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Liquid−Liquid Equilibria of Aqueous Acetic Acid Derivatives with Trioctylamine and Select Organic Diluents

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Liquid−liquid equilibria for aqueous solutions of acetic acid derivatives, formic, monochloroacetic, dichloroacetic, and trichloroacetic acids, with trioctylamine in various diluents, 1-octanol, chloroform, hexane, and tetrachloromethane, were determined at 298 K. The loading of trioctylamine was calculated, and the extraction behavior was discussed on the basis of the loading. The degrees of extraction of these medium-strong carboxylic acids with trioctylamine are in the order 1-octanol ≥ chloroform > tetrachloromethane > hexane at $Z_{exp} < 1$. The strong acid provides a larger loading of trioctylamine than the weak acid; that is, the consequence is that trichloroacetic acid > dichloroacetic acid > monochloroacetic acid > formic acid > acetic acid, and this result depends on both the acidity and hydrophobicity of the acid.

Introduction

Long-chain, aliphatic amines are effective extractants for separation of carboxylic acids from dilute aqueous solution.[1−5] Generally, the use of a diluent with an amine is necessary to improve the physical properties of the extractant, such as viscosity and density, to make the mixture much easier to handle to allow the amine to be used in any extraction process. Many factors have been found to influence the equilibrium extraction characteristics of these systems. Three important variables are the nature of the acid extracted, the concentration of extractant, and the type of diluent.[6] The nature of the acids mainly concerns the strength of the acid (pK_a)[7,8] and the hydrophobicity of the acid (log P).[9,10]

King et al.[7] proposed that the equilibrium constant of the (1,1) complex decreases about 1 log unit with each unit increase in pK_a for the extraction equilibrium of carboxylic acids (acetic, lactic, succinic, malonic, fumaric, and maleic acids) with amines, but the results from the experimental data did not fit the above rule well.

Hano et al.[9] investigated the extraction equilibria of organic acids (acetic, glycolic, propionic, lactic, pyruvic, butyric, succinic, fumaric, maleic, itaconic, tartaric, citric, and isocitric) with trioctylphosphine oxide in hexane and concluded that the number of carboxyl groups and the extraction equilibrium were controlled by the hydrophobicity of the acid, not by the pK_a value. However, the degree of extraction of trioctylamine is quite different from that of trioctylphospine oxide.

The authors of this paper[10] studied the liquid−liquid equilibria of acetic, propionic, butyric, and valeric acids with trioctylamine in 1-octanol, chloroform, methyl isobutyl ketone, and tetrachloromethane, and the relationship between the equilibrium constant of the (1,1) complex, K_{11}, and the hydrophobicity of the acid was discussed. Log K_{11} is linear with log P of the carboxylic acid, and the slope is about 1.3 for all four diluents.

In the present work, the extraction equilibria for aqueous solutions of acetic acid derivatives, formic, monochloroacetic, dichloroacetic, and trichloroacetic acids, with trioctylamine were investigated. Equilibrium data are presented for the system of carboxylic acids with trioctylamine in 1-octanol, chloroform, hexane, and tetrachloromethane. The dependence of the degree of extraction on the acidity of carboxylic acids was discussed further.

Table 1. Physical Properties of Carboxylic Acids

chemical	pK_a[11]	hydrophobicity, log$P$
formic acid	3.75	−0.538
monochloroacetic acid	2.87	0.139
dichloroacetic acid	1.26	0.705
trichloroacetic acid	0.52	0.713

Table 2. Distribution Ratio of the Acid between the Pure Diluent and Water

solute	1-octanol	chloroform	hexane	CCl_4
formic acid	0.2902	0.0069	0	0
acetic acid[12]	0.4861	0.0976	0	0
monochloroacetic acid	1.3773	0.0492	0.0009	0.0227
dichloroacetic acid	5.0748	0.0833	0.0021	0.0079
trichloroacetic acid	5.1694	0.0011	0	0.0009

Materials and Methods

Chemicals. All of the carboxylic acids used were analytical reagents with purity > 99 mass %. Trioctylamine with purity > 99 mass % (Fluka) was used as extractant. The four diluents, 1-octanol, chloroform, hexane, and tetrachloromethane, from Beijing Chemical Plant, were analytical reagent grade with purity > 99 mass %. The characteristics of the carboxylic acids are presented in Table 1, and the log P in Table 1 was reported in this paper.

It is obvious that all of the acetic acid derivatives in this paper, formic, monochloroacetic, dichloroacetic, and trichloroacetic acids, especially the chloroacetic acids, have stronger acidity than acetic acid, and they are medium-strong or strong carboxylic acids.

