REFERENCES

1. Stokes, R.H. and Levien, B.J. "Transference Numbers and Activity Coefficients in Zinc Iodide Solutions at 25° ." J.Amer. Chem. Soc. 68(1946) : 1852-1854.

2. Wolten, W.G. and King, C.V. "Transference Numbers of Zinc and Cadmium Sulfates at 25°, as Function of the Concentration." J. Amer. Chem. Soc. 71(1949) : 576-578.

3. Breck, W.G. "The Cation Transport Numbers of Certain Cadmium and Tallous Solutions." Trans. Faraday Soc. 52(1956) : 247-250.

4. Alberty, R.A. and King, E.L. "Moving Boundary Systems Formed by Weak Electrolytes. Study of Cadmium Iodide Complex." J. Amer. Chem. Soc. 73(1951) : 517-523.

5. Lang, R.E. and King, C.V. "Transference Numbers in Aqueous Zinc and Cadmium Sulfates" J. Amer. Chem. Soc. 76(1954) : 4716-4718.

6. Spiro, M. Transference Numbers in Physical Methods of Chemistry Part II A pp. 205-295. A. Weiss berger, Ed., Wiley & Sons, New York, 1971.

7. Cady, H.P. and Longsworth, L.G. "Modification of the Moving Boundary Method for the Determination of Transference Numbers." J. Amer. Chem. Soc. 51(1929) : 1656-1664.

8. Hartley, G.S., Drew, E. and Collie, B. "A New Method for the Determination of Transport Numbers. III The Balance - Boundary Apparatus." Trans. Faraday Soc. 30(1934) : 657-662 appeared in C.A. 28(1934) : 7115^7.

9. Gardon, A.R. and Kay, R.L. " Anomalous Adjustment of Indicator Concentration in Moving Boundary Measurements of Transference Numbers." J. Chem. Phys. 21(1953) : 131-135.

10. Muir, D.R. Graham, J.R., and Gordon, A.R. "The Determination of the Adjusted Indicator Concentration behind a Moving Boundary in Dilute Solution; the system KCl - NaCl in Water at 25°." J. Amer. Chem. Soc. 76(1954) : 2157-2160.

11. Longsworth, L.G. "Transference Numbers of Aqueous Solutions of KCl, LiCl and HCl at 25° by the Moving Boundary Method." J. Amer. Chem. Soc. 54(1932) : 2741-2758.

12. Gwyther, J.R. and Spiro, M. "Volume Correction for Direct and Indirect Moving Boundary Transference Measurements." J.C.S. Faraday I 72(1976) : 1410-1418.

13. Kay, R.L., Vidulich, G.A. and Fratiello, A. "Potentiometric Method of Direct Moving Boundary in the Determination of Transference Numbers." Chem. Instrum. 1(1969) : 361-382 appeared in C.A. 71(1969) : 84674.

14. Indaratna, K. "Transport Properties of Dilute Aqueous Cadmium Chloride Solutions." Ph.D. Thesis, Otago University, 1980.

15. Kruh, R.F. and Standley, C.L. "An X-ray Diffraction Study of Aqueous Zinc Chloride Solutions" Inorg. Chem. 1(1962) : 941-943.

16. Irish, D.E., Macarrol, B. and Young, T.E. "Raman Study of Zinc Chloride Solutions" J.Chem. Phys. 39(1964): 3436-3444.

17. Lutfullah, Dunsmore, H.S. and Paterson, R. "Re-Determination of the Standard Electrode Potential of Zinc and Mean Molal Activity Coefficients for Aqueous Zinc Chloride at 298.15 K" J.C.S. Faraday I 72(1976) : 495-503.

18. Stokes, R.H. "Thermodynamic Study of Bivalent Metal Halides in Aqueous Solution. XVI. Complex-ion Formation in Zinc Halides solutions" Trans. Faraday Soc. 44(1948) : 137-141 appeared in C.A. 42(1948) : 6698 b.

19. Shedlovsky, T. and Brown, A.S. "The Electrolytic Conductivity of Alkaline Earth Chlorides in Water at 25° " J. Amer. Chem. Soc. 56(1934) : 1066-1071.

20. Longsworth, L.G. "Transference Numbers of Aqueous Solutions of Some Electrolytes at 25° by the Moving Boundary Method" J. Amer. Chem. Soc. 57(1935) : 1185-1191

21. Agnew, A. and Paterson, R. "Transport in Aqueous Solutions of Group IIB Metal Salts at 298.15 K. V. Irreversible Thermodynamic Parameters for $Zn(ClO_4)_2$ and Verification of Onsager's Reciprocal Relationships" J.C.S. Faraday I 74(1978) : 2885-2895.

22. Egan, D.M. and Partington, J.R. "Transport Numbers of Zinc Halides" J. Chem. Soc. 67(1945) : 191-197.

23. Harris, A.C. and Parton, H.N. "The Transport Numbers of Zinc Chloride From E.M.F. Measurements" Trans. Faraday Soc. 36(1940) : 1139-1141.

