The Influence of Uranyl and Thorium Salts on the Miscibility of Phenol and Water.

By S. T. BOWDEN and J. H. PURNELL.

[Reprint Order No. 4629.]

The critical solution temperature (C.S.T.) of phenol and water is depressed by uranyl acetate but raised by uranyl nitrate or sulphate and by thorium nitrate or sulphate. At certain concentrations precipitation of a basic sulphate occurs in the systems containing thorium sulphate. For the other systems a logarithmic relation exists between the concentration of the salt and the depression or elevation of the C.S.T. The depression constant is 0·96 and the elevation constant is 0·86, which is identical with that found for systems containing salts of the light metals. In the lyotropic series representing the influence of ions on the C.S.T. of phenol and water, UO_2^{2+} lies between Be^{2+} and Pb^{2+}, while Th^{4+} falls between K^+ and NH_4^+.

THE influence of uranyl acetate, nitrate, and sulphate, and of thorium nitrate and sulphate on the miscibility of phenol and water has been examined in order to ascertain the relation between concentration and the change in C.S.T., and to establish on this basis the position of UO_2^{2+} and Th^{4+} in the lyotropic series.

EXPERIMENTAL

Purification of Materials.—Water was freed from grease by distillation in an all-glass apparatus. Phenol was purified by repeated distillation in an apparatus provided with a guard tube ($CaCl_2$) until it had m. p. 40·75°. Uranyl nitrate hexahydrate was twice crystallised from dilute nitric acid; gravimetric determination of the uranium content showed that the salt was 99·97% pure. Uranyl sulphate trihydrate was thrice crystallised from dilute sulphuric acid, and was 99·95% pure. Uranyl acetate dihydrate was recrystallised from dilute acetic acid, and had a purity of 99·93%.

Commercial thorium sulphate, after two crystallisations from dilute sulphuric acid in a desiccator over concentrated sulphuric acid, gave a product corresponding to the nonahydrate. Owing to the low solubility of the substance in the liquids under study, it was dehydrated by heating it at 360° for 1 hr. The anhydrous thorium sulphate thus obtained had a purity of 99·69%. Thorium nitrate hexahydrate was obtained by crystallisation of the commercial hydrate from dilute nitric acid in a desiccator containing sulphuric acid. The largest crop of crystals consisted of hexahydrate of purity 99·56%.

Determination of Miscibility Points.—A known weight of phenol was placed in a constricted, thin-walled test-tube, and a pre-determined volume of water or of a standard aqueous solution of the third component was introduced by means of a pipette. After being weighed, the tube was hermetically sealed to prevent evaporation losses.

The miscibility tube, which was fixed by a spring clip to the extended armature of an electric buzzer in series with a switch and 6-v battery, was completely immersed in the water contained in a 2-l. beaker, and could be brought into rapid oscillation by closing the circuit. This arrangement served not only to agitate the contents of the miscibility tube but also to stir the heating bath and thus ensure rapid thermal equilibration. The bath was heated by a micro-burner, and

TABLE 1. *Phenol and water.*

Phenol, %	9·93	12·53	15·02	17·89	20·00	24·76	31·86	35·21	40·52
t	34·00°	51·90°	55·90°	61·70°	63·20°	65·40°	65·55°	65·65°	65·50°
Phenol, %	45·66	49·64	55·09	60·75	62·48	65·29	67·31	70·84	
t	65·20°	63·20°	59·55°	52·60°	48·50°	42·85°	36·20°	23·80°	

