[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

TERNARY SYSTEMS: WATER, TERTIARY BUTANOL AND SALTS AT 30°

BY P. M. GINNINGS AND DOROTHY ROBBINS

RECEIVED FEBRUARY 5, 1930 PUBLISHED JUNE 6, 1930

Tertiary butanol has been more or less a laboratory curiosity until recent years but economical methods of manufacture from the by-products of cracking petroleum have opened up a new field of potential uses. A résumé is given by Davis and Murray[1] concerning the chemical properties, solvent powers and physiological properties of the aliphatic tertiary alcohols and their industrial possibilities. Investigation of some of the physical properties of one of these, tertiary butanol, seems to have lagged behind that relative to the chemical properties. For example, while most of the aliphatic alcohols entirely miscible with water have been investigated as regards the two liquid phase formation in the familiar salting out phenomena when an aqueous solution of the alcohol is shaken with various salts, little has been done with tertiary butanol. Search of the literature revealed that the ternary systems water, tertiary butanol and salts had been investigated only partially in one paper,[2] in which potassium chloride was the only salt tried with the tertiary butanol. Investigation of this set of ternary systems seemed desirable for two reasons: first, tertiary butanol is the only aliphatic tertiary alcohol entirely miscible with water; second, it has the highest molecular weight of any simple aliphatic alcohol that is entirely miscible with water. The other butanols are only partially miscible with water.

While there are many inorganic salts that will cause the formation of two liquid phases in the above three-component system, only ten diversified salts were investigated in detail here. Some of these salts had been used in investigations of analogous systems; some were chosen in order to find the most effective salting-out agent; and the four potassium halides were selected primarily in order to compare their respective binodal curves. The system of graphical representation of the binodal and conjugation curves, interpolation to the plait point and phase composition used here is similar to that used in the "International Critical Tables," Vol. III, p. 398.

The aliphatic alcohols entirely miscible with water are methanol, ethanol, propanol, isopropanol, 1-propenol (allyl alcohol) and tertiary butanol. Fortunately, for the sake of comparison, all of the above alcohols have now been investigated as regards their behavior with aqueous

---

[1] Davis and Murray, *Ind. Eng. Chem.*, **18**, 844 (1926).

[2] Timmermans, *Z. physik. Chem.*, **58**, 129 (1907).

potassium carbonate solutions. If the binodal curves of all are plotted upon the conventional triangular diagram and a perpendicular line is drawn from the alcohol–salt axis to the water apex, there will be a series of intersections between this line and the respective binodals in the following order: methanol, ethanol, isopropanol, 1-propenol, tertiary butanol and propanol. The tertiary butanol binodal lies very close to the propanol binodal. A little inspection here of the order reveals how unsaturation, branched carbon chain and progression in the homologous series affect the binodals in these ternary systems.

Sodium carbonate seems to have the highest *specific* salting-out effect because the binodal curve approaches nearest to the water apex. However, the ratio of the concentration of the alcohol to that of the water, in the salt-rich phase, is probably a better measure of the salting-out effectiveness; the smaller the ratio, the more effective the salt. In this respect, potassium carbonate and potassium fluoride in concentrated solutions surpass the sodium carbonate and seem to be the most effective of the ten salts investigated. This seems to be in agreement with the results from several investigations of salting-out agents.[3] In some cases, such as potassium iodide, the binodal curve terminates abruptly at both ends because the two liquid phase formation ceases. In other cases, such as potassium carbonate and potassium fluoride, the binodal curves approach the alcohol–water and water–salt axes with a very small slope. If a comparison is made of the four binodal curves of the potassium halides, the effectiveness seems to be an inverse function of the molecular weight of the potassium halide, potassium fluoride being the most effective.

