[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Ternary Systems: Water, Tertiary Butanol and Salts at 25°

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Results of an investigation of this group of systems were published in a paper[1] but it was not until later[2] that the idea occurred to investigate the mathematical aspects of these systems. In the latter paper the concentration of the isopropanol as a function of the concentration of the salt was investigated and it seemed desirable to supplement the work on tertiary butanol by an analogous investigation. This has been done with thirty diversified salts in their thirty ternary systems. The purpose of the unusual number of systems was to render improbable any coincidental relationships which might occur if only a few systems were investigated. Tertiary butanol is especially suitable here on account of the ease with which it is salted out from its homogeneous aqueous solutions by a large number of salts.

In the preliminary work, a temperature of 30° was used, the idea being that the higher temperature would be above the critical temperatures for some systems. However, the necessity for increased accuracy in the experimental data made it imperative that the room temperature be maintained constant also. Everything considered, 25° seemed to be the optimum temperature and was used in preference to the 30°. The thirty systems investigated here at 25° include the ten systems previously reported upon at 30°.

The primary purpose was to ascertain what mathematical relationships, if any, could be found between the components of the systems. The concentration of the tertiary butanol as a function of the concentration of the salt seemed of greatest interest and received most attention. Experimental points of the binodal curves were first determined and the weight per cent. of tertiary butanol plotted as a function of the weight per cent. of the salt. Then the empirical mathematical equations were derived which seemed to approximate the experimental data the best. Because of a few coincidences at first, the tentative assumption was made that the two mathematical equations would always intersect in the plait point, but later results on other systems showed conclusively that this was not necessarily true in all systems. Consequently, the binodal curves were divided into two sections, the alcohol-rich section and the salt-rich section. Examination of the empirical equations which fit the alcohol-rich sections revealed that all thirty systems followed the exponential equation, $y = a + b(10)^{-cx}$ (y is weight per cent. of tertiary butanol and x the weight per cent. salt; a, b and c are arbitrary constants). From this can be derived the differential equation $-\mathrm{d}(y - a)/\mathrm{d}x = ky$. In one-half of the systems,

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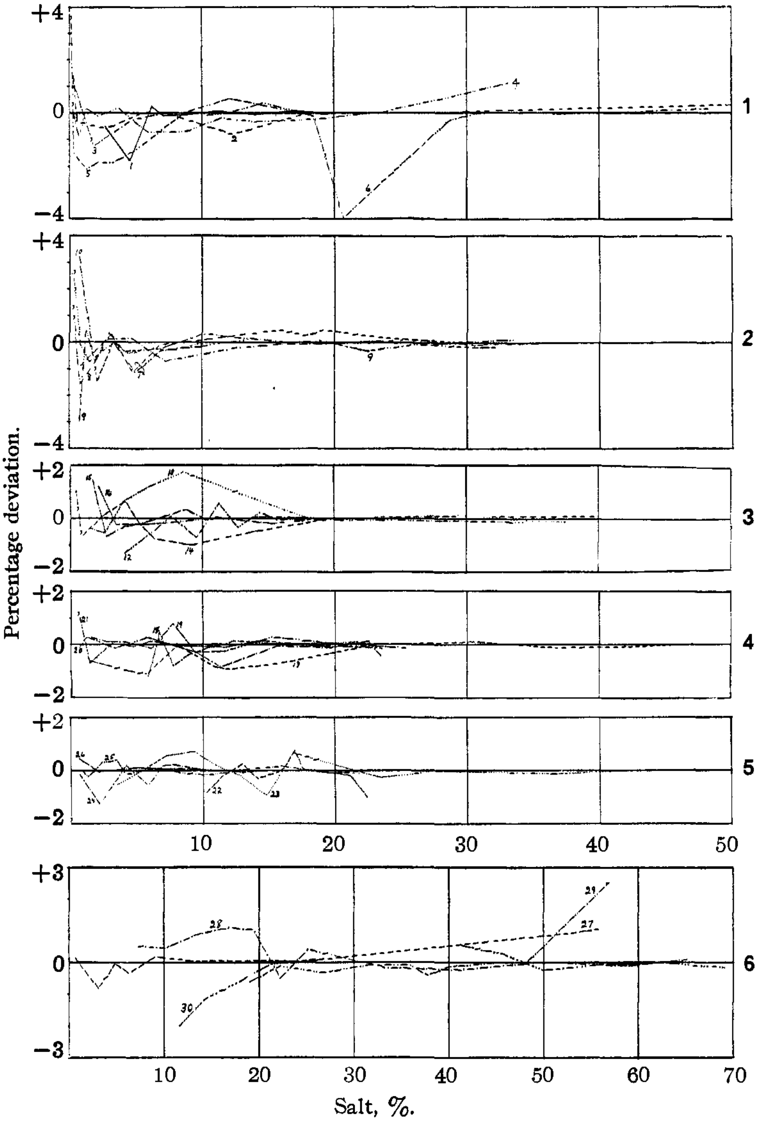
(1) Ginnings and Robbins, THIS JOURNAL, **52**, 2282–2286 (1930).

