
**CORRELATION OF SOLUBILITIES IN SYSTEMS WITH COMPONENTS
FORMING SOLID SOLUTIONS;
THE SYSTEM KBr-KCl-H₂O**

S. NIKL* and J. NÝVLT

*Research Institute of Inorganic Chemistry,
400 60 Ústí nad Labem*

Received August 1st, 1975

Relations were derived correlating equilibrium data of solid and liquid phases in systems with components forming solid solutions. The equation has been applied to the system KBr-KCl-H₂O at 25, 30 and 35°C. Data for 25 and 35°C were taken from literature, for 30°C they were obtained experimentally. The derived relations are with a reasonable accuracy expressing the equilibrium compositions of the liquid and solid phases.

Relations were derived in recent publications on which basis the calculation of the equilibrium composition of phases in a three-phase system formed by two salts and one solvent is possible^{1,2}. In comparison to the graphical evaluation, the numerical calculation is advantageous for data tabulating, solution of material balances, and calculation of derived values (*e.g.* the coefficient of solubility in dependence on temperature) as in these cases the algorithm of calculation is of considerable complexity due to the reading of data from the graphs.

For saturated solutions of soluble compounds the concentration region is reached in which the present state of theory does not enable calculation of chemical potentials and the exact thermodynamic procedure cannot be used for calculation of the phase equilibria. For numerical calculation under these conditions it is advantageous to start from the exact thermodynamic relations defining the equilibrium and to substitute the calculation of activities by the empirical development of relative activity coefficients^{3,4} which is also applicable for cases where the components of the system form solid solutions^{2,4}.

In this study the published relations are generalized and verified by a suitable aqueous system of two salts with the same cation forming solid solutions.

THEORETICAL

Simultaneous crystallization of components at formation of a solid solution takes place in a way similar to isomorphous coprecipitation. From four groups into which

* Present address: Spolchemie, 407 11 Boletice nad Labem.

Hahn has subdivided the mechanisms of co-crystallizations, just the isomorphous coprecipitation is best described^{5,6}. The mechanism of establishing the equilibrium in the system which forms solid solutions is at best expressed by the distribution law⁶, where it is assumed that ions of both components are at crystallization in steady equilibrium with the ions inside the crystal. The relations given in the quoted paper are of course suitable only for simultaneous precipitation at small concentration changes where activities can be approximatively substituted by concentrations.

From the condition of equality of chemical potentials of individual components in both equilibrium phases for the case in which a mutual interaction of two types of molecules of the dissolved non-electrolyte and the solvent takes place in the solution, the relation

$$\log(x_i/y_i) = \varphi_i \quad [T, P \text{ sat}] \quad (1)$$

was derived² where $x_i = m_i/m_{i0}$ is the relative molality of the i -th component in the liquid phase and y_i is the molar ratio of the same component in the equilibrium solid phase. If solutions of strong electrolytes are considered, it is advantageous to use for description of the behaviour of the system the mean molality⁷

$$m_{i\pm} = m_i(v_{i+}^{v_{i+}} + v_{i-}^{v_{i-}})^{1/v_i} = (m_{i+}^{v_{i+}} m_{i-}^{v_{i-}})^{1/v_i} \quad (2)$$

Eq. (1) then becomes

$$\begin{aligned} v_i^{-1} [(v_{i+} \log m_{i+} + v_{i-} \log m_{i-}) / (v_{i+} \log m_{i0+} + v_{i-} \log m_{i0-})] = \\ = \varphi_i + \log y_i. \end{aligned} \quad (3)$$

If all dissolved compounds have the same cation, then it holds

$$m_{j+} = \sum_{i=1}^k v_j + m_i / m_{i-} = v_i - m_i \quad (4)$$

and Eq. (5) becomes

$$\begin{aligned} v_i^{-1} \log \left[\left(\sum_{i=1}^k v_j m_i \right)^{v_j+} (v_i - m_i)^{v_j-} (v_j m_{i0})^{-v_j+} (v_i m_{i0})^{-v_j-} \right] = \\ = \varphi_i + \log y_i. \end{aligned} \quad (5)$$

