A Study of Concentrated Solutions of Mixed Electrolytes. Ultrasonic Velocities and Viscosities of Mixtures of Aqueous Solutions of Potassium and Sodium Chlorides at High Concentrations

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Stearn,[1] Ruby and Kawai,[2] and Smith and Gortner[3] determined the conductivity of concentrated aqueous mixtures of alkali halides. The conductivity of mixed salt solutions is not strictly additive. In these mixtures, the ion of a higher mobility is slowed down while that of a lower mobility is speeded up. Onsager and Fuoss[4] and Van Rysselberghe and Nutting[5] gave quantitative theories for the mobility changes occuring in mixed electrolyte solutions. However, the rather anomalous behaviour of mixtures of electrolyte solutions has not been properly explained; often such behaviour may be attributed to the ion pairing on complex formation and ionic hydration. O'Connor[6] examined mixtures of calcium and strontium dithionates in different proportions and found the same equivalent conductivity throughout the concentration range examined. It has been felt by previous workers that the effect of the hydration of the ions on the electrical conductivity is a factor of major importance. Against this background, we have undertaken a very systematic study of mixtures of potassium and sodium chlorides from the points of view of ionic hydration and viscosity.

Experimental Procedure

The Preparation of Solutions.—All solutions were made by weighing the constituents. At a chosen constant molality of one salt, mixtures were made in such a way that the molality of the other salt was increased in steps. This was repeated systematically by choosing different increasing molalities of the first salt. For instance, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 m of sodium chloride could be obtained at each of the potassium chloride molalities of 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5, subject to both the constituents being soluble. The potassium and sodium chlorides used were of the B. D. H. Analar variety. Solutions were prepared in distilled water.

Ultrasonic Velocities.—The measurements of ultrasonic velocities were made by the Debye and Sears[7] diffraction method. The frequency of the piezo-electric quartz oscillator used in our experiments was 5 Mc./s. The third-order diffraction fringes were taken in all the cases for measurement. Hilger's X-ray microphotometer L 486 was used with a Multiflex galvanometer with a sensitivity of 8×10^{-9} amp./mm. to measure the distance between the fringes.

The hydration numbers were calculated by Passynsky's method:[8]

$$\text{Hydration number}=\frac{n_1}{n_2}\left\{1-\frac{\beta}{\beta_0}\right\} \tag{1}$$

where n_1 and n_2 are the numbers of the moles of the solvent and of the solute respectively, and β and β_0 are the adiabatic compressibilities of the solution and solvent respectively. The adiabatic compressibility is given by:

$$\beta_s=\frac{1}{u^2\rho} \tag{2}$$

where u is the ultrasonic velocity and ρ, the density of the medium.

For measuring the ultrasonic velocity of the solutions at 34.9±0.05°C, a special water-jacketted stainless-steel cubical cell with a chromium-plated inside was fabricated with two optical-plane glass windows cemented on opposite faces to give a perfect transmission of the sodium light. The cell was thermostated at 34.9±0.05°C.

The Measurement of Viscosities.—A Cannon-Fenske type viscometer was used, immersed in a glass-walled thermostat at 34.9±0.05°C. The viscosity values reported herein are subject to an error of ±0.5%. The flow time of the solutions ranged from 62.0 sec. to 93.0 sec. measured to an accuracy of ±0.2 sec.

Density.—A 10 ml. picnometer was used. Care was taken that the picnometer and its contents attained the thermostat temperature before they were weighed. A Sartorius semi-micro single-pan balance accurate to the fifth place was used for weighing.

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[1] A. E. Stearn, *J. Am. Chem. Soc.*, **44**, 670 (1922).

[2] C. E. Ruby and J. Kawai, ibid., **48**, 1119 (1926).

[3] A. K. Smith and R. A. Gortner, *J. Phys. Chem.*, **37**, 79 (1933).

[4] L. Onsager and R. M. Fuoss, ibid., **36**, 2689 (1932).

[5] P. Van Rysselberghe and L. Nutting, *J. Am. Chem. Soc.*, **56**, 1435 (1934).

[6] E. A. O'Connor, *Nature*, **139**, 151 (1937).

[7] P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci.*, **18**, 409 (1932).

[8] A. Passinski, *Acta Physicochimica*, **8**, 385 (1938).

