Density and Excess Molar Volume of Tri-*n*-Octylamine + Propionic Acid + Diluent at 298.15 K

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The densities and excess molar volumes (V^E) for tri-*n*-octylamine (TOA) + propionic acid, TOA + diluent, and propionic acid + diluent binary systems were measured under the full range of composition at 298.15 K, respectively. The excess molar volumes of TOA + propionic acid + diluent ternary systems were also measured at 298.15 K. Benzene, toluene, *p*-xylene, ethanol, hexane, and cyclohexane were used as the diluent. The $|V^E_{MAX}|$ of TOA + propionic acid is found to be about 6 $cm^3 \cdot mol^{-1}$ at $x_A = 0.75$. The maximum values of excess molar volume (V^E_{MAX}) for the ternary systems showed smaller values than that of TOA + propionic acid.

Introduction

Some long-chain alkylamines are considered as the effective extractant for carboxylic acids. According to the studies by Chen et al. (1988, 1989) it is considered that the association of an amine and a carboxylic acid plays an important role in the extraction process.

On the other hand, if amines are used as an extractant without a diluent, an effective extraction operation has difficulty because amines have a high viscosity. Diluents are added to amines in an extraction process for the purpose of decreasing the viscosity and increasing the distribution ratio (Kohler et al., 1981; Noda et al., 1983). Hence, the selection of the diluent is important for the effective extraction. The effect of a diluent on the excess volume of amine + carboxylic acid has not been studied.

In this study, the densities for tri-*n*-octylamine (TOA) + propionic acid, TOA + diluent, and propionic acid + diluent binary systems were measured at 298.15 K. The excess molar volumes were calculated from the observed densities. Furthermore, densities for (TOA + diluent) + propionic acid pseudobinary systems where six diluents (benzene, toluene, *p*-xylene, ethanol, hexane, or cyclohexane) were used, were measured at 298.15 K. The diluent effect on the excess molar volumes for the solvent mixtures of TOA, carboxylic acid, and diluents were calculated in this paper.

Experimental Section

Materials. TOA, propionic acid, benzene, toluene, *p*-xylene, ethanol, hexane, and cyclohexane of guaranteed reagent grade were supplied by Wako Chemicals Co., Japan. Their minimum purities were 99.7%, 99.0%, 99.5%, 99.5%, 98.0%, 99.5%, 99.0%, and 99.5%, respectively. Since the impurity in ethanol was mostly water, it was dehydrated by molecular sieves 3A, $^1/_{16}$ in. (pellets) and the extent of dehydration was confirmed by gas chromatography. Water was purified by use of Milli-Q Labo manufactured by Millipore Ltd., after distillation and ion exchange.

Excess Molar Volume for Each Binary System. The samples of TOA and carboxylic acid were prepared by mass in a bottle (15 cm^3). The sample solution was stirred using Mix Rotor MR-5 manufactured by Iuchi Co. Ltd. for one night. Then, the sample solution was shaken for 10.8 ks in a constant temperature water bath at 298.15 K (±0.05 K) before density measurement. The density was measured by a Digital Density/Specific Gravity Meter DA-210 manufactured by Kyoto Electronics Co. Ltd., Japan. The temperature was maintained constant within ±0.01 K. The accuracy of the density mea-

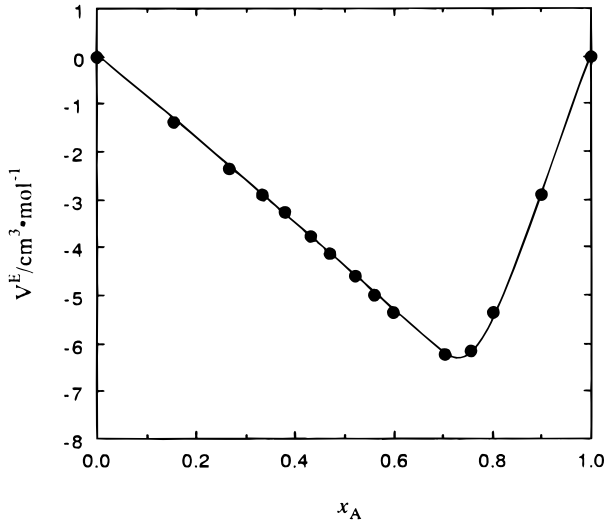

Figure 1. Excess molar volume of TOA (B) + propionic acid (A) at 298.15 K.

