

### S 61. *The Activity Coefficient of Uranyl Nitrate in the Presence of Sodium Nitrate.*

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The activity coefficient  $\gamma_1$  of uranyl nitrate in presence of sodium nitrate has been measured by a solvent-extraction method, using a technique of circulating an organic uranyl nitrate solution through a series of aqueous solutions. At constant ionic strength it has been found that  $\log \gamma_1$  varies linearly with the sodium nitrate molality. Thermodynamic arguments show, however, that  $\log \gamma_2$ , where  $\gamma_2$  is the activity coefficient of the sodium nitrate, cannot be a simple linear function of the uranyl nitrate molarity.

THERE have been few determinations hitherto of the activity coefficients of the individual electrolytes in mixtures of strong electrolytes. The difficulty is to find suitable methods: E.M.F. measurements can be used in a limited number of cases, *e.g.*, for hydrochloric acid in presence of chlorides, and a certain amount of information can be obtained from solubility measurements (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, Chap. 14), but general methods applicable to all electrolytes are lacking.

Uranyl nitrate is a favourable case on account of its solubility in organic solvents such as ethers and ketones. Its activity in mixed nitrate solutions can be determined by partition experiments with such solvents. If two aqueous solutions *A* and *B* come to equilibrium with the same concentration of uranyl nitrate in the organic phase, then *A* and *B* contain uranyl nitrate at the same activity. If *A* is a pure uranyl nitrate solution, this activity is already known from isopiestic work (Robinson, Wilson, and Ayling, *J. Amer. Chem. Soc.*, 1942, **64**, 1469). We know, therefore, the activity in solution *B*, which may be a mixed nitrate solution. The organic phase acts, as it were, as a semipermeable membrane between solutions *A* and *B*, through which uranyl but not other nitrates can come to equilibrium.

For the mixed solutions of uranyl nitrate and sodium nitrate employed in the present work, the theory is as follows. Let the *m*'s be molarities and the  $\gamma$ 's mean total activity coefficients, and let subscripts 1 and 2 refer to uranyl nitrate and sodium nitrate respectively. Then the activity of uranyl nitrate in a mixed solution is  $m_1(2m_1 + m_2)^2\gamma_1^3$ . For a series of "iso-active" solutions, this quantity is a constant. In particular, if one of the iso-active solutions contains no sodium nitrate we have

$$m_1(2m_1 + m_2)^2\gamma_1^3 = 4\bar{m}_1^3\bar{\gamma}_1^3 \dots \dots \dots (1)$$

where  $\bar{m}_1$  and  $\bar{\gamma}_1$  refer to the pure uranyl nitrate solution. Since  $\bar{\gamma}_1$  is known as a function of  $\bar{m}_1$  this equation enables us to determine  $\gamma_1$ .

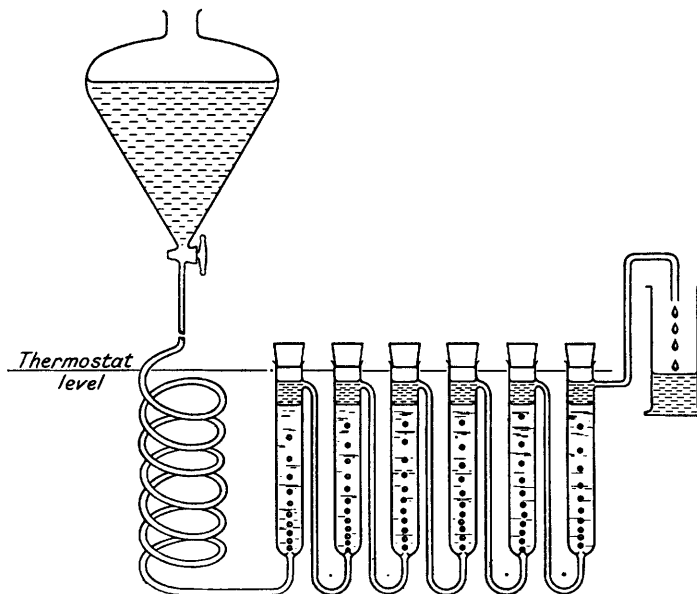
Among the conditions for success are: (1) Low solubility of the organic solvent in the aqueous phase; otherwise the solvent may modify the solute activities. (2) Low solubility of water and of the second nitrate in the organic phase; otherwise it may not be possible to assume that the activity of uranyl nitrate in the organic phase is a function only of its concentration in that phase. (3) For practical reasons, uranyl nitrate partitions that are not too heavily in favour of the aqueous phase. Solvents which appear to fulfil these conditions are dibutyl and higher ethers.