Results and Discussion

Figures 1A and 1B show that the viscosity varies exponentially with the ionic strength of the electrolyte mixture:

$$\eta = A\exp[B\mu] \tag{3}$$

where A and B are constants, and μ and η are the ionic strength and viscosity of the solution respectively. In Fig. 1A, a few points at a higher ionic strength in a solution of lower potassium chloride concentrations are off the straight line. In Fig. 1B, the exponential relationship is valid in most cases, except at low ionic strengths containing lower sodium chloride concentrations. Up to a 1.0 m sodium chloride concentration, the viscosity falls or remains almost constant initially, and then there is a linear rise. The initial effect may be ascribed to the well-known negative viscosity effects due to potassium chloride.

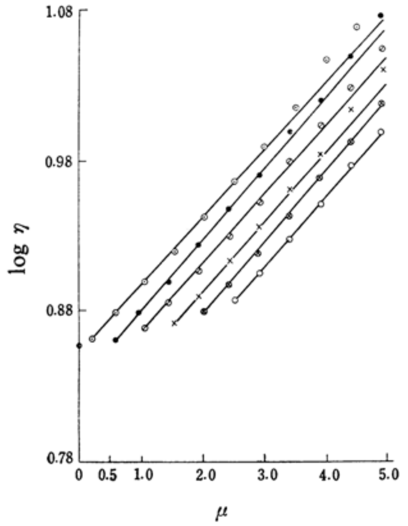

Fig. 1A

⊙——⊙ 0.1 m kcl Base
●——● 0.5 m kcl Base
⊖——⊖ 1.0 m kcl Base
×——× 1.5 m kcl Base
⊗——⊗ 2.0 m kcl Base
○——○ 2.5 m kcl Base

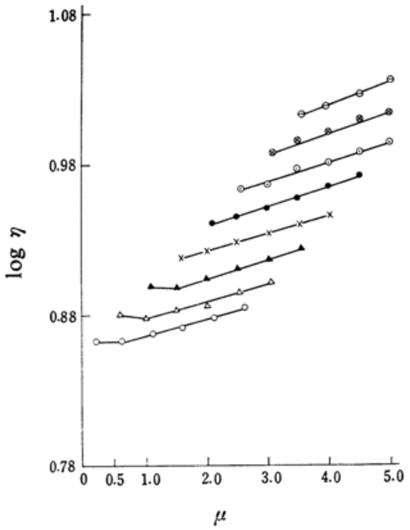

Fig. 1B

○——○ 0.1 m NaCl
△——△ 0.5 m NaCl
▲——▲ 1.0 m NaCl
×——× 1.5 m NaCl
●——● 2.0 m NaCl
⊙——⊙ 2.5 m NaCl
⊗——⊗ 3.0 m NaCl
⊖——⊖ 3.5 m NaCl

Table IIA gives the intercepts and slopes of the linear plots of Figs. 1A and 1B. In all the cases, the intercepts, ideally speaking should have corresponded to $\log_{10} \eta_{H_2O}$, which is 0.858. In Fig. 1A all intercept values are less than 0.858, whereas the reverse is the case with the intercepts in Fig. 1B, excepting that which corresponds to 0.1 m sodium chloride. One interesting observation is that, for purposes of viscosity, the solution of a constant molality chosen as the base of reference, in which varying concentrations of the other salts are investigated, acts as the

TABLE I. DENSITY OF THE MIXED ELECTROLYTE SOLUTIONS (ρ in g./ml.)

Molal concn. of NaCl	Molal concn. of KCl					
	0.1	0.5	1.0	1.5	2.0	2.5
0.1	1.00253	1.02144	1.04194	1.06310	1.08098	1.10225
0.5	1.01807	1.03636	1.05631	1.07760	1.09489	1.11368
1.0	1.03683	1.05437	1.07343	1.09806	1.11016	1.12972
1.5	1.05421	1.07248	1.09004	1.10960	1.12588	1.14371
2.0	1.07230	1.09071	1.10607	1.12523	1.14085	1.15895
2.5	1.08870	1.10449	1.12246	1.13824	1.15435	1.16478
3.0	1.10482	1.12344	1.13649	1.15440	1.16845	—
3.5	1.12058	1.13575	1.15105	1.16946	—	—
4.0	1.14251	1.15162	1.16521	—	—	—
4.5	1.15056	1.16811	1.17921	—	—	—

