007
$NaNO_2$	0.013	0.015
KNO_2	0.017	0.013
NaBr	0.019	0.018
KBr	0.018	0.018
NH_4Br	0.014	0.011
CH_3CO_2Na	0.015	0.018
CH_3CO_2K	0.014	0.015
$CH_3CO_2NH_4$	0025	0.026

3.1.2. *Kobatake et al Method*

Equation (3) [3] indicates that a value of β and a relation between α and X can be obtained from a plot of $|\Delta E_{mr}|$ against C_2 at fixed $\gamma = 10$ (in the region of very low concentration, from 0.05 M to 0.005 M – Figure 2). The values of β and the relation between α and X can be determined by evaluating the intercept and initial slope. The value of intercept is equal to (1/β) ln γ, from which β may be evaluated.

$$|\Delta E_{mr}| = \left(\frac{1}{\beta}\right)\ln\gamma - \left(\frac{\gamma-1}{\alpha\beta\gamma}\right)\left(1+\frac{1}{\beta}\right)\left(\frac{C_2}{X}\right) \qquad (3)$$

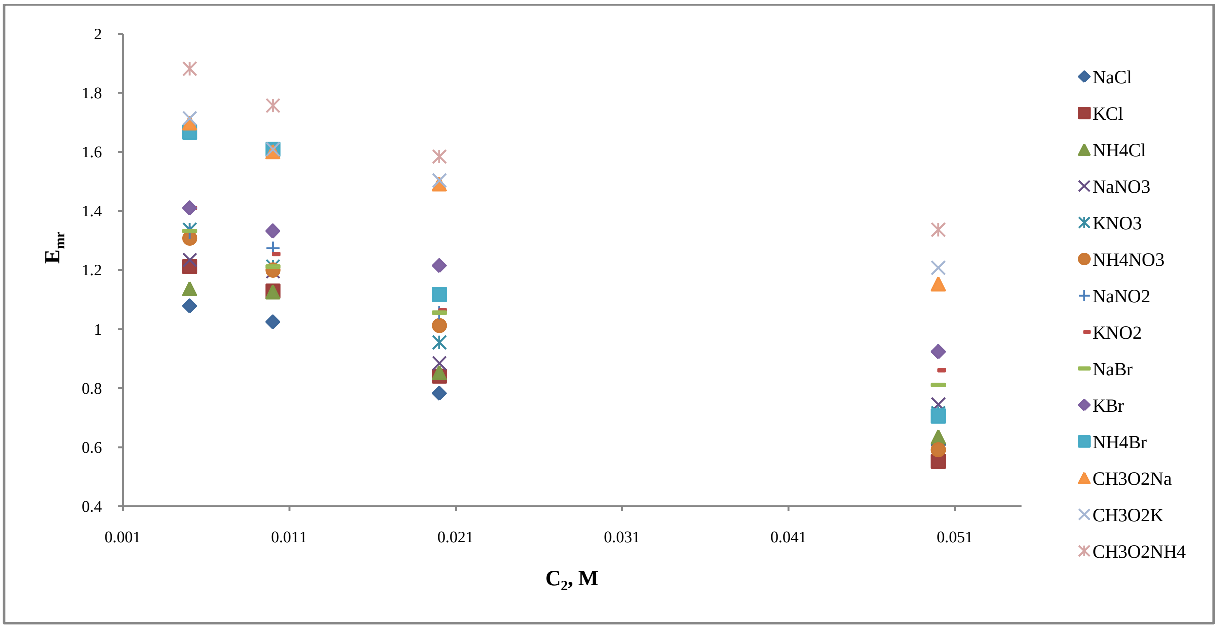


Figure 2. $|E_{mr}|$ vs. C_2 in contact with different electrolytes (at low concentrations).

