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Quaternary phase equilibrium of water–carboxylic acid mixture (formic–propionic acid or acetic–propionic acid)–solvent liquid systems at 298.15 K

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ABSTRACT

Liquid–liquid equilibrium data of water–acid mixture (formic–propionic acid or acetic–propionic acid)–solvent (amyl acetate, diisobutyl ketone, and diisopropyl ether) quaternary systems were measured at 298.15 K. Complete phase diagrams were obtained by determining solubility curves and tie-lines. A comparison of the extracting capabilities of the solvents was made with respect to distribution coefficients, separation factors and solvent-free selectivity bases. Reliability of the data was ascertained from Othmer–Tobias plots. It is concluded that the used solvents can be treated as suitable separating agents for dilute aqueous formic–propionic acid or acetic–propionic acid mixtures.

1. Introduction

In the carboxylic acid production through fermentation processes, aqueous solutions of acid occur in the broth about in 10% (w/w) concentrations. The economics of the process depends strongly on the development of an effective recovery method of organic acids from the broth medium. Therefore, the selective recovery of organic acids from dilute aqueous solutions has become of interest.

Formic, acetic and propionic acids are the most important carboxylic acids that are widely used in industry, which makes the biotechnological production of these acids important. Formic acid is used as a preservative and antibacterial agent in livestock feed and also used in textile industry [1]. Acetic acid is an important chemical reagent and industrial chemical and has been extensively used in many manufacturing processes of organic chemicals such as polyethylene terephthalate (the material for making soft drink bottles), cellulose acetate (the material for making photographic film), and polyvinyl acetate (the material for wood glue, as well as synthetic fibers and fabrics) [2]. Also propionic acid is used in the manufacture of herbicides, chemical intermediates, artificial fruit flavors, pharmaceuticals, and preservatives for food, animal feed, and grain [3].

The solvent is the key to a successful separation by liquid–liquid extraction. Among several solvent selection criteria, the distribution coefficient and selectivity are of considerable value since they measure the separating power of a solvent.

Reliable data of a physical–chemical nature are necessary for the development of liquid–liquid extraction processes and the design of equipment for them [4]. Although liquid–liquid equilibrium (LLE) data of aqueous formic, acetic and propionic acids solutions with various solvents have been performed and reported by several researchers in ternary basis [5–50], the quaternary LLE data on related acids are scarce in the literature [51–57]. In this study, quaternary LLE data of water–formic acid–propionic acid–solvent (amyl acetate, diisobutyl ketone, and diisopropyl ether) and of water–acetic acid–propionic acid–solvent (amyl acetate, diisobutyl ketone, and diisopropyl ether) systems were determined at 298.15 K, where no such data are available in the literature. Complete phase diagrams were obtained by solubility and tie-line data simultaneously for each solvent. A comparison of the extracting capabilities of the solvents was made with respect to distribution coefficients (d), separation factors (S) and solvent-free selectivity bases. Reliability of the data was ascertained by Othmer–Tobias plots [58].

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Table 1
Refractive indexes n_D and densities ρ at 20 °C, and boiling points t_b at 101.33 kPa of chemicals [59].

Compound	n_D		ρ (g cm^{-3})		t_b (°C)	
	Meas'd.	Lit.	Meas'd.	Lit.	Meas'd.	Lit.
Formic acid	1.3711	1.3714	1.2185	1.2200	100.9	101.0
Acetic acid	1.3721	1.3720	1.0445[a]	1.0446[a]	117.9	117.9
Propionic acid	1.3808	1.3809	0.9881[a]	0.9882[a]	141.1	141.15
Amyl acetate	1.4025	1.4023	0.8759	0.8756	149.1	149.2
Diisobutyl ketone	1.4118[b]	1.4120[b]	0.8065	0.8062	169.6	169.4
Diisopropyl ether	1.3655[a]	1.3658[a]	0.7190[a]	0.7192[a]	68.2	68.4

[a] At 25 °C.
[b] At 21 °C.

2. Experimental

2.1. Chemicals

Formic acid (Merck, >98%), acetic acid (Merck, >99%), propionic acid (Merck, >99%), amyl acetate (Merck, 98%), diisobutyl ketone (Merck, ~75% 2,6-dimethyl-4-heptanone + ~25% 2,4-dimethyl-6-heptanone), and diisopropyl ether (Merck, ≥99%) were used without further purification. Deionized and redistilled water was used throughout all experiments. The purity of the chemicals was checked on the basis of their refractive indexes and densities at 293 ± 0.20 K. Refractive indexes and densities were measured with Anton Paar densimeter (Model DMA 4500) integrated with

Table 2
Solubility data for water (1)–formic acid (2)–propionic acid (3)–solvent (4) quaternary systems at 298.15 K.