TABLE IIA. VALUES OF INTERCEPTS AND SLOPES OF PLOTS IN GRAPHS IA AND IB

Graph IA

Molality of KCl kept constant	Intercept	Slope	0.858−Col. (2)
0.1	0.8493	0.0445	+0.0087
0.5	0.8250	0.0483	+0.033
1.0	0.8099	0.0476	0.0481
1.5	0.7909	0.0454	0.0671
2.0	0.7758	0.0472	0.0822
2.5	0.7686	0.0456	0.0894

Graph IB

Molality of NaCl kept constant	Intercept	Slope	0.858−Col. (2)
0.1	0.8546	0.0119	+0.0034
0.5	0.8646	0.0126	−0.0066
1.0	0.8815	0.0132	−0.0235
1.5	0.8994	0.0118	−0.0414
2.0	0.9115	0.0134	−0.0535
2.5	0.9299	0.0129	−0.0719
3.0	0.9543	0.0125	−0.0963

solvent. For example, mixtures of varying concentrations of sodium chloride in a solution of 2.5 m potassium chloride of a constant molality, give, on extrapolation, an intercept of 0.881 at an ionic strength of 2.5; the $\log_{10}$ of the viscosity of a 2.5 m potassium chloride solution alone is 0.879. In the case of almost all the plots of Figs. 1A and 1B the above observation is fully verified when compared with the respective viscosities of individual solutions of sodium and potassium chloride reported earlier.9)

The intercept corresponding to zero ionic strength is always lower than for pure water in the case of the plots in Fig. 1A. In general, this may be ascribed to the lowering of the viscosity by potassium chloride. From Table IIA the ratio of the corresponding slopes of the plots in Figs. IA and IB may be seen to be a constant around 3.68.

Table III gives the ultrasonic velocities measured by us in different mixtures. Table IV gives the compressibility values calculated using Eq. 2.

Table V gives hydration numbers calculated from Eq. 1.

Figures 2A and 2B give plots of the hydration numbers vs. the total concentrations the mixtures. The plots in Fig. 2A are from the point of view of potassium chloride solutions to which varying amounts of sodium chloride have been added, whereas Fig. 2B gives the plots from the point of view of sodium chloride as the base of reference. For one thing, these

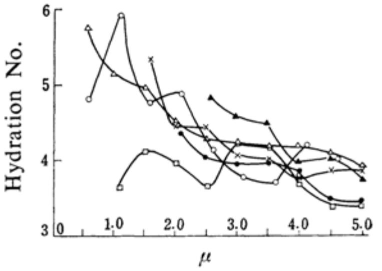

Fig. 2A

○—○ 0.1 m KCl △—△ 0.5 m KCl
□—□ 1.0 m KCl ×—× 1.5 m KCl
●—● 2.0 m KCl ▲—▲ 2.5 m KCl

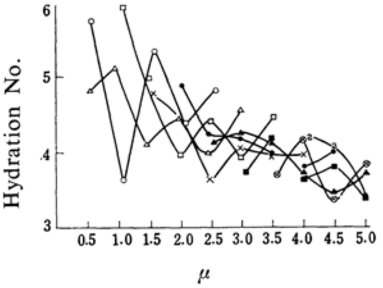

Fig. 2B

○—○ 0.1 m NaCl △—△ 0.5 m NaCl
□—□ 1.0 m NaCl ×—× 1.5 m NaCl
●—● 2.0 m NaCl ▲—▲ 2.5 m NaCl
■—■ 3.0 m NaCl ⊗—⊗ 3.5 m NaCl
8—2 4.0 m NaCl

hydration number plots do not satisfactorily explain the conductance data obtained by previous workers. No single plot in any graph gives a uniform variation. Peaks and troughs occur too often, and both the sets of graphs are rather difficult to explain. A very broad trend seems, however, to be that, with an increasing total molality, the hydration declines.

With an increasing salt mixture concentration, either the water molecules required for the hydration of ions are not enough to go around all the ions, or ion pairing occurs preferentially. The viscosity behaviour and the hydration data of these mixed electrolyte solutions do not throw any light on the conductivity behaviour they exhibit and they at last leave us in the same position we were in previously.

