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Dimitrios P. Koullas[a]; Okechukwu S. Umealu[a]; Emmanuel G. Koukios[a]
[a] BIORESOURCE TECHNOLOGY UNIT DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL TECHNICAL UNIVERSITY OF ATHENS, ATHENS, GREECE

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Solvent Selection for the Extraction of Ethanol from Aqueous Solutions

DIMITRIOS P. KOULLAS,* OKECHUKWU S. UMEALU, and
EMMANUEL G. KOUKIOS
BIORESOURCE TECHNOLOGY UNIT
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TECHNICAL UNIVERSITY OF ATHENS
ZOGRAFOU CAMPUS, GR-157 00 ATHENS, GREECE

ABSTRACT

Several organic solvents were examined as potential separating agents for ethanol recovery from aqueous solutions by liquid–liquid extraction. Phase composition determinations for five promising ethanol–water–solvent systems at 20 and 40°C and two solvent-to-feed ratios show that isoamyl acetate (IAA) and isooctyl alcohol (IOA) along with *n*-butyl acetate (BA) present a greater potential than dibutyl ether and dibutyl oxalate. Tie-line liquid–liquid equilibrium data at 25°C for the three promising solvents (IAA, IOA, and BA) were collected and analyzed. Both IAA and IOA were found to be very good separating agents, exhibiting ethanol distribution coefficients greater than 1, and separation factors in Bancroft coordinates of the order of 70 and 2000, respectively.

INTRODUCTION

It is a well-known fact that the production of transportation biofuels through bioconversion involves bioethanol fermentation. A major problem of ethanol–water separation, i.e., the downstream process which follows the fermentation, is the rather high energy requirement of the operation process. The recovery of anhydrous ethanol from the aqueous fermentation broth by liquid–liquid extraction is a particularly promising solution of the energy-balance problems usually associated with ethanol–water separation (1, 2).

According to the most recent research work, the separation of ethanol from water can be achieved by a variety of technologies, such as sorptive separation

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* To whom correspondence should be addressed.

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by molecular sieves (3), by (pervaporation) with a zeolite membrane (4) or a zeolite-filled composite membrane (5), by selective desorption of water (6), etc.

As far as extraction methods are concerned, various types of approaches have been reported in the literature, including extraction by gasoline for the use of the extract directly as fuel (7, 8), supercritical extraction (9, 10) extraction based on the upper solution temperature (11), and examination of a variety of solvents as candidates for conventional liquid–liquid extraction (12–14). Some efforts have been made to combine the characteristics of technologies which are even diverse in some cases (10).

All those studies have, among other things, strongly reconfirmed that selection of the separating agent is the key stage for the success of the whole process by major technical, economic, energetic, and environmental criteria (15). Theoretical investigations on the best potential solvent for ethanol–water separation by liquid–liquid extraction have considerably improved knowledge in this area (16). Nevertheless, experimental studies are necessary in all cases to verify predictions.

The object of this paper, the first in a series on ethanol–water separation by liquid extraction, is to experimentally screen several organic compounds taken from a long list of potential solvents (17) in order to select some promising ones. A step-by-step procedure was employed for this selection, starting with a fast screening test and ending with detailed equilibrium experiments. In the following papers in this series the technical design and economics of the separation process using the chosen solvents will be addressed in order to provide an integrated view of the whole research work.

EXPERIMENTAL

All organic chemicals used in this paper were of analytical reagent grade. Water was further purified by means of an ion-exchange column. Only glass apparatus were used throughout the experiments.

The experimental procedure consisted of mixing, under stirring, premeasured volumes of ethanol and water in a glass cell, placing them in a thermostatically heated water bath (temperature control within ±0.2°C), and then adding the premeasured volume of the organic solvent. After vigorous mixing for 2 minutes, the system was allowed to stand for 8 hours under constant stirring. Then it was transferred in a glass settler/decanter where it was left undisturbed overnight (approximately 12 hours for complete phase separation). Finally, the aqueous or water-rich phase and the organic or solvent-rich phase were separately recovered for analysis.