24. Agnew, A. and Paterson, R. "Transport in Aqueous Solutions of Group IIB Metal Salts at 298.15 K. VI. Irreversible Thermodynamic Palameters for Zinc Chloride and Verification of Onsager's Reciprocal Relationships" J.C.S. Faraday I 74(1978) : 2896-2906.

25. Robinson, R.A. and Stokes, R.H. in Electrolyte Solutions 2nd Ed., Butterworth, London, 1959.

26. McInnes, D.A. and Longsworth, L.G. "Transference Numbers" Chem. Rev. 11(1932) : 171-228.

27. Longsworth. L.G. "Moving Boundary Studies on Salt Mixtures" J. Amer. Chem. Soc. 67(1945) : 1109-1119.

28. Dole, V.P. "A Theory of Moving Boundary Systems Formed by Strong Electrolytes" J. Amer. Chem. Soc. 67(1945) : 1119-1125.

29. Longworth, L.G. "The Concentration Distribution in two-Salt Moving Boundaries" J.Amer.Chem.Soc. 66(1944):449-453.

30. Lewis, G.N. "The Theory of the Determination of Transference Number by the Moving Boundaries" J. Amer. Chem. Soc. 32(1910) : 862-869.

31. Bearman, R.J. "Nonequilibrium Thermodynamics of the Simple Moving Boundary Experiment" J. Chem. Phys. 36(1962) : 2432-2436.

32. Milios, P. and Newman, J. "Moving Boundary Measurement of Transference Numbers" J. Phys. Chem. 73(1969) : 298-303.

33. Smits, L.J.M. and Duyvis, E.M. "Transport Numbers of Concentrated Sodium Chloride Solution at 25° " J. Phys. Chem. 70(1966) : 2747-2753.

34. Spiro, M. "Determination of Transference Numbers of Weak Electrolyte Solutions by the Moving Boundary Method" Trans. Faraday Soc. 61(1965) : 350-359.

35. Smith, E.R. and McInnes, D.A. " The Moving-Boundary Method for Determining Transference Numbers. IV. The Transference Numbers of Some Chloride Solutions" J. Amer. Chem. Soc. 47(1925) : 1009-1015.

36. Tamas, J., Kaposi, O. and Scheiber, P. "Application of the Moving-Boundary Method to the Determination of the Ion Transport Number of Concentrated Aqueous Solutions" Acta. Chim. Acad. Sci. Hung. 48(1966) : 309 appeared in C.A. 65(1966) : 11364 c.

37. Gwyther, J.R. and Spiro, M. "Solvent Correction for Hittorf and Direct and Indirect Moving Boundary Transference Measurements" J.C.S. Faraday I 72(1976) : 1419-1424.

38. Vogel, A.I. in Quantitative Inorganic Analysis, 3rd Ed., Longmans, London, 1971.

39. Stokes, R.H. "The Conductance of Hydrochloric acid at 25° " J. Phys. Chem. 65(1961) : 1242-1247.

40. Daniels, F. in Experimental Physical Chemistry, 5th.Edition, Mc-Graw Hill company, INC, 1956.

41. Stokes, R.H. "The Soret Effect as a Source of Error in Conductance Measurements" J. Phys. Chem. 65(1961) : 1277-1278.

42. Jones, G. and Bradshaw, B.C. "The Measurement of the Conductance of Electrolytes. V. A Redetermination of the Conductance of Standard Potassium Chloride Solutions in Absolute Units" J. Amer. Chem. Soc. 55(1933) : 1780-1800.

43. Shedlovsky, T. "The Electrolytic Conductivity of Some Uni-Univalent Electrolytes in Water at 25° " J. Amer. Chem. Soc. 54(1932) : 1411-1428.

44. Lind, J.E., Zwolenik, J.J. and Fuoss, R.M. "Calibration of Conductance Cells at 25° with Aqueous Solutions of Potassium Chloride" J. Amer. Chem. Soc. 81(1959) : 1557-1559.

45. Miller, D.G. "Application of Irreversible Thermodynamics to Electrolyte Solutions. I. Determination of Ionic Transport Coefficient l_{ij} for Isothermal Vector Transport Processes in Binary Electrolyte System" J. Phys. Chem. 70(1966) : 2639-2659.

46. Owen, B.B. and Gery, R.W. "The Electrolytic Conductivity of Zinc Sulfate and Copper Sulfate in Water at 25 " J. Amer. Chem. Soc. 60(1938) : 3074-3078.

47. Purser, E,P. and Stokes, R.H. "Transference Numbers in Aqueous Solutions of Zinc Sulfate" J. Amer. Chem. Soc. 73(1951) : 5650-5652.

48. Paterson, R., anderson, J. and Anderson, S.S. "Transport in Aqueous Solutions of Group IIB Metal Salts at 298.15 K Part I. Isothermal Transport Properties of Cadmium Iodide" J.C.S. Faraday I 73(1977) : 1763-1771.