Equation (4) [3] indicates that the intercept of a plot of $(1/t_{-app})$ against $(1/C_2)$ at fixed $\gamma = 10$ allow the values of α to be determined in the region of high salt concentrations (from 1 M to 0.05 M). The values of the apparent transference number of co-ion calculated using equation (5) [3] are given in Table 3. Plots of $(1/t_{-app})$ against $(1/C_2)$ for various 1:1 electrolytes are given in Figure 3. From the value of intercept, γ may be evaluated.

$$\frac{1}{t_{-app}} = \frac{1}{1-\alpha}\left[\frac{(1+\beta-2\alpha\beta)(\gamma-1)\alpha}{2(1-\alpha)^2\ln\gamma}\right]\frac{X}{C_2} \qquad (4)$$

$$\Delta E_{mr} = (1-t_{-app})ln\gamma \qquad (5)$$

Where:
α and β: Parameters independent of salt concentration
ΔE_{mr}: Reduced membrane potential
$\gamma = \frac{C_2}{C_1}$
t_{-app}: Apparent transference number for co-ion in a negatively charged membrane

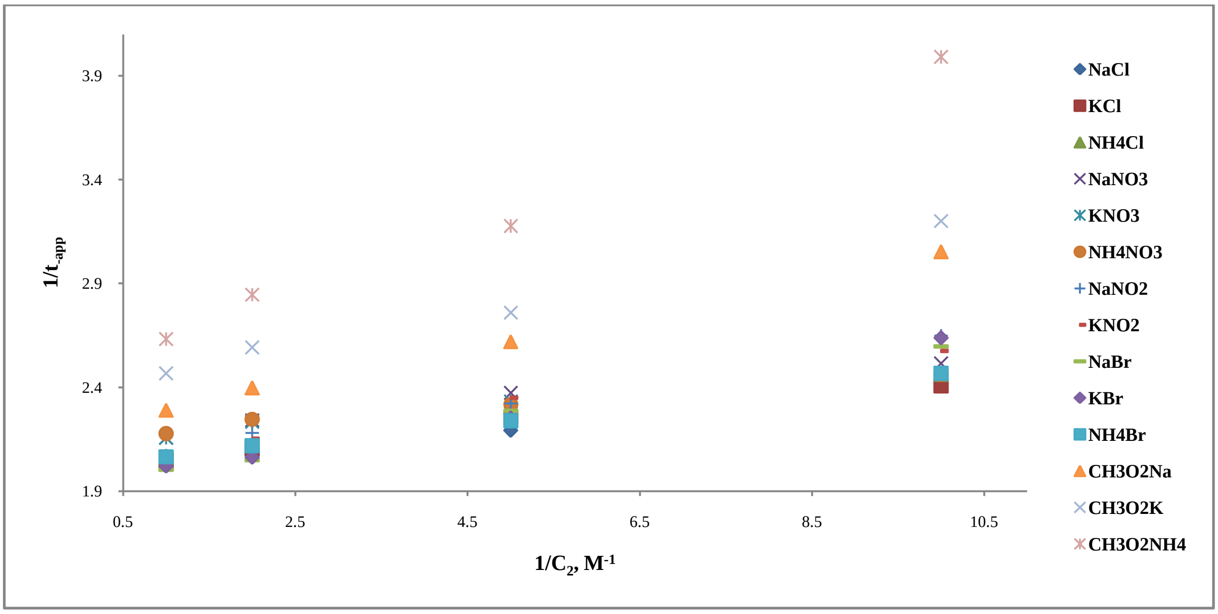


Figure 3. $1/t_{-app}$ vs. $1/C_2$ in contact with different electrolytes (at high concentrations).

Table 3. Values of apparent transference number t_{-app} at 30°C across silver oxalate membrane calculated from membrane potentials for various uni-univalent electrolytes of different concentrations at γ = 10.