w_1	w_2	w_3	w_4
Amyl acetate			
0.9950	0.0000	0.0000	0.0050
0.8893	0.0531	0.0526	0.0050
0.7914	0.1006	0.0999	0.0081
0.6882	0.1496	0.1485	0.0137
0.5815	0.1940	0.1926	0.0319
0.4510	0.2262	0.2245	0.0983
0.2976	0.2235	0.2228	0.2561
0.2653	0.2209	0.2193	0.2945
0.1943	0.2020	0.2005	0.4032
0.1398	0.1726	0.1712	0.5164
0.0974	0.1388	0.1377	0.6261
0.0655	0.0994	0.0987	0.7364
0.0358	0.0499	0.0496	0.8647
0.0105	0.0000	0.0000	0.9895
Diisobutyl ketone			
0.9961	0.0000	0.0000	0.0039
0.8960	0.0506	0.0502	0.0032
0.7945	0.1007	0.0999	0.0049
0.6951	0.1501	0.1489	0.0059
0.5964	0.1976	0.1961	0.0099
0.4904	0.2438	0.2420	0.0238
0.4309	0.2659	0.2638	0.0394
0.3784	0.2757	0.2736	0.0723
0.3015	0.2857	0.2836	0.1292
0.2206	0.2808	0.2786	0.2200
0.1403	0.2591	0.2572	0.3434
0.1009	0.2299	0.2282	0.4410
0.0692	0.1876	0.1861	0.5571
0.0591	0.1440	0.1429	0.6540
0.0453	0.0957	0.0950	0.7640
0.0327	0.0496	0.0493	0.8684
0.0103	0.0000	0.0000	0.9897
Diisopropyl ether			
0.9706	0.0000	0.0000	0.0294
0.8653	0.0499	0.0495	0.0353
0.7725	0.0964	0.0956	0.0355
0.6735	0.1452	0.1442	0.0371
0.5692	0.1902	0.1888	0.0518
0.4441	0.2237	0.2220	0.1102
0.3160	0.2381	0.2362	0.2097
0.2376	0.2295	0.2278	0.3051
0.1673	0.2093	0.2078	0.4156
0.1213	0.1768	0.1755	0.5264
0.0945	0.1374	0.1364	0.6317
0.0670	0.0941	0.0933	0.7456
0.0326	0.0500	0.0496	0.8678
0.0053	0.0000	0.0000	0.9947

Table 3
Solubility data for water (1)–acetic acid (2)–propionic acid (3)–solvent (4) quaternary systems at 298.15 K.

w_1	w_2	w_3	w_4
Amyl acetate			
0.9950	0.0000	0.0000	0.0050
0.8919	0.0505	0.0509	0.0067
0.7919	0.0993	0.1001	0.0087
0.6842	0.1467	0.1479	0.0212
0.5739	0.1910	0.1925	0.0426
0.4391	0.2172	0.2189	0.1248
0.2962	0.2181	0.2198	0.2659
0.2786	0.2157	0.2175	0.2882
0.1892	0.2011	0.2027	0.4070
0.1257	0.1747	0.1761	0.5235
0.0817	0.1371	0.1383	0.6429
0.0476	0.0954	0.0961	0.7609
0.0298	0.0500	0.0504	0.8698
0.0105	0.0000	0.0000	0.9895
Diisobutyl ketone			
0.9961	0.0000	0.0000	0.0039
0.8945	0.0504	0.0509	0.0042
0.7859	0.1044	0.1054	0.0043
0.6945	0.1490	0.1504	0.0061
0.5941	0.1953	0.1972	0.0134
0.4835	0.2400	0.2425	0.0340
0.3619	0.2694	0.2721	0.0966
0.2564	0.2686	0.2713	0.2037
0.1743	0.2467	0.2492	0.3298
0.1275	0.2170	0.2191	0.4364
0.0785	0.1832	0.1851	0.5532
0.0531	0.1423	0.1438	0.6608
0.0342	0.0959	0.0968	0.7731
0.0179	0.0509	0.0514	0.8798
0.0103	0.0000	0.0000	0.9897
Diisopropyl ether			
0.9706	0.0000	0.0000	0.0294
0.8694	0.0485	0.0489	0.0332
0.7696	0.0946	0.0954	0.0404
0.6625	0.1410	0.1422	0.0543
0.5576	0.1836	0.1850	0.0738
0.4434	0.2186	0.2204	0.1176
0.3086	0.2337	0.2356	0.2221
0.2387	0.2274	0.2293	0.3046
0.1582	0.2098	0.2114	0.4206
0.1048	0.1793	0.1807	0.5352
0.0676	0.1399	0.1411	0.6514
0.0366	0.0958	0.0965	0.7711
0.0147	0.0500	0.0505	0.8848
0.0053	0.0000	0.0000	0.9947