\* Contribution to the Discussion of paper No. S 59, "The Hydrolysis of Uranyl Salts," by J. Sutton.

Rather surprisingly, partition experiments have been little used hitherto for the determination of activity coefficients in aqueous solution; yet the principle employed in the present work is well known in metallurgy for the determination, for instance, of the activity coefficient of FeO in slags consisting of FeO, SiO<sub>2</sub>, CaO, and MgO, where partitions of FeO with molten iron are measured (Chipman, Faraday Soc. Discussion, No. 4, 1948, p. 23).

#### EXPERIMENTAL.

The apparatus is shown in the figure. A solution of uranyl nitrate in the organic solvent was circulated through a series of tubes containing mixed aqueous solutions of uranyl nitrate and sodium nitrate at different concentrations. The first tube contained uranyl nitrate only. In each tube, uranyl nitrate was transferred from the organic solvent into the aqueous solution, or in the opposite direction, until equilibrium had been achieved. Thereafter, the organic solution passed through the apparatus unchanged, and it could be assumed that the uranyl nitrate activity was the same in all six tubes. Analysis of the six solutions then gave the data required.



Apparatus for equilibration of solutions.

**Materials.**—The ethers used as solvents were commercial products which were purified by distillation, followed by treatment with alkaline permanganate until no further reduction occurred; finally, they were washed with water. The nitrates were "AnalaR" grade materials, and were not further purified.

**Solutions.**—The apparatus was filled initially with a series of solutions known to be approximately in equilibrium with the organic uranyl nitrate solution. The concentration of uranyl nitrate decreased, and that of sodium nitrate increased from left to right in the figure. The first tube on the left-hand side contained pure uranyl nitrate solution.

**Equilibrations.**—The organic solution was allowed to flow through the apparatus at 5–10 ml./minute. For the first hour or so the apparatus stood on the bench, and then for a further hour at least it was immersed in a thermostat at 25°. Before it was placed in the thermostat, the rubber bungs were removed, and the solutions stirred. This was to overcome a minor design defect, *viz.*, the existence of a small "dead" volume of aqueous solution at the base of each tube, which did not automatically mix with the bulk.

No visible entrainment of aqueous phase by the organic phase could be detected, and both phases remained perfectly clear throughout.

Two tests were made to check the completeness of the equilibrations. On one occasion the organic solution which had passed through the apparatus was compared colorimetrically, by means of a Spekker absorptiometer, with that being fed in. After only 30 minutes' running, no composition change could be detected. The second check was made as follows. At the start of the run, the fourth, fifth, and sixth tubes were filled respectively with the same solutions as the first, second, and third tubes. All the solutions were analysed as usual at the end of the run with the following results:

Molarities,			Molarities,		
Tube no.	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .	NaNO <sub>3</sub> .	Tube no.	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .	NaNO <sub>3</sub> .
1	1.075	—	4	1.053	—
2	0.676	2.35	5	0.658	2.33
3	0.283	5.25	6	0.290	5.16

The agreement of the analyses for the respective pairs of tubes indicates that equilibrium had been attained.

*Analyses.*—Uranium was precipitated with tannic acid, and weighed as  $U_3O_8$ . Sodium was weighed as sodium zinc uranyl acetate. The accuracy of the individual analyses is estimated as  $\pm 2\%$ .

RESULTS AND DISCUSSION.

The results are given in Table I. The solutions in each run are iso-active in uranyl nitrate. The activity coefficients have been calculated according to equation (1), using the figures in Table II for  $\bar{\gamma}_1$ , which contains the results of Robinson, Wilson, and Ayling (*loc. cit.*) reduced by a constant factor in accordance with the later work of Stokes (private communication based on *Trans. Faraday Soc.*, 1948, **44**, 295).

TABLE I.