(C_2/C_1) M	Apparent transference number, t_{-app}													
	NaCl	KCl	NH_4Cl	$NaNO_3$	KNO_3	NH_4NO_3	$NaNO_2$	KNO_2	NaBr	KBr	NH_4Br	CH_3O_2Na	CH_3O_2K	$CH_3O_2NH_4$
1/0.1	0.493	0.492	0.485	0.464	0.464	0.459	0.483	0.481	0.499	0.495	0.484	0.437	0.405	0.380
0.5/0.05	0.483	0.475	0.471	0.446	0.448	0.445	0.459	0.464	0.488	0.485	0.472	0.417	0.386	0.351
0.2/0.02	0.456	0.443	0.441	0.421	0.429	0.432	0.431	0.426	0.437	0.444	0.447	0.382	0.362	0.315
0.1/0.01	0.414	0.415	0.406	0.398	0.406	0.406	0.377	0.388	0.385	0.379	0.405	0.328	0.312	0.251
0.05/0.005	0.368	0.380	0.362	0.339	0.344	0.371	0.299	0.313	0.324	0.300	0.347	0.250	0.238	0.210
0.02/0.002	0.330	0.317	0.315	0.308	0.293	0.280	0.271	0.269	0.271	0.236	0.257	0.176	0.174	0.156
0.01/0.001	0.278	0.255	0.256	0.240	0.237	0.240	0.224	0.228	0.237	0.211	0.151	0.153	0.151	0.119
0.005/0.0005	0.266	0.237	0.253	0.232	0.210	0.216	0.212	0.194	0.211	0.194	0.138	0.131	0.128	0.092

For the evaluation of X, there are two limiting cases: (a) in dilute range from the slope of equation (3). This value of X is designated by X_d; (b) in the concentrated range from the slope of equation (4). This value of X is designated by X_c. The values of α, β, X_d, and X_c derived in this way for membrane and 1:1 electrolytes are given in Table 4

In the present investigation with parchment-supported silver oxalate membrane, the X_d values are found to be higher than X_c values. It is also noted that the lower values of X (X_c) are closer to the charge density values determined by TMS method.

3.2.*Evaluation of Thermodynamically Effective Fixed Charge Density at different concentration ratios*

Membrane potentials through a parchment-supported silver oxalate membrane at different concentration ratios (γ = 2, 5, 10, 15, and 20) for a wide interval concentration have been studied. The results have been analyzed by Kobatake theory.

Figure 4 illustrates plots of $|\Delta E_{mr}|$ against C_2 in the region of low concentrations for different 1:1 electrolytes at different γ values. However, Figure 5 shows plots of $1/t_{-app}$ against $1/C_2$ in the region of high concentrations also at different γ values.

Table 4. Derived values of silver oxalate membrane parameters (α, β, X_d, X_c) at 30°C with different electrolytes at γ = 10 using Kobatake et. Al. theory.

Electrolytes	α	β	X_d, eq/l	X_c, eq/l
NaCl	0.496	2.229	0.045	0.011
KCl	0.505	1.970	0.038	0.010
NH_4Cl	0.508	2.067	0.044	0.011
$NaNO_3$	0.534	1.966	0.046	0.009
KNO_3	0.535	1.819	0.041	0.007
NH_4NO_3	0.538	1.764	0.005	0.007
$NaNO_2$	0.507	1.812	0.078	0.015
KNO_2	0.510	1.734	0.060	0.013
NaBr	0.483	1.792	0.065	0.018
KBr	0.482	1.645	0.077	0.018
NH_4Br	0.506	1.421	0.050	0.011
CH_3CO_2Na	0.548	1.365	0.072	0.018
CH_3CO_2K	0.582	1.358	0.066	0.015
$CH_3CO_2NH_4$	0.599	1.264	0.072	0.026