Extraction Experiments. All extraction experiments were conducted with 100 mL flasks at 25 ± 0.5 °C. Twenty milliliters of the extractant and 20 mL of the acid solution were added to each flask. The flask containing the mixture

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Table 3. Equilibrium Data for the System Formic Acid + Trioctylamine in Diluent

tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}		tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}	
acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase	acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase
1-Octanol as the Diluent									
0.0635	0.500	4.95	0.00041	0.0631	0.1229	1.000	4.98	0.0011	0.1218
0.1226	0.500	4.52	0.00079	0.1218	0.2683	1.000	4.44	0.0038	0.2645
0.1938	0.500	4.51	0.0016	0.1922	0.3907	1.000	4.19	0.0065	0.3842
0.2686	0.500	4.42	0.0029	0.2657	0.5964	1.000	3.82	0.0152	0.5812
0.4287	0.500	4.25	0.0086	0.4201	0.7730	1.000	3.51	0.0301	0.7429
0.5143	0.500	3.67	0.0411	0.4732	0.9115	1.000	3.28	0.0523	0.8592
0.5958	0.500	2.93	0.0812	0.5146	1.1881	1.000	2.92	0.1251	1.0630
0.7724	0.500	2.61	0.1804	0.5920	1.6769	1.000	2.55	0.3238	1.3531
0.9113	0.500	2.49	0.2600	0.6513	2.1054	1.000	2.35	0.5407	1.5647
1.0165	0.500	2.41	0.3233	0.6932	2.4428	1.000	2.24	0.6892	1.7536
Chloroform as the Diluent									
0.0636	0.500	4.51	0.00042	0.0632	0.1234	1.000	4.42	0.0045	0.1189
0.1237	0.500	4.43	0.0016	0.1221	0.2693	1.000	4.25	0.0049	0.2644
0.1937	0.500	4.26	0.0024	0.1913	0.3901	1.000	4.02	0.0070	0.3831
0.2689	0.500	4.20	0.0039	0.2650	0.5953	1.000	3.95	0.0130	0.5823
0.3906	0.500	3.93	0.0102	0.3804	0.7723	1.000	3.74	0.0211	0.7512
0.5151	0.500	3.50	0.0373	0.4778	0.9110	1.000	3.54	0.0354	0.8756
0.5948	0.500	2.88	0.0667	0.5281	1.1878	1.000	3.16	0.0867	1.1011
0.7728	0.500	2.57	0.1539	0.6189	1.6776	1.000	2.55	0.2612	1.4164
0.9118	0.500	2.44	0.2394	0.6724	2.1070	1.000	2.48	0.4903	1.6167
1.0162	0.500	2.32	0.3072	0.7090	2.4440	1.000	2.40	0.7541	1.6899
Hexane as the Diluent									
0.1261	0.500	2.93	0.1029	0.0232	0.9627	0.500	2.29	0.4513	0.5114
0.1968	0.500	2.87	0.1567	0.0401	1.0745	0.500	2.25	0.4856	0.5889
0.2765	0.500	2.71	0.2154	0.0611	1.2589	0.500	2.20	0.5467	0.7122
0.5344	0.500	2.39	0.3451	0.1893	1.3715	0.500	2.18	0.5964	0.7751
0.6200	0.500	2.38	0.3722	0.2478	1.7750	0.500	2.08	0.7961	0.9789
Tetrachloromethane as the Diluent									
0.1289	0.500	2.96	0.0678	0.0611	0.9742	0.500	2.45	0.3430	0.6312
0.2028	0.500	2.88	0.1011	0.1017	1.0860	0.500	2.40	0.3893	0.6967
0.2846	0.500	2.79	0.1333	0.1513	1.2673	0.500	2.33	0.4744	0.7929
0.5479	0.500	2.64	0.2142	0.3337	1.3788	0.500	2.31	0.5321	0.8467
0.6348	0.500	2.58	0.2389	0.3959	1.7732	0.500	2.16	0.8084	0.9648

Table 4. Equilibrium Data for the System of Monochloroacetic Acid+ Trioctylamine in Diluent

tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}		tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}	
acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase	acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase
1-Octanol as the Diluent									
0.1469	0.500	5.90	0.00015	0.1467	0.3058	1.000	5.21	0.00065	0.3052
0.3066	0.500	5.11	0.00020	0.3064	0.4397	1.000	4.90	0.00086	0.4389
0.4400	0.500	4.12	0.00081	0.4392	0.6341	1.000	4.55	0.00078	0.6333
0.6041	0.500	2.41	0.0280	0.5761	0.7422	1.000	4.42	0.00097	0.7412
0.7412	0.500	2.12	0.0579	0.6833	0.8795	1.000	4.21	0.0021	0.8774
0.8794	0.500	1.96	0.0962	0.7832	0.9744	1.000	3.41	0.0047	0.9697
0.9748	0.500	1.89	0.1311	0.8437	1.1772	1.000	2.45	0.0202	1.1570
1.1772	0.500	1.77	0.1742	1.0030	1.2551	1.000	2.38	0.0339	1.2212
1.2545	0.500	1.73	0.2078	1.0467	1.3575	1.000	2.33	0.0511	1.3064
1.3572	0.500	1.66	0.2433	1.1139	1.4353	1.000	2.24	0.0612	1.3741
1.4356	0.500	1.63	0.2704	1.1652	1.5370	1.000	2.15	0.0803	1.4567
1.5374	0.500	1.60	0.3121	1.2253	1.6371	1.000	2.10	0.0982	1.5389
1.6358	0.500	1.51	0.3428	1.2930	1.9932	1.000	1.92	0.1589	1.8343
0.1471	1.000	5.50	0.00039	0.1467					
Chloroform as the Diluent									
0.1513	0.500	5.60	0.00020	0.1511	0.3126	1.000	5.91	0.00025	0.3123
0.3112	0.500	5.06	0.00040	0.3108	0.4507	1.000	5.31	0.00032	0.4504
0.4508	0.500	4.27	0.00071	0.4501	0.6093	1.000	5.08	0.00042	0.6089
0.6089	0.500	2.49	0.0222	0.5867	0.7500	1.000	4.80	0.00062	0.7494
0.7499	0.500	2.12	0.0556	0.6943	0.8961	1.000	4.40	0.00091	0.8952
0.8959	0.500	1.91	0.1061	0.7898	0.9997	1.000	3.72	0.0027	0.9970
1.0004	0.500	1.79	0.1552	0.8452	1.2374	1.000	2.67	0.0252	1.2122
1.2369	0.500	1.59	0.2767	0.9602	1.3288	1.000	2.53	0.0343	1.2945
1.3293	0.500	1.55	0.3261	1.0032	1.4140	1.000	2.44	0.0451	1.3689
1.4146	0.500	1.50	0.3744	1.0402	1.5013	1.000	2.33	0.0612	1.4401
1.5004	0.500	1.45	0.4440	1.0564	1.6060	1.000	2.24	0.0808	1.5252
1.6061	0.500	1.41	0.5089	1.0972	1.7110	1.000	2.13	0.1092	1.6018
1.7112	0.500	1.37	0.5951	1.1161	1.9941	1.000	1.93	0.1817	1.8124
1.9936	0.500	1.27	0.8103	1.1833	2.3158	1.000	1.77	0.2989	2.0169
2.3109	0.500	1.19	1.0720	1.2389	2.8444	1.000	1.57	0.5733	2.2711
2.8445	0.500	1.08	1.5523	1.2922	2.9877	1.000	1.52	0.6798	2.3079
3.6880	0.500	0.94	2.4017	1.2863	3.6891	1.000	1.38	1.2021	2.4870
0.1513	1.000	6.03	0.00020	0.1511					

Table 4 (Continued)

tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}		tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}	
acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase	acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase
Hexane as the Diluent									
0.1511	0.500	2.66	0.0133	0.1378	0.2631	1.000	2.99	0.0103	0.2528
0.3121	0.500	2.51	0.0199	0.2922	0.3689	1.000	2.92	0.0122	0.3567
0.4507	0.500	2.42	0.0256	0.4251	0.5270	1.000	2.84	0.0137	0.5133
0.6087	0.500	2.29	0.0367	0.5720	0.5983	1.000	2.81	0.0152	0.5831
0.7500	0.500	2.16	0.0533	0.6967	0.7495	1.000	2.72	0.0191	0.7304
0.8975	0.500	2.02	0.0821	0.8154	0.8992	1.000	2.67	0.0214	0.8778
1.0003	0.500	1.92	0.1131	0.8872	1.1231	1.000	2.53	0.0278	1.0953
1.3282	0.500	1.56	0.2774	1.0508	1.2730	1.000	2.43	0.0354	1.2376
1.4141	0.500	1.55	0.3452	1.0689	1.4216	1.000	2.31	0.0456	1.3760
1.5006	0.500	1.54	0.4049	1.0957	1.5743	1.000	2.19	0.0588	1.5155
1.6052	0.500	1.51	0.4807	1.1245	1.7506	1.000	2.03	0.0874	1.6632
0.7114	0.500	1.45	0.5862	1.1252	2.0669	1.000	1.76	0.1679	1.8990
1.9929	0.500	1.37	0.8078	1.1851	2.3412	1.000	1.58	0.2731	2.0681
2.5539	0.500	1.22	1.3256	1.2283	2.8964	1.000	1.33	0.6042	2.2922
0.1525	1.000	3.10	0.0084	0.1441	3.1496	1.000	1.26	0.7889	2.3607
Tetrachloromethane as the Diluent									
0.1589	0.500	2.97	0.0048	0.1541	0.2285	1.000	3.53	0.0033	0.2252
0.3024	0.500	2.78	0.0086	0.2938	0.3979	1.000	3.37	0.0046	0.3933
0.4559	0.500	2.58	0.0142	0.4417	0.6095	1.000	3.26	0.0054	0.6041
0.6089	0.500	2.38	0.0238	0.5851	0.8003	1.000	3.13	0.0081	0.7922
0.7841	0.500	2.13	0.0489	0.7352	1.0306	1.000	2.97	0.0113	1.0193
0.9612	0.500	1.89	0.1011	0.8601	1.2369	1.000	2.78	0.0172	1.2197
0.9985	0.500	1.86	0.1162	0.8823	1.3295	1.000	2.67	0.0213	1.3082
1.2367	0.500	1.61	0.2231	1.0136	1.4138	1.000	2.58	0.0249	1.3889
1.3280	0.500	1.55	0.2729	1.0551	1.5007	1.000	2.49	0.0311	1.4696
1.4140	0.500	1.50	0.3276	1.0864	1.6062	1.000	2.37	0.0408	1.5654
1.5014	0.500	1.44	0.3981	1.1033	1.9328	1.000	1.91	0.1316	1.8012
1.6065	0.500	1.40	0.4593	1.1472	2.5543	1.000	1.56	0.3322	2.2221
1.7107	0.500	1.36	0.5467	1.1640	2.9882	1.000	1.35	0.5799	2.4083
0.1504	1.000	3.67	0.0026	0.1478					

Table 5. Equilibrium Data for the System Dichloroacetic Acid + Trioctylamine in Diluent

tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}		tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}	
acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase	acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase
1-Octanol as the Diluent									
0.1535	0.500	6.26	0.00015	0.1533	0.1534	1.000	6.45	0.00026	0.1531
0.2914	0.500	6.26	0.00034	0.2911	0.2911	1.000	6.43	0.00033	0.2908
0.4485	0.500	5.75	0.0013	0.4472	0.4482	1.000	6.25	0.00039	0.4478
0.5993	0.500	1.88	0.0159	0.5834	0.5993	1.000	6.18	0.00043	0.5989
0.7135	0.500	1.67	0.0290	0.6845	0.7138	1.000	6.04	0.00046	0.7133
0.8827	0.500	1.52	0.0471	0.8356	0.8829	1.000	5.46	0.00048	0.8824
1.0823	0.500	1.40	0.0713	1.0110	1.0827	1.000	2.26	0.0089	1.0738
1.3430	0.500	1.30	0.0989	1.2441	1.2854	1.000	1.85	0.0222	1.2632
1.5121	0.500	1.23	0.1193	1.3928	1.4841	1.000	1.66	0.0361	1.4480
1.7422	0.500	1.16	0.1478	1.5944	1.6749	1.000	1.52	0.0523	1.6226
1.9757	0.500	1.10	0.1864	1.7893	1.8723	1.000	1.40	0.0745	1.7978
2.3042	0.500	1.02	0.2511	2.0531	2.1799	1.000	1.27	0.1123	2.0676
2.6509	0.500	0.95	0.3223	2.3286	2.4518	1.000	1.17	0.1427	2.3091
3.1192	0.500	0.86	0.4341	2.6851	2.7801	1.000	1.05	0.1989	2.5812
Chloroform as the Diluent									
0.1533	0.500	4.95	0.00034	0.1530	0.1534	1.000	6.25	0.00026	0.1531
0.2916	0.500	4.52	0.00048	0.2911	0.2911	1.000	5.72	0.00037	0.2907
0.4530	0.500	4.16	0.00072	0.4523	0.4525	1.000	6.05	0.00030	0.4522
0.6014	0.500	1.72	0.0225	0.5789	0.6013	1.000	5.93	0.00037	0.6009
0.7121	0.500	1.47	0.0454	0.6667	0.7129	1.000	5.89	0.00046	0.7124
0.8945	0.500	1.25	0.0911	0.8034	0.8938	1.000	5.09	0.00052	0.8933
1.1062	0.500	1.06	0.1667	0.9395	1.1060	1.000	2.32	0.0071	1.0989
1.3355	0.500	0.90	0.2904	1.0451	1.3345	1.000	1.70	0.0268	1.3077
1.5028	0.500	0.81	0.3883	1.1145	1.5028	1.000	1.50	0.0417	1.4611
1.7330	0.500	0.75	0.5278	1.2052	1.7335	1.000	1.33	0.0722	1.6613
1.9629	0.500	0.67	0.6951	1.2678	1.9635	1.000	1.20	0.1181	1.8454
2.2896	0.500	0.60	0.9630	1.3266	2.2901	1.000	1.02	0.2123	2.0778
2.6365	0.500	0.55	1.2083	1.4282	2.6349	1.000	0.85	0.3614	2.2735
3.1007	0.500	0.50	1.6011	1.4996	3.1011	1.000	0.69	0.6070	2.4941