Run no.	Molarities,					Run no.	Molarities,				
	$UO_2(NO_3)_2$	$NaNO_3$	$\mu$	$\gamma_1$	$\alpha_{12}$		$UO_2(NO_3)_2$	$NaNO_3$	$\mu$	$\gamma_1$	$\alpha_{12}$
1	0.796	—	2.38	0.630	—	5	1.064	—	3.19	0.735	—
	0.531	1.067	2.66	0.612	0.035		0.667	2.34	4.34	0.652	0.066
	0.381	2.20	3.35	0.574	0.055		0.287	5.21	6.07	0.721	0.051
	0.192	3.38	3.96	0.650	0.035		1.285	—	3.86	0.840	—
	0.161	4.43	4.91	0.617	0.052		1.110	0.945	4.28	0.794	0.065
2	0.828	—	2.49	0.641	—	6	0.921	1.910	4.67	0.805	0.048
	0.600	1.076	2.88	0.598	0.057		0.774	3.06	5.38	0.758	0.059
	0.432	2.06	3.36	0.585	0.055		0.571	4.09	5.80	0.797	0.051
	0.291	3.17	4.04	0.592	0.054		0.418	5.53	6.78	0.831	0.059
	0.187	4.12	4.68	0.635	0.047		1.359	—	4.08	0.878	—
3	0.1122	5.21	5.55	0.721	0.042	7	1.188	0.987	4.55	0.828	0.069
	0.933	—	2.80	0.678	—		0.975	2.06	4.99	0.816	0.055
	0.693	1.089	3.17	0.642	0.052		0.807	3.15	5.57	0.810	0.054
	0.516	2.03	3.58	0.634	0.048		0.639	4.19	6.11	0.830	0.049
	0.362	3.20	4.29	0.634	0.047		0.469	6.42	7.83	0.847	0.053
4	0.247	4.22	4.97	0.668	0.053	8	1.731	—	5.19	1.106	—
	0.1456	5.42	5.86	0.741	0.043		1.545	0.956	5.59	1.071	0.050
	0.998	—	2.99	0.705	—		1.373	2.01	6.13	1.044	0.047
	0.793	0.886	3.27	0.678	0.047		1.210	3.17	6.79	1.030	0.054
	0.611	1.875	3.71	0.662	0.048		1.041	4.64	7.77	1.031	0.054
	0.426	3.03	4.31	0.669	0.046	0.758	5.93	8.20	1.116	0.042	
	0.333	4.05	5.05	0.668	0.051						
	0.232	5.50	6.19	0.693	0.050						

*Added in proof*, 22.11.49. It has lately been found that each molecule of uranyl nitrate carries four water molecules into solution in the solvents used. The assumption that water is not significantly soluble in the organic phase in our experiments was therefore invalid. The fourth power of the appropriate water activity should thus be added on each side of equation (1). The values of  $\gamma_1$  and  $\alpha_{12}$  in Table I have been corrected to the new basis. A full account will be published later.

TABLE II.

Uranyl nitrate.

Molarity .....	0.8	1.0	1.2	1.4	1.6	1.8	2.0
$\gamma$ .....	0.632	0.706	0.796	0.899	1.018	1.153	1.297

Now, it is often assumed that when the proportions of two electrolytes in a mixture are varied at constant total ionic strength, then the logarithms of their activity coefficients vary linearly, *i.e.*,

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12} m_2 \dots \dots \dots (3)$$

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21} m_1 \dots \dots \dots (4)$$

where the  $\gamma_{(0)}$ 's are the activity coefficients of the pure solutes at the ionic strength  $\mu$  of the mixture, and the  $\alpha$ 's vary slightly with  $\mu$ , but are otherwise constant. Experimental evidence shows that in certain cases (3) holds to a high degree of accuracy (Harned and Owen, *op. cit.*, p. 459). Values of  $\alpha_{12}$  have accordingly been calculated from our results, and are given in the last columns of Table I. It should be noted that these are independent of the constant factor introduced into Table II, which affects  $\gamma_1$  [calculated from equation (1)] and  $\gamma_{1(0)}$  equally.

The accuracy of any given  $\alpha_{12}$  value is roughly proportional to  $m_2$ . The later values on any run are therefore more accurate than the earlier. The weighted mean of all the results is  $0.051 \pm 0.001$  (standard deviation).

No significant trend in the  $\alpha_{12}$  values can be detected, either with  $\mu$  or with  $m_1$  or  $m_2$  separately.

