unitarian entropy of dimerization (entropy corrected for the effect of the disappearance of a solute mole on dimerization) (*15*).

This result is in good agreement with our previous results on acridine orange *N*-alkyl derivatives (*6*, *7*) and is in favor of our suggestion, also proposed by other authors (*16*–*20*), on the dominant contribution of hydrophobic interactions to the association of these dyes in aqueous solution.

Registry No. Acridine orange hydrochloride, 65-61-2.

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Composition of Ternary Systems Comprising Water, *n*-Butyl or Isobutyl Alcohol, and One of the Four Mineral Acids $HClO_4$, HNO_3, HCl or H_2SO_4

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Phase boundary data of the following ternary systems are presented: water–*n*-butyl alcohol–perchloric acid; water–isobutyl alcohol–perchloric acid; water–*n*-butyl alcohol–nitric acid; water–*n*-butyl alcohol–hydrochloric acid; water–isobutyl alcohol–hydrochloric acid; water–*n*-butyl alcohol–sulfuric acid; water–isobutyl alcohol–sulfuric acid; water–*n*-butyl alcohol–phosphoric acid. A well-defined correlation is suggested between the composition and the extent of the homogeneous region and the mineral acids contained in it.

Introduction

The investigation was undertaken to provide some basic analytical information concerning the various butyl alcohol–water–mineral acid systems used in esterification of fatty acids with butyl alcohol in solutions containing different amounts of water.

In the preceding papers (*1*–*7*), the liquid equilibria of ternary systems of water–a butyl alcohol isomer–a mineral acid were investigated for practical extraction purposes. Reburn and Shearer (*1*) determined the parameters of the water–isobutyl alcohol, isoamyl alcohol–HBr, HI, HCl systems, the nonaqueous phases of which are good electric conductors. Legge and Morieson (*2*) studied various butyl alcohol–water–acetic acid systems used in the countercurrent distribution of peptides and proteins. Further observations were reported on the optimal

Table I. Phase Boundary Data of Water–Perchloric Acid–*n*-Butyl Alcohol System

	[component], mol %		
no.[a]	water	perchloric acid	*n*-butyl alcohol
1	98.08	0	1.92
2	94.45	2.58	2.97
3	93.91	2.80	3.29
4	91.45	3.37	5.18
5	91.41	3.78	6.81
6	90.42	3.47	6.11
7	88.92	3.63	7.45
8	87.62	3.63	8.75
9	86.73	3.69	9.58
10	85.67	3.75	10.59
11	85.07	3.74	11.19
12	84.64	3.76	11.73
13	82.66	3.89	13.46
14	80.51	3.84	15.65
15	79.75	3.84	16.41
16	79.14	3.83	17.05
17	78.22	3.71	18.07
18	75.94	3.71	20.35
19	73.26	3.50	23.47
20	68.68	3.28	28.04
21	65.04	3.04	31.92
22	60.01	2.36	37.63
23	53.24	2.09	44.67
24	50.06	1.36	48.58
25	47.43	0	52.57

[a] Number of measurement (in this table and in all following tables).

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Table II. Phase Boundary Data of Water-Perchloric Acid-Isobutyl Alcohol System

no.	[component], mol % water	 perchloric acid	 isobutyl alcohol
1	89.00	0	2.91
2	95.09	2.06	2.85
3	93.41	2.97	3.62
4	91.80	3.65	5.05
5	91.20	3.59	5.21
6	90.05	4.09	5.86
7	88.62	4.20	7.18
8	87.35	4.26	8.40
9	86.53	4.24	9.23
10	85.32	4.34	10.33
11	84.89	4.36	10.75
12	84.53	4.31	11.16
13	82.62	4.41	12.97
14	80.51	4.70	14.79
15	80.03	4.52	15.45
16	79.21	4.34	13.02
17	77.58	4.55	17.87
18	76.13	4.47	19.40
19	73.33	4.44	22.23
20	69.35	4.26	26.39
21	67.23	3.88	28.89
22	60.56	2.78	36.67
23	55.15	2.29	42.56
24	53.30	1.58	45.09
25	40.92	0	59.08

Table III. Phase Boundary Data of Water-Nitric Acid-*n*-Butyl Alcohol System

no.	[component], mol % water	 nitric acid	 *n*-butyl alcohol
1	98.08	0	1.92
2	93.12	4.07	2.81
3	92.25	4.45	3.30
4	91.04	4.94	4.06
5	89.00	5.90	5.11
6	87.84	6.15	6.01
7	86.33	6.32	7.35
8	84.96	6.44	8.60
9	84.02	6.58	9.40
10	82.94	6.68	10.38
11	82.32	6.71	10.97
12	82.00	6.58	11.42
13	80.11	6.83	13.07
14	77.80	6.88	15.32
15	77.28	6.90	15.82
16	76.78	6.75	16.47
17	74.85	6.73	18.45
18	73.61	6.94	19.45
19	70.50	7.05	22.45
20	66.56	5.84	27.60
21	63.86	5.31	30.85
22	58.53	3.96	37.50
23	53.62	3.93	42.45
24	49.86	4.43	45.76
25	47.43	0	52.57

