A transition was found at 103.52°K. and a region of large energy absorption, possibly ending in a transition, was found near 126°K. The abnormal rise in heat capacity extended for many degrees below this temperature but a large proportion of the energy was absorbed nearly isothermally at 126.22°K.

The melting and boiling points were found to be 187.61 and 212.77°K., respectively.

The heat of transition at 103.52 is 368.2 cal./mole. The total heat absorption between 126 and 127°K. is 121.3 cal./mole. The heat of fusion is 568.1 cal./mole. The heat of vaporization is 4463 cal./mole at the boiling point.

The vapor pressure of solid and liquid hydrogen sulfide was measured and the results are represented by the equations:

Solid hydrogen sulfide, 164.90 to 187.61°K.

$$\log_{10} P \text{ (int. cm. Hg)} = -(1329/T) + 9.28588 - 0.0051263T$$

Liquid hydrogen sulfide, 187.61 to 213.17°K.

$$\log_{10} P \text{ (int. cm. Hg)} = -(1145/T) + 7.94746 - 0.00322T$$

The experimental data and the third law of thermodynamics have been used to calculate the molal entropy of the gas at the boiling point. The value found, 46.38 ± 0.1 E. U., is in excellent agreement with the spectroscopic value, 46.441 E. U. calculated by Cross. Each of the above values neglects the nuclear spin entropy.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 2, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 365]

The Freezing Points of Aqueous Solutions. X. Dioxane and its Mixtures with Lithium, Sodium and Potassium Chlorides[1]

BY GEORGE SCATCHARD AND MARJORIE ALLEN BENEDICT

Debye and McAulay's application of the Born theory to the interaction of electrolytes and non-electrolytes in dilute solutions[2] indicates that the sodium ion should be more effective in salting out non-electrolytes than the potassium ion and that the lithium ion should be considerably more effective than the sodium ion. Debye's later theory,[3] which takes into account the variations from random distribution, indicates very much smaller differences, though in the same order. The experimental measurements of the salting out of non-electrolytes, on the other hand, disagree as to whether the sodium ion or the potassium ion is the more effective, but generally make the lithium ion much the least effective of the three. Since these measurements have been made at rather high concentrations of salt, and sometimes also of non-electrolyte, the following measurements were made of the freezing points of aqueous solutions of mixtures of each of the three chlorides with dioxane in order to obtain the limiting law at low concentrations with which the theories might be tested.

Dioxane was chosen as the non-electrolyte solute because it has a very large effect on the dielectric constant and also because its simple ether structure makes any specific chemical action improbable. Since dioxane–water mixtures are finding so much use in physico-chemical studies, and because such an ether might well be expected to be only slightly miscible with water, the study of the freezing points of dioxane solutions without added salt is also of importance.

Materials and Procedure

The salts were prepared as in earlier papers in this series.[4] The sodium and potassium chlorides were weighed into the mixtures as the dried salts, and the lithium chloride was weighed as an analyzed concentrated solution. All water used was from the laboratory conductivity water still.

Commercial dioxane ($C_4H_8O_2$) was refluxed eight hours with one-tenth its weight of concentrated hydrochloric acid, decanted from the acid layer, shaken with enough sodium hydroxide pellets to neutralize the acid and dried with calcium chloride and then with sodium, being refluxed during the drying with sodium.[5] It was then fractionated twice through a Davis column, the middle two-thirds being retained. By comparison with water in a carefully designed boiling point apparatus with a closed atmosphere of helium[6] and a Beckmann thermometer, the

---

[1] From a thesis submitted in October, 1935, by Mrs. Marjorie Allen Benedict in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] P. Debye and J. McAulay, *Physik. Z.*, **26**, 22 (1925).

[3] P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

[4] G. Scatchard and S. S. Prentiss, THIS JOURNAL, **55**, 4355 (1933).

[5] B. D. Kribben, Thesis, M. I. T., 1933; C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934).

[6] J. A. Beattie, J. M. Gaines, Jr., and B. E. Blaisdell, unpublished.

normal boiling point was found to be 101.22°; Kraus and Vingee report 101.24° at 761 mm. The density at 20°, d^{20}_4, was found to be 1.0377.

