[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Calculation of the Composition of an Aqueous Solution Saturated with an Arbitrary Number of Highly Soluble Strong Electrolytes

BY GÖSTA ÅKERLÖF

In a previous paper[1] a method was given for the calculation of the composition of the solution phase in a three component system with water as solvent and two strong electrolytes present as solutes. This method may without any theoretical difficulties be extended to poly-component systems where the solution phase is saturated with respect to an arbitrary number of co-existent solid phases, which do not form molecular compounds or solid solutions with each other. In this study will be given the generalized calculation method to be employed in the case of uni-univalent strong electrolytes and also an experimental test of its validity for the quaternary system hydrochloric acid–sodium chloride–potassium chloride–water. Unfortunately a search of the literature has not revealed any other cases for which all the data necessary for a complete test may be calculated directly. In the case of the system potassium hydroxide–potassium chloride–potassium nitrate–water all the experimental data that presumably would be necessary are available but they are generally of such a low accuracy that they cannot be used for our purposes. However, we will show how it may be possible to obtain indirectly at least a partial solution of the problem of getting the constants necessary.

As was shown previously, the activity coefficient γ of a given uni-univalent strong electrolyte may be expressed in terms of the activity coefficient γ_R of a reference electrolyte of the same valence type by the simple relation

$$\log (\gamma/\gamma_R) = k_1 m \qquad (1)$$

where k_1 is an empirical constant and m the molality. Using this equation and the principle of the linear variation of the logarithm of the activity coefficient of a strong electrolyte in mixed solution with another strong electrolyte at constant total ionic strength, the following equation was deduced for the solubility of the electrolyte forming the solid phase in a ternary system with two homo-ionic, uni-univalent solutes

$$\log \gamma_{R(\mu_T)} + k_{1(x)}\,\mu_T + k_{2(x)}(\mu_T - \mu_x) + {}^1/_2 (\log \mu_T + \log \mu_x) = \log a_x \qquad (2a)$$

where μ designates ionic strength, a_x the activity of the electrolyte forming the solid phase and k_2 is the slope of the curve for the logarithm of the activity coefficient of the same electrolyte in solutions of constant total ionic strength as plotted against its concentration. In the case of hetero-ionic, uni-univalent co-solutes the equation takes the form

$$\log \gamma_{R(\mu_T)} + k_{1(x)}\,\mu_T + k_{2(x)}\,(\mu_T - \mu_x) + \log \mu_x = \log a_x \qquad (2b)$$

Considering the previously demonstrated simple geometry of the curves for the variations of the logarithm of the activity coefficient of a strong electrolyte it is apparently evident that the influence of a number of different co-solutes A, B, C, . . ., with the respective concentrations m_A, m_B, m_C, . . ., on the logarithm of the activity coefficient of a given electrolyte present as a solid phase is equal to the sum of the products of their concentrations and k_2 values, which in the case of homo-ionic, uni-univalent electrolytes gives the following equation

$$\log \gamma_{R(\mu_T)} + k_{1(n)}\,\mu_T + \Sigma k_{2(n_i)}\cdot m_i + {}^1/_2 (\log \mu_T + \log \mu_n) = \log a_n \qquad (3a)$$

where n indicates an arbitrary electrolyte present as a solid phase. For hetero-ionic solutes the concentration term has the same form as in equation (2b). The case of both homo- and hetero-ionic electrolytes present simultaneously does not change the equations to be used since the solubility of each solid phase is represented by a separate equation. Further, the presence of co-solutes of different valence types does not introduce additional terms since in mixed solutions of two electrolytes with constant total ionic strength the logarithm of the activity coefficient of either one of the two varies linearly independently of the valence type of the co-solute.