For the preliminary screening stage, a fast, short-cut method was employed, based on the relative volumes of the organic and aqueous phases separated after mixing 2 volumetric parts of solvent with 1 part of a 50/50 (v/v) ethanol–water solution. The selection of the latter initial composition for fast screening of potential solvents was determined by the fact that, as also verified in this work, most solvents examined present different separation performance at different initial compositions of the ethanol–water system.

The composition of the organic phase in ethanol and the solvent used each time was determined by gas chromatography (N_2 as carrier gas). Mixtures of known composition were used for reference. In the case of high-water content samples, CaO was used in order to dehydrate the solvent-rich phase before gas chromatography. The water content in the organic phase was measured by the Karl Fischer titrimetric method (18). The composition of the aqueous phase was then determined by calculation of the differences from the initial quantities of the three components. The mass balances of the two phases provided additional checking of the experimental determinations.

RESULTS AND DISCUSSION

A fast preliminary screening of a multitude of organic solvents, identified on the basis of their physical properties (17, 19) was first done according to phase separation data. A number of good ethanol solvents, which at the same time show a very low miscibility with water, were tested in that way (Table 1). Several of them were found particularly interesting for more detailed evaluation.

TABLE 1
Phase Separation Data for Ethanol (E)–Water (W)–Organic Solvent (S) Systems at 20°C—Preliminary Screening Stage[a]

System	Organic phase (relative volume)[b]	Aqueous phase (relative volume)[b]
E–W	—	200
S (all used)	100	—
E–W–2,2,4-trimethylpentane	87	213
E–W–3-Methylpentane	90	210
E–W–4-chlorotoluene (*para*)	95	205
E–W–2-chlorotoluene (*ortho*)	100	200
E–W–1,2-dichloroethane	100	200
E–W–cyclohexane	110	190
E–W–di-*n*-butyl ether[c]	126	184
E–W–isoamyl acetate[c,d]	155	125
E–W–1-octanol	160	140
E–W–isooctyl alcohol[c,e]	160	140
E–W–*n*-butyl acetate[c]	165	130
E–W–di-*n*-butyl oxalate[c]	170	105
E–W–bis(2-ethylhexylester) phthalate	195	90

[a] Phase separation obtained after mixing 200 volumetric parts of a 50/50 (v/v) ethanol–water solution with 100 volumetric parts of an organic solvent.
[b] Volumetric parts after phase separation.
[c] Selected for more detailed investigation.
[d] 3-Methyl butyl acetate.
[e] 6-Methyl-1-heptanol.

The results of phase composition determination for five solvents, considered as potential ethanol–water separating agents by liquid–liquid extraction, i.e., one alcohol, one ether, and three esters, are shown in Table 2. Experiments were carried out at two temperatures and two solvent-to-feed ratios of technical importance. For two of them, isoamyl acetate and isooctyl alcohol,

TABLE 2

Phase Composition Data for Ethanol (E)–Water (W)–Organic Solvent (S) Systems at 20 and 40°C—Preliminary Evaluation Stage[a]