The procedure was the same as that used with ethyl alcohol or glycine and their mixtures with sodium chloride.[7] With solutions of pure dioxane, nitrogen was bubbled through the solutions during the measurements, and the equilibrium concentrations were determined from the indices of refraction in a Zeiss portable interferometer. The weight percentage of dioxane was determined as a quadratic function of the interferometer reading by the method of least squares.

Mixtures of dioxane with the salts were made up with constant ratios, approximately one mole ions to two moles dioxane, and two moles ions to one mole dioxane (designated hereafter as 1:2 and 2:1, respectively), and the freezing point depressions of each mixture were determined up to a total concentration (assuming complete ionization) of two molal. The concentrations were determined from the conductances by the use of our customary deviation curves. Before each run with dilute solutions nitrogen was passed through each side of the apparatus, but the gas current had to be stopped before adding the solute in order not to change the ratio of dioxane to salt.

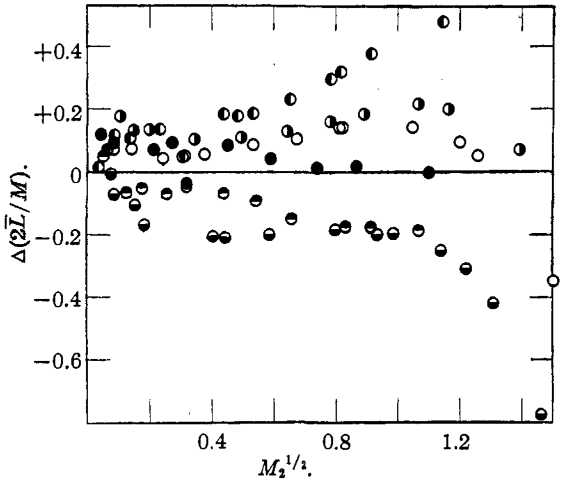

Fig. 1.—Deviations from conductance functions: ◐, LiCl 2:1; ◑, LiCl, 1:2; ●, NaCl 2:1; ○, NaCl 1:2; ◓. KCl 2:1; ◒, KCl 1:2.

The forty-eight junction thermocouple was rebuilt. Bakelite lacquer baked on for half an hour at 125° was found much more satisfactory than cellulose acetate as an insulating medium, and purified vaseline was found to be much superior to paraffin, which shrinks on solidifying, for filling the spaces in the tube. Calibrated as before against a platinum resistance thermometer between −10 and +10°, the new couple gave depressions, θ, in degrees centigrade related to the electromotive force, E, in microvolts by the equation (determined by the method of least squares) $\theta = 0.53793 \times 10^{-3} E + 0.2905 \times 10^{-9} E^2 + 0.1431 \times 10^{-14} E^3 + 0.141 \times 10^{-18} E^4$. The average deviation was 0.03%. The agreement with the equation

$$\theta = 0.53787 \times 10^{-3} E + 0.32714 \times 10^{-9} E^2 + 0.1651 \times 10^{-14} E^3$$

was only slightly less satisfactory. For our purposes the most important point is that the two equations give practically the same values for small depressions. Otherwise the apparatus was the same as that used in previous papers in this series.

Results

The measurements of conductance may be expressed to a first approximation as a function of the salt concentration in moles per kilogram water multiplied by another function of the dioxane concentration. The functions of salt concentrations used are those previously found by the method of least squares. The function of the dioxane concentrations chosen is the same for all the salts. The complete equations are

LiCl: $2\overline{L}/M_1 = (80.634 - 41.383\, M_1^{1/2} + 36.463\, M_1 - 27.108\, M_1^{3/2} + 10.255\, M_1^2 - 1.564\, M_1^{5/2})\,(1 - 0.25\, M_2 + 0.035\, M_2^2)$

NaCl: $2\overline{L}/M_1 = (89.132 - 42.720\, M_1^{1/2} + 35.664\, M_1 - 19.832\, M_1^{3/2} + 4.328\, M_1^2 - 0.094\, M_1^{5/2})\,(1 - 0.25\, M_2 + 0.035\, M_2^2)$