Table 5 (Continued)

tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}		tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}	
acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase	acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase
				Hexane as the Diluent					
0.1538	0.500	4.18	0.00047	0.1533	0.2842	1.000	4.34	0.00060	0.2836
0.2916	0.500	3.87	0.00052	0.2911	0.5698	1.000	4.09	0.00064	0.5692
0.4487	0.500	3.16	0.0013	0.4474	0.9252	1.000	3.42	0.0009	0.9243
0.5985	0.500	2.39	0.0047	0.5938	1.2050	1.000	2.37	0.0059	1.1991
0.7135	0.500	2.04	0.0139	0.6996	1.4531	1.000	1.88	0.0167	1.4364
0.8827	0.500	1.62	0.0405	0.8422	1.7810	1.000	1.42	0.0499	1.7311
1.0830	0.500	1.29	0.1076	0.9754	2.0997	1.000	1.12	0.1141	1.9856
1.2842	0.500	1.30	0.2131	1.0711	2.4363	1.000	0.89	0.2352	2.2011
1.4845	0.500	1.17	0.3472	1.1373	2.6592	1.000	0.78	0.3471	2.3121
1.6742	0.500	1.02	0.4894	1.1848	2.9526	1.000	0.70	0.5133	2.4393
1.8722	0.500	0.94	0.6695	1.2027	3.2391	1.000	0.64	0.6867	2.5524
2.1794	0.500	0.87	0.9052	1.2742	3.5876	1.000	0.60	0.9934	2.5942
2.4518	0.500	0.81	1.1321	1.3197	3.9786	1.000	0.57	1.2921	2.6865
2.7796	0.500	0.75	1.4223	1.3573	4.4285	1.000	0.53	1.7763	2.6522
				Tetrachloromethane as the Diluent					
0.1537	0.500	4.35	0.00044	0.1533	0.1537	1.000	5.13	0.00046	0.1532
0.2917	0.500	4.01	0.00065	0.2911	0.2916	1.000	4.98	0.00049	0.2911
0.4477	0.500	3.43	0.0010	0.4467	0.4490	1.000	4.66	0.00058	0.4484
0.5999	0.500	2.41	0.0086	0.5913	0.5994	1.000	4.62	0.00064	0.5988
0.7137	0.500	1.99	0.0181	0.6956	0.7140	1.000	4.34	0.00066	0.7133
0.8838	0.500	1.61	0.0464	0.8374	0.8830	1.000	3.98	0.00078	0.8822
1.0819	0.500	1.30	0.1133	0.9686	1.0829	1.000	2.52	0.0038	1.0791
1.2866	0.500	0.90	0.2142	1.0724	1.2847	1.000	2.02	0.0104	1.2743
1.4838	0.500	0.81	0.3455	1.1383	1.4846	1.000	1.72	0.0222	1.4624
1.6742	0.500	0.70	0.4784	1.1958	1.6732	1.000	1.56	0.0397	1.6335
1.8722	0.500	0.63	0.6378	1.2344	1.8733	1.000	1.30	0.0792	1.7941
2.1793	0.500	0.57	0.8892	1.2901	2.1804	1.000	1.07	0.1593	2.0211
2.4526	0.500	0.50	1.1454	1.3072	2.4518	1.000	0.87	0.2695	2.1823
2.7793	0.500	0.46	1.4442	1.3351	2.7806	1.000	0.75	0.4322	2.3484

Table 6. Equilibrium Data for the System Trichloroacetic Acid + Trioctylamine in Diluent

tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}		tot init conc/mol·L^{-1}			tot equil conc/mol·L^{-1}	
acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase	acid conc in aq phase	trioctylamine conc in org phase	equil pH in aq phase	acid conc in aq phase	acid conc in org phase
				1-Octanol as the Diluent					
0.1205	0.500	6.99	0.00004	0.1204	0.6024	0.500	1.79	0.0211	0.5813
0.1990	0.500	6.82	0.00005	0.1989	0.8087	0.500	1.51	0.0442	0.7645
0.3004	0.500	6.65	0.00007	0.3003	1.0122	0.500	1.35	0.0678	0.9444
0.3503	0.500	6.55	0.00009	0.3502	1.1365	0.500	1.28	0.0813	1.0552
0.3975	0.500	6.42	0.00012	0.3974	1.6530	0.500	1.17	0.1389	1.5141
0.5043	0.500	4.48	0.00052	0.5038					
				Chloroform as the Diluent					
0.1203	0.500	6.63	0.000058	0.1202	0.6013	0.500	1.41	0.0531	0.5482
0.1992	0.500	6.61	0.000058	0.1991	0.8093	0.500	1.12	0.1204	0.6889
0.2996	0.500	6.61	0.000058	0.2995	1.0118	0.500	1.01	0.1967	0.8151
0.3504	0.500	6.02	0.00012	0.3503	1.1358	0.500	0.94	0.2593	0.8765
0.3973	0.500	6.04	0.00017	0.3971	1.6538	0.500	0.74	0.5344	1.1194
0.5040	0.500	1.99	0.0162	0.4878	1.8443	0.500	0.65	0.6581	1.1862
				Hexane as the Diluent					
0.1208	0.500	5.42	0.00036	0.1204	0.6019	0.500	3.91	0.0021	0.5998
0.1998	0.500	5.58	0.00043	0.1984	0.8103	0.500	1.53	0.0440	0.7663
0.2997	0.500	5.27	0.00086	0.2988	1.0131	0.500	1.14	0.1243	0.8888
0.3506	0.500	5.24	0.00052	0.3501	1.1362	0.500	0.98	0.2051	0.9311
0.3976	0.500	5.07	0.0012	0.3964	1.6527	0.500	0.66	0.5845	1.0682
0.5049	0.500	4.59	0.0016	0.5033	1.8445	0.500	0.58	0.7421	1.1024
				Tetrachloromethane as the Diluent					
0.1192	0.500	4.48	0.00012	0.1191	0.6022	0.500	1.85	0.0171	0.5851
0.1987	0.500	4.54	0.00029	0.1984	0.8093	0.500	1.38	0.0611	0.7482
0.2993	0.500	4.50	0.00050	0.2988	1.0128	0.500	1.07	0.1484	0.8644
0.3513	0.500	4.25	0.00086	0.3504	1.1350	0.500	0.96	0.2172	0.9178
0.3971	0.500	4.29	0.0011	0.3960	1.6536	0.500	0.69	0.5903	1.0633
0.5048	0.500	3.91	0.0015	0.5033	1.8442	0.500	0.59	0.7311	1.1131

was shaken for about 6 h in a shaker bath with a vibrating rate of 200 rpm and then was left to equilibrate for 1−2 h, followed by separating the two phases. The upper layer (extractant phase) was removed, and an aqueous-phase sample was taken from the bottom layer (aqueous phase) for pH and solute concentration analyses.