In the three-component system the last relation is simplified to

$$v_1^{-1} \log [(x_1 + x_2 m_{20} / m_{10})^{v_1+} x_1^{v_1-}] - \log y_1 = \varphi_1 \quad (6)$$

(for common anion, the sign in indices changes). The molar ratio $y_{i\pm} = (y_{i+}^{v_{i+}} y_{i-}^{v_{i-}})^{1/v_i}$ can be, for the case with all components in the solid solution having the same cation expressed by use of the relations $y_{1+} = v_{1+} y_1 / (v_{1+} + v_{1-} y_1 + v_{2-} y_2)$ and $y_{1-} = v_{1-} y_1 / (v_{1+} + v_{1-} y_1 + v_{2-} y_2)$ so that *e.g.* for the uniunivalent electrolytes ($v_{1+} = v_{2+}$, $v_{1-} = v_{2-}$, $v_{1+} = v_{1-}$) there results

$$\frac{1}{2} \log [(x_1 + x_2 m_{20} / m_{10}) x_1] - \frac{1}{2} \log (y_1 / 4) = \varphi_1. \quad (7)$$

The three-component system with two phases has only one degree of freedom at a constant temperature and pressure, which means that by choosing the concentration of one component all other concentrations are defined. After introduction of the relation $y_1 = y_2 = 1$ are only 3 Eqs for 4 unknowns available so that by selecting one of the variables the others can be calculated. The disadvantage is the tedious and time-consuming solution of a system of transcendental equations. Thus the function Φ_i has been defined² which describes relations in the liquid phase

$$\Phi_1 = \frac{1}{2} \log [x_1 (x_1 + x_2 m_{20} / m_{10})], \quad (8)$$

$$\Phi_2 = \frac{1}{2} \log [x_2 (x_2 + x_1 m_{10} / m_{20})]$$

and both functions φ and Φ can be then expressed in the form of a power series

$$\varphi_i = \sum_{n=1}^n A_{ni} m_{j\neq i}^n, \quad (9)$$

$$\Phi_i = \sum_{n=1}^n C_{ni} m_{j\neq i}^n. \quad (10)$$

EXPERIMENTAL

For determination of phase equilibrium analytical grade reagents KCl and KBr (Lachema) and redistilled water were used.

The samples were weighed in 150 ml flasks closed with rubber stopper and were kept at constant temperature in the steel bath with the capacity of about 120 l. The vessel was heated by 2 submerged heaters equipped with contact relay. The relay was controlled by a contact thermometer, the accurate setting was made by use of the mercury thermometer controlled according to the standard. The temperature in the vessel was kept constant with the accuracy $\pm 0.15^\circ\text{C}$. The content of the vessel was mixed by the revolving holder with sampling flasks. By revolving the flasks a good contact of both phases has been reached and made the dissolving easier.

The equilibrium time, *i.e.* the time necessary for reaching the equilibrium has been found by weighing 2 sets of 10 samples^{4,11} each with the initial composition of 35 g KBr — 20 g KCl — 55 g H₂O. The first half of samples was prepared so that KBr was dissolved, the sample had been kept overnight and then KCl was added; the procedure was reversed with the second set. From the graphical plot of dependence of composition on the time is obvious that equilibrium has been

reached practically in 12 days. Samples for determination of phase equilibrium were taken after 20 days. Sampling was made by the method described earlier⁴.

For determination of chlorides and bromides in the same sample was used, after testing of 4 methods, the direct titration of AgNO_3 with the potentiometric indication. The Silver electrode was used as indicator with the calomel electrode^{7,8} as reference.

The effect of rough, random errors was eliminated by preparing always two samples at the same time. Dissolving of the components in the reversed sequence has enabled to determine the imperfect steadying of equilibrium for each sample. To be able to compare the results of 2 parallel samples, the dissolved components have to be weighed with an accuracy of 10^{-3} g; water with an accuracy of 0.1 g. The point of equivalency on the titration curve was performed according to the isoplane method⁸.