KCl: $2\overline{L}/M_1 = (107.377 - 45.587\, M_1^{1/2} + 37.602\, M_1 - 18.004\, M_1^{3/2} + 3.662\, M_1^2 - 0.159\, M_1^{5/2})\,(1 - 0.25\, M_2 + 0.035\, M_2^2)$

in which $\overline{L}/1000$ is the specific conductance at 10°, M_1 the weight molality of the ions (twice that of the salt) and M_2 is the weight molality of dioxane. $2\overline{L}/M_1$ is the equivalent conductance multiplied by the number of grams of water in a cubic centimeter of solution. Approximately half of the decrease in conductance on the addition of dioxane is caused by the dilution. Figure 1 shows the deviations of the individual measurements from the equations, $\Delta(2\overline{L}/M)$, plotted against the square root of the dioxane molality. This method of plotting is used merely to spread the points in dilute solutions and not because a variation proportional to the square root is to be expected. For each salt the molality of the ions is half that of dioxane in one series, and twice that of dioxane in the other. The fact that the two series do not superimpose exactly shows that the effect of dioxane depends somewhat on the salt concentration, but no simple generalizations can be made concerning this dependence except that it is small. The measurements do show that the decrease is slightly larger for sodium chloride than for lithium chloride, and still larger for potassium chloride, but the greatest difference is only a few per cent. of the equivalent conductance, which varies from 104 for the most dilute potassium chloride solution

---

(7) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 1486, 2314 (1934).

to 19 for the most concentrated lithium chloride solution.

The freezing point depressions are expressed as the osmotic coefficient for the chemical potential of the solvent at the freezing point of the solution

$$\phi' = \frac{\mu_0^* - \mu_0}{0.018015\,RTM} = \frac{\theta}{1.858\,M}\left(1 + \frac{\theta}{1858}\right) \quad (1)$$

ϕ' is this osmotic coefficient, μ_0^* the chemical potential (partial molal free energy) of pure water, μ_0 is the potential of water in the solution, and θ is the freezing point depression. For a solution containing m_1 moles of univalent ions ($m_1/2$ moles of salt) and m_2 moles of non-electrolyte per kilogram of water, $M = m_1 + m_2$, $x_1 = m_1/M$, $x_2 = m_2/M$. Constants for equation (4) of Paper VIII[7] were obtained by the method of least squares as in that paper, with the use of the values of Papers VIII and IX[8] for the coefficients of the salt solutions. For this special case, this equation reduces to

$$\begin{aligned}\phi' = 1 &+ 0.5\,A_1x_1^{3/2}M^{1/2} + (B_{11}x_1^2 + 2B_{12}x_1x_2 + \\ &B_{22}x_2^2)M + 1.5(C_{11}x_1^{5/2} + 2C_{12}x_1^{3/2}x_2)M^{3/2} + \\ &2(D_{111}x_1^3 + 3D_{112}x_1^2x_2 + 3D_{122}x_1x_2^2 + D_{222}x_2^3)M^2 + \\ &2.5(E_{111}x_1^{7/2} + 3E_{112}x_1^{5/2}x_2 + 3E_{122}x_1^{3/2}x_2^2)M^{5/2}\end{aligned}$$

It was found, however, that the measurements in dilute solutions were not sufficiently precise to determine both B_{12} and C_{12} accurately. Therefore, C_{12} was determined from the Debye–Hückel limiting law and the effect of dioxane on the dielectric constant of water. Professor Jeffries Wyman of the Department of Biology of Harvard University very kindly measured the dielectric constants for us. From his results, which are given in Table I, we obtain the limiting law

$$D_0/D = 1 + 0.091\,M_2 \quad (2)$$

The agreement with the measurements is almost as good as when C_{12} is allowed to vary, and determined from the freezing point measurements.

TABLE I

DIELECTRIC CONSTANTS OF DIOXANE SOLUTIONS AT 1.4°

Wt. % dioxane	0.000	1.740	3.132	4.482	5.439	6.468
D	87.64	86.00	84.79	83.63	82.73	81.76

TABLE II

CONSTANTS FOR OSMOTIC COEFFICIENTS

For all series: $A_1 = 0.52864$, $A_2 = 0$, $B_{22} = +0.00534$, $C_{22} = 0$, $D_{222} = +0.00013$, $E_{222} = 0$, $C_{12} = -0.032$.