Table IV. Phase Boundary Data of Water-Hydrochloric Acid-*n*-Butyl Alcohol System

no.	[component], mol % water	 hydrochloric acid	 *n*-butyl alcohol
1	98.08	0	1.92
2	93.57	4.54	1.89
3	92.88	5.02	2.10
4	92.05	5.61	2.35
5	91.15	5.98	2.87
6	90.53	6.22	3.25
7	89.72	6.54	3.74
8	89.05	6.64	4.32
9	88.64	6.68	4.68
10	88.11	6.72	5.17
11	87.86	6.80	5.38
12	87.64	6.77	5.58
13	86.76	6.91	6.43
14	85.69	6.82	7.49
15	85.47	6.87	7.66
16	85.07	6.87	8.07
17	84.27	6.93	8.82
18	83.60	6.92	9.48
19	82.23	6.95	10.81
20	80.47	6.98	12.55
21	79.03	7.01	13.96
22	76.08	6.84	17.08
23	73.46	6.44	19.80
24	68.17	5.80	26.03
25	47.43	0	52.57

Table V. Phase Boundary Data of Water-Hydrochloric Acid-Isobutyl Alcohol System

no.	[component], mol % water	 hydrochloric acid	 isobutyl alcohol
1	89.00	0	2.91
2	94.61	3.22	2.17
3	93.51	4.30	2.19
4	92.68	4.89	2.43
5	91.63	5.56	2.81
6	91.01	5.90	3.09
7	90.27	6.26	3.47
8	89.65	6.40	3.95
9	89.28	6.61	4.11
10	88.86	6.69	4.45
11	88.62	6.77	4.61
12	88.47	6.79	4.74
13	87.76	6.97	5.27
14	86.98	7.02	6.00
15	86.79	7.04	6.17
16	86.74	7.03	6.50
17	85.64	7.09	7.27
18	85.31	7.09	7.60
19	84.30	7.15	8.55
20	82.95	7.20	9.85
21	81.81	7.22	10.97
22	79.87	7.26	12.87
23	78.29	7.28	14.43
24	76.74	7.21	16.05
25	47.43	0	52.57

conditions for extraction of mineral acids contained in the following systems: water-isobutyl alcohol-H_3PO_4, HCl (*3*); water-isobutyl alcohol, *n*-butyl alcohol-HF (*4*); water, 2-5 wt % of $CaCl_2$ contained in water-*n*-butyl alcohol-H_3PO_4 (*5*, *6*).

The aim of our work—for completing those available in the literature—was to elucidate the relationship of the origin and composition of the homogeneous zone to the mineral acid contained in it.

Experimental Section

All measurements were made in a 25-cm^3 glass-stoppered Erlenmeyer flask. Analytical-grade chemicals (Reanal, Budapest, Hungary) were used in all cases. The alcohol and water were pipetted with analytical accuracy into the flask and titrated from a microburet with the acid until the mixture became homogeneous. The results of measurements in a water bath at 25 ± 0.1 °C were not different (within the experimental error) from those performed at room temperature (without thermostating), in accordance with earlier data (*2*, *3*).

Discussion

Our results show that the amount of acid necessary to form

Table VI. Phase Boundary Data of Water-Sulfuric Acid-*n*-Butyl Alcohol System

no.	[component], mol % water	sulfuric acid	*n*-butyl alcohol
1	98.08	0	1.96
2	90.09	6.95	2.95
3	89.00	7.50	3.50
4	88.10	7.56	4.34
5	86.48	7.84	5.68
6	85.41	7.86	6.73
7	83.83	7.90	8.27
8	82.19	8.10	9.71
9	81.40	7.91	10.69
10	79.97	8.22	11.81
11	79.41	8.08	12.51
12	79.02	8.06	12.96
13	76.95	7.86	15.19
14	74.30	8.14	17.56
15	74.00	7.79	18.21
16	73.26	7.51	19.23
17	71.15	7.75	21.10
18	70.05	6.96	22.99
19	66.85	6.70	26.45
20	62.77	6.05	31.18
21	59.71	5.03	35.26
22	53.89	3.67	42.44
23	49.11	2.55	48.35
24	44.97	1.89	53.13
25	47.43	0	52.57