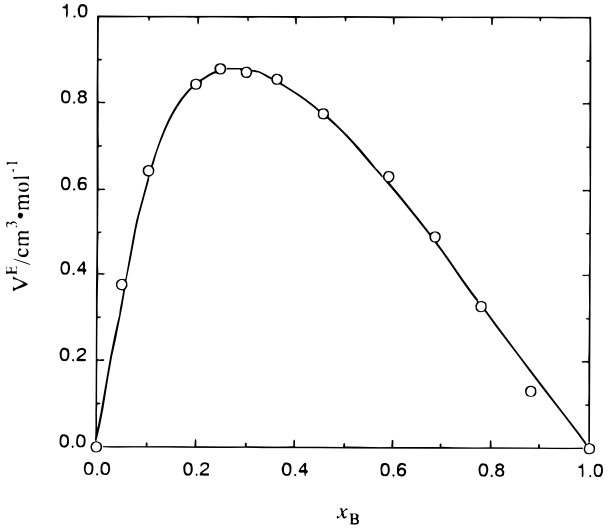

Figure 2. Excess molar volume of TOA (B) + benzene (D) at 298.15 K.

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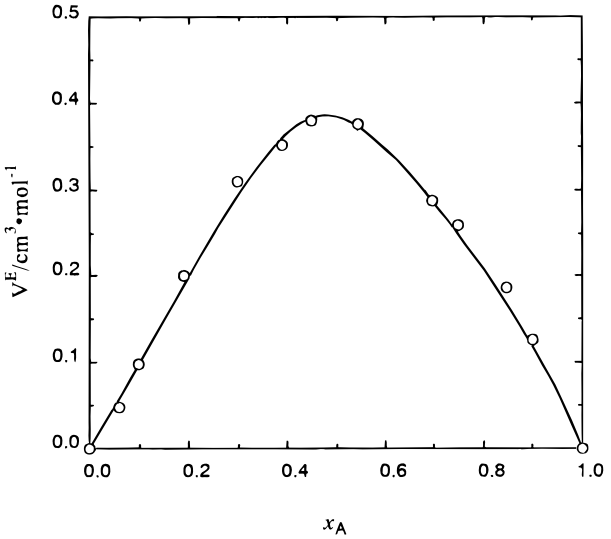

Figure 3. Excess molar volume of propionic acid (A) + benzene (D) at 298.15 K.

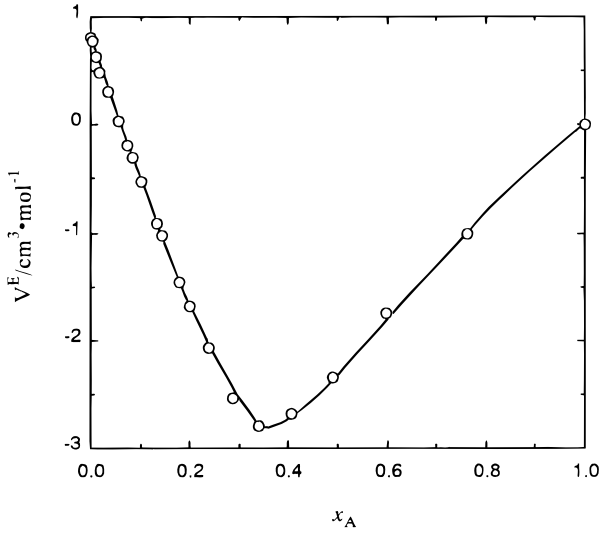

Figure 4. Excess molar volume TOA (B) + benzene (D) + propionic acid (A) ternary system at 298.15 K. (Volume ratio TOA: benzene = 1:1.)