TABLE 2. *Phenol, water, and specified third component.*

PhOH, %		PhOH, %	t	PhOH, %	t	PhOH, %	t	PhOH, %	
Uranyl acetate									
$m = 0·01945$		$m = 0·03441$		$m = 0·05822$		$m = 0·09872$		$m = 0·14730$	
10·33	38·5°	10·25	40·6°	14·61	53·0°	15·00	51·2°	15·01	48·3°
20·46	61·6	19·90	60·4	19·16	58·2	19·62	55·6	20·95	52·1
30·92	64·1	25·53	62·1	24·27	60·4	24·25	57·5	24·18	54·0
35·58	64·3	30·14	63·1	29·55	61·3	29·52	58·3	29·20	54·9
42·55	64·2	34·71	63·3	34·93	61·6	34·69	58·8	34·67	55·7
50·93	61·5	40·00	63·3	39·69	61·6	39·89	59·0	39·08	56·0
59·60	52·7	49·52	61·1	48·04	59·6	49·84	56·9	49·64	53·8
		50·12	60·9	56·69	48·3	59·68	45·8		
Uranyl nitrate									
$m = 0·01800$		$m = 0·02982$		$m = 0·05122$		$m = 0·07900$		$m = 0·16981$	
14·67	59·7	14·67	62·3	17·19	65·3	16·28	66·9	16·50	73·3
20·07	65·3	20·50	66·3	22·37	68·9	21·68	71·4	22·12	77·5
24·72	67·2	24·30	68·3	30·86	70·8	30·17	73·0	29·23	79·5
29·86	68·0	29·41	69·3	36·55	71·3	35·30	73·6	34·25	80·6
34·83	67·9	33·82	69·4	41·00	71·5	39·36	74·2	39·79	81·8
39·97	68·0	39·20	69·4	45·25	71·4	45·06	73·6	44·32	82·6
45·10	67·5	45·35	69·2	50·41	70·5	50·40	74·2	49·23	83·3
50·52	66·2	50·11	68·2	60·07	63·9	60·05	69·4	59·43	81·2
59·59	58·6	59·09	60·2						
Uranyl sulphate									
$m = 0·01126$		$m = 0·02482$		$m = 0·04643$		$m = 0·07597$		$m = 0·12210$	
12·30	58·4	12·17	56·1	12·17	58·5	12·07	59·4	17·17	72·1
18·40	62·8	17·40	63·4	17·96	65·9	17·91	67·7	24·37	78·6
24·94	67·3	23·45	67·6	25·08	70·6	24·60	73·1	29·32	80·3
30·11	68·2	29·62	69·4	29·07	71·7	29·53	74·2	34·91	84·0
34·90	67·9	35·45	69·9	35·45	73·1	34·28	75·7	39·34	87·2
40·29	68·0	40·27	70·4	39·78	74·2	40·02	77·7	45·20	95·4
50·37	67·5	50·22	81·5	49·91	77·6	45·57	80·4	49·92	100·00
59·57	59·2	60·40	71·4	59·00	85·0	50·57	84·9		
						60·51	100·0		
Thorium nitrate									
$m = 0·02081$		$m = 0·04736$		$m = 0·06015$		$m = 0·10845$		$m = 0·14341$	
12·44	54·7	9·51	42·4	12·23	61·4	12·38	62·4	10·00	57·0
17·77	66·4	17·38	68·2	18·18	71·0	17·15	73·7	12·17	70·4
25·11	70·0	24·67	71·7	30·05	76·0	24·34	79·4	17·84	79·5
30·01	70·4	29·74	73·1	35·77	77·1	28·76	81·2	24·39	84·5
34·95	70·6	34·82	73·5	40·33	77·8	33·88	82·6	29·30	86·4
39·88	70·9	39·57	74·2	49·79	79·4	39·49	83·9	34·11	88·0
50·39	69·9	42·35	74·4	58·81	76·7	50·13	87·2	39·75	90·3
59·61	63·5	49·79	74·2			59·53	89·2	43·70	92·0
								47·95	93·5
Thorium sulphate									
$m = 0·00371$		$m = 0·00665$		$m = 0·00798$		$m = 0·01565$		$m = 0·02281$	
9·89	41·6	12·33	53·5	12·52	53·2	17·35	63·3	12·60	54·9
14·45	60·2	17·48	62·4	17·62	62·7	19·97	65·6	17·43	64·8
20·02	64·3	25·17	66·7	24·99	67·3	24·86	68·0	19·89	66·8
24·94	66·5	30·29	67·5	30·32	67·9	29·83	68·7	24·89	68·9
29·90	66·7	35·17	67·8	34·91	68·2	34·54	69·0	29·81	69·4
35·09	67·3	40·42	67·7	39·93	68·4	37·75	69·4	34·88	69·8
40·62	67·3	50·29	66·1	50·33	66·5 *	39·88	69·4 *	39·77	70·4 *
49·46	65·3	60·16	58·0	59·64	59·7 *	44·60	69·6 *	44·51	70·6 *