(2) Ginnings and Chen, *ibid.*, **53**, 3765–3769 (1931).

constant "*a*" approaches zero with the resulting simplification of the two equations. Of lesser importance but of some interest are the constants in the equations for the potassium halides. Constant "*b*" is a direct function



Deviation charts of experimental values of weight % of tertiary butyl alcohol from values calculated using the empirical equations.

and "*c*" an inverse function of the molecular weight of the halide. The case of the salt-rich sections of the binodal curves is not so distinct. Eighteen systems followed the above-mentioned exponential law and the other twelve seemed to be power functions of the type form $y = a + bx^{-c}$. No important relationship in this section was obvious although the exponential equation was evidently the one favored. Apparently, the salt component predominates here to such an extent that each system is primarily a function of the specific salt used.

Experimental

The experimental method was essentially identical with that used before[3] with minor improvements tending toward greater precision. The synthetical method was used to determine the plait point and seemed to be distinctly superior to the analytical method. In some cases interpolation between two binodal points to find the plait point was more convenient. This was done on the curve obtained by plotting the volume per cent. of one

TABLE I

(A) $y = a + b(10)^{-cx}$ (B) $y = a + bx^{-c}$

y = wt. % of *tert*-butanol; x = wt. % of salt; a, b, c are numerical constants

Dev.			Alcohol-rich section			Limit		Salt-rich section		
curve no.	Salt	Eq.	a	b	c	for x	Eq.	a	b	c
1	NH_4Cl	A	0	117.4	0.0748	9.7	B	0	325	1.189
2	KF	A	0	71.7	.1330	5.0	A	0	30.3	0.0583
3	$(NH_4)_2HPO_4$	A	5.9	59.25	.0835	16.1	A	− 0.67	33.1	.0328
28	NH_4NO_3	A	0	121.6	.0266	21.6	B	− 1.65	17458	2.016
29	KI	A	−44.9	158.3	.00969	38.4	A	−13.0	277.0	0.0233
19	KCl	A	14.2	74.4	.0992	5.4	B	0	331	1.326
4	$CdSO_4$	A	30.64	33.1	.2867	4.5	B	−34.0	112.2	0.3320
20	$K_3Fe(CN)_6$	A	33.9	38.8	.2185	4.3	B	− 3.5	125.8	.7635
12	KBr	A	0	99.5	.0391	11.5	B	0	2690	1.750
30	KSCN	A	−44.5	164 7	.0109	37.9	A	0.63	4840	0.0624
10	Na acetate	A	0	89 1	.0787	4.7	B	0	269	1.215
14	$NaAl(SO_4)_2$	A	21.2	36.55	.1503	5.4	A	0	46.4	0.0440
11	Na_2SO_4	A	0	60.7	.0987	5.6	A	−22	51.2	.0209
5	$Na_2S_2O_3$	A	4.57	62.2	.0955	18.4	A	0	50.0	.0513
8	$ZnSO_4$	A	21.55	36.35	.1610	6.0	A	0	45.9	.0441
17	NaBr	A	0	101.8	.0403	11.0	B	− 1.47	2175	1.682
9	$NaKCO_3$	A	0	68.1	.1284	4.0	A	0	37.1	0.0621
26	$(NH_4)_2SO_4$	A	2.95	63.05	.0909	8.3	A	0	30.46	.0405
18	$BaCl_2$	A	0	95.5	.0617	11.6	A	0	47.6	.0358
24	NaCl	A	0	88.5	.1030	6.6	B	0	214.6	1.298
16	$NaHSO_4$	A	0	61.1	.0518	8.0	B	− 3.9	240.3	1.020
23	$NaNO_3$	A	0	93.5	.0399	11.6	B	− 2.63	1523	1.540
22	$LiNO_3$	A	−75	218.5	.0218	16.0	A	3.88	1505	0.1186
13	KNa tartrate	A	3.70	59.8	.0849	11.0	A	− 0.455	30.2	.0326
6	$SrBr_2$	A	30.75	323.3	.1030	20.7	B	− 1.095	$1.986\,(10)^5$	2.845
7	$SrCl_2$	A	0	87.2	.0669	10.7	A	0	45.5	0.0398
27	K_2CO_3	A	0	63.1	.1014	6.9	A	−0.87	26.90	.0441
21	$MgSO_4$	A	5.50	45.75	.0988	8.0	A	0	34.65	.0530
25	Na_2CO_3	A	5.48	57.42	.1759	4.1	A	0	32.04	.0700
15	Na tartrate	A	0	58.6	.0710	7.8	A	0.895	33.87	.0432