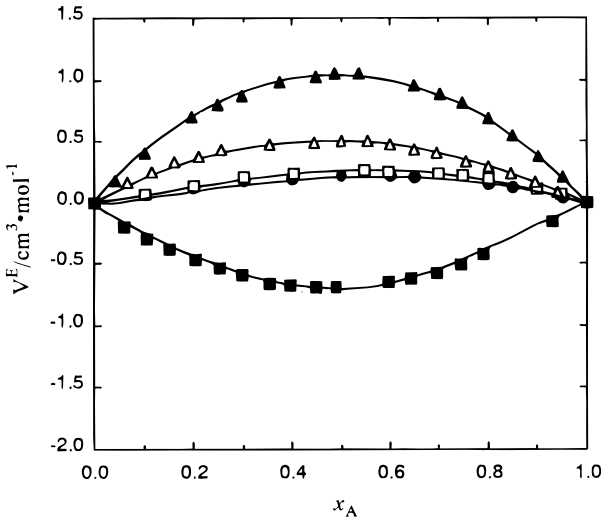

Figure 5. Excess molar volume of propionic acid + diluent binary systems at 298.15 K: (●) toluene; (□) *p*-xylene; (■) ethanol; (△) hexane; (▲) cyclohexane.

surement is $\pm 10^{-5}$ g·cm^{-3}. Under these experimental conditions the V^E value has been estimated to be $\pm 10^{-4}$ g·cm^{-3}. The excess molar volumes (V^E) calculated from the measured

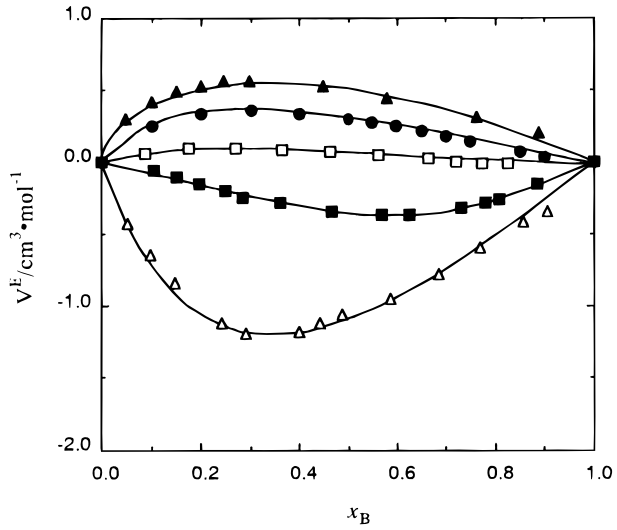

Figure 6. Excess molar volume of TOA + diluent binary systems at 298.15 K: (●) toluene; (□) *p*-xylene; (■) ethanol; (△) hexane; (▲) cyclohexane.

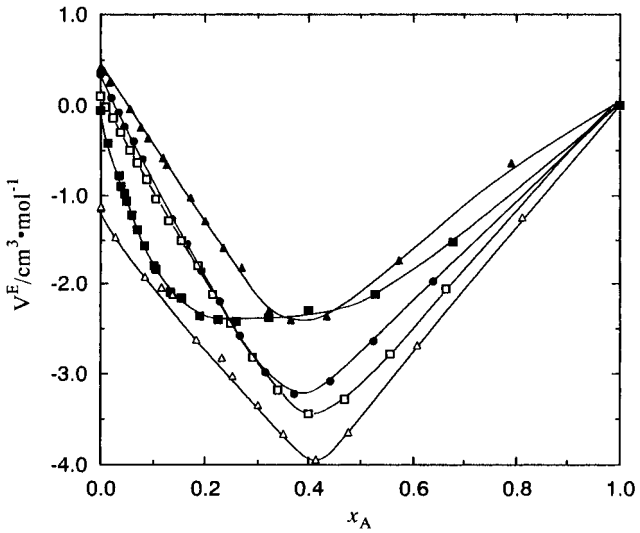

Figure 7. Excess molar volume of TOA + propionic acid + diluent pseudobinary systems at 298.15 K: (●) toluene; (□) *p*-xylene; (■) ethanol; (△) hexane; (▲) cyclohexane. (Volume ratio TOA:diluent = 1:1.)