APPENDIX 1

Calculation of the Concentration of Solutions from Conductometric Analysis

From the conductometric analysis, solvent corrected conductivities of diluted samples, amounts of samples and added conductivity water are obtained. Three values are used to determine the concentrations of sample solutions. The general procedure is outlined as follows :

1) A molar concentration of the diluted solution is assumed or estimated from knowledge of the weight dilution and crude estimate of the concentration of the sample or from some available K vs. concentration charts.

2) From linear deviation function or apparent limiting equivalent conductance vs. concentration equations or plots, (see Appendix 2), first approximated Λ corresponding to the value of concentration M estimated in (1) can be obtained.

3) Calculate a more accurate concentration value from

$$\frac{10^3 K}{\Lambda} = |Z| M$$

4) Use the new value of M from (3) and repeat the procedure from (1) to (3) until the same value of M is obtained. Usually, self-consistency is achieved after 2-3 cycles.

5) Conversion of molar concentration of the diluted solution obtained in (4) to a molal scale is done by successive approximation method described in Appendix 3.

6) From known weights of a sample solution used and amount of conductivity water added, the concentration of the sample solution can then be determined.

APPENDIX 2

Linear Deviation Function vs. Concentration of Some Dilute Solutions

For dilute 1:1 electrolytes the Shedlovsky apparent limiting equivalent conductance defined as

$$\Lambda^{o'} = \frac{\Lambda + 60.65\sqrt{M}}{1 - 0.23\sqrt{M}}$$

give a linear function with concentration M (25).

Plots of $\Lambda^{o'}$ vs. M were prepared from different values of Λ and M available from some literature data. For KCl solutions between 0 to 0.01 mol dm^{-3} both Λ and $\Lambda^{o'}$ vary only slightly with concentration (45). $\Lambda^{o'}_{KCl}$ varies from 149.96 to 150.80 $cm^2\Omega^{-1}equiv^{-1}$., while $\Lambda^{o}_{KCl} = 149.86$ $cm^2\Omega^{-1}equiv^{-1}$ (45).

For HCl solutions, R.H. Stokes (39) has derived a deviation function,

$$x = \Lambda + \frac{158.74\sqrt{M}}{1 + 1.316\sqrt{M}}$$

for the range of concentration between 0 to 0.18 mol dm^{-3} x lies in a narrow range of 426.06 - 426.84 $cm^2\Omega^{-1}equiv^{-1}$.

Inspection of Λ vs. concentration of $ZnCl_2$ solutions obtained in this work suggest that in the concentration range 0.001 to 0.01 mol dm^{-3},

$$f(\Lambda) = \Lambda + 208\sqrt{M}$$

varies linearly with concentration. This function changes value from 129.90 to 130.86 $cm^2\ \Omega^{-1}\ equiv^{-1}$. between 0.001 to 0.01 mol dm^{-3} $ZnCl_2$ solutions.

These functions allow close estimation of Λ from approximation values of concentration of the electrolyte solution under study.

APPENDIX 3

Successive Approximation Method for Conversion of Molar to Molal Concentration in Dilute Solutions

Three useful expressions are :

$$m = \frac{M}{d - M M_W \times 10^{-3}} \quad \text{mol kg}^{-1} \qquad (1)$$

$$M = \frac{md}{1 + mM_W \times 10^{-3}} \quad \text{mol dm}^{-3} \qquad (2)$$

Molar masses, M_W of electrolytes used in this work were obtained from the tabulated atomic weights. The densities of electrolytes solution, d are calculated from linear equations of d vs. weight percent , or given in Appendix 4.

Conversion of molar concentration to molal scale was done by first assuming any value of m close to the known value of M. From this value the obtained weight percent can be used to calculate the corresponding density. Substituting these values of d and m into equation (2) then M is calculated. This value of M is somewhat different from the original value. By varying the value of m and repeat the procedure the exact value of M can be obtained.

APPENDIX 4

The Density Equations of Some Dilute Electrolyte Solutions

Electrolytes	Density at 25 C/gm cm^{-3}	Concentration range/weight%
KCl	$d^{25} = 0.99707+0.00635W$	0-3
HCl	$d^{25} = 0.99707+0.0049W$	0-4
$ZnCl_2$	$d^{25*} = 0.99704+(8.958W + 0.928751W^2)\times 10^{-3}$	0.1-1
$ZnCl_2$	$d^{25*} = 0.99704 + 0.00923W$	0-0.1

* From the analysis of the density data.

W is the weight percent of the electrolytes.

The data of density KCl and HCl were obtained from reference (14).

VITA

Miss Benchang Sangchakr was graduated from Faculty of Science, Sri Nakharinwirot University (Prasarn Mitr Campus). She recieved her B.Sc. in Chemistry in 1979. During the study towards the Master's degree of Science, she was supported by Dr. Thab Neelaniti Foundation Scholarship.