The empirical equation for the alcohol-rich section of the binodal curve of any specific system is valid for the interval between the smallest value of "x" in Dev. Ch. to the value in the column headed "limit for x" in Table I. Similarly, the empirical equation for the salt-rich section covers the interval between value for "x" in the column "limit for x" to the largest value in the deviation chart.

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(3) Ref. 2, p. 3767.

liquid phase as a function of the weight per cent. of salt. Interpolation to the 50% intersection gave the desired plait point. The highest weight per cent. salt in a system in a Chart is approximately conjugate with the highest weight per cent. of tertiary butanol; and the lowest weight per cent. salt is conjugate with the lowest weight per cent. of tertiary butanol. Eastman's best grade of tertiary butanol, d_4^{20} 0.7872, and C. P. chemicals were used throughout. Whenever hydrates of salts were used, the calculations were corrected to the basis of anhydrous salts. The authors feel that the error in binodal data does not exceed 1.0% in any case and is usually less than 0.5%.

TABLE II

PLAIT POINTS

Salt	Wt. % t-BuOH	Wt. % salt	Salt	Wt. % t-BuOH	Wt. % salt
NH_4Cl	37.6	6.6	KF	36.3	2.2
$(NH_4)_2HPO_4$	33.8	3.8	NH_4NO_3	33.1	21.6
KI	22.2	38.4	KCl	41.0	4.5
$CdSO_4$	21.3	8.1	$K_3Fe(CN)_6$	38.0	4.3
KBr	35.1	11.5	KSCN	19.3	37.9
Na acetate	38.0	4.7	$NaAl(SO_4)_2$	26.9	5.4
Na_2SO_4	31.4	2.8	$Na_2S_2O_3$	33.6	3.2
$ZnSO_4$	25.5	6.0	NaBr	36.3	11.0
$NaKCO_3$	31.6	2.6	$(NH_4)_2SO_4$	35.4	3.2
$BaCl_2$	34.1	7.2	NaCl	36.7	3.7
$NaHSO_4$	29.5	6.1	$NaNO_3$	32.4	11.6
$LiNO_3$	23.0	16.0	KNa tartrate	31.1	4.0
$SrBr_2$	29.8	20.4	$SrCl_2$	33.1	6.3
K_2CO_3	36.3	2.3	$MgSO_4$	27.2	3.3
Na_2CO_3	32.2	2.1	Na tartrate	31.4	3.8

Summary

Data are given for the ternary systems of water and tertiary butanol with thirty salts at 25°. In the case of the alcohol-rich section of the binodal curves for the thirty systems, the rate of decrease of the weight per cent. of the tertiary butanol with respect to the weight per cent. of salt in a liquid phase seems to be a direct function of the weight per cent. of tertiary butanol. The constants in the equations for the four potassium halides are compared. Values for the numerical constants in the empirical equations and deviation charts are given for all of the systems.

GREENSBORO, NORTH CAROLINA

RECEIVED JUNE 27, 1932
PUBLISHED MARCH 7, 1933