Table 1. Physical Properties of Pure Components at 298.15 K

component	molar mass	ρ/g·cm^{-3} exp	ρ/g·cm^{-3} lit.
propionic acid	74.08	0.987 98	0.9880[a]
tri-*n*-octylamine	353.68	0.806 89	
benzene	78.11	0.873 57	0.8737[b]
toluene	92.10	0.862 19	0.8623[c]
p-xylene	106.17	0.856 61	0.8565[d]
ethanol	46.07	0.785 70	0.7853[e]
hexane	86.18	0.655 92	0.6562[f]
cyclohexane	84.16	0.773 99	0.7740[g]

[a] Juan and Angulo, 1984. [b] Wei and Rowley, 1984. [c] Timmermans, 1965. [d] Kawano et al., 1982. [e] Yu and Tsai, 1994. [f] Petrino and Gaston-Bonhomme, 1995. [g] Asfour and Dullien, 1981.

densities using the following equation.

$$V^E = V - V^{id}$$

$$V^E = \frac{(x_A M_A + x_B M_B)}{\rho} - \left[\frac{x_A M_A}{\rho_A} + \frac{x_B M_B}{\rho_B}\right] \qquad (1)$$

Subscripts B, A, and D denote TOA, propionic acid, and diluent.

Excess Molar Volume for TOA + Propionic Acid + Diluent Ternary Systems. Then, the measurement of densi-

Table 2. Densities (ρ) and Excess Molar Volumes (V^E) of Trioctylamine (B) + Propionic Acid (A) at 298.15 K

x_B	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}	x_B	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}
0.0000	0.987 98	0.0000	0.5303	0.843 73	−4.1383
0.1009	0.940 61	−2.8948	0.5704	0.838 74	−3.7717
0.1976	0.914 46	−5.3545	0.6226	0.832 94	−3.2786
0.2481	0.902 39	−6.1647	0.6671	0.828 70	−2.9079
0.2955	0.889 72	−6.2289	0.7339	0.823 15	−2.3706
0.4007	0.864 80	−5.3657	0.8460	0.815 30	−1.3923
0.4399	0.857 51	−5.0004	1.0000	0.806 86	0.0000
0.4803	0.850 84	−4.6034			

Table 3. Densities (ρ) and Excess Molar Volumes (V^E) of Trioctylamine (B) + Diluent (D) at 298.15 K