A simple general method for the mathematical solution of a system of simultaneous equations of the type represented by (3a) is not known and it is necessary to solve by successive approximation, eventually aided by graphical interpolation or possibly expanding the logarithm of the variables in power series. However, in the test case to be considered below only two different solid phases are present simultaneously and the numerical

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[1] Åkerlöf and Thomas, THIS JOURNAL, **56**, 593 (1934).

calculations are relatively very simple. Further, the computations are simplified by the fact that in the test case referred to, the concentration of the third electrolyte may be chosen arbitrarily since it is not present in its own saturated solution. Therefore the total ionic strength may also be chosen arbitrarily within the limits necessary to obtain positive values for the solubilities of the solid phases. Naturally only when this is the case the corresponding liquid phase is able to have real existence. In the presence of strong electrolytes decreasing the solubility of a given solid phase, the upper limiting value of the same is given by the solubility in the pure solvent. The lower limiting value is determined either by a minimum in the solubility curve or by the appearance of a new solid phase. The extensions of the solubility curves for the old and the new solid phases beyond their crossing points represent metastable states and returning to more probable states the previous solid phase must disappear since the solution phase becomes unsaturated with respect to the same. In the case of continually increasing solubility of a given solid phase with increasing concentration of the co-solutes, the conditions are reversed. The lower limiting value is the solubility in the pure solvent and when the upper value is reached a new solid phase has appeared. In the following for a comparison between actually measured and calculated solubilities, the values of the experimentally determined total ionic strengths will be employed to avoid interpolation difficulties.

Solubilities of the Solid Phases in the System Hydrochloric Acid–Sodium Chloride–Potassium Chloride–Water at 25°.—In order to carry out the solubility calculations, we must first of all compute the values of the necessary constants. Since the details of the computation may be omitted, only a summary of the data employed and the results is given in Part I of Table I. The solubility data are taken from "International Critical Tables," Vol. IV, pages 313 and 314. The values for the activity coefficient of the reference electrolyte for which purpose hydrochloric acid was used, were obtained by interpolation of the data given by Randall and Young.[2] The values of k_1 were calculated using the activity coefficient measurements of Harned and of Harned and Nims[2] for solutions of sodium chloride and of Harned[2] for solutions of potassium chloride. The two simultaneous equations obtained for the solubilities of sodium and potassium chloride, respectively, from the general equation (3a) and the data in Table I have the following form:

(A) Solubility of sodium chloride: $\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.088\,\mu_T + 0.0459\,\mu_{\mathrm{HCl}} - 0.0208\,\mu_{\mathrm{KCl}} + {}^1/_2\,(\log \mu_T + \log \mu_{\mathrm{NaCl}}) = 0.7766$ (4a)

(B) Solubility of potassium chloride: $\log \gamma_{\mathrm{HCl}(\mu_T)} - 0.118\,\mu_T + 0.0431\,\mu_{\mathrm{HCl}} + 0.0088\,\mu_{\mathrm{NaCl}} + {}^1/_2\,(\log \mu_T + \log \mu_{\mathrm{KCl}}) = 0.4661$ (4b)

As previously mentioned, we will use for the solubility calculations the same values for the total ionic strength and the acid concentration as those experimentally determined. The system considered has been investigated by Hicks.[3] In Part II of Table I is given a comparison between the solubilities calculated according to equations (4a) and (4b), respectively, and the values observed by Hicks. The agreement between observed and calculated values is quite satisfactory considering the difficulties usually encountered in solubility measurements of the type employed and also the number of different sources from which the data used for the computation of the necessary constants have been derived. The practical application to technically important

TABLE I

PART I. CONSTANTS FOR THE SYSTEM HYDROCHLORIC ACID–SODIUM CHLORIDE–POTASSIUM CHLORIDE–WATER AT 25°

Electrolyte	KCl	NaCl
Solubility of the salt in pure water, s_0	4.819	6.160
Solubility of the salt in 1-molal HCl, s_1	3.885	5.100
Log γ for HCl at the concentration s_0	0.3517	0.5291
Log γ for HCl at the concentration $s_1 + 1$	.3602	.5210
Value of k_1 for the salt in reference to HCl	−.118	−.088
Log γ for the salt in pure saturated soln.	−.2169	−.0130
Value of k_2 for the salt in solution of HCl	.0431	.0459
Value of k_2 for one salt in solution of the other	.0088	−.0208