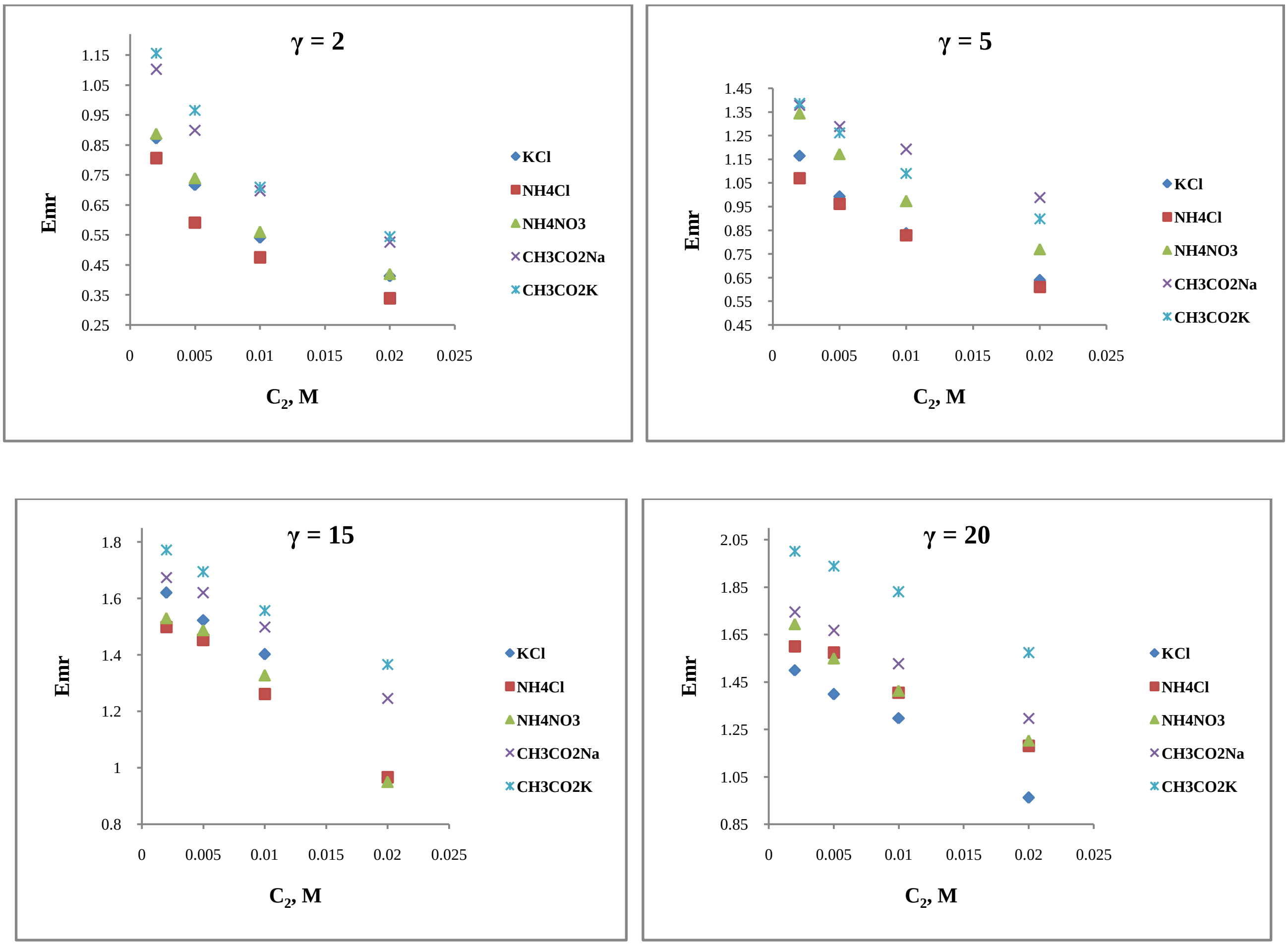


Figure 4. $|E_{mr}|$ vs. C_2 in contact with different electrolytes (at low concentrations) at different γ values.

Values of α, β, and X are given in Table 5. For each electrolyte, these values are essentially independent of γ.