x_B	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}	x_B	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}
TOA (B) + Benzene (D)					
0.0000	0.873 57	0.0000	0.4556	0.817 38	0.7754
0.0502	0.856 80	0.3778	0.5905	0.813 39	0.6309
0.1023	0.845 30	0.6437	0.6837	0.811 40	0.4902
0.1964	0.832 76	0.8422	0.7783	0.809 78	0.3310
0.2442	0.828 50	0.8792	0.8797	0.808 40	0.1323
0.2981	0.824 78	0.8730	1.0000	0.806 86	0.0000
0.3590	0.821 39	0.8561			
TOA (B) + *p*-Xylene (D)					
0.0000	0.856 61	0.0000	0.5627	0.815 70	0.0457
0.0869	0.843 72	0.0647	0.6650	0.813 01	0.0217
0.1762	0.834 73	0.0968	0.7195	0.811 79	0.0037
0.2683	0.828 13	0.0981	0.7744	0.810 66	−0.0063
0.3627	0.823 07	0.0882	0.8267	0.809 68	−0.0171
0.4607	0.819 02	0.0695	1.0000	0.806 86	0.0000
TOA (B) + Hexane (D)					
0.0000	0.655 90	0.0000	0.4861	0.773 59	−1.0565
0.0516	0.681 09	−0.4287	0.5859	0.783 04	−0.9566
0.0992	0.699 28	−0.6542	0.6868	0.790 73	−0.7817
0.1459	0.714 21	−0.8424	0.7689	0.795 90	−0.6054
0.2417	0.737 82	−1.1150	0.8580	0.800 72	−0.4211
0.2906	0.747 23	−1.1884	0.9047	0.803 11	−0.3449
0.3974	0.763 41	−1.1844	1.0000	0.806 86	0.0000
0.4410	0.768 60	−1.1149			
TOA (B) + Toluene (D)					
0.0000	0.862 19	0.0000	0.5993	0.813 94	0.2524
0.1000	0.843 37	0.2485	0.6501	0.812 74	0.2129
0.1999	0.832 55	0.3387	0.6990	0.811 67	0.1860
0.2994	0.825 51	0.3597	0.7496	0.810 69	0.1470
0.4001	0.820 50	0.3406	0.8496	0.809 00	0.0716
0.4999	0.816 79	0.3057	0.8993	0.808 26	0.0350
0.5488	0.815 30	0.2814	1.0000	0.806 86	0.0000
TOA (B) + Ethanol (D)					
0.0000	0.785 72	0.0000	0.5715	0.806 13	−0.3745
0.1032	0.795 70	−0.0555	0.6275	0.806 42	−0.3718
0.1494	0.798 31	−0.1038	0.7297	0.806 81	−0.3300
0.1961	0.800 22	−0.1598	0.7805	0.806 90	−0.2919
0.2467	0.801 69	−0.2009	0.8074	0.806 92	−0.2656
0.2841	0.802 68	−0.2502	0.8848	0.807 03	−0.1588
0.3613	0.804 01	−0.2935	1.0000	0.806 92	0.0000
0.4666	0.805 33	−0.3552			
TOA (B) + Cyclohexane (D)					
0.0000	0.774 00	0.0000	0.2986	0.792 92	0.5667
0.0488	0.778 32	0.3023	0.4459	0.797 81	0.5251
0.1000	0.782 33	0.4231	0.5811	0.800 90	0.4503
0.1503	0.785 59	0.4950	0.7606	0.804 01	0.3136
0.1988	0.788 42	0.5431	0.8867	0.805 60	0.2060
0.2456	0.790 63	0.5698	1.0000	0.806 89	0.0000

ties of TOA + propionic acid + diluent ternary systems was carried out by the same method as that of the binary systems. In the ternary systems, various quantities of propionic acid were added to the TOA + diluent mixture with keeping the constant volume ratio of TOA:diluent = 1:1.

Results and Discussion

Density of Pure Solvent. Densities of all pure substances (TOA, propionic acid, benzene, toluene, *p*-xylene, ethanol, hexane, and cyclohexane) at 298.15 K are listed in Table 1 and are in satisfactory agreement with a deviation of 0.05% from the literature value (Juan and Angulo, 1984; Wei and Rowley, 1984; Timmermans, 1965; Kawano et al., 1982; Yu and Tsai, 1994; Petrino and Gaston-Bonhomme, 1995; Asfour and Dullien, 1981).

Table 4. Densities (ρ) and Excess Molar Volumes (V^E) of Propionic Acid (A) + Diluent (D) at 298.15 K