PART II. CALCULATED AND OBSERVED SOLUBILITIES OF SODIUM AND POTASSIUM CHLORIDES IN ABOVE SYSTEM AT 25°

Acid concn. m_{HCl}	Ionic strength μ_T	log γ_{HCl} at μ_T	Solubility of sodium chloride Calcd.	Obs.	Solubility of potassium chloride Calcd.	Obs.
0.00	7.29[a]	0.6792	5.09	5.09	2.20	2.20
3.23	7.11	.6550	2.53	2.49	1.34	1.39
6.23	7.71	.7333	1.00	0.81	0.70	0.68
7.60	8.58	.8460	0.57	0.46	0.45	0.51

[a] Ionic strength at this triple point the calculated value.

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[2] Randall and Young, THIS JOURNAL, **50**, 989 (1928); Harned, *ibid.*, **51**, 416 (1929); Harned and Nims, *ibid.*, **54**, 423 (1932).

[3] Hicks, *ibid.*, **37**, 844 (1915).

equilibria or a more thorough testing of the calculation method indicated above is as yet hindered, mostly by insufficient accuracy of the solubility data available. Since two constants have to be derived simultaneously for each electrolyte concerned, relatively small experimental errors cause considerable fluctuations in the apparent magnitude of these constants. As regards the calculation of the composition of the solution phase in a poly-component system at different temperatures, not a single case for which all the data necessary are available has been found in the literature. However, as far as can be judged the k_1 values seem to vary linearly with the temperature and in several cases the slopes of the lines appear to be practically identical. The temperature coefficients of the k_2 values may be obtained only in very few cases but it seems as if they as a rule are very small.

TABLE II

VALUES OF k_2 FOR VARIOUS UNI-UNIVALENT STRONG ELECTROLYTES IN THE PRESENCE OF DIFFERENT CO-SOLUTES AT 25°

Solute A	k_1 of A	Co-sol. B	k_1 of B	k_2 of A
HCl	0.000	LiCl	−0.015	−0.0013
HCl	.000	NaCl	− .088	− .0275
HCl	.000	KCl	− .118	− .0620
HCl	.000	CsCl	− .147	− .0978
HBr	.034	NaBr	− .068	− .0391
HBr	.034	KBr	− .112	− .0831
NaCl	− .088	HCl	.000	.0459
KCl	− .118	HCl	.000	.0431
H_4NCl	− .146	HCl	.000	.0408
NaCl	− .088	KCl	− .118	− .0208
KCl	− .118	NaCl	− .088	.0088
LiOH	− .139	LiCl	− .015	− .0038
NaOH	− .077	NaCl	− .088	...
KOH	− .030	KCl	− .118	...
CsOH	− .020	CsCl	− .147	− .0832
$NaBrO_3$	− .161	NaCl	− .088	.0380
$NaBrO_3$	− .161	NaBr	− .068	.0396
$NaBrO_3$	− .161	NaI	− .043	.0430
$KBrO_3$	− .207	KCl	− .118	.0431
$KBrO_3$	− .207	KBr	− .112	.0381
$KBrO_3$	− .207	KI	− .097	.0355
KIO_3	− .228	KCl	− .118	.0540
KIO_3	− .228	KBr	− .112	.0400