Temperature (°C)	Organic phase[b]			Aqueous phase[b]			Distribution coefficients		
	Y_E	Y_W	Y_S	X_E	X_W	X_S	K_E	K_W	α[c]
(i) Di-n-Butyl Oxalate									
20	8.3	8.9	82.8	15.2	64.8	20.0	0.55	0.14	3.9
20	16.0	13.8	70.2	12.2	69.4	18.4	1.31	0.20	6.6
40	22.7	10.4	66.2	19.0	42.8	38.2	1.19	0.24	5.0
40	28.2	12.8	59.0	8.7	72.9	18.4	3.24	0.18	18
(ii) Di-n-Butyl Ether									
20	22.6	2.0	75.4	24.7	59.4	15.9	0.91	0.034	27
20	22.2	1.9	75.9	15.5	56.2	28.3	1.43	0.034	42
40	18.2	2.3	79.5	29.2	59.2	11.6	0.62	0.030	16
40	10.1	1.9	88.0	29.9	63.3	6.8	0.34	0.030	11
(iii) Isoamyl Acetate[d]									
20	25.8	7.2	67.0	14.0	75.1	10.9	1.84	0.096	19
20	17.2	5.8	77.0	3.9	78.1	18.0	4.41	0.074	60
40	22.0	8.2	69.8	4.1	73.5	22.4	5.37	0.112	48
40	17.2	5.9	76.9	2.9	83.3	13.8	5.93	0.071	84
(iv) Isooctyl Alcohol[d]									
20	31.7	4.8	63.5	3.3	83.0	13.7	9.61	0.058	166
20	19.0	3.3	77.7	0.5	89.6	9.9	38.0	0.037	1027
40	29.5	5.4	65.1	8.0	81.9	10.1	3.69	0.066	56
40	18.6	3.8	77.6	0.5	95.9	3.6	37.2	0.040	930
(v) n-Butyl Acetate[d]									
20	18.8	6.4	74.8	28.0	71.3	0.7	0.67	0.090	7.4
20	13.2	4.1	82.8	20.6	79.3	0.1	0.65	0.052	13.0
40	20.2	8.2	71.6	25.4	70.1	0.5	0.80	0.117	6.8
40	14.9	4.8	80.3	12.9	79.6	7.5	1.16	0.060	19.0

[a] See Table 1, Footnote *a*; for each temperature, 1:1 and 2:1 (v/v) solvent-to-feed ratios were used.

[b] Mass fractions (% w/w) of the particular phase.

[c] Separation factor, $\alpha = K_E K_W^{-1}$.

[d] Selected for more detailed investigation.

TABLE 3
Tie-Line Liquid–Liquid Equilibrium Data for Selected Ethanol (E)–Water (W)–Organic Solvents (S) Systems at 25°C[a]

Solvent and initial system, E (% v/v)	Organic phase[a]			Aqueous phase[a]			Distribution coefficients			
	Y_E	Y_W	Y_S	X_E	X_W	X_S	K_E	K'^{b}_{E}	$K_W\,(10^{-1})$	$K'^{b}_{W}\,(10^{-3})$
(i) Isoamyl Acetate							4.55[c]	4.38[c]	0.65[c]	1.95[c]
10.0	4.4	2.2	93.4	0.1	89.6	10.2	44.0	42.2	0.25	0.03
20.0	7.4	3.2	89.4	2.4	85.2	12.4	3.08	2.94	0.38	1.02
30.0	10.7	4.2	85.1	3.9	84.6	11.5	2.74	2.72	0.50	2.29
40.0	13.9	5.8	80.3	5.0	73.7	21.3	2.78	2.55	0.79	4.92
60.0	16.1	8.3	75.6	4.9	64.7	30.4	3.29	2.81	1.28	8.30
70.0	21.4	11.9	66.7	8.2	75.2	16.6	2.61	2.94	1.58	19.4
(ii) Isooctyl Alcohol							4.27[c]	3.99[c]	0.62[c]	9.00[c]
10.0	4.4	3.3	92.3	0.3	93.7	6.0	14.7	14.9	0.35	0.11
20.0	8.7	3.8	87.5	0.8	83.7	15.5	10.9	10.4	0.45	0.41
30.0	10.9	4.3	84.8	5.1	78.8	16.1	2.14	2.00	0.55	3.31
60.0	18.4	6.0	75.6	9.8	70.0	20.2	1.88	1.74	0.86	11.2
70.0	23.1	7.5	69.4	10.5	59.3	30.2	2.20	1.88	1.26	19.1
(iii) n-Butyl Acetate							0.56[c]	0.44[c]	0.56[c]	9.22[c]
10.0	2.4	2.0	95.6	3.7	91.4	4.9	0.65	0.62	0.22	0.85
20.0	3.6	1.9	94.5	10.0	84.0	6.0	0.36	0.32	0.23	2.43
30.0	6.8	2.4	90.8	12.7	80.5	6.8	0.54	0.48	0.30	4.20
40.0	12.1	4.3	83.6	19.5	70.3	10.2	0.62	0.52	0.61	14.2
60.0	15.1	7.2	77.7	23.0	63.6	13.4	0.66	0.54	1.13	33.5
70.0	20.2	10.4	69.4	35.6	35.6	28.8	0.57	0.29	2.92	149.8