x_B	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}	x_B	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}
Propionic Acid (A) + Benzene (D)					
0.0000	0.873 57	0.0000	0.5439	0.926 51	0.3750
0.0610	0.878 99	0.0487	0.6956	0.945 32	0.2867
0.0989	0.882 21	0.0985	0.7496	0.952 23	0.2599
0.1902	0.890 32	0.2010	0.8458	0.965 21	0.1866
0.2969	0.900 20	0.3096	0.8998	0.972 96	0.1256
0.3878	0.909 29	0.3524	1.0000	0.987 98	0.0000
0.4460	0.915 48	0.3794			
Propionic Acid (A) + *p*-Xylene (D)					
0.0000	0.856 61	0.0000	0.6998	0.931 05	0.2336
0.1000	0.864 45	0.0597	0.7496	0.938 90	0.2177
0.2005	0.872 84	0.1399	0.7998	0.947 41	0.1899
0.3002	0.882 06	0.2000	0.9001	0.966 24	0.1131
0.4007	0.892 44	0.2343	0.9483	0.976 32	0.0620
0.5505	0.910 10	0.2567	1.0000	0.987 98	0.0000
0.5992	0.916 52	0.2559			
Propionic Acid (A) + Hexane (D)					
0.0000	0.655 92	0.0000	0.6006	0.805 49	0.4742
0.0651	0.667 99	0.1617	0.6494	0.822 89	0.4380
0.1156	0.677 85	0.2470	0.6953	0.841 05	0.4061
0.1614	0.687 10	0.3344	0.7543	0.864 15	0.3348
0.2091	0.697 47	0.3737	0.7990	0.883 54	0.2870
0.2568	0.708 23	0.4262	0.8466	0.905 42	0.2419
0.3531	0.731 87	0.4731	0.8967	0.930 18	0.1635
0.4457	0.757 02	0.4940	0.9418	0.954 63	0.0763
0.4994	0.772 79	0.5011	1.0000	0.987 98	0.0000
0.5545	0.790 04	0.4974			
Propionic Acid (A) + Toluene (D)					
0.0000	0.862 19	0.0000	0.6000	0.924 45	0.2139
0.1001	0.870 73	0.0678	0.6498	0.931 10	0.2075
0.1998	0.879 84	0.1264	0.8001	0.953 21	0.1488
0.3002	0.889 71	0.1739	0.8499	0.961 27	0.1177
0.3999	0.900 36	0.1995	0.9508	0.978 88	0.0352
0.4996	0.911 80	0.2205	1.0000	0.987 98	0.0000
Propionic Acid (A) + Ethanol (D)					
0.0000	0.785 70	0.0000	0.4474	0.897 78	-0.6903
0.0581	0.802 75	−0.1945	0.4884	0.906 21	−0.6990
0.1061	0.815 99	−0.2939	0.5985	0.927 06	−0.6531
0.1519	0.828 83	0.3888	0.6419	0.934 84	−0.6244
0.2026	0.841 37	−0.4696	0.6962	0.944 13	−0.5741
0.2517	0.853 62	−0.5425	0.7438	0.951 72	−0.5033
0.2962	0.864 38	−0.6011	0.7916	0.959 08	−0.4726
0.3516	0.877 27	−0.6604	0.9287	0.978 66	−0.1641
0.3963	0.887 08	−0.6823	1.0000	0.987 98	0.0000
Propionic Acid (A) + Cyclohexane (D)					
0.0000	0.773 99	0.0000	0.5394	0.869 56	1.0434
0.0410	0.778 61	0.1794	0.6503	0.884 37	0.9556
0.1004	0.786 06	0.4045	0.7011	0.896 78	0.8860
0.1958	0.799 10	0.6985	0.7477	0.908 79	0.8070
0.2487	0.807 17	0.7966	0.8012	0.923 51	0.6880
0.2966	0.814 88	0.8663	0.8487	0.937 59	0.5436
0.3741	0.827 88	0.9765	0.9013	0.953 95	0.3820
0.4465	0.841 11	1.0262	0.9501	0.970 19	0.2068
0.4876	0.849 02	1.0454	1.0000	0.987 98	0.0000

Excess Molar Volumes for TOA (B) + Propionic Acid (A) Binary Systems. The excess molar volumes of TOA (B) + propionic acid (A) binary systems were measured at 298.15 K are in Figure 1, and the observed densities are given in Table 2. The $|V^E_{MAX}|$ is found to be about 6 cm^3 mol^{-1} at $x_A = 0.75$.