Experimental data employed for the calculation of the k_2 constants given in Table II: activity coefficient of hydrochloric acid in pure aqueous solutions, Randall and Young, THIS JOURNAL, **50**, 989 (1928); Harned and Ehlers, *ibid.*, **55**, 2179 (1933); hydrochloric acid in solutions of lithium, sodium and potassium chlorides, Harned, THIS JOURNAL, **48**, 326 (1926), Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); in solutions of lithium chloride, Harned and Copson, THIS JOURNAL, **55**, 2206 (1933); in solutions of potassium chloride, Harned and Hamer, *ibid.*, **55**, 2194 (1933); in solutions of cesium chloride, Harned and Schupp, *ibid.*, **52**, 3892 (1930); hydrobromic acid in pure aqueous solutions according to measurements of James published by Harned, *ibid.*, **51**, 416 (1929); hydrobromic acid in solutions of sodium and potassium bromides, Harned and Hamer, *ibid.*, **55**, 4496 (1933); in the case of sodium bromide the k_2 value obtained for 0.5 *m* has been chosen; using the measurements of Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926), the point given in Fig. 2 of this paper for sodium bromide as co-solute would fall practically right on the curve, instead of being the only one to be slightly off; ammonium chloride in solutions of hydrochloric acid, solubility measurements of Ingham, *J. Chem. Soc.*, **129**, 2059 (1929); lithium hydroxide in solutions of lithium chloride, Harned and Swindells, THIS JOURNAL, **48**, 126 (1926); sodium and potassium hydroxides in solutions of sodium and potassium chlorides, respectively, Harned and Harris, *ibid.*, **50**, 2633 (1928); these measurements show appreciable differences with those of Harned and Hecker, *ibid.*, **55**, 4838 (1933); compare also Harned, *ibid.*, **47**, 676, 686 and 689 (1925); cesium hydroxide in solutions of cesium chloride, Harned and Schupp, *ibid.*, **52**, 3886 and 3892 (1930); sodium and potassium bromates in solutions of the corresponding halides, Ricci, *ibid.*, **56**, 299 (1934); potassium iodate measurements of Comstock of this Laboratory, and Ricci, *ibid.*, **56**, 290 (1934).

An Empirical Relation between k_1 and k_2 Values of Uni-univalent Strong Electrolytes.—Due to the reasons indicated above the tracing of a definite rule for the variation of the k_1 and k_2 values relative to each other is connected with considerable difficulties. The k_2 value of one electrolyte in solution with some other electrolyte does not have the same magnitude with reversed sign as the k_2 value of the other electrolyte with respect to the first one. To advance further we will study the summary given in Table II of the k_1 and k_2 values obtained for a number of the cases where the most reliable measurements are available. Plotting the k_2 values of different electrolytes having the same co-solute against their respective k_1 values we obtain curves which apparently within the limits of the experimental uncertainties are straight lines as shown in Fig. 1. Computing the slopes k_3 of these lines and plotting the values obtained against the k_1 values of the different co-solutes, the result is another straight line which is demonstrated in Fig. 2. Thus it would appear that the slopes along which the k_2 value of an arbitrary uni-univalent electrolyte in solution with a given co-solute of the same valence type is determined by the sum of the intercept with the k_3 axis and the product of a universal constant equal to about 5.20 with the k_1 value of the co-solute. However, in order to fix the position of the lines in Fig. 1 it is also necessary to know the values of their intercepts with the k_2 axis. The latter do not appear to be related directly to the k_1 values of the co-solutes and have to be determined separately for each case. In Table III is given a summary of the data for Fig. 2 and the values of these intercepts for the electrolytes indicated. Using the equations discussed above and the constants in Table III the solubility curve for any one of the electrolytes forming a solid phase at 25° and for which data are given, may thus be calculated in an arbitrary mixture of the same, provided that chemical reactions do not occur or unknown solid phases or solid solutions are not formed. Within these restrictions the solubility curves for any other uni-univalent strong electrolytes with known k_1 values may be calculated for solutions containing as co-solutes any one of the electrolytes treated in Table III.