Although determination of the binodal curves was the main object of this investigation, the conjugation curves were determined approximately, and also the intersection of the two, the plait point. The authors believe that the binodal curves here are in error by less than 1% in any case, and probably within 0.3% in many cases. However, the method used for the determination of the conjugation points allows a large possible error in some of the systems; this is especially true where the binodal curve follows quite closely and almost parallel to the alcohol–water axis. Here the $dC_{\mathrm{alc.}}/dC_{\mathrm{salt}}$ is very large, making the exact composition of the alcohol-rich phase as regards alcohol content difficult of determination by the indirect method used. Where the binodal curve is neither near nor almost parallel to the alcohol–water axis—as in the system with potassium iodide—the conjugation curve is relatively accurate. Usually, the sum of the weights of the three components in the mixture was from five to fifteen grams.

---

[3] Frankforter and Frary, "Orig. Com. 8th Intern. Congr. Appl. Chem.," **22**, 87–127; *C. A.*, **7**, 44 (1913); Frankforter and Frary, *J. Phys. Chem.*, **17**, 402–473 (1913); Frankforter and Cohen, THIS JOURNAL, **36**, 1103–1134 (1914).

Experimental

The synthetical method was used throughout in the determination of the binodal curves. Known weights of each of the three components were introduced into a tapered centrifuge tube; the salt (c. p.) from a weighing tube weighed accurately to one centigram, the tertiary butanol (Eastman) and water from their respective burets. By careful and repeated trials with much shaking, the quantities of the three components in the tube were so regulated that the second liquid phase was at the point of appearance or disappearance. Observation of the cloudiness along with the use of the centrifuge to estimate the volume of the second liquid phase seemed to be the best method for the determination of the binodal points. The tube was shaken thoroughly in a well-stirred water-bath at 30° (plus or minus 0.2°) as the last step in the determination of each binodal point. The quantities of the three components were expressed as weight percentages, and so graphed on the triangular diagram.

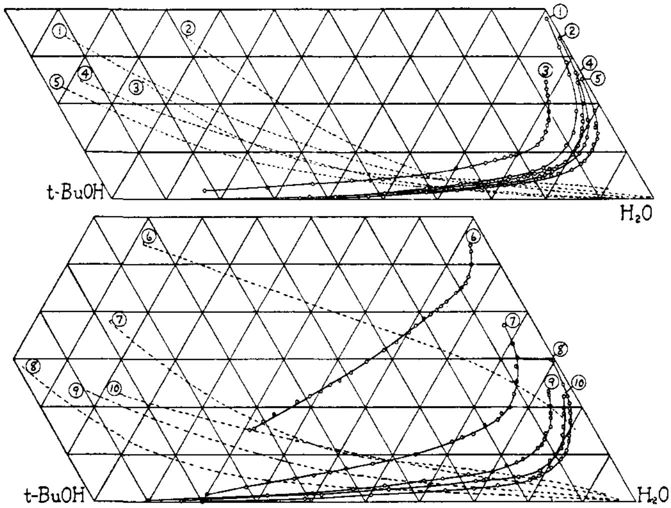

Fig. 1.—1, $(NH_4)_2SO_4$; 2, K_2CO_3; 3, NH_4Cl; 4, Na_2SO_4; 5, Na_2CO_3; 6, KI; 7, KBr; 8, KF; 9, KCl; 10, NaCl; ——, binodal; - - - - - -, conjugation.

An indirect analytical method was used for the determination of the conjugation points; indirect in the case of the alcohol-rich layer and direct in the case of the salt-rich layer. Two liquid phases were set up in equilibrium in the tube and brought to the correct temperature of 30° in the water-bath. Then a rubber stopper, perforated with two glass tubes, was inserted into the centrifuge tube, thereby producing a miniature wash bottle. By obtaining the difference between weighings (plus or minus 1 cg.), known weights of the two liquid phases were withdrawn into two weighed crucibles. Evaporation to dryness of the pair of crucibles corresponding to the two liquid phases and weighing gave the salt content of both phases. But according to the custom of preparation of the conjugation curves in the "International Critical Tables," the salt content of the salt-rich phase is plotted against the alcohol content of the alcohol-rich phase, so the alcohol content of the alcohol-rich phase was determined by notation of the salt content, reference to the binodal curve and intrapolation or extrapolation to the point required. Similarly, the segment of the conjugation curve on the opposite side of the binodal curve was obtained by plotting the alcohol content of the salt-rich phase against the salt content of the alcohol-rich phase. The intersection of the line uniting the two segments, just mentioned, with the binodal curve gave the plait point.