	KCl	NaCl	LiCl
B_{11}	+0.32640	+0.38628	+0.40156
B_{12}	+ .05939	+ .07330	+ .06851
C_{11}	− .18650	− .24194	− .17019
D_{111}	+ .06935	+ .09600	+ .04950
D_{112}	+ .02229	+ .01732	+ .00927
D_{122}	+ .01234	+ .00483	− .00197
E_{111}	− .01144	− .01603	− .00557
E_{112}	− .00566	− .00471	− .00247
E_{122}	− .01164	− .00506	+ .00058

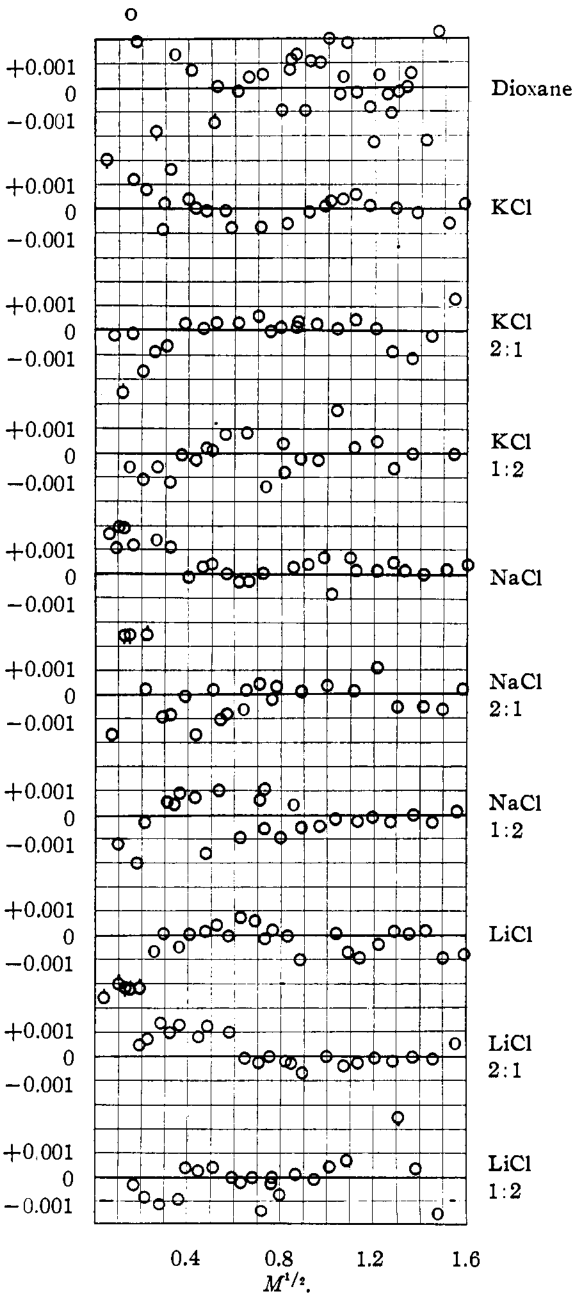

Fig. 2.—Deviations of osmotic coefficients.

The constants thus obtained are given in Table II, and the deviations of the measured ϕ' from those calculated are shown in Fig. 2.

---

(8) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 2320 (1934).

The osmotic coefficients themselves are shown in Figs. 3, 4 and 5.

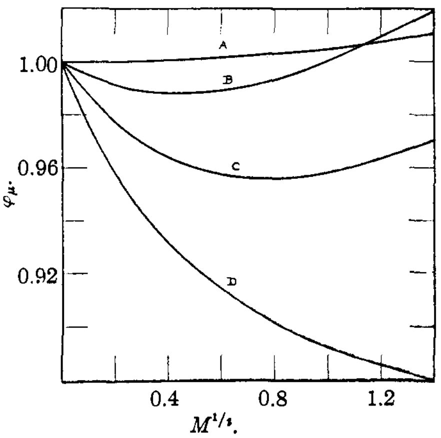

Fig. 3.—Osmotic coefficients of dioxane–KCl mixtures: A, dioxane; B, 1:2; C, 2:1; D, KCl.