Excess Molar Volumes for TOA (B) + Diluent (D) and Propionic Acid (A) + Diluent (D) Systems. Figures 2 and 3 show the TOA + benzene and propionic acid + benzene system at 298.15 K. Figure 4 shows the V^E for the (TOA + benzene) + propionic acid system with keeping the volume ratio of TOA:benzene = 1:1.

The densities and V^E for TOA + diluent and propionic acid + diluent where the diluents were cyclohexane, hexane, toluene, *p*-xylene, and ethanol are given in Tables 3 and 4. The results are plotted in Figures 5 and 6, respectively. $|V^E_{MAX}|$ for TOA + diluent and propionic acid + diluent systems are much smaller than that for TOA + propionic acid.

Density and Excess Molar Volume for TOA (B) + Propionic Acid (A) + Diluent (D) Ternary Systems. The excess molar volumes of TOA + propionic acid systems

Table 5. Densities (ρ) and Excess Molar Volumes (V^E) of Trioctylamine (B) + Propionic Acid (A) at 298.15 K

x_A	x_B	x_D	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}	x_A	x_B	x_D	ρ/g·cm^{-3}	V^E/ cm^3·mol^{-1}
TOA (B) + Benzene (D) + Propionic Acid (A)									
0.0000	0.1694	0.8306	0.835 65	0.8109	0.1795	0.1403	0.6802	0.864 03	−1.4613
0.0025	0.1688	0.8287	0.836 11	0.7722	0.1992	0.1338	0.6669	0.868 04	−1.6854
0.0119	0.1695	0.8186	0.837 31	0.6356	0.2363	0.1313	0.6324	0.873 53	−2.0633
0.0179	0.1657	0.8164	0.838 93	0.4845	0.2870	0.1215	0.5914	0.882 56	−2.5324
0.0357	0.1687	0.7956	0.840 54	0.3090	0.3408	0.1129	0.5463	0.890 66	−2.7943
0.0554	0.1606	0.7840	0.844 26	0.0306	0.4048	0.1009	0.4943	0.898 19	−2.6709
0.0727	0.1565	0.7708	0.847 09	−0.1910	0.4887	0.0877	0.4236	0.906 86	−2.3469
0.0828	0.1594	0.7578	0.847 89	−0.2959	0.5995	0.0675	0.3331	0.919 45	−1.7531
0.1010	0.1549	0.7441	0.851 02	−0.5336	0.7612	0.0409	0.1979	0.941 28	−1.0011
0.1345	0.1464	0.7191	0.856 71	−0.9156	1.0000	0.0000	0.0000	0.987 98	0.0000
0.1435	0.1465	0.7100	0.857 95	−1.0306					
TOA (B) + *p*-Xylene (D) + Propionic Acid (A)									
0.0000	0.2204	0.7796	0.831 31	0.0989	0.1805	0.1807	0.6389	0.852 97	−1.7933
0.0120	0.2177	0.7703	0.832 60	−0.0201	0.2129	0.1737	0.6134	0.857 33	−2.1050
0.0239	0.2151	0.7610	0.833 93	−0.1544	0.2485	0.1657	0.5858	0.862 36	−2.4388
0.0375	0.2122	0.7503	0.835 49	−0.3143	0.2904	0.1564	0.5532	0.868 54	−2.8104
0.0557	0.2081	0.7361	0.837 59	−0.5159	0.3390	0.1453	0.5157	0.875 98	−3.1834
0.0682	0.2055	0.7263	0.839 01	−0.6462	0.3980	0.1328	0.4693	0.884 51	−3.4466
0.0860	0.2013	0.7127	0.841 12	−0.8314	0.4686	0.1172	0.414	0.892 80	−3.2734