RESULTS AND DISCUSSION

By the described method, 8 points on the equilibrium curve were determined always simultaneously in two samples. The experimental results and the procedure of calculation are given in Table I together with data for 25 and 35°C taken from literature.

Interaction coefficients in Eqs (13) and (14) were evaluated by combination of the graphical and numerical procedures. As this procedure is rather cumbersome a program was set for the Cellatron computer. For individual temperatures the following correlation relations were found:

For temperature 25°C:

$$\begin{aligned}
 \Phi_1 &= -0.0160m_2 + 0.0035m_2^2 - 0.0049m_2^3 \\
 \Phi_2 &= -0.0080m_1^2 \\
 \varphi_1 &= -0.035m_2 + 0.0015m_2^2 + 0.0036m_2^3 \\
 \varphi_2 &= -0.0008m_1 - 0.0063m_1^2 + 0.0025m_1^3 \\
 \log y_1 &= -0.0250m_2 + 0.0040m_2^2 - 0.0170m_2^3 \\
 \log y_2 &= -0.0015m_1 - 0.0034m_1^2 - 0.0050m_1^3
 \end{aligned} \tag{11}$$

For temperature 30°C:

$$\begin{aligned}
 \Phi_1 &= -0.0016m_2 + 0.0045m_2^2 - 0.0049m_2^3 \\
 \Phi_2 &= -0.0020m_1 - 0.0034m_1^2 - 0.0003m_1^3 \\
 \varphi_1 &= -0.0010m_2 - 0.0015m_2^2 + 0.0038m_2^3 \\
 \varphi_2 &= -0.0032m_1 - 0.0040m_1^2 + 0.0025m_1^3 \\
 \log y_1 &= 0.0280m_2 + 0.0098m_2^2 - 0.0210m_2^3 \\
 \log y_2 &= 0.0044m_1 - 0.0198m_1^2 + 0.0020m_1^3.
 \end{aligned} \tag{12}$$

For temperature 35°C:

$$\begin{aligned}
 \Phi_1 &= -0.0160m_2 + 0.0058m_2^2 - 0.0049m_2^3 \\
 \Phi_2 &= -0.0090m_1 - 0.0042m_1^2 \\
 \varphi_1 &= -0.0010m_2 - 0.0017m_2^2 + 0.0036m_2^3 \\
 \varphi_2 &= -0.0055m_1 - 0.0020m_1^2 + 0.0010m_1^3 \\
 \log y_1 &= -0.0300m_2 + 0.0150m_2^2 - 0.0174m_2^3 \quad (13) \\
 &\quad (\text{for } m_1 = 5.80 - 4.28) \\
 \log y_2 &= -0.0070m_1 - 0.0044m_1^2 - 0.0020m_1^3 \\
 &\quad (\text{for } m_2 = 5.24 - 3.00)
 \end{aligned}$$

If the interaction coefficients in the above given equations are known, a selection of a single concentration in the solid or liquid phase enables the calculation of the remaining three concentrations.

By arranging Eq. (8) the quadratic Eq. can be obtained *e.g.*

$$x_2^2 + \frac{m_2}{m_{10}} x_2 - 10^{\Phi_2} = 0, \quad (14)$$

which can be solved in the usual way.

The system KCl-KBr-H₂O was described for temperatures 25 and 35°C⁹⁻¹², mostly as the composition of the liquid phase only. For 30°C the solubility data

TABLE I
Experimental Data on System Composition at 30°C

a_1 g/100 g H ₂ O	a_2 g/100 g H ₂ O	x_1	x_2	w_1 wt %	w_2 wt %	y_1	y_2
41.62	0	1.000	0		100		
34.29	6.66	0.8146	0.3126	1.89	98.11	0.0298	0.9702
28.05	11.45	0.6504	0.5246	14.00	86.00	0.2260	0.7740
24.30	13.40	0.5472	0.5962	16.33	83.67	0.2376	0.7624
20.00	16.05	0.4387	0.6957	39.19	60.81	0.5071	0.4929
14.03	18.82	0.2931	0.7769	59.20	40.80	0.6985	0.3015
9.42	21.88	0.1924	0.8828	88.70	11.30	0.9261	0.0739
0	26.51	0	1	100		0	