Table VII. Phase Boundary Data of Water-Sulfuric Acid-Isobutyl Alcohol System

no.	[component], mol % water	sulfuric acid	isobutyl alcohol
1	89.00	0	2.91
2	89.15	7.95	2.90
3	87.95	8.61	3.44
4	86.95	8.80	4.05
5	85.47	8.95	5.58
6	84.28	9.12	6.60
7	82.73	9.00	8.28
8	81.36	9.10	9.55
9	80.10	9.46	10.45
10	78.92	9.50	11.58
11	78.47	9.25	12.29
12	77.79	9.53	12.68
13	75.90	9.11	14.89
14	73.65	9.07	17.30
15	73.34	8.72	17.94
16	72.25	8.90	18.85
17	70.16	9.40	20.69
18	68.90	8.70	22.46
19	65.66	8.42	25.82
20	61.81	7.69	30.51
21	58.14	7.42	34.44
22	52.18	5.93	41.27
23	48.30	4.53	47.17
24	44.23	3.93	51.84
25	40.96	0	59.08

Table VIII. Phase Boundary Data of Water-Phosphoric Acid-*n*-Butyl Alcohol System

no.	[component], mol % water	phosphoric acid	*n*-butyl alcohol
1	98.08	0	1.92
2	87.37	10.61	2.02
3	86.34	11.19	2.47
4	83.49	13.04	3.47
5	83.56	12.53	4.89
6	83.03	12.30	4.67
7	82.36	12.55	5.09
8	80.89	12.35	6.76
9	79.40	11.65	8.95
10	79.25	12.90	7.86
11	78.90	12.30	8.80
12	77.11	13.49	9.40
13	75.35	12.10	12.55
14	74.32	13.61	12.06
15	72.25	13.20	14.55
16	71.00	13.85	15.15
17	69.90	13.19	16.92
18	68.51	13.16	18.35
19	66.85	12.89	20.06
20	62.71	11.76	25.53
21	60.37	11.02	28.61
22	56.09	8.39	35.52
23	51.65	5.41	42.94
24	47.48	2.24	50.27
25	47.43	0	52.57

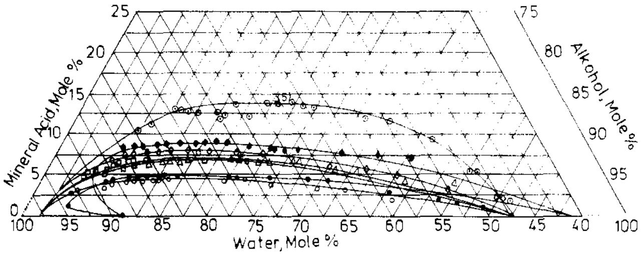

Figure 1. Phase boundary data of ternary systems: (○) water–*n*-butyl alcohol–perchloric acid, (●) water–isobutyl alcohol–perchloric acid, (△) water–*n*-butyl alcohol–nitric acid, (□) water–*n*-butyl alcohol–hydrochloric acid, (◇) water–*n*-butyl alcohol–sulfuric acid, (◆) water–isobutyl alcohol–sulfuric acid, (⊙) water–*n*-butyl alcohol–phosphoric acid, (5, ⊗) measured by Muralimohan (*5*).

a homogeneous ternary system from water–*n*-butyl alcohol, isobutyl alcohol mixtures present in two phases depends on the strength of the mineral acid applied (Tables I–VIII). All data of the binodal curves are means of three parallel titrations which agreed satisfactorily within the experimental error. We determined the composition of the homogeneous ternary system by the molar ratio of water/acid calculated from titrations (Table IX, Figure 1). The mean values of ratios were taken from tests of no. 10–19, which represent the most reliable points of the binodal curves, derived from the titration method, according to the literature (*7*).

The obtained ratios suggest that the acid content of the given homogeneous ternary system decreases proportionally (H_3PO_4 > H_2SO_4 > HCl > HNO_3 > $HClO_4$) with the basicity of the anions according to Lewis concepts. We consider that the relationship observed between the extent of heterogeneous zones and the Lewis basicity of the mineral acid in the given system may be of theoretical importance.