* In these systems there was precipitation of a basic sulphate at the compositions indicated.

the temperature was registered by a calibrated thermometer with its bulb set in the vicinity of the miscibillity tube. The system was heated to a temperature 4—5° above the clearing point, and then allowed to cool at a rate of about 0·5°/min. The temperature at which the system became turbid was taken as the miscibility temperature, since the development of turbidity was rapid and more readily observed than the reverse change to homogeneous solution. Each value recorded is the mean of at least three determinations.

Mixtures covering the range 10—70% of phenol were examined in this way, and the results for the binary system are recorded in Table 1, where t is the miscibility temperature. The C.S.T. is 65·65—65·70° and the critical solution composition corresponds to 38·4% of phenol; these values agree closely with those obtained by Hill and Malisoff (*J. Amer. Chem. Soc.*, 1926, **48**, 918) and McKinney (*Trans. Roy. Soc. Canada*, 1927, iii, **21**, III, 256). In common with the majority of mutual solubility curves for mixtures of organic compounds, the curve for phenol and water has a flat maximum (Woodburn, Smith, and Tetewsky, *Ind. Eng. Chem.*, 1944, **36**, 588), owing to the conditions obtaining in the system when the interfacial tension between the solution and the molecular clusters vanished (Rice, *J. Chem. Phys.*, 1947, **15**, 314; *Chem. Reviews*, 1949, **44**, 69). In this region we found that the change from homogeneity to heterogeneity was sharp, but the miscibility temperatures corresponding to the steep parts of the curve were not so readily ascertained in view of the fact that the change was much more gradual. Strong opalescence was observed at all compositions in the neighbourhood of the critical point, and this persisted in the presence of high concentrations of the various third components.

The miscibility data for the ternary systems are listed in Table 2, where m is the molality with reference to the aqueous solution.

DISCUSSION

In accordance with the Timmermans's rules, salts generally cause an elevation of the C.S.T. when one of the components of the binary mixture is water. Among the exceptions for the phenol–water system is sodium acetate, and we find a similar behaviour with uranyl acetate.

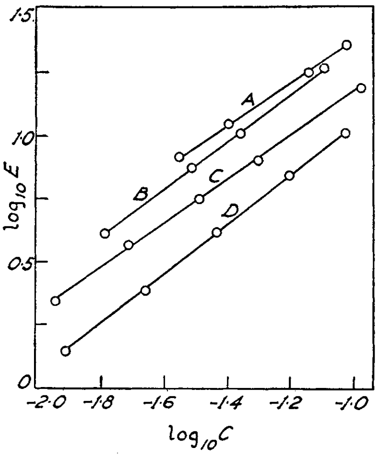
According to Carrington, Hickson, and Patterson (*J.*, 1925, **127**, 2544) the elevation or depression for concentrations greater than about 0·01 mole per 1000 g. of the mixture for systems which do not undergo hydrolysis or form complexes in solution is related to the concentration by the equation $e = aC^b$, where a is a constant characteristic of the third component and b is a constant characteristic of the binary system. The data obtained in the present work are listed in Table 3, where C is the concentration in moles of third component per 1000 g. of the ternary mixture, t_c is the corresponding C.S.T., e is the elevation in °c, and E is the molecular elevation.