Discussion

The freezing points of dioxane–water mixtures are given by the equation

$$\phi' = 1 + 0.00534M + 0.00026M^2$$

and the deviations from ideal solutions are given by

$$\phi' - \phi_{\mathrm{I}} = 0.01435M + 0.00015/M^2$$

Either of these expressions is linear within the limits of our measurements. Not only is dioxane completely miscible with water, but its dilute solutions are very nearly ideal. The fact that the deviations in the osmotic coefficient are positive corresponds to negative deviations from Raoult's law and may possibly be related to the fact that this system forms stable hydrates. Preliminary measurements of one of us (GS) with L. F. Epstein[9] confirm the earlier measurements[10] in the indication that the solid phases, $C_4H_8O_2 \cdot H_2O$ and probably $2C_4H_8O_2 \cdot H_2O$ and $3C_4H_8O_2 \cdot H_2O$ are in equilibrium with the liquid solution.

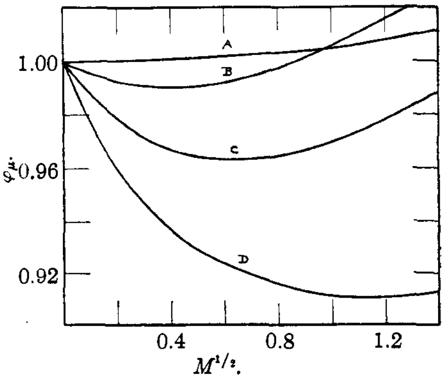

Fig. 4.—Osmotic coefficients of dioxane–NaCl mixtures: A, dioxane; B, 1:2; C, 2:1; D, NaCl.

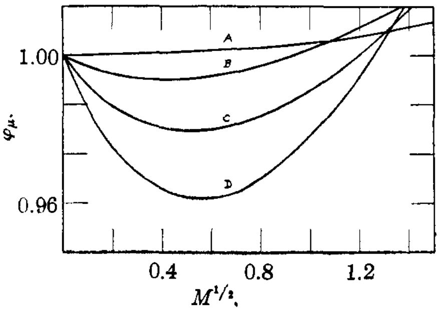

Fig. 5.—Osmotic coefficients of dioxane–LiCl mixtures; A, dioxane; B, 1:2; C, 2:1; D, LiCl.

The relative interaction of the electrolytes with dioxane may be shown most clearly by considering the mixed parameters in Table II or by plotting the osmotic coefficient of each mixture minus the product of the osmotic coefficient of each component at the same concentration and its mole fraction in the solute, x, $\phi' - x_1\phi_1' - x_2\phi_2'$, which should be equal to

$$2B_{12}Mx_1x_2 + 2.5C_{12}M^{3/2}x_1^{3/2}x_2 + 6D_{112}M^2x_1^2x_2 + 6D_{122}M^2x_1x_2^2 + 7.5E_{112}M^{5/2}x_1^{5/2}x_2 + 7.5E_{122}M^{5/2}x_1^{3/2}x_2^2$$

Figure 6 shows the curves corresponding to this equation. The deviations of the experimental points from these curves are the same as the corresponding deviations in Fig. 2. In dilute solutions the results for the two mixtures with any one salt fall on the same curve. This is demanded by the theory since the product x_1x_2 is the same in each. In the more concentrated solutions the curves separate.

These curves show that the initial slope increases very slightly in the order of potassium, lithium, sodium, but that in concentrated solutions the order is lithium, potassium, sodium. The behavior in dilute solutions is brought out more clearly from the constants B_{12}, and preferably from the differences of these quantities from B_{I}, which are given in Table III together with the corresponding quantities calculated from the Debye–McAulay theory[2] and from the later theory of Debye.[3] For both these calculations are used Wyman's measurements of the dielectric

---

[9] L. F. Epstein, Bachelor's Thesis, M. I. T., 1935.