[a] Procedure and symbols as in Table 2 (Footnotes *a* and *b*), solvent-to-feed ratio 2:1 (v/v).
[b] In Bancroft coordinates.
[c] Geometric mean values.

the findings are definitely positive; significantly higher ethanol concentrations in the organic phase than that in the aqueous one, in conjunction with low water contents in the solvent-rich phase, as well as low solvent contents in the water-rich phase, make these solvents particularly attractive for further examination. For the opposite reasons, di-*n*-butyl oxalate shows a low potential, whereas of the remaining two solvents which appear to be in an intermediate situation, *n*-butyl acetate was selected for more detailed study, mainly due to its considerably lower solvent content in the raffinate (aqueous phase).

Liquid–liquid equilibrium data required for the construction of tie-line diagrams involving the three selected solvents are presented in Table 3. It should be noted that as the system enriches in ethanol, extraction becomes progressively more efficient and, therefore, advantageous in contrast to other separation methods. A comparison of the separation selectivity when those solvents are used as separating agents in liquid–liquid extraction is shown in Table 4. Separation factors in the usual as well as in Bancroft coordinates, which are useful for short-cut design calculations (20), are used. The results from this comparison are illustrated in Fig. 1, where separation factors in Bancroft coordinates are plotted versus the concentration of ethanol in the extract.

Overall, both isoamyl acetate and isooctyl alcohol are found to satisfy all criteria for this stage of the analysis. Distribution coefficients for ethanol are significantly higher than 1 (Table 3); this fact, along with the very low values of distribution coefficients for water (Table 3), lead to very high values of the separation factor (Table 4), thus guaranteeing an efficient extraction. Although the overall average potentials of the two solvents appear to be the same, Fig. 1 shows that isoamyl acetate is more selective for obtaining ethanol concentrations of more than 10% (w/w) in the extract whereas isooctyl alcohol is more selective for lower ethanol concentration values. On the other hand, *n*-butyl acetate is clearly an inferior solvent (Fig. 1, Table 4); however, it shows a separation efficiency similar to other compounds examined in the literature (13, 14).

Moreover, as shown in Table 3, the distribution coefficient for ethanol in both coordinates remains rather constant and, with the exception of some extreme points, does not change with the initial feed concentration. This finding could considerably simplify process design calculations (17).

Based on the experimental results of Table 3, the equilibrium diagrams of Figs. 2, 3, and 4 were constructed for the three solvents under investigation.

TABLE 4
Separation Selectivity for the Liquid–Liquid Extraction of Ethanol (E) from Aqueous Solutions by Selected Organic Solvents (S) at 25°C[a]

Initial system, E (%, v/v)	Isoamyl acetate		Isooctyl alcohol		*n*-Butyl acetate	
	α	α'[b]	α	α'[b]	α	α'[b]
10.0	1760.0	1405×10^3	419.0	135×10^3	29.5	729.0
20.0	81.1	2880	242	25.4×10^3	15.7	132
30.0	54.8	1190	38.9	602	18.0	114
40.0	35.2	518	—	—	10.2	36.5
60.0	25.7	339	21.9	156	5.8	16.1
70.0	16.5	151	17.5	99	2.0	1.9
Mean, values[a]	70	2250	69	2000	10	48

[a] Based on the data in Table 3.

[b] Separation factors: $\alpha = K_E K_W^{-1}$; $\alpha' = K'_E K'^{-1}_W$.