Our work was aimed primarily to clarify the phase boundary data of homogeneous and heterogeneous zones in order to esterify in homogeneous aqueous solutions. These data were applied for esterifications in aqueous solutions within quite a wide range of compositions. The members of the homologous series of normal fatty acids could be esterified quantitatively with *n*-butyl and isobutyl alcohols in water–alcohol mixtures in a volume ratio of 1:1 (that corresponds to a molar ratio of 5:1). Though our results are mainly of analytical character (*8*, *9*), in

Table IX. Phase Boundary Data of All Systems Investigated Expressed in Mole Ratio of Water to Acid

	mol of water/mol of acid[a]							
no.	I	II	III	IV	V	VI	VII	VIII
2	36.60	46.16	22.88	20.61	29.38	12.96	11.21	8.23
3	33.54	31.45	20.73	18.50	21.75	11.87	10.21	7.72
4	27.13	25.15	18.43	16.41	18.95	11.65	9.88	6.40
5	24.18	25.40	15.08	15.24	16.48	11.03	9.55	6.67
6	26.06	22.02	14.28	14.55	15.43	10.87	9.24	6.75
7	24.50	21.10	13.66	13.72	14.42	10.61	9.19	6.56
8	24.14	20.50	13.19	13.41	14.01	10.15	8.94	6.55
9	23.50	20.41	12.77	13.27	13.51	10.29	8.47	6.82
10	22.85	19.66	12.42	13.11	13.28	9.73	8.31	6.14
11	22.75	19.47	12.27	12.92	13.09	9.83	8.48	6.41
12	22.51	19.61	12.46	12.95	13.02	9.80	8.16	5.72
13	21.25	18.73	11.73	12.56	12.59	9.79	8.33	6.23
14	20.97	17.13	11.31	12.56	12.39	9.13	8.12	5.46
15	20.77	17.71	11.20	12.44	12.33	9.50	8.41	5.47
16	20.66	18.25	11.37	12.38	12.34	9.75	8.12	5.13
17	21.08	17.05	11.12	12.16	12.08	9.18	7.46	5.30
18	20.47	17.03	10.61	12.08	12.03	10.06	7.92	5.21
19	20.93	16.52	10.00	11.83	11.79	9.98	7.80	5.19
20	20.94	16.28	11.40	11.53	11.52	10.38	8.04	5.33
21	21.39	17.33	12.03	11.27	11.33	11.87	7.84	5.48
22	25.43	21.78	14.78	11.12	11.00	14.68	8.80	6.69
23	25.47	24.08	13.64	11.41	10.75	19.26	10.66	9.55
24	36.80	33.75	11.26	11.75	10.64	23.79	11.25	21.20
av[b]	21.43	18.12	11.45	12.50	12.49	9.68	8.11	5.63
SD[c]	0.91	1.20	0.80	0.41	0.50	0.31	0.32	0.47
CV[d]	4.3 (20.7)[e]	6.6 (23.5)	7.0 (23.4)	3.3 (14.0)	4.0 (14.0)	3.2 (36.0)	3.8 (40.2)	8.4 (49.2)

[a] Ratios calculated from Tables I-VIII. [b] Average of measurement no. 10-19. [c] Standard deviation calculated according to the instructions of: *Anal. Chem.* **1983**, *55*, 173. [d] Coefficient of variation calculated according to the instructions of: *Anal. Chem.* **1983**, *55*, 173. [e] In parentheses: acid content of the aqueous solution in weight percent; calculated from the mean value (av) of mole ratios (water/acid) of the given system.

addition to the rapid preparation for gas-chromatographic analysis, they may also be of some technological importance.

The synergetic effect of *n*-butyl and isobutyl alcohols in extraction is well-known. Our results may help support the use of butyl alcohol as an auxiliary material in extractants.

On the basis of our results, the use of butyl alcohol as an extractant from concentrated aqueous solutions of mineral acids is limited: As is shown (data in parentheses in Table IX), one can extract neither with *n*-butyl alcohol nor with isobutyl alcohol from mixtures containing more than about 14 wt % of hydrochloric acid solutions. But, for example, *n*-butyl alcohol is a good extractant up to about 50 wt % of phosphoric acid content.

Registry No. Butyl alcohol, 71-36-3; isobutyl alcohol, 78-83-1; hydrochloric acid, 7647-01-0; perchloric acid, 7601-90-3; nitric acid, 7697-37-2; sulfuric acid, 7664-93-9; phosphoric acid, 7664-38-2.

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Excess Volumes for Mixtures of Benzene with Some Cycloalkanes at 293.15, 298.15, and 303.15 K

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Excess volumes were determined from density measurements for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 293.15, 298.15, and 303.15 K.

This paper reports excess volumes for binary mixtures of benzene with cyclopentane, methylcyclohexane, and cyclooctane at 293.15, 298.15, and 303.15 K. The measurements were undertaken to provide information about thermodynamic properties of benzene-cycloalkane systems; determinations for the mixture of benzene-cyclohexane which were carried out as a part of the present series have been published previously (*1*).

Experimental Section

Excess volumes were determined from densities measured by use of a vibrating densimeter (Model 01D, Sodev Inc.,

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