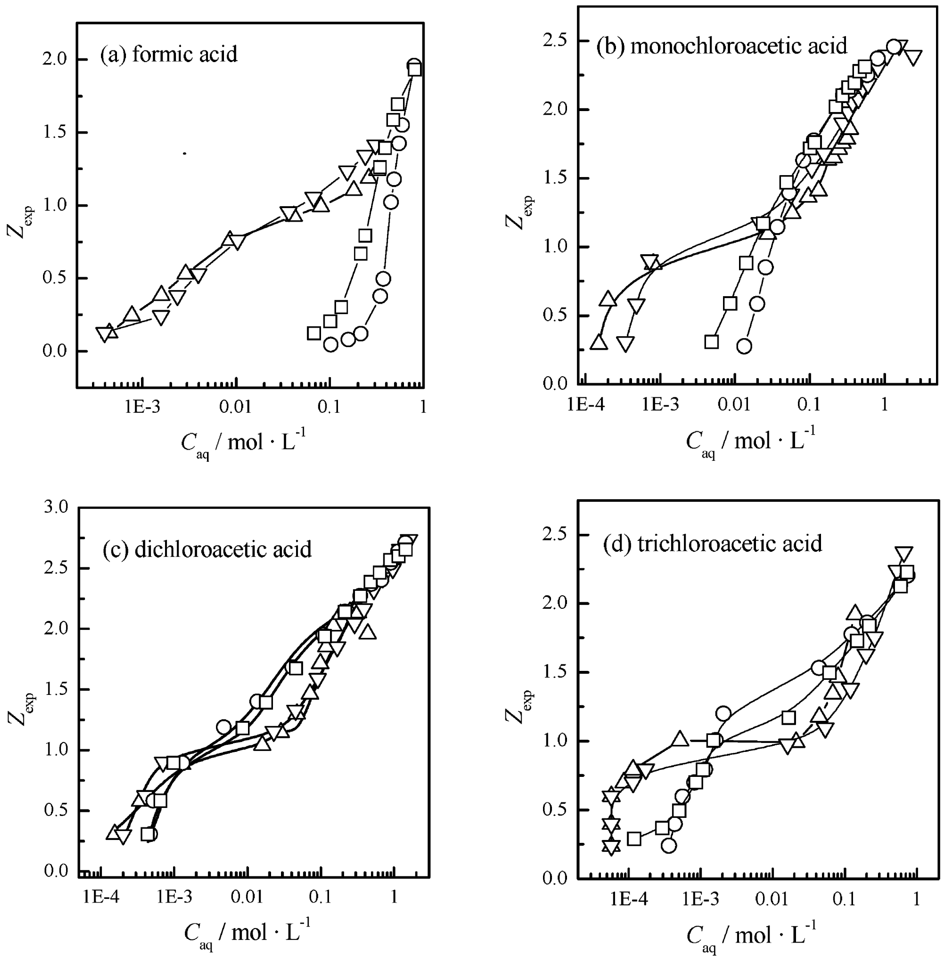

Figure 1. Loading curve of carboxylic acids in 0.500 mol·L^{-1} trioctylamine−diluent systems: △, 1-octanol; ▽, chloroform; ○, hexane; □, tetrachloromethane.

Sample Analysis. The concentration of carboxylic acid in the aqueous phase (C_{aq}) was determined by colorimetric titration with aqueous NaOH solution, using phenolphthalein as an indicator, and duplicated. The carboxylic acid concentrations in the extractant phase (C_{org}) were calculated by material balance. However, the acid concentration in the organic phase was also determined by first stripping the organic phase with a small amount of NaOH solution (pH = 12). The alkaline solution containing the organic salt was then acidified with sulfuric acid and analyzed by using a high-pressure liquid chromatography (HPLC) system with an organic acid analysis column (RSpak KC-811) and a UV spectrophotometer (Waters 2487 at 210 nm wavelength). The eluent was 0.1% phosphoric acid. The results from these two methods agreed well, within 3%, which probably resulted from the volume changing for each phase and the error of the analysis method.

The pH value of the aqueous phase was determined with a pH meter, Hanna pH 201 models.

Results and Discussion

The loading of trioctylamine, Z_{exp}, is defined as the total concentration of acid (all forms) bonded to trioctylamine in the organic phase divided by the total concentration of trioctylamine (all forms) in the organic phase. With appropriate material balance, Z_{exp} is determined for a given set of stoichiometries as

$$Z_{exp} = \frac{C_{org} - [HA]_{org}}{S_0} = \frac{C_{org} - \Phi m[HA]_{aq}}{S_0} \qquad (1)$$

and $[HA]_{aq}$ and was obtained from eq 2

$$[HA]_{aq} = \frac{C_{aq}}{1 + 10^{pH-pK_a}} \qquad (2)$$

where pK_a is the dissociation constant of the acid in the aqueous phase, Φ is the volume fraction of diluent in the extractant phase, S_0 is the initial concentration of trioctylamine in the extractant phase, m is the physical distribution ratio of the acid between the pure diluent and water, and the extents of the acid extractions by the various diluents were determined experimentally and listed in Table 2.

Most of the complexes exist in the (1, 1) form when the carboxylic acid concentration is low ($Z_{exp} < 1$).[13] Thus, the degree of extraction has the same sequence as Z_{exp} for the various diluents.

Diluent Type. The equilibrium data in various trioctylamine−diluent systems are given in Tables 3−6, and the degrees of extraction of carboxylic acids with trioctylamine show the order 1-octanol ≥ chloroform > tetrachloromethane > hexane at $Z_{exp} < 1$ (Figure 1), which is the same as the extraction result for the weak carboxylic acids such as acetic acid.[10] Also, the solvation of the complex by the diluent is one of the most important factors in extraction of the medium-strong carboxylic acid in this paper. A polar diluent increases the extracting power of nonpolar amines by providing additional solvating power that allows higher levels of polar acid−amine complexes to stay in the organic phase. Especially, protic halogenated hydrocarbons