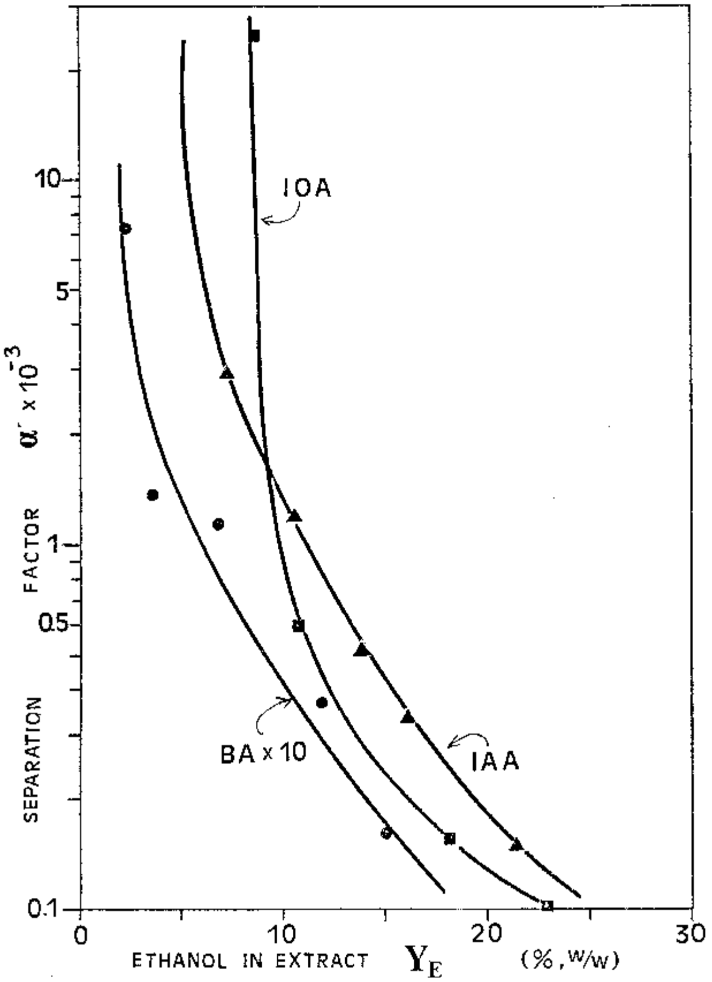

FIG. 1 Comparative separation efficiency of the selected solvents: Isoamyl acetate (IAA, ▲); isooctyl alcohol (IOA, ■); *n*-butyl acetate (BA, ●).

Orthogonal-type diagrams in solvent-free coordinates were preferred due to their usefulness in design calculations. In another aspect of comparison between the three candidates, we observe that maximum values in the 70–75% range of ethanol concentration in the extraction solvent-free coordinates can be obtained by all three solvents. Nevertheless, this phenomenon requires the presence of solvent in significantly different ratios to the recovered ethanol as measured by the Y'_S in Figs. 2–4: 2 for isooctyl alcohol, 5 for isoamyl acetate, and 8 for *n*-butyl acetate. Obviously, better differentiation between the three solvents is possible only through preliminary design of the corresponding extraction systems.

Finally, the tie-line data of the three systems (Table 3) were correlated with the use of the Othmer–Tobias correlation (Fig. 5). The fitting was satisfactory, as verified by the values of the correlation coefficient (0.96–0.98).

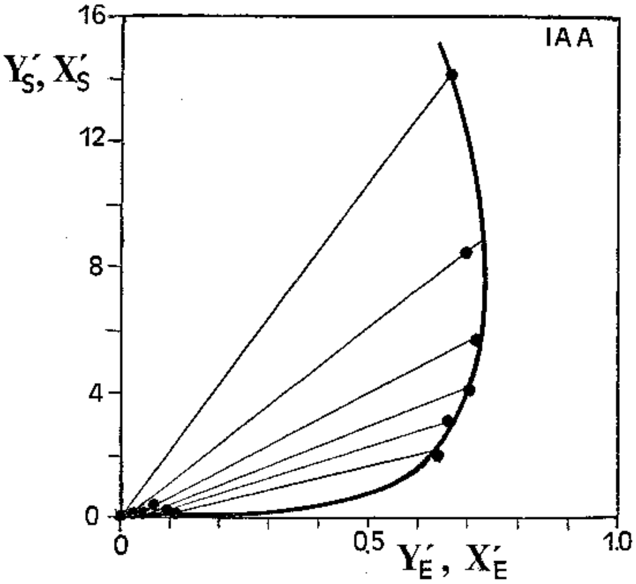

FIG. 2 Liquid–liquid orthogonal equilibrium diagram in solvent-free-based coordinates for the system ethanol (E)–water (W)–isoamyl acetate (S) at 25°C.