[10] Unkowskaja, *J. Russ. Phys.-Chem. Soc.*, **45**, 1099 (1913); Gillis and Delaunois, *Rec. trav. chim.*, **53**, 186 (1934).

constants of dioxane solutions and the atomic radii calculated by Pauling[11] from crystallographic measurements.

TABLE III

B_{12}–B_I

	Debye–McAulay	Debye	Experimental
KCl	0.12	0.072	0.068
NaCl	.14	.0725	.082
LiCl	.18	.073	.078

The Debye–McAulay theory gives much too large values of B_{12}, and the spread from potassium to lithium is also much too large. The second Debye theory gives values slightly smaller than our measurements and a smaller spread. The small differences might easily be accounted for by errors in the atomic radii, most probably in the assumption that the radii are the same in aqueous solutions as in the crystals, by errors in the simplifying assumptions of the Debye theory, or by experimental errors in our measurements. In particular the change in the order of the sodium and lithium chlorides may be due to the fact that our series expansion gives slightly larger values than our measurements for very dilute lithium chloride solutions.

The agreement with Debye's second theory is so good that we may well consider its basis, and particularly the differences between the two theories. Both theories consider the ions as rigid spheres and the non-electrolytes as a continuous medium whose interaction with the ions is determined by the macroscopic dielectric constant. The first theory ignores the effect of the ions on the distribution of the non-electrolytes and treats the medium as though its dielectric constant were uniform, calculating the free energy of the solution from the reversible work of transferring the ions from water to the solution. The calculations of the second theory are based entirely upon the change of concentration of the non-electrolyte solute with changing distance from the ion. The concentration c at any point is given by $c = c_0e^{-R^4/r^4}$, in which c_0 is the concentration at infinite distance, r is the distance from the center of the ion and

$$R^4 = \frac{\epsilon^2z^2}{0.008\pi kT}\frac{(D_0 - D)}{D_0DM_2}$$

D is the dielectric constant of the solution and D_0 that of the solvent. For dioxane in water R is 2.53 Å. The concentration decreases rapidly as the ion is approached. The value of c/c_0 is calculated as 6×10^{-3} at the surface of the chloride ion (1.59 Å.), as 3×10^{-10} at the surface of the potassium ion (1.17 Å.) and still very much smaller at the surface of the sodium or lithium ion. There is little probability that short range forces between the dioxane molecule and an ion be effective unless they are very large. Experimentally we do find no evidence of the effects of such forces.

The very rapid change in relative concentration with distance from the ion may also explain the fact that the limiting salting out effect calculated is smaller than the effects measured for the lithium or sodium ions. The calculated relative concentration changes enormously within the diameter of a dioxane molecule. The theory assumes that the decrease in concentration very close to the ion does not affect the concentration at greater distances, but actually this concentration must also be decreased if the dioxane in the two regions are parts of the same molecule.

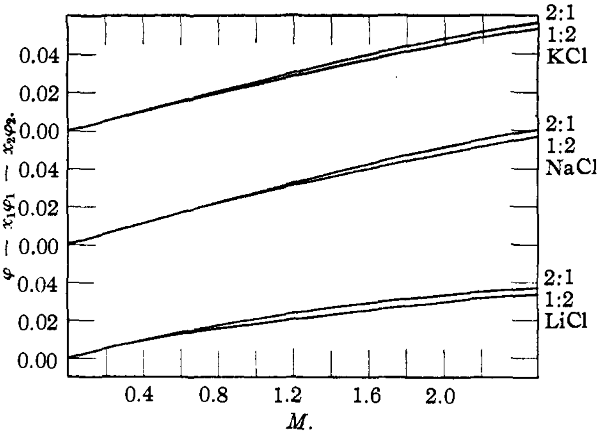

Fig. 6.—Deviations of osmotic coefficients from additivity.