TABLE II
Calculated Composition of Phases

m_1 , mol/kg	m_2 , mol/kg	Φ_1/m_2	Φ_2/m_1	x_2	$x_2(\text{exp.})$	y_1	$y_1(\text{exp.})$	y_2	$y_2(\text{exp.})$
25°C, Eq. (II)									
0.3307	4.5842	0.1424	0.0086	0.9689	0.9595	0.0196	—	0.9976	+
0.6695	4.4058	0.1118	0.0067	0.9241	0.9221	0.0302	—	0.9908	—
1.0281	4.2353	0.0930	0.0050	0.8778	0.8864	0.0441	—	0.9760	—
1.2716	4.0796	0.0855	0.0076	0.8466	0.8539	0.0607	0.0579	0.9597	0.9421
1.2348	4.0395	0.0884	0.0148	0.8520	0.8390	0.0657	0.0678	0.9628	0.9322
1.8073	3.6305	0.0781	0.0174	0.7712	0.7599	0.1347	—	0.9050	—
2.1895	3.5118	0.0599	0.0130	0.7151	0.7350	0.1614	—	0.8471	—
2.4812	3.2597	0.0557	0.0174	0.6701	0.6823	0.2282	0.1827	0.7925	0.8173
2.6276	3.1924	0.0521	0.0183	0.6492	0.6631	0.2482	0.1877	0.7619	0.8123
2.9725	3.0294	0.0438	0.0166	0.4875	0.5184	0.3000	0.2834	0.6826	0.7166
3.0246	2.9395	0.0443	0.0201	0.5102	0.5275	0.3304	0.2756	0.6699	0.7244
3.6017	2.5216	0.0344	0.0245	0.6102	0.6281	0.4824	0.4844	0.5210	0.5156
3.6504	2.4264	0.0352	0.0260	0.6316	0.6366	0.5180	0.5389	0.5077	0.4611
3.9695	2.1576	0.0303	0.0299	0.6885	0.6923	0.6165	—	0.4244	—
4.1033	2.0953	0.0266	0.0299	0.7009	0.7156	0.6385	0.6783	0.3901	0.3217
4.2111	1.9233	0.0272	0.0348	0.7337	0.7344	0.6966	0.7275	0.3631	0.2725
4.5552	1.5567	0.0232	0.0417	0.7970	0.7944	0.8037	0.7992	0.2818	0.2008
4.9200	1.0767	0.0219	0.0564	0.8628	0.8557	0.9028	0.8910	0.2064	0.1090
4.9198	1.0487	0.0234	0.0605	0.8708	0.8580	0.9080	0.8839	0.2065	0.1161
5.3994	0.4726	0.0177	0.0854	0.9416	0.9416	0.9710	0.9576	0.1276	0.0424

30°C, Eq. (12)

1-1518	4-2709	-0-0895	-0-0020	0-8720	0-8828	0-0208	0-0119	0-9870	0-9792
1-7551	3-7584	-0-0800	-0-0151	0-8002	0-7769	0-0925	0-0829	0-9380	0-8975
2-6270	3-3656	-0-0531	-0-0123	0-6918	0-6957	0-1089	0-1045	0-7850	0-8911
3-2764	2-8843	-0-0433	-0-0183	0-6077	0-5962	0-2867	0-3139	0-6140	0-7124
3-8945	2-5379	-0-0307	-0-0201	0-5266	0-5246	0-4762	0-4454	0-4340	0-5238
4-8778	1-5125	-0-0201	-0-0394	0-3988	0-3126	0-8310	0-8079	0-1880	0-1690

35°C, Eq. (13)