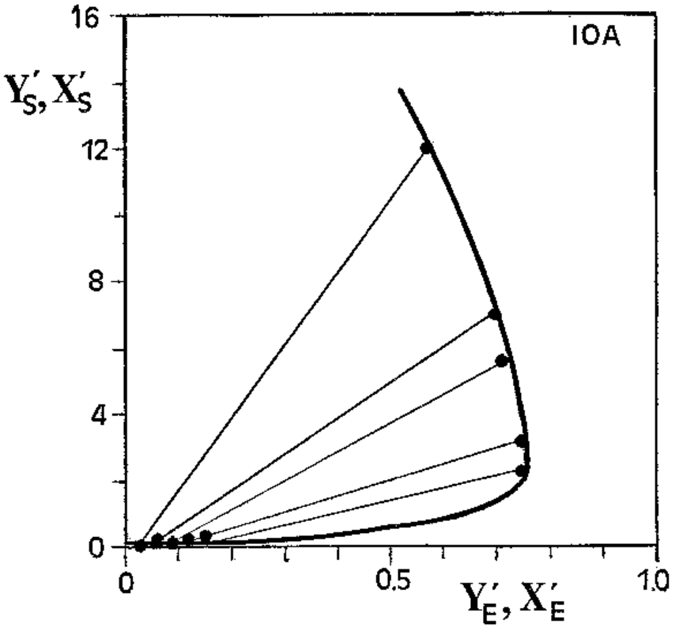

FIG. 3 Liquid–liquid orthogonal equilibrium diagram in solvent-free-based coordinates for the system ethanol (E)–water (W)–isooctyl alcohol (S) at 25°C.

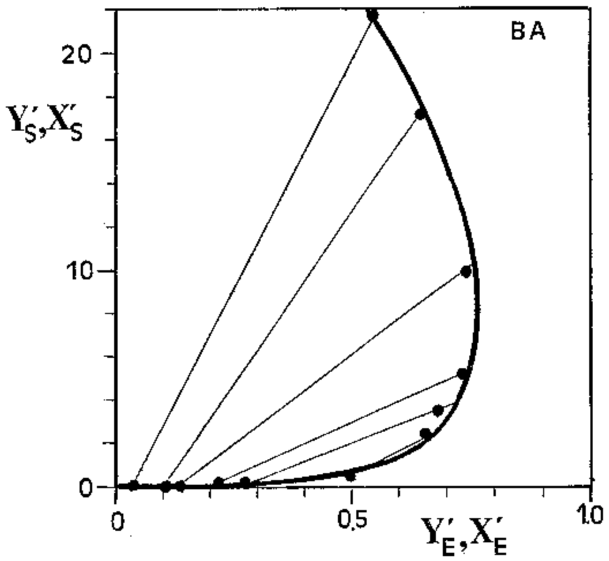

FIG. 4 Liquid–liquid orthogonal equilibrium diagram in solvent-free-based coordinates for the system ethanol (E)–water (W)–*n*-butyl acetate (S) at 25°C.