A quantity called "Relative Association" was defined by some previous workers10,11) as:

$$\text{R. A.} = \frac{\rho_c}{\rho_0} \cdot \left(\frac{u_0}{u_c}\right)^{1/3} \tag{4}$$

where ρ_0 and ρ_c are the densities of water at 0°C and of a solution at room temperature,

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9) C. V. Suryanarayana and V. K. Venkatesan, This Bulletin, 31, 442 (1958).

10) G. W. Marks, *J. Acoust. Soc. Am.*, 31, 936 (1959).

11) S. V. Subrahmanyam and I. Bhimasenachar, ibid., 32, 835 (1960).

TABLE II. VISCOSITIES OF THE MIXED ELECTROLYTE SOLUTIONS IN MILLIPOISES

Molal concn. of NaCl	Molal concn. of KCl					
	0.1	0.5	1.0	1.5	2.0	2.5
0.1	7.292	7.291	7.390	7.444	7.558	7.694
0.5	7.589	7.562	7.683	7.729	7.865	7.999
1.0	7.940	7.931	8.075	8.198	8.250	8.421
1.5	8.311	8.394	8.495	8.597	8.736	8.861
2.0	8.744	8.845	8.945	9.074	9.239	9.398
2.5	9.222	9.269	9.496	9.578	9.739	9.867
3.0	9.708	9.910	10.012	10.222	10.307	—
3.5	10.302	10.416	10.582	10.857	—	—
4.0	11.020	11.095	11.213	—	—	—
4.5	11.540	11.795	11.933	—	—	—

TABLE III. ULTRASONIC VELOCITIES IN (KCl+NaCl) MIXTURES IN METRES PER SECOND

Molal concn. of NaCl	Molal concn. of KCl					
	0.1	0.5	1.0	1.5	2.0	2.5
0.1	1514	1546	1540	1595	1593	1637
0.5	1541	1560	1562	1592	1599	1653
1.0	1582	1584	1578	1612	1619	1679
1.5	1587	1596	1585	1625	1646	1674
2.0	1618	1611	1635	1649	1664	1710
2.5	1615	1639	1660	1661	1662	1717
3.0	1620	1662	1656	1696	1682	—
3.5	1641	1696	1656	1731	—	—
4.0	1703	1722	1685	—	—	—
4.5	1732	1735	—	—	—	—

TABLE IV. COMPRESSIBILITIES OF (KCl+NaCl) MIXTURES ($\beta \times 10^6$ atm^{-1})

Molal concn. of NaCl	Molal concn. of KCl					
	0.1	0.5	1.0	1.5	2.0	2.5
0.1	43.51	40.91	40.47	36.95	36.45	33.82
0.5	41.36	39.61	38.80	36.61	35.71	32.84
1.0	38.52	37.77	37.38	35.01	34.35	31.38
1.5	37.66	36.56	36.48	34.10	32.77	31.2
2.0	35.62	35.31	33.78	32.68	31.63	29.48
2.5	35.19	33.67	32.30	31.83	31.36	29.09
3.0	34.46	32.22	32.05	30.11	30.23	—
3.5	33.14	30.60	31.65	28.52	—	—
4.0	30.18	29.25	30.22	—	—	—
4.5	28.94	28.41	—	—	—	—

TABLE V. HYDRATION NUMBERS IN (KCl+NaCl) MIXTURES

Molal concn. of NaCl	Molal concn. of KCl					
	0.1	0.5	1.0	1.5	2.0	2.5
0.1	0.83	5.74	3.64	5.31	4.36	4.81
0.5	4.81	5.11	4.11	4.47	4.02	4.57
1.0	5.91	4.96	3.97	4.40	3.94	4.46
1.5	4.76	4.50	3.64	4.04	3.95	3.96
2.0	4.87	4.24	4.19	3.98	3.82	4.00
2.5	4.12	4.22	4.13	3.75	3.47	3.71
3.0	3.76	4.14	3.68	3.83	3.41	—
3.5	3.70	4.15	3.39	3.84	—	—
4.0	4.17	4.07	3.41	—	—	—
4.5	4.07	3.88	—	—	—	—