TABLE 3. *Elevation of C.S.T.*

C	t_c	e	E	C	t_c	e	E	C	t_c	e	E
Uranyl acetate				Uranyl nitrate				Uranyl sulphate			
0·01258	64·3°	1·40°	−111·3°	0·01165	67·9°	2·20°	188·8°	0·00751	68·2°	2·50°	333·3°
0·02219	63·3	2·40	−108·2	0·01924	69·4	3·70	192·3	0·01655	70·0	4·25	257·0
0·03730	61·6	4·10	−109·9	0·03288	71·2	5·55	168·8	0·03095	73·0	7·30	235·8
0·06261	58·8	6·85	−109·4	0·05032	73·6	7·90	157·0	0·04398	75·6	9·90	225·0
0·09234	55·7	10·00	−108·3	0·10580	80·7	15·05	142·2	0·08140	85·9	18·20	223·6
Thorium nitrate				Thorium sulphate							
0·01386	70·7	5·00	360·4	0·00241	67·3	1·65	684·8				
0·02824	73·8	8·10	287·0	0·00432	67·8	2·15	497·5				
0·04010	77·3	11·60	289·3	0·00519	68·2	2·50	481·7				
0·07230	83·0	17·30	236·5	0·01017	69·1	3·40	334·2				
0·09561	88·0	22·30	233·2	0·01482	69·8	4·15	280·0				

Ionisation of uranyl salts in water is accompanied by formation of complex ions which undergo constitutional changes with dilution (Dittrich, *Z. physikal. Chem.*, 1899, **29**, 465; Gomez, *Anal. Fís. Quím.*, 1919, **17**, 24; Guiter, *Bull. Soc. chim.*, 1947, **14**, 64), and the behaviour of the salts in hydroxylic organic solvents is considered to be due either to direct co-ordination of the solvent molecule to the central atom or to hydrogen bonding between the solvent molecule and the water of hydration (Glueckauf, McKay, and

Mathieson, *Trans. Faraday Soc.*, 1951, **48**, 438). However, as shown in the Figure, the plots of log e against log C for the systems containing uranyl salts (the sign of the elevation for the acetate being ignored) are straight lines, and it is evident, therefore, that Patterson's equation is obeyed by these systems. The values of the constants are as follows : uranyl acetate, $a = -99{\cdot}5$, $b = 0{\cdot}96$; uranyl nitrate, $a = 101{\cdot}0$, $b = 0{\cdot}85$; uranyl sulphate, $a = 163{\cdot}3$, $b = 0{\cdot}89$; thorium nitrate, $a = 178{\cdot}6$, $b = 0{\cdot}85$. As found by previous workers, the binary system constant varies according as there is elevation or depression of the C.S.T., but the average value of b for systems exhibiting elevation (0·86) agrees with that found (0·87) by Carrington *et al.* (*loc. cit.*). For the systems containing uranyl salts the values of a furnish further confirmation of the rule that sulphates produce greater elevation than the corresponding nitrates. The system containing thorium nitrate also conforms to Patterson's equation despite the fact that complexes are formed through co-ordination of the thorium with the oxygen atoms of the solvent molecule (Templeton, Rothschild, and Hall, *J. Phys. Coll. Chem.*, 1949, **53**, 838). The linear relation is not obeyed by the thorium sulphate system, but this behaviour is to be expected inasmuch as the concentrations lie outside the range to which Patterson's rule is applicable.



A, Thorium nitrate.
B, Uranyl sulphate.
C, Uranyl nitrate.
D, Uranyl acetate.

The influence of a series of ions on the C.S.T. of a binary system is similar to that shown by the Hofmeister series in the coagulation of neutral egg albumin. The positions of the uranyl and thorium ions in the series may be ascertained by comparing the elevations of the C.S.T. with the values found for other salts at corresponding concentrations (Duckett and Patterson, *J. Phys. Chem.*, 1925, **29**, 295); this places the uranyl ion between the beryllium and lead ions, and the thorium ion between the alkali-metal and ammonium ions.

The effects of the alkali-metal ions and of the ammonium and hydrogen ions on the C.S.T. of phenol and water are in the reverse order of those found by Briggs (*ibid.*, 1928, **32**, 1646) for the change in zeta potential at the cellulose–water interface. It is evident from the present work also that there is a reversal of order with respect to the effects of the thorium and alkali-metal ions, and that the thorium ion has a greater effect than the ammonium and hydrogen ions on the C.S.T.

Tatem Laboratories, University College, Cardiff.

[*Received, September 4th,* 1953.]