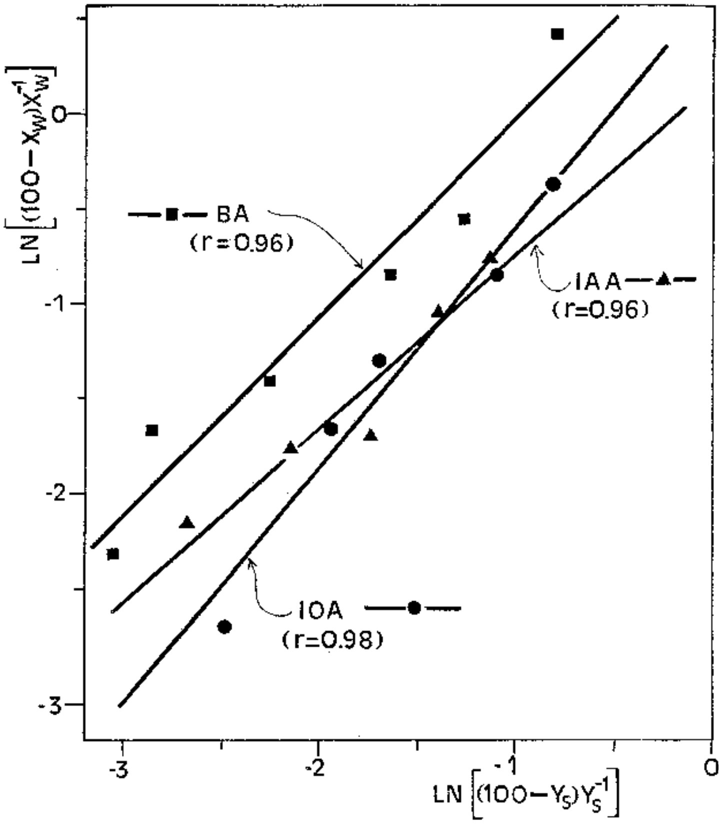

FIG. 5 Othmer–Tobias correlation of experimental results for the selected solvents: Isoamyl acetate (IAA), isooctyl alcohol (IOA), *n*-butyl acetate (BA).

TABLE 5
Ranking of Solvents According to Various Criteria

Solvents examined	Ethanol separation	Ethanol losses	Solvent losses	Overall performance
Isoamyl acetate	1, 2[a]	1	3	1, 2[a]
Isooctyl alcohol	1, 2[a]	2	2	1, 2[a]
n-Butyl acetate	3	3	1	3

[a] Further refinement is necessary for a final ranking.

Final ranking of the three solvents was based on (a) their relative separation efficiency, as determined by the ethanol concentration in the extract, as well as on the potential losses of (b) ethanol, and (c) solvent, as indicated by the respective concentrations in the aqueous phase. As seen in Table 3, under optimal conditions the aqueous phase was found to contain less than 5% (M/M) ethanol and less than 15% (M/M) solvent, which at the present stage of the work could be assumed for the most part to be separated from water by distillation and recycled to the appropriate points of the whole process.

The results of such a ranking, as summarized in Table 5, confirm that at this stage of the work no differentiation is possible between isoamyl acetate and isooctyl alcohol, whereas *n*-butyl acetate is found to be of inferior potential overall. A more specific evaluation of the two higher ranking solvents can only be based on technical and economic aspects to be addressed in a subsequent publication.

SYMBOLS

Y_i	weight fraction of solute in the organic (extract) phase (i = E for ethanol, W for water, S for solvent)
X_i	weight fraction of solute in the aqueous (raffinate) phase (i = E for ethanol, W for water, S for solvent)
y_i	weight fraction of solute to extraction solvent in the organic (extract) phase (i = E for ethanol, W for water, S for solvent)
x_i	weight fraction of solute to feed solvent in the aqueous (raffinate) phase (i = E for ethanol, W for water, S for solvent)
K_i	distribution coefficient, equal to Y_i/X_i (i = E for ethanol, W for water, S for solvent)
K'_i	distribution coefficient in Bancroft coordinates, equal to y_i/x_i (i = E for ethanol, W for water, S for solvent)
α	separation factor, equal to $K_{\mathrm{E}}K_{\mathrm{w}}^{-1}$
α'	separation factor in Bancroft coordinates, equal to $K'_{\mathrm{E}}\mathrm{K}'_{\mathrm{w}^{-1}}$

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