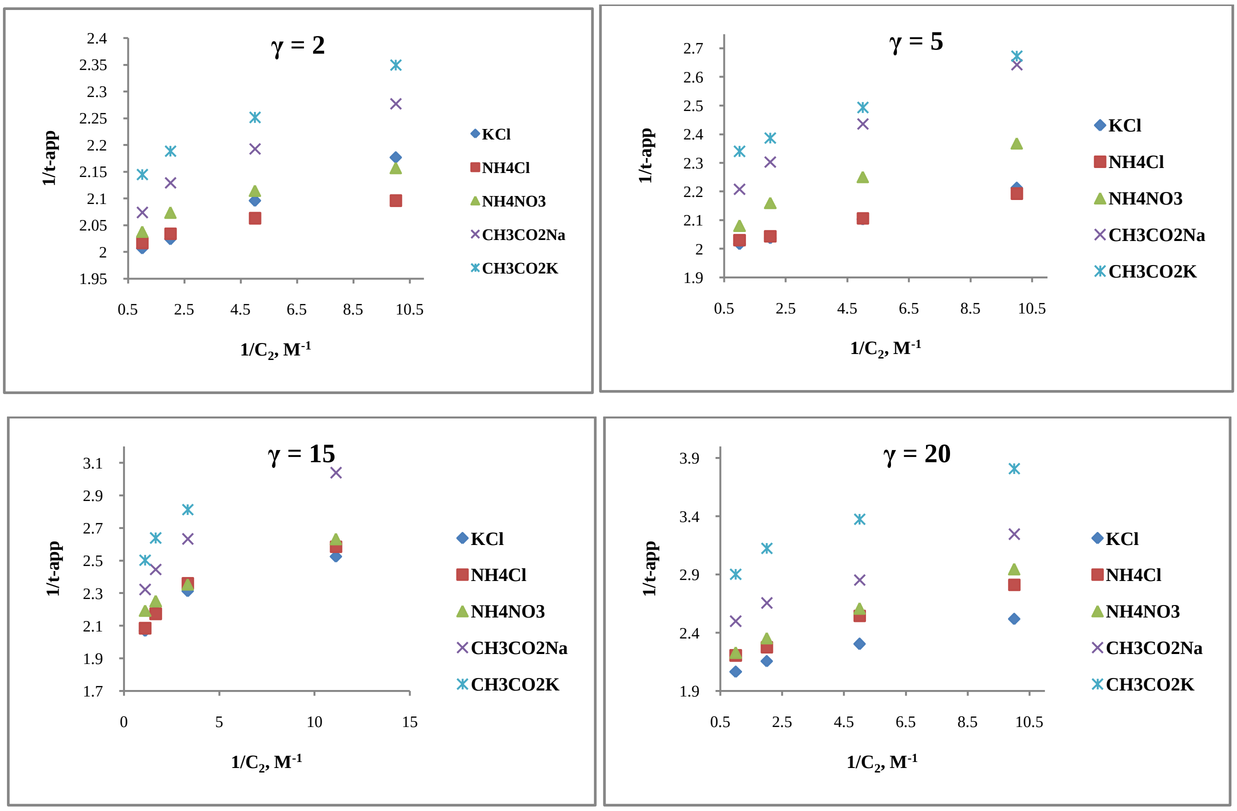


Figure 5. $1/t_{app}$ vs. $1/C_2$ in contact with different electrolytes (at high concentrations) at different γ values.

Table 5. Derived values of silver oxalate membrane parameters (α, β, X_c) at 30°C with different electrolytes at different concentration ratios (γ) using Kobatake et. al. theory.

Electrolytes	γ	α	β	X_c, eq/l
KCl	2	0.484	0.944	0.019
	5	0.497	1.548	0.013
	10	0.505	1.889	0.010
	15	0.521	1.734	0.006
	20	0.509	1.664	0.005
NH_4Cl	2	0.511	1.057	0.007
	5	0.504	1.621	0.011
	10	0.508	1.983	0.011
	15	0.521	1.874	0.007
	20	0.528	1.636	0.007
NH_4NO_3	2	0.510	0.919	0.011
	5	0.519	0.809	0.011
	10	0.538	1.722	0.007
	15	0.535	1.830	0.006
	20	0.534	1.817	0.007
CH_3CO_2Na	2	0.549	0.749	0.021
	5	0.559	1.230	0.026
	10	0.548	1.350	0.018
	15	0.559	1.670	0.008
	20	0.572	1.713	0.007
CH_3CO_2K	2	0.592	0.718	0.022
	5	0.593	1.273	0.019
	10	0.582	1.349	0.015
	15	0.586	1.589	0.007
	20	0.616	1.522	0.006

Conclusions

The analytical methods based on T. M. S. and Kobatake et. al. for membrane potential gave satisfactory values for fixed charge densities. The values of which were quite low (in order of 0.01-0.001) and hence very difficult to determine by the usual exchange methods.