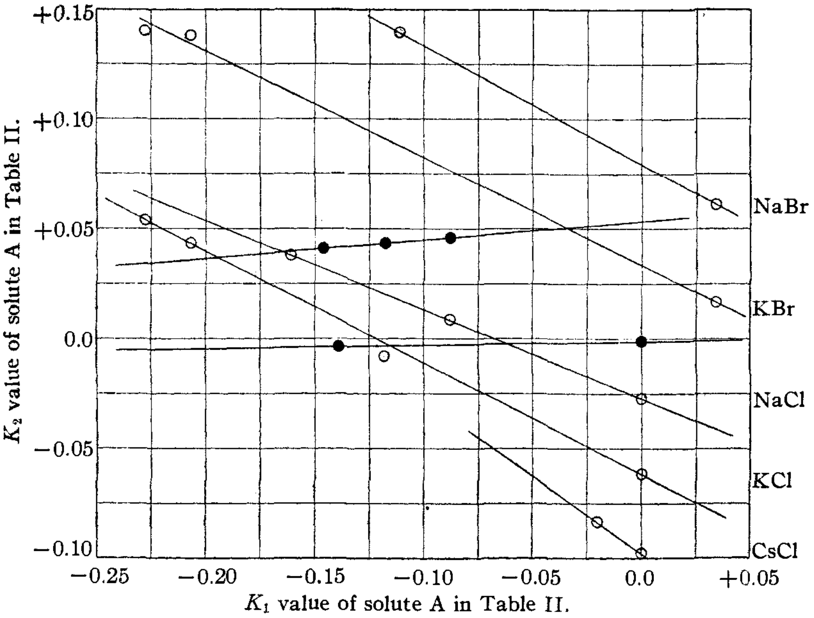

Fig. 1.—Curves for the K_2 values of electrolytes having the same co-solute. Upper curve with black dots hydrochloric acid, lower curve lithium chloride as co-solute. To avoid confusion of the points curves for potassium and sodium bromide are moved up 0.1.

TABLE III

VALUES OF SLOPES AND INTERCEPTS OF THE CURVES IN FIG. 1

Co-solute	k_1	k_3	Intercept
Hydrochloric acid	0.000	0.09	0.053
Lithium chloride	− .015	.02	− .001
Sodium chloride	− .088	− .40	− .027
Potassium chloride	− .118	− .51	− .062
Cesium chloride	− .147	− .73	− .098
Sodium bromide	− .068	− .39	− .021
Potassium bromide	− .112	− .49	− .067

An Application of the Relations Found between the k_1 and k_2 Values to the Study of Solid Solutions.—A thermodynamic approach to a numerical study of the properties of solid solutions appearing as solid phases in systems composed of strong electrolytes and a solvent has previously not been possible due to the absence of any data on the activities of the component electrolytes in the liquid phase, which must equal those of the same components in the solid solution. This obstacle may now be removed by using the relations developed above for the variations of the k_1 and k_2 values of the electrolytes concerned relative to each other.

As an example we will choose the system potassium chloride–potassium bromide–water studied by Amadori and Pampini[4] at 25°. The two electrolytes form as solid phases a continuous series of solid solutions. Their activities in the liquid phase may be calculated from the equations

$$\log a_{KCl} = \log \gamma_{HCl(\mu_T)} - 0.118\,\mu_T - 0.0064\,\mu_{KBr} + {}^1/_2\,(\log \mu_T + \log \mu_{KCl})$$

$$\log a_{KBr} = \log \gamma_{HCl(\mu_T)} - 0.112\,\mu_T - 0.0055\,\mu_{KCl} + {}^1/_2\,(\log \mu_T + \log \mu_{KBr})$$

The two k_2 values were derived from the data in Table II according to the rules given above. The experimental data and the calculations are summarized in Table IV and graphically treated in

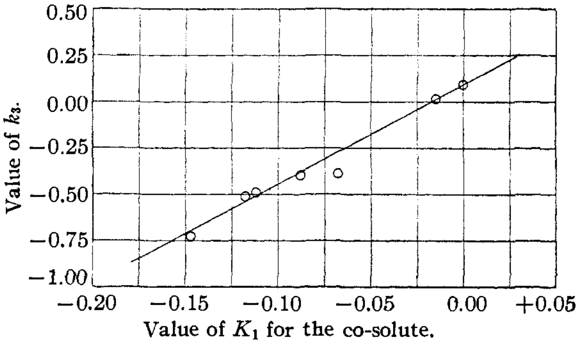

Fig. 2.—The slopes of the curves in Fig. 1 as plotted against the K_1 values of the co-solutes.