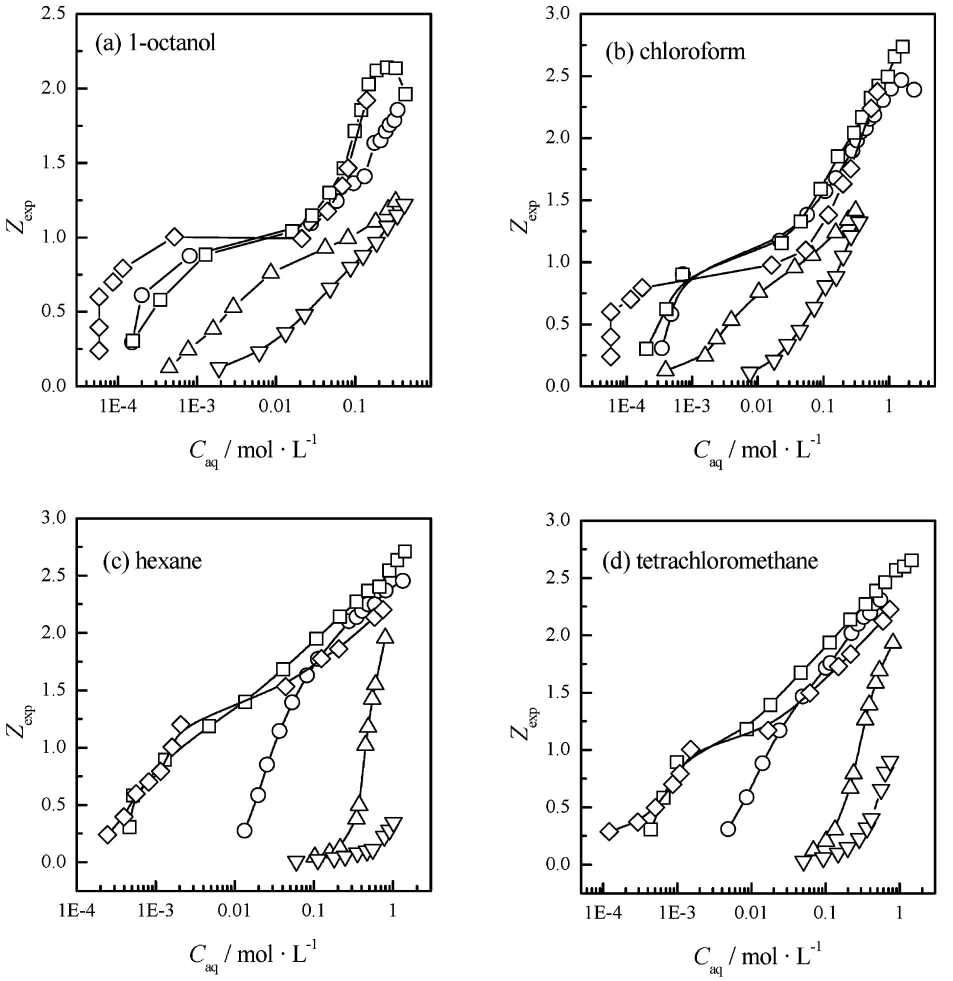

Figure 2. Loading curve of carboxylic acids in 0.500 mol·L^{-1} trioctylamine–diluent systems: △, formic acid; ▽, acetic acid;[16] ○, monochloroacetic acid; □, dichloroacetic acid; ◇, trichloroacetic acid.

and alcohol diluents, chloroform and 1-octanol, give an unusually high degree of extraction through the specific hydrogen bonding between the proton of the diluent and the acid–amine complex.[14–16] Therefore, the optimal composition for the trioctylamine–diluent mixture is trioctylamine–stronger polar diluent in extraction of a medium-stronger carboxylic acid.

Acid Type. In general**,** the degree of extraction depends on the nature of the acid extracted. A strong acid increases the bonding power between the acid and an amine so as to obtain a high degree of extraction. As shown in Figure 2, a similar result was obtained in this work; that is, a strong acid provides a larger loading of trioctylamine than a weak acid, and the consequence is that trichloroacetic acid > dichloroacetic acid > monochloroacetic acid > formic acid > acetic acid.

Extraction is expected to increase with increasing acidity and increasing hydrophobicity of the acid. Generally, the greater the ionizing acidity of the acid, the weaker the hydrophobicity of the acid is. However, a reverse of the behavior appears for the solutes in this paper; that is, the hydrophobicity of the acid has the same order as the acidity of the acid. Therefore, the order of the degree of extraction for the various acids above results from both the acidity and hydrophobicity of the acid, and the degree of extraction is more sensitive to the acidity than the hydrophobicity of the carboxylic acid according to the experimental data of acetic acid and formic acid.

Conclusions

Extraction equilibrium studies for the systems of acetic acid derivatives (formic, monochloroacetic, dichloroacetic, and trichloroacetic acids) + trioctylamine in various diluents (1-octanol, chloroform, hexane, and tetrachloromethane) were conducted at various trioctylamine concentrations. The strength of solvation of the complex by the diluent for the acids studied decreases in the order 1-octanol chloroform > tetrachloromethane > hexane. The strong acid provides a larger loading of trioctylamine than the weak acid, and the consequence is that trichloroacetic acid > dichloroacetic acid > monochloroacetic acid > formic acid > acetic acid. This result depends on both the acidity and hydrophobicity of the acid.

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