The values of fixed charge density is a parameter characteristic of a given pair of membrane and electrolyte, not a given membrane only. It was also noted that for a given membrane-electrolyte system the values of α, β, and X are essentially independent of γ, although there was observed such trend that X decreases systematically as γ increases.

It was observed a good agreement between values obtained by different theories and the fixed charge density values were the same order of magnitude.

Acknowledgments-The authors are pleased to acknowledge University of Benghazi (UOB) and Chemistry Department for providing the facilities for the research.

References

1. Teorell T., *Proc. Soc. Exp. Biol. Med.* 33 (1935) 282
2. Meyer K. H., Sievers J. F., *Helv. Chem. Acta* 19 (1936) 649
3. Kobatake Y., Noriaki T., Toyoshima Y., Fujita H., *J. Phys. Chem.* 69 (1965) 3981
4. Shahi V. K., Gohil G. S., Nagarale R. K., Binsu V. V., *J. Colloid Interface Sci.* 298 (2006) 845
5. Shahi V. K., Mahendra K., Bijay P. T., *J. Membr. Sci.* 340 (2009) 52
6. Khan M. M. A., Rafiuddin, Inamuddin, *J. Ind. Eng. Chem.* 18 (2012) 1391
7. Shahi V. K., Amaranadh J., Prakash S., *React. Funct. Polym.* 72 (2012) 115
8. Khan M. M. A., Rafiuddin, Inamuddin, *J. of Ind. Eng. Chem.* 18 (2012) 1813
9. Lin Y. S., Burggraaf A. J., J. *Am. Ceram. Soc.* 74 (1991) 219
10. Badrul Islam, Elhaddad S., *Int. J. Chem. Sci.* 10 (2012) 1043
11. Ansari M. A., Manoj K., Neelam S., Dadoriya K. S., Kushwaha R. S., Shahnaz Ayub, *.Adv. Appl. Sci. Res.* 3 (2012) 251
12. Kumar, Rakesh, Obrai, Sangeeta, Harmaz, Aparna, *Der. Chem. Sinica.* 4 (2011) 219
13. Demisch, Pusch W., *J. Electrochem. Soc.* 123 (1976) 370
14. Toyoshima Y., Nozaki H., *J. Phys. Chem.* 73 (1969) 2134
15. Aizawa M., Tomono S., Suzuki S., *J. Membr. Sci.* 6 (1980) 235
16. Higa M., Tonioka A., Miyasaka K., J. Membr. Sci., (1990), 49, 145
17. Elsherif K. M., El-Hashani A., El-Dali A., *J. Appl. Chem.* 2 (2013) 1543
18. Elsherif K. M., El-Hashani A., El-Dali A., *Ann Chemischen Forschung* 1 (2013) 15
19. Elsherif K. M., El-Hashani A., El-Dali A., *Der Chem. Sin.* 4 (2013) 13
20. Elsherif K. M., El-Hashani A., El-Dali A., *Int. J. Adv. Sci. Tech. Res.* 1 (2014) 638
21. Elsherif K. M., El-Hashani A., El-Dali A., Saad M., *Int. J. Chem. Pharm. Sci.* 2 (2014) 890
22. Elsherif K. M., El-Hashani A., El-Dali A., Musa M., *Int. J. Anal. Bioanal. Chem.* 4 (2014) 58
23. Elsherif K. M., El-Hashani A., El-Dali A., *Int. J. Res. Pharm. Chem.* 4 (2014) 267
24. Siddiqi F. A., Lakshminarayanaiah N., Mohammad N. B., *J. Polym. Sci.* 9 (1971) 2853
25. Siddiqi F. A., Lakshminarayanaiah N., Mohammad N. B., *J. Polym. Sci.* 9 (1971) 2869
26. Siddiqi F. A., NasimBeg N., Abdul Haque, Surendra P. S., *Bull. Chem. Soc. Jpn.* 49 (1976) 2858
27. Siddiqi F. A., NasimBeg N., Abdul Haque, Surendra P. S., *Bull. Chem. Soc. Jpn.* 49 (1976) 2864
28. Siddiqi F. A., Pratap S., J. Electroanal. Chem., 1969, 23, 137

(2017) ; http://www.jmaterenvironsci.com