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(4) Amadori and Pampini, *Att. Accad. Lincei* [V], **21**, I, 667 (1911).

Fig. 3. From the curves shown in this figure we find that if larger amounts of both salts are present in the solid phase, their activity product is approximately constant as had to be expected if a true equilibrium had been established. Plotting the values of a/N, where N is the mole fraction, the decrease observed at low concentrations is comparable to that of the activity coefficient of strong electrolytes in media of very low dielectric constant.

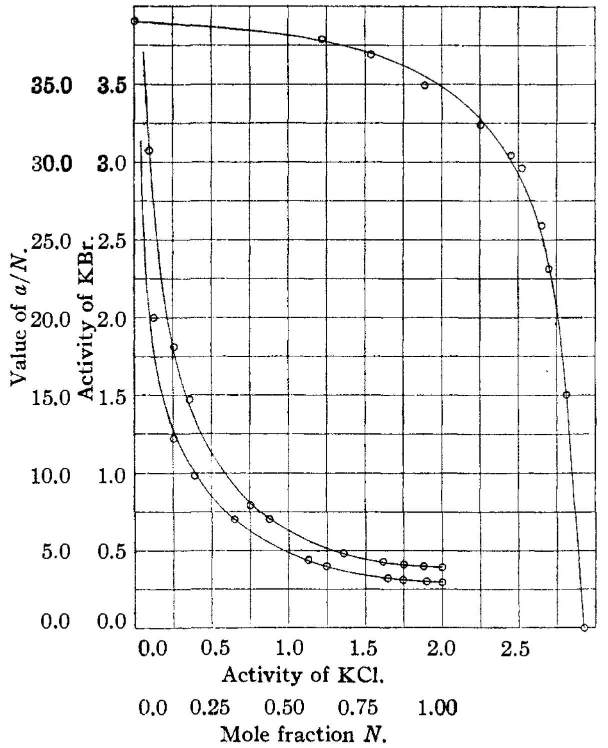

Fig. 3.—The curve for the activities of the salts in the system potassium chloride–potassium bromide–water at 25° as plotted against each other and the curves for the ratio a/N as plotted against N.

TABLE IV

ACTIVITIES OF THE SALTS IN THE SYSTEM POTASSIUM CHLORIDE–POTASSIUM BROMIDE–WATER AT 25°

Composition of solid solutions		Composition of liquid phase					
N KCl	N KBr	m KCl	m KBr	μ total	$\log \gamma_{HCl}$	a KCl	a KBr
1.000	0.000	4.819	0.000	4.819	0.3517	2.93	0.00
0.951	.049	4.161	1.087	5.248	.4096	2.84	1.50
.872	.128	3.472	2.237	5.709	.4700	2.70	2.31
.823	.177	3.248	2.649	5.897	.4948	2.65	2.59
.624	.376	2.848	3.252	6.100	.5216	2.52	2.96
.564	.436	2.707	3.406	6.113	.5232	2.45	3.04
.323	.677	2.304	3.816	6.120	.5241	2.25	3.24
.194	.806	1.674	4.407	6.081	.5190	1.89	3.49
.126	.874	1.135	4.916	6.051	.5152	1.54	3.69
.061	.939	0.728	5.231	5.959	.5030	1.22	3.79
.000	1.000	0.000	5.753	5.753	.4760	0.00	3.91

Summary

The method given in a previous paper for the calculation of the composition of the liquid phase in a ternary system formed by two strong electrolytes and water as a solvent has been extended to poly-component systems with an arbitrary number of uni-univalent, strong electrolytes present in the solid or the liquid phase. A study of the constants needed for the equations employed has shown that they follow rules that are unexpectedly simple. Using a new universal constant, the known k_1 and k_2 values for some reference electrolyte, the composition of the liquid phase may be calculated for any poly-component system containing as pure solid phases any electrolyte with known k_1 values. The relations obtained for the variations of the k_1 and k_2 values relative to each other have been used for a computation of the activities of the components in solid solutions formed by potassium chloride and potassium bromide.

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