TABLE I

EXPERIMENTAL RESULTS

T-BuOH, wt. %	KI, wt. %	T-BuOH, wt. %	KF, wt. %	T-BuOH, wt. %	NH_4Cl, wt. %	T-BuOH, wt. %	Na_2SO_4, wt. %	T-BuOH, wt. %	Na_2CO_3, wt. %
62.8	15.5	60.6	0.8	82.0	2.0	58.6	0.3	52.3	0.7
60.3	16.9	48.3	1.4	70.2	2.4	47.0	1.2	50.0	1.0
57.7	18.5	34.1	2.3	61.2	3.3	42.2	1.6	41.3	1.3
52.0	20.9	28.6	2.8	54.1	3.7	37.2	2.2	35.4	1.8
49.2	22.1	24.1	3.3	47.9	4.2	33.7	2.6	30.8	2.1
46.5	23.4	20.4	3.7	39.3	5.0	31.1	2.9	26.2	2.8
44.3	24.6	17.7	4.5	33.4	6.4	28.8	3.4	22.4	3.3
42.0	25.5	16.6	5.1	30.2	6.6	26.3	3.6	19.7	4.0
39.2	27.0	15.4	5.6	27.5	7.4	24.9	3.9	18.1	4.6
35.1	29.5	14.9	5.7	25.3	8.0	22.9	4.2	16.6	5.0
30.6	31.9	12.5	7.0	23.2	8.6	21.5	4.6	15.3	5.4
27.6	33.4	9.7	8.8	22.0	9.0	20.8	4.9	11.9	6.0
24.2	35.6	8.7	9.6	20.7	9.4	19.5	5.3	9.9	7.2
22.1	37.0	8.2	10.0	19.8	10.0	17.5	5.8	8.6	8.0
19.9	38.6	7.7	10.9	15.7	11.5	16.4	6.2	6.8	9.7
17.9	39.6	6.3	12.7	14.1	12.7	14.3	6.9	6.1	10.4
16.6	40.3	5.6	14.0	12.9	14.3	12.4	7.8	5.2	11.2
15.4	41.1	3.8	16.9	11.8	15.6	10.2	9.5	4.0	12.9
13.9	42.3	2.8	18.7	11.0	16.8	8.1	11.4	3.3	14.1
11.3	44.0	2.4	19.7	10.2	18.4	6.7	13.3	3.1	15.3
9.6	45.4	1.9	20.7	9.2	20.3	6.1	14.2	2.5	16.0
8.4	46.1	1.6	22.2	8.7	21.7	5.5	15.2	1.5	18.9
7.2	47.3	1.2	24.6	8.1	23.2	4.8	16.5	0.6	25.2
5.2	49.8	0.7	29.8	7.6	24.7	3.9	17.9		
4.0	52.9	0.2	51.9			3.0	19.8		
3.3	54.7					1.8	24.5		