It can therefore be concluded that equation (3) holds within the experimental error for mixed solutions of uranyl nitrate and sodium nitrate. It must, however, be remarked that, owing to the scatter of the results, a variation of  $\alpha_{12}$  by, say,  $\pm 0.005$  over the whole range would probably pass undetected.

If equations (3) and (4) both hold, then  $\alpha_{21}$  can be calculated from the equation

$$3\alpha_{12} - 2\alpha_{21} = \frac{6}{[\mu]^2} \int_{\mu=0}^{\mu=\mu} \mu d \log \gamma_{1(0)}/\gamma_{2(0)}^2 \quad \dots \quad (5)$$

which holds for a mixture of a 2 : 1- with 1 : 1-electrolyte. Equation (5) is obtained by inserting (3) and (4) into the Gibbs–Duhem relation, and is the analogue of Harned and Owen's equation (14-5-8), which applies to two 1 : 1-electrolytes (Harned and Owen, *op. cit.*, p. 453). The expression on the right-hand side of (5) varies somewhat with  $\mu$  in the uranyl nitrate–sodium nitrate system :

$$\left. \begin{array}{l} \text{At } \mu = 3, 3\alpha_{12} - 2\alpha_{21} = 0.488 \\ \text{At } \mu = 6, 3\alpha_{12} - 2\alpha_{21} = 0.420 \end{array} \right\} \quad \dots \quad (6)$$

With the experimental value of  $\alpha_{12} = 0.051$ , the corresponding values of  $\alpha_{21}$  would be  $-0.168$  and  $-0.134$ , respectively.

There is, however, another consequence of equations (3) and (4) which appears to have been overlooked hitherto. It is a thermodynamic necessity that

$$3(\partial \log \gamma_1 / \partial m_2)_{m_1} = 2(\partial \log \gamma_2 / \partial m_1)_{m_2}$$

(The numerical coefficients are the numbers of ions from a 2 : 1- and a 1 : 1-electrolyte, respectively.) Since  $\mu = 3m_1 + m_2$ , this can be rewritten as

$$(\partial \log \gamma_1 / \partial \mu)_{m_1} = 2(\partial \log \gamma_2 / \partial \mu)_{m_2}$$

Hence from (3) and (4)

$$\frac{d \log \gamma_{1(0)}}{d\mu} - \alpha_{12} - (\mu - 3m_1) \frac{d\alpha_{12}}{d\mu} = 2 \frac{d \log \gamma_{2(0)}}{d\mu} - \frac{2}{3} \alpha_{21} - 2m_1 \frac{d\alpha_{21}}{d\mu}$$

Since the  $\gamma_{(0)}$ 's and the  $\alpha$ 's are functions of  $\mu$  only, it follows that the coefficient of  $m_1$  in this equation must vanish, *i.e.*,

$$d(3\alpha_{12} + 2\alpha_{21})/d\mu = 0 \quad \dots \quad (7)$$

$(3\alpha_{12} + 2\alpha_{21})$  should therefore be a constant for all values of  $\mu$ .

It is difficult, for the uranyl nitrate–sodium nitrate system, to reconcile this requirement with equations (6). We have

$$\left. \begin{array}{l} 3\Delta\alpha_{12} - 2\Delta\alpha_{21} = -0.068 \\ 3\Delta\alpha_{12} + 2\Delta\alpha_{21} = 0 \end{array} \right\}$$

where the  $\Delta$ 's refer to changes between  $\mu = 3$  and  $\mu = 6$ . Hence  $\Delta\alpha_{12} = -0.011$  and  $\Delta\alpha_{21} = 0.017$ .

The  $\alpha_{12}$  results, despite their scatter, hardly permit a decrease as large as 0.011 between  $\mu = 3$  and  $\mu = 6$ . The only alternative is to abandon the linear relationship (4) for the activity coefficient of sodium nitrate in presence of uranyl nitrate. This means that none of the subsequent equations can be applied in this case.

It may be noted, too, that Glueckauf's recent expressions (*Nature*, 1949, **163**, 414) for  $\alpha_{12}$  and  $\alpha_{21}$  are inapplicable unless both (3) and (4) are valid, and there is therefore no point in comparing the predictions of his theory with the present experimental data.

The arguments used here are of far-reaching consequence, and it is intended to elaborate them more generally in a future paper.

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