TABLE VI. RELATIVE ASSOCIATION

Molal concn. of NaCl	Molal concn. of KCl					
	0.1	0.5	1.0	1.5	2.0	2.5
0.1	0.9825	0.9929	1.0149	1.0236	1.0416	1.0523
0.5	0.9911	1.0044	1.0245	1.0387	1.0533	1.0593
1.0	1.0017	1.0171	1.0359	1.0533	1.0633	1.0704
1.5	1.0171	1.033	1.0514	1.0623	1.0724	1.0838
2.0	1.0273	1.0474	1.0563	1.0714	1.0827	1.0901
2.5	1.0445	1.0543	1.0663	1.0817	1.0964	1.0943
3.0	1.0583	1.0673	1.0806	1.088	1.104	—
3.5	1.0693	1.0714	1.0943	1.0964	—	—
4.0	1.0765	1.0806	1.1007	—	—	—
4.5	1.0786	1.0932	—	—	—	—

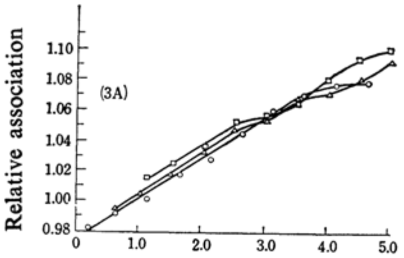

Fig. 3A

○—○ 0.1 m KCl base
△—△ 0.5 m KCl base
□—□ 1.0 m KCl base

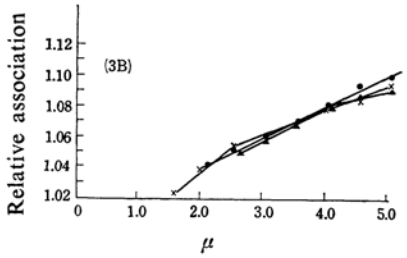

Fig. 3B

×—× 1.5 m KCl base
●—● 2.0 m KCl base
▲—▲ 2.5 m KCl base

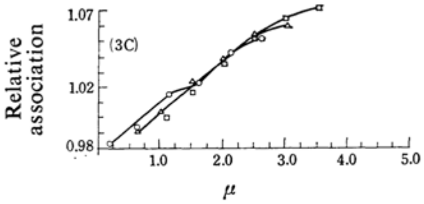

Fig. 3C

○—○ 0.1 m NaCl
△—△ 0.5 m NaCl
□—□ 1.0 m NaCl

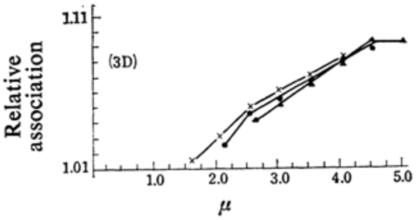

Fig. 3D

×—× 1.5 m NaCl
●—● 2.0 m NaCl
▲—▲ 2.5 m NaCl

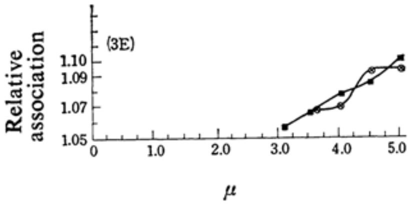

Fig. 3E

■—■ 3.0 m NaCl
⊗—⊗ 3.5 m NaCl

and u_0 and u_c are the velocities of ultrasonic waves in water at 0°C and in a solution at room temperature. Figures 3A, 3B, 3C, 3D and 3E show the plots of the "Relative Association" vs. the total molality. The general trend is for relative association to increase steadily, almost linearly, in most of the cases examined. All the plots have approximately the same slope. One must, therefore, doubt whether "Relative Association" is a measure of the hydration at all.

Summary

The electrical conductance of mixtures of aqueous solutions of potassium and sodium chlorides has been studied by previous workers. However, no valid explanation has been given for the conductance behaviour of the mixtures.

We have reported herein the results of our ultrasonic and viscometric studies of the same mixtures. Even now the hydration numbers and the viscosity variation are inadequate to explain the conductance behaviour of the mixtures. We have observed that all the mixtures follow the exponential relation, $\eta = Ae^{B\mu}$, where A and B are constants; η the viscosity of the mixture, and μ, the ionic strength.

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