The activity coefficients of the ions and of dioxane may be determined from the parameters in Table II by the equations

$$\ln \gamma_1 = 1.5A_1M_1^{1/2} + 2B_{11}M_1 + 2.5C_{11}M_1^{3/2} + 3D_{111}M_1^2 + 3.5E_{111}M_1^{5/2} + (2B_{12} + 3C_{12}M_1^{1/2} + 6D_{112}M_1 + 7.5E_{112}M_1^{3/2})M_2 + (3D_{122} + 4.5E_{122}M_1^{1/2})M_2^2$$

$$\ln \gamma_2 = 2B_{22}M_2 + 3D_{222}M_2^2 + (2B_{12} + 6D_{122}M_2)M_1 + (2C_{12} + 6E_{122}M_2)M_1^{3/2} + 3D_{112}M_1^2 + 2E_{112}M_1^{5/2}$$

The first of these quantities might be determined from the electromotive force of cells in which the cell process is the transfer of the salt in question from one solution to another, for example with alkali amalgam and silver–silver chloride electrodes, and is analogous to the effect of the non-electrolyte on the solubility of slightly soluble salts. The second might be determined from the

---

(11) L. Pauling, THIS JOURNAL, 50, 1036 (1928).

ratio of the vapor pressure of dioxane to its molality, and is analogous to the salting out of slightly soluble non-electrolytes.

The discussion of the general cases in which M_1 and M_2 is each allowed to vary from 0 to 2 would require much more space than is available. We shall limit ourselves to the case of zero concentration of the substance whose activity coefficient is being measured, and we shall designate the corresponding activity coefficients with a superscript^0. The equations are:

$$\text{KCl} \quad \ln \gamma_1^0 = 0.11878\, M_2 + 0.03702\, M_2^2$$

$$\text{NaCl} \quad \ln \gamma_1^0 = 0.14660\, M_2 + 0.01449\, M_2^2$$

$$\text{LiCl} \quad \ln \gamma_1^0 = 0.13702\, M_2 - 0.00591\, M_2^2$$

$$\text{KCl} \quad \ln \gamma_2^0 = 0.11878\, M_1 - 0.064\, M_1^{3/2} + 0.06687\, M_1^2 - 0.01698\, M_1^{5/2}$$

$$\text{NaCl} \quad \ln \gamma_2^0 = 0.14660\, M_1 - 0.064\, M_1^{3/2} + 0.03200\, M_1^2 - 0.01413\, M_1^{5/2}$$

$$\text{LiCl} \quad \ln \gamma_2^0 = 0.13702\, M_1 - 0.064\, M_1^{3/2} + 0.02781\, M_1^2 - 0.00741\, M_1^{5/2}$$

The effect of dioxane on the activity coefficients of the ions, when the concentration of the latter is zero, is greater for KCl than for LiCl when M_2 is greater than 0.43, and is greater for KCl than for NaCl when M_2 is greater than 1.24. The effect of KCl on dioxane, when the dioxane concentration is zero, is greater than the effect of LiCl when M_1 is greater than 0.57. At and above this concentration the difference between KCl and NaCl remains nearly constant at 0.015 greater for NaCl. In one molal salt solutions ($M_1 = 2$), the relative values of $\ln \gamma_2^0$ are: KCl − 0.95, NaCl − 1.00, LiCl − 0.68. These may be compared with the relative values calculated from Euler's measurements[12] of the salting out of diethyl ether at the same salt concentration: KCl − 0.94, NaCl − 1.00, LiCl − 0.73. Better agreement could scarcely be hoped for.

The results of our measurements are therefore in accord both with the measurements of salting out, and, except for the slight discrepancy between the sodium and lithium ions, with the theory of Debye. They show that the difference between the theory and the salting out measurements must be due to the fact that the measurements are made in a concentration range too high for the limiting law of the theory.

Summary

1. The freezing points of aqueous solutions of dioxane have been measured up to a concentration of 2 *M*. The osmotic coefficient is found to increase slightly and almost linearly with increasing concentration.

2. The freezing points of aqueous solutions of two mixtures each of potassium, sodium and lithium chlorides with dioxane have been measured up to a total concentration of dioxane plus ions of 2 *M*. The results are expressed analytically as functions of the concentrations.

3. At low concentrations the osmotic coefficients of the mixtures are smaller than the Debye–McAulay theory demands, but agree well with the second theory of Debye.

4. The salting out effects of molal salt solutions calculated from these measurements have nearly the same relative values as those directly measured for diethyl ether.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 27, 1936

---

[12] H. Euler, *Z. physik. Chem.*, **49**, 304 (1903).