## 594. *The Activity Coefficients of Aqueous Solutions of Choline Chloride at 25°.*

By R. Fleming.

The isopiestic method has been used to determine the activity coefficients of aqueous solutions of choline chloride over the concentration range 0·1—4 molal. Fitting Robinson and Stokes's two-parameter equation to the experimental results requires a value of $\mathring{a} = 3{\cdot}08$ and a hydration number of 2·65. Senko has found that the distance of closest approach between the choline and chlorine atoms in the crystal state is 3·04 Å.

The activity coefficients of aqueous choline chloride solutions being important for another research we have determined them by the isopiestic method and have calculated the hydration number and distance of closest approach of the ions.

### Experimental

The isopiestic apparatus was based on Robinson and Sinclair's design.[1] It consisted of four stainless-steel crucibles, each with a rhodium-plated hinged lid, and they rested on a circular

[1] Robinson and Sinclair, *J. Amer. Chem. Soc.*, 1934, **56**, 1830.

piece of brass, 1" thick and 6" in diameter. This ensured a good thermal contact between the crucibles. The brass plate, the crucibles, and the mechanism that operated the lids, were housed in a vacuum-desiccator inside a pivoted metal can, and the can was placed in a thermostat bath at 25° ± 0·01° kept in a cupboard at 25° ± 1°. Turning the tap of the desiccator opened or closed the lids of the crucibles. The can was rocked with a cam-mechanism and this caused glass balls placed in the crucibles to move, preventing the formation of diffusion gradients.

" AnalaR " potassium chloride, used as the reference substance, was dried at 110° for several hours before use. Choline chloride (B.D.H.) was purified by recrystallisation from absolute ethanol and its purity was checked by methods previously described.[2]

TABLE 1. *Isopiestic ratios.*

| $m_B$ | $m_C$ | $R$ | $m_B$ | $m_C$ | $R$ | $m_B$ | $m_C$ | $R$ |
|---|---|---|---|---|---|---|---|---|
| 0·2000 | 0·1975 | 1·013 | 1·000 | 0·9606 | 1·041 | 1·600 | 1·510 | 1·060 |
| 0·4000 | 0·3923 | 1·020 | 1·200 | 1·145 | 1·048 | 1·800 | 1·690 | 1·065 |
| 0·6000 | 0·5842 | 1·027 | 1·400 | 1·328 | 1·054 | 2·000 | 1·868 | 1·071 |
| 0·8000 | 0·7737 | 1·034 | | | | | | |

Two crucibles were used for the potassium chloride; the remaining two contained choline chloride. The required amount of substance was weighed into each crucible, triply distilled water was added, and the crucibles were placed in the apparatus which was then evacuated (water-pump) until the pressure was 10—12 mm. The apparatus was allowed to remain undisturbed for 3—7 days depending on the concentration of the solutions. Then the crucibles were reweighed and the concentrations of the solutions were calculated.

*Results.*—The apparatus was checked by determining the isopiestic ratio of potassium and sodium chloride solutions. The values obtained agree closely with those given by Robinson and Sinclair.[1] The results are shown in Table 1 where $m_B$ and $m_C$ are the molalities of potassium and sodium chloride respectively and $R$ is the isopiestic ratio $(m_B/m_C)$.

Experimental results for choline chloride, obtained with potassium chloride as reference substance, are shown in Table 2; they represent the summation of 3 runs over the concentration

TABLE 2. *Activity coefficient, $\gamma_C$, of choline chloride.*

| $m_B$ | $m_C$ | $R$ | $\phi_C$ | $\gamma_C$ | $\gamma_C$ (calc. $n = 2·65$, $\mathring{a} = 3·08$) | $m_B$ | $m_C$ | $R$ | $\phi_C$ | $\gamma_C$ | $\gamma_C$ (calc. $n = 2·65$, $\mathring{a} = 3·08$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·1 | 0·1002 | 0·998 | 0·9247 | 0·769 | 0·759 | 1·4 | 1·410 | 0·992 | 0·8938 | 0·572 | 0·574 |
| 0·2 | 0·2005 | 0·997 | 0·9103 | 0·714 | 0·704 | 1·6 | 1·610 | 0·994 | 0·8988 | 0·567 | 0·570 |
| 0·3 | 0·301 | 0·996 | 0·9027 | 0·682 | 0·672 | 1·8 | 1·806 | 0·997 | 0·9054 | 0·564 | 0·567 |
| 0·4 | 0·402 | 0·995 | 0·8972 | 0·659 | 0·650 | 2·0 | 2·000 | 1·000 | 0·9124 | 0·563 | 0·565 |
| 0·5 | 0·503 | 0·994 | 0·8935 | 0·641 | 0·633 | 2·4 | 2·390 | 1·004 | 0·9251 | 0·562 | 0·564 |
| 0·6 | 0·605 | 0·992 | 0·8904 | 0·626 | 0·620 | 2·8 | 2·780 | 1·007 | 0·9380 | 0·564 | 0·566 |
| 0·7 | 0·707 | 0·990 | 0·8880 | 0·614 | 0·610 | 3·0 | 2·967 | 1·011 | 0·9470 | 0·567 | 0·568 |
| 0·8 | 0·809 | 0·988 | 0·8862 | 0·604 | 0·602 | 3·4 | 3·330 | 1·021 | 0·9676 | 0·576 | 0·573 |
| 0·9 | 0·910 | 0·989 | 0·8872 | 0·596 | 0·595 | 3·8 | 3·693 | 1·029 | 0·9866 | 0·585 | 0·579 |
| 1·0 | 1·010 | 0·990 | 0·8884 | 0·590 | 0·591 | 4·0 | 3·878 | 1·032 | 0·9956 | 0·590 | 0·583 |
| 1·2 | 1·210 | 0·991 | 0·8905 | 0·580 | 0·580 | | | | | | |