5-7818	0-6450	-0-0147	-0-0707	0-9975	1-0068	0-0005	0-0008	0-9995	0-9992
5-2491	1-1686	-0-0263	-0-0564	0-9918	0-9810	0-0014	0-0026	0-9986	0-9974
4-6527	2-9995	-0-0241	-0-0247	0-9780	0-9642	0-0043	0-0070	0-9957	0-9930
4-3091	2-3398	-0-0282	-0-0279	0-9591	0-9656	0-0086	0-0145	0-9914	0-9855
4-2837	2-4110	-0-0273	-0-0262	0-8926	0-8848	0-0299	0-0395	0-9701	0-9605
3-4718	3-0240	-0-0390	-0-0201	0-8791	0-8650	0-0368	0-0456	0-9632	0-9544
3-3092	3-1013	-0-0423	-0-0203	0-8376	0-8246	0-0595	0-0625	0-9405	0-9375
1-8840	4-1404	-0-0693	-0-0094	0-8293	0-8351	0-0649	0-0674	0-9351	0-9326
1-6493	4-1801	-0-0755	-0-0139	0-7962	0-8034	0-0823	0-0812	0-9177	0-9188
1-3915	4-3448	-0-0806	-0-0129	0-7656	0-7958	0-1142	0-1032	0-8858	0-8968
1-3257	4-2903	-0-0847	-0-0191	0-5800	0-5961	0-3406	0-3281	0-6594	0-6719
0-9955	4-5005	-0-0947	-0-0197	0-5593	0-5812	0-3674	0-3585	0-6326	0-6417
0-8886	4-6034	-0-0979	-0-0167	0-4580	0-4634	0-5902	0-6211	0-4098	0-3789
0-3461	5-0238	-0-1314	-0-0021	0-4497	0-4497	0-6152	0-6390	0-3848	0-3610
0-1877	5-0168	-0-1620	-0-0418	0-4145	0-4410	0-6952	0-7127	0-3048	0-2873
0-0712	5-1040	-0-1982	-0-0747	0-3480	0-2246	0-9070	0-8696	0-0930	0-1304
0-0211	5-2385	-0-2463	-0-1813	0-2514	0-1240	0-9598	0-9365	0-0402	0-0635
	5-2021								

were not found. The data taken from literature for 25 and 35°C were correlated in the same manner as our own experimental data for 30°C. The results of correlations are summarized in Table II. The calculated compositions of the solid phase at 30 and 35°C are in a good agreement with the experimental data. The maximum deviation is $\Delta y = 0.0375$ which corresponds to the maximum error of 4%. At 25°C the data are more scattered with a greater maximum deviation $\Delta y = 0.0843$. In the liquid phase, the experimental data were correlated satisfactorily by the used equations with the exception of the smallest concentrations. With low concentrations the error is largely due to inaccuracy in the analytical method or to reading off the values from the graph. For temperatures 25 and 30°C, the derived relations hold for the whole concentration range, for 35°C they can be also satisfactorily used for concentrations larger than 0.2 mol/kg.

REFERENCES

1. Nývlt J.: This Journal 34, 2348 (1969).
2. Nývlt J., Majrich A., Kočová H.: This Journal 35, 165 (1970).
3. Erdős E.: Chem. Listy 51, 1632 (1957).
4. Nývlt J.: *Rovnováhy tuhá fáze-kapalina*. Academia, Prague 1975.
5. Doerner H. A., Hoskins W. M.: J. Amer. Chem. Soc. 47, 662 (1925).
6. Chlopin V. G.: Z. Anorg. Allg. Chem. 143, 97 (1925).
7. Níkl S.: *Thesis*. Institute of Chemical Technology, Prague 1970.
8. *Analytická příručka* (J. Zýka, Ed.). SNTL, Prague 1966.
9. Linke W. F., Seidell A.: *Solubilities*, Vol. II. Amer. Chem. Soc., Washington 1965.
10. Bergman A. G., Vlasov N. A.: Izv. Akad. Nauk SSSR 36, 57 (1942).
11. Durham G. S., Rock E. J., Frayn J. S.: J. Amer. Chem. Soc. 75, 5792 (1953).
12. Flatt R., Burghardt G.: Helv. Chim. Acta 27, 1605 (1944).

Translated by M. Rylek.