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Abstract

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A. N. KIRGINTSEV, I. I. YAKOVLEV

EXTRACTION EQUATION
FOR TERNARY AQUEOUS-SALT SOLUTIONS

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In studying extraction in ternary aqueous-salt solutions with an extractant insoluble in these solutions, we obtain data on the composition of the coexisting phases. The dependence of the composition of one phase on the composition of the other is ultimately determined by the thermodynamic characteristics of these phases. Therefore, naturally, the question arises of obtaining information on the thermodynamic properties of one phase if the thermodynamic properties of the other phase are known.

The thermodynamic properties of ternary aqueous-salt solutions can be studied most simply by means of isopiestic investigations. It can be shown that, in a first approximation, for solutions of the type AC_{n_2}—BC_{n_4}—H_2O, integration of the McKay-Perring differential equation (1) gives (see, for example, (2))

$$\ln \frac{a_i}{a_{i0}} = K(1-y_i)^2 \ln \frac{1}{a_w} + \ln y_1, \quad [a_w], \tag{1}$$

where a_w is the activity of water; K is a constant; y_i and a_i are the mole fraction and activity of the salt of the i-th component in the ternary solution ($i = 1, 2$), with y_i calculated without taking water into account; $a_i = a_{i0}$ when $y_i \to 1$ ($a_w = \text{const}$).

Let us consider the extraction of salts AC_{n_2} and BC_{n_4} from an aqueous solution by an extractant insoluble in this solution, at constant temperature and pressure. In the state of equilibrium

$$\mu_i' = \mu_i'', \tag{2}$$

where the prime denotes the organic phase, and the double prime the aqueous phase. We express the chemical potential in terms of activities, i.e.

$$\mu_i' = \mu_{i0}' + RT \ln a_i',$$

$$\mu_i'' = \mu_{i0}'' + RT \ln a_i''. \tag{3}$$

Taking (1) into account, the last of these equations may be written as

$$\mu_i'' = \mu_{i0}'' + RT\ln a_{i0}'' + RTK(1-y_i)^2 \ln\frac{1}{a_w} + RT\ln y_i, \quad [a_w]. \tag{4}$$

From (2) we obtain the usual thermodynamic relation

$$\lg a_i' = \lg a_{i0}'' + K(1-y_i)^2 \lg\frac{1}{a_w} + \lg y_1 + K_i^0, \quad [a_w], \tag{5}$$

where

$$K_i^0 = \frac{1}{2.3}\frac{\mu_{i0}'' - \mu_{i0}'}{RT}. \tag{6}$$

Equation (5) makes it possible to determine the activity of the salt of the i-th component in the extractant up to the constant K_i^0. Indeed, the quantity a_{i0}'' is the activity of the salt of the i-th component in the binary salt-water solution at water activity a_w. These quantities are known for many solutions (3). The numerical value of the quantity K is determined from isopiestic measurements. Therefore, all terms on the right-hand side of equation (5), with the exception of the quantity K_i^0, are known.

For practical application of equation (5), it is convenient to represent the quantity a_i' in the form

$$\lg a_i' = \lg x_i + f(x_i), \tag{7}$$

where x_i is the mole fraction of component i in the organic phase.

Table 1

Extraction with tributyl phosphate from ternary solutions NH_4NO_3–$Ca(NO_3)_2$–H_2O at 25°

$Ca(NO_3)_2$, wt. %	H_2O, wt. %	x_2	x_w	NH_4NO_3, wt. %	$Ca(NO_3)_2$, wt. %	m	y_2	$\lg a_2' - K_2^0$
				$a_w = 0.6734$; $\lg a_{20}'' = 1.52$				
0.00	3.40	0.000	0.345	62.25	0.00	20.494	0.000	
4.10	3.20	0.047	0.336	55.50	5.58	18.683	0.047	−0.513
5.50	3.06	0.065	0.329	49.60	11.02	17.310	0.095	−0.138
6.90	3.06	0.081	0.328	41.80	17.00	15.496	0.165	+0.198
8.30	3.15	0.097	0.341	34.90	22.96	13.692	0.243	+0.463
9.40	3.24	0.111	0.350	28.30	28.20	12.052	0.327	+0.685