T-BuOH, wt. %	KCl, wt. %	T-BuOH, wt. %	KBr, wt. %	T-BuOH, wt. %	NaCl, wt. %	T-BuOH, wt. %	$(NH_4)_2SO_4$, wt. %	T-BuOH, wt. %	K_2SO_3, wt. %
67.3	1.4	70.2	3.1	83.8	0.3	63.4	0.4	57.8	0.7
58.4	2.0	65.7	4.2	57.3	1.5	48.8	1.4	39.3	1.8
50.9	2.6	60.7	4.8	44.4	2.4	40.7	2.4	26.9	3.1
43.8	3.3	56.9	5.4	36.4	3.2	34.3	3.2	18.9	4.8
36.6	4.5	53.4	6.1	27.7	4.3	28.2	4.0	17.7	5.1
33.3	4.8	50.3	6.7	26.0	4.5	24.6	4.6	16.1	5.8
28.3	5.6	44.7	7.8	19.4	5.1	19.8	5.7	12.8	7.2
23.9	6.2	35.7	10.0	14.5	6.7	17.4	6.5	9.1	9.8
20.5	7.4	29.7	11.9	11.5	9.0	8.9	13.0	7.5	11.4
18.2	8.1	27.7	12.6	10.0	10.0	7.7	14.1	5.9	13.3
16.5	9.0	25.6	13.4	8.5	11.2	5.3	18.2	4.5	15.4
12.5	11.4	22.8	14.3	7.5	12.5	2.5	26.1	3.5	17.0
11.5	12.2	20.0	15.7	6.7	14.1	1.8	28.7	0.9	26.7
10.5	13.3	17.0	17.0	5.8	15.6	1.4	32.1	0.4	34.2
9.4	14.6	13.4	19.8	5.6	15.7	0.8	37.8		
7.9	15.9	11.3	22.6	4.2	18.4				

TABLE I (*Concluded*)

T-BuOH, wt. %	KCl, wt. %	T-BuOH, wt. %	KBr, wt. %	T-BuOH, wt. %	NaCl wt. %
7.0	17.6	9.2	25.3	3.6	19.8
6.4	18.6	7.7	28.5	2.7	22.4
5.9	20.0	6.8	30.4		
4.8	22.6	6.1	33.1		
4.5	23.3				

TABLE II

CONJUGATION DATA

(A) Tertiary butanol in the tertiary butanol-rich phase, weight per cent. (B) Salt in the salt-rich phase, weight per cent. (P. P.) Plait point.

(A)	(B)	(A)	(B)
99	29.8 KF	82	24.7 NH_4Cl
64	4.3 KF	80	22.7 NH_4Cl
60	4.1 KF	65	10.1 NH_4Cl
55	3.4 KF	44	5.0 NH_4Cl P. P.
36	2.2 KF P. P.	99	37.8 $(NH_4)_2SO_4$
90	23.3 KCl	82	27.4 $(NH_4)_2SO_4$
57	7.1 KCl	60	12.1 $(NH_4)_2SO_4$
53	6.7 KCl	42	5.1 $(NH_4)_2SO_4$
39	4.2 KCl P. P.	32	3.7 $(NH_4)_2SO_4$ P. P.
78	37.0 KBr	93	24.5 Na_2SO_4
76	34.2 KBr	68	11.5 Na_2SO_4
64	19.1 KBr	66	10.5 Na_2SO_4
42	8.7 KBr P. P.	50	4.6 Na_2SO_4
63	54.7 KI	37	2.5 Na_2SO_4 P. P.
50	47.1 KI	69	34.2 K_2CO_3
45	45.5 KI	62	24.4 K_2CO_3
26	34.6 KI P. P.	53	14.8 K_2CO_3
84	22.4 NaCl	27	3.2 K_2CO_3 P. P.
60	13.9 NaCl	97	25.2 Na_2CO_3
48	10.7 NaCl	70	7.7 Na_2CO_3
23	4.6 NaCl P. P.	55	4.5 Na_2CO_3
		35	2.0 Na_2CO_3 P. P.

Summary

1. Tabular data, binodal curves, conjugation curves and plait points are given for the ternary systems of tertiary butanol and water with ten inorganic salts.

2. A comparison is made between the binodal curves of the systems water, alcohol and potassium carbonate, when the alcohol varies among the water-miscible aliphatic alcohols.

3. Potassium carbonate and potassium fluoride are the most effective salting-out agents of the ten salts investigated.

4. The value of the respective potassium halides as salting-out agents seems to be an inverse function of the molecular weight of the halide, potassium fluoride being the most effective of the four.

GREENSBORO, NORTH CAROLINA