range studied. In this Table, $m_B$ is the molality of potassium chloride and $m_C$ is the molality of choline chloride. $R$ is the isopiestic ratio $(m_B/m_C)$ and $\phi_C$ is the osmotic coefficient of the choline chloride calculated according to the equation $\phi_C = R\phi_B$. Values of $\phi_B$ for potassium chloride were taken from Appendix 8.3 of Robinson and Stokes's [3] book. The column $\gamma_C$ shows the experimental value of the activity coefficient of choline chloride, $c$, calculated according to the equation: [1]

$$\ln \gamma_C = \ln \gamma_B + \ln R + \int_0^{m_B} (R - 1)\mathrm{d} \ln \gamma_B m_B.$$

The last term was evaluated graphically by using the equivalent form $2\int[(R - 1)/\sqrt{a_B}].\mathrm{d}\sqrt{a_B}$, $(R - 1)/\sqrt{a_B}$ being plotted against $\sqrt{a_B}$. The curve was extrapolated to zero concentration.

[2] Fleming, *J.*, 1960, 4914.

[3] Robinson and Stokes, " Electrolyte Solutions," Butterworths Scientific Publications, London, 1st edn., 1955, p. 461.

Values for the activity of potassium chloride were obtained from Robinson and Stokes (Appendix 8.3).[3]

The calculated activity coefficients were obtained from Stokes and Robinson's two-parameter equation:[4]

$$\log \gamma_C = -\frac{A|Z_1Z_2|\sqrt{I}}{1 + Ba\sqrt{I}} - \frac{n}{\nu}\log a_A - \log [1 + 0{\cdot}001W_A(\nu - n)m].$$

The second term was taken to be equivalent to $0{\cdot}007824 \times m \times \phi_C \times n$ where $n$ is the hydration number. It was found that values of the parameters $a = 3{\cdot}08$ and $n = 2{\cdot}65$ gave activity coefficients best fitting the experimental values. In the above equation $A = 0{\cdot}5092$, $W_A = 0{\cdot}018$, and $B$ was taken to be $0{\cdot}3286 \times 10^8$.

## Discussion

Varimbi and Fuoss[5] have recently measured the conductance of choline iodide in dilute solution (0·001—0·021M) and have found that this salt shows no evidence of hydrogen bonding between the solvent molecules and the hydroxy-groups. These workers have found that the closest distance of approach between the choline and iodide ions is 5·39 Å ($3{\cdot}19 = r_+$) and that there is little evidence of ionic association. If it is assumed that

Table 3. *Calculations.* (*n and å refer to the two-parameter equations*).

| | | $n = 0$ | $n = 2{\cdot}65$ | $n = 3{\cdot}65$ |
|---|---|---|---|---|
| $m$ | Expt. | $å = 3{\cdot}85$ | $å = 4{\cdot}52$ | $å = 3{\cdot}08$ |
| 0·503 | 0·641 | 0·645 | 0·686 | 0·633 |
| 1·010 | 0·590 | 0·595 | 0·595 | 0·591 |
| 2·000 | 0·563 | 0·552 | 0·552 | 0·565 |
| 2·967 | 0·567 | 0·530 | 0·530 | 0·568 |
| 3·878 | 0·590 | 0·516 | 0·516 | 0·583 |

there is no ion association in the more concentrated solutions used in this work, then it is possible to use Stokes and Robinson's two-parameter equation to calculate theoretical activity coefficients which will match the experimental values. The values of $a$ and $n$ required to give a close fit are 3·08 and 2·65 respectively, and the distance 3·08 Å seems too small, especially in view of the closest distance of approach found by Varimbi and Fuoss. Senko[6] has found that in the crystal state the distance between the chloride ion and oxygen atom is 3·04 Å and it appears that in concentrated solutions the distance between the choline and chlorine ions approaches that in the crystal state, although of course this is not the distance of closest approach between the ionic centres, as the oxygen atom is at the periphery of the choline ion.

An attempt was made to use the one-parameter equation of Robinson and Stokes:[7]

$$\log \gamma_1 = \frac{0{\cdot}5092|Z_1Z_2|\sqrt{I}}{1 + 0{\cdot}3286\sqrt{I}(\frac{3}{4}\pi(30n + V_1)^{\frac{1}{3}} + r_2 - \Delta)} - \frac{n}{\nu}\log A_W - \log [1 - 0{\cdot}018\,(n - \nu)m]$$

where $n$ is the hydration number, $V_1$ is the apparent molal volume of the ion in Å$^3$, and $\Delta = 0{\cdot}7$ represents "penetration distance." $V_1$ was estimated by using the relation $V_1 = V_{app} - 6{\cdot}47Z_1r_2^3$ where $V_{app}$ was taken as 124·1 c.c. and the radius of chloride ion $r_2$ was taken as 1·81 Å. Activity coefficients were first calculated by assuming that $n = 0$ ($å = 3{\cdot}85$ Å), and then with $n = 2{\cdot}65$ ($å = 4{\cdot}52$). The results are summarised in Table 3. They show that only the two-parameter equation fits the experimental results satisfactorily.

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[4] Stokes and Robinson, *J. Amer. Chem. Soc.*, 1948, **70**, 1870.
[5] Varimbi and Fuoss, *J. Phys. Chem.*, 1960, **64**, 1335.
[6] Senko, U.S. Atomic Energy Comm. Report, 1957, U.C.R.L. 3521.
[7] Robinson and Stokes, ref. 3, p. 249.