$Ca(NO_3)_2$, wt. %	H_2O, wt. %	x_2	x_w	NH_4NO_3, wt. %	$Ca(NO_3)_2$, wt. %	m	y_2	$\lg a'_2 - K_2^0$
10.30	3.36	0.121	0.361	22.36	32.60	10.651	0.415	+0.873
11.30	3.50	0.132	0.373	16.04	37.20	9.125	0.532	+1.077
12.00	3.60	0.139	0.381	10.44	41.10	7.844	0.657	+1.247
13.30	3.85	0.150	0.400	0.00	47.75	5.582	1.000	
				$a_w = 0.7532$; $\lg a''_{20} = 0.91$				
0.00	4.00	0.000	0.381	51.80	0.00	13.639	0.000	
1.92	3.77	0.020	0.364	47.25	4.72	12.710	0.047	−0.922
3.33	3.66	0.035	0.355	42.30	9.07	11.874	0.095	−0.567
4.90	3.62	0.052	0.350	35.93	14.55	10.936	0.165	−0.259
6.30	3.70	0.066	0.353	30.50	19.76	9.890	0.243	−0.022
7.40	3.85	0.077	0.361	24.40	24.40	8.868	0.327	+0.175
8.30	3.95	0.084	0.366	19.43	28.40	7.955	0.415	+0.338
9.15	4.10	0.091	0.374	13.90	32.40	6.924	0.532	+0.515
9.80	4.17	0.097	0.377	9.07	35.70	6.043	0.657	+0.663
10.46	4.25	0.103	0.381	4.46	38.70	5.198	0.811	+0.799
11.30	4.33	0.110	0.384	0.00	41.86	1.000	1.000	
				$a_w = 0.8618$; $\lg a''_{20} = -0.06$				
0	4.95	0.000	0.435	33.00	0.00	6.172	0.000	
0.62	4.73	0.006	0.422	30.20	3.03	5.924	0.047	−1.653
1.30	4.66	0.012	0.417	27.46	5.88	5.692	0.095	−1.348
2.10	4.70	0.021	0.418	24.10	9.64	5.399	0.165	−1.045
2.90	4.75	0.028	0.419	20.20	13.30	5.025	0.243	−0.841
3.70	4.80	0.035	0.419	16.65	16.61	4.646	0.327	−0.677
4.40	4.90	0.042	0.425	13.43	19.53	4.283	0.415	−0.542
5.20	5.00	0.049	0.429	9.76	22.80	3.863	0.532	−0.397
5.85	5.05	0.055	0.431	6.50	25.55	3.486	0.657	−0.276
6.50	5.07	0.061	0.431	3.20	28.23	3.090	0.811	−0.161
7.10	5.10	0.066	4.431	0.00	30.05	2.699	1.000	

If the composition of coexisting phases is known at some water activity a_w, then from equation (5) the quantity $\lg a'_i - K_i^0$ can be determined and, consequently, the dependence of the quantity $f(x_i) - K_i^0$ on the composition can be found empirically. Using this dependence, from (5) we obtain an extraction equation valid for any water activity.

As an example, let us consider extraction from ternary solutions NH_4NO_3–$Ca(NO_3)_2$–H_2O with tributyl phosphate (TBP). In studying extraction in the indicated system it turned out that ammonium nitrate is practically not extracted. Table 1 gives the results of studying the composition of equilibrium phases at constant water activity. In this table x_2 and x_w denote the mole fraction of calcium nitrate and water in the organic phase, m and y_2 the total molality and the mole fraction of calcium nitrate, not counting water, in the aqueous solution. The last column of the table gives the value of the quantity $\lg a_2' - K_2^0$ (a_2 is the activity of calcium nitrate in the organic phase), calculated from equation (5). This calculation was carried out as follows. First, the ternary ...

solutions NH_4NO_3—$Ca(NO_3)_2$—H_2O. It turned out that, to a good approximation, the value K in equation (1) is equal to -4.5. The value of $\lg a_{20}''$ corresponding to the given value of a_w was found from the graph in Fig. 1, constructed from the data given in monograph (3).

(Figure: Fig. 1)

Fig. 1. Dependence of the logarithm of the activity of calcium nitrate on the activity of water in the binary solution $Ca(NO_3)_2$—H_2O at 25°

(Figure: Fig. 2)

Fig. 2. 1—$a_w = 0.6734$; 2—$a_w = 0.7532$; 3—$a_w = 0.8618$

In Fig. 2 the dependence $r = \lg a_2' - \lg x_2 - K_2^0$ on x_2 is plotted. The quantity r was calculated from the data of Table 1. All the experimental points satisfactorily fall on the straight line $r = 0.40 + 10x_2$.

In accordance with (7),

$$f(x_2) = r + K_2^0 = K_2^0 + 0.40 + 10x_2, \tag{8}$$

$$\lg a_2' - K_2^0 = 0.40 + 10x_2 + \lg x_2. \tag{9}$$

From (9) and (5) we obtain

$$\lg \frac{x_2}{y_2} = \lg a_{20}'' - 0.40 + 4.5y_1^2 \lg a_w - 10x_2,\ [a_w]$$

—the extraction equation for calcium nitrate in the system under consideration. Let us note that the first, second, and last terms of the right-hand side of this equation depend only on the properties of the binary solutions calcium nitrate—water and on the interaction of calcium nitrate with TBP. The third term of the right-hand side is determined by the properties of the ternary solutions NH_4NO_3—$Ca(NO_3)_2$—H_2O. If NH_4NO_3 is replaced by some other salt not extracted by TBP, only the value of this term will change, i.e. the quantity in equation (5) will assume another value.

From equation (9) the value of the quantity K_2^0 can be formally calculated. Indeed, in accordance with (6), the quantity K_i^0 is determined by the standard states of the solutions salt of the i-th component—water and salt of the i-th component—extractant. As the standard state in the first solution an infinitely dilute solution is adopted, and in the second solution we shall take the pure substance as the standard state, i.e. $a_i' \to 1$ as $x_i \to 1$. Then in equation (9) $\lg a_2' \to 0$ as $x_2 \to 1$. Therefore $K_2^0 = -10.4$.

In an analogous manner, extraction equations with an insoluble extractant can also be found in other ternary aqueous-salt solutions. For this, as we have seen, it is necessary to study the composition of coexisting phases under isopiestic conditions and to have data from isopiestic measurements in ternary aqueous-salt solutions. With a well-established technique, carrying out isopiestic measurements presents no difficulties. Therefore the method described in this work for obtaining information on the thermodynamic features of the organic phase (the extraction equation) can be used to clarify the mechanism of extraction processes.

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.