0.1060	0.1969	0.6971	0.843 51	−1.0395	0.5555	0.0980	0.3466	0.902 37	−2.7684
0.1293	0.1920	0.6788	0.846 38	−1.2823	0.6649	0.0739	0.2612	0.916 14	−2.0551
0.1528	0.1867	0.6605	0.849 35	−1.5167	1.0000	0.0000	0.0000	0.987 98	0.0000
TOA (B) + Hexane (D) + Propionic Acid (A)									
0.0000	0.2644	0.7356	0.742 22	−1.1466	0.2324	0.1806	0.5870	0.770 50	−2.8079
0.0003	0.2325	0.7673	0.735 95	−1.1261	0.2505	0.1709	0.5786	0.773 08	−3.0174
0.0266	0.2250	0.7485	0.739 53	−1.4618	0.3023	0.1635	0.5343	0.783 37	−3.3444
0.0545	0.2173	0.7282	0.742 43	−1.5221	0.3484	0.1486	0.5030	0.792 02	−3.6664
0.0852	0.2120	0.7028	0.747 65	−1.9077	0.4124	0.1361	0.4515	0.805 66	−3.9334
0.1157	0.2037	0.6807	0.751 35	−2.0243	0.4747	0.1203	0.4050	0.816 68	−3.6382
0.1347	0.1994	0.6659	0.754 01	−2.1135	0.6094	0.0887	0.3019	0.843 48	−2.6781
0.1557	0.1931	0.6512	0.758 43	−2.6168	0.8105	0.0418	0.1477	0.900 23	−1.2439
0.1828	0.1896	0.6276	0.762 39	−2.6055	1.0000	0.0000	0.0000	0.987 98	0.0000
TOA (B) + Toluene (D) + Propionic Acid (A)									
0.0000	0.1959	0.8041	0.832 88	0.3397	0.2270	0.1515	0.6216	0.864 65	−2.1920
0.0208	0.1917	0.7875	0.835 63	0.0734	0.2672	0.1437	0.5892	0.871 00	−2.5768
0.0335	0.1894	0.7772	0.837 22	−0.0745	0.3140	0.1344	0.5516	0.878 55	−2.9662
0.0467	0.1865	0.7668	0.839 00	−0.2380	0.3700	0.1233	0.5067	0.886 92	−3.2222
0.0614	0.1840	0.7546	0.840 90	−0.4109	0.4398	0.1097	0.4505	0.890 04	−3.0757
0.0788	0.1806	0.7406	0.843 24	−0.6156	0.5261	0.0928	0.3810	0.904 35	−2.6317
0.1379	0.1687	0.6934	0.851 39	−1.2627	0.6382	0.0710	0.2908	0.917 81	−1.9805
0.1637	0.1637	0.6726	0.855 15	−1.5473	1.0000	0.0000	0.0000	0.987 98	0.0000
0.1931	0.1580	0.6489	0.859 49	−1.8521					
TOA (B) + Ethanol (D) + Propionic Acid (A)									
0.0000	0.1180	0.8820	0.796 83	−0.0708	0.1342	0.1027	0.7631	0.833 11	−2.0904
0.0148	0.1297	0.8555	0.802 11	−0.4265	0.1523	0.0999	0.7479	0.836 65	−2.1599
0.0356	0.1135	0.8509	0.807 57	−0.7939	0.1884	0.0962	0.7155	0.844 13	−2.3542
0.0400	0.1106	0.8494	0.809 12	−0.9093	0.2229	0.0922	0.6849	0.850 26	−2.4004
0.0446	0.1137	0.8416	0.810 37	−0.9802	0.2573	0.0883	0.6545	0.856 21	−2.4189
0.0504	0.1105	0.8391	0.811 89	−1.0628	0.3219	0.0792	0.5989	0.867 44	−2.3758
0.0598	0.1132	0.8270	0.814 59	−1.2315	0.3978	0.0711	0.5311	0.880 30	−2.2958
0.0689	0.1078	0.8233	0.817 31	−1.3875	0.5267	0.0583	0.4149	0.902 38	−2.1038
0.0824	0.1108	0.8068	0.820 65	−1.5655	0.6777	0.0376	0.2847	0.929 26	−1.5376
0.1016	0.1060	0.7924	0.825 55	−1.7916	1.0000	0.0000	0.0000	0.987 98	0.0000
0.1058	0.0989	0.7954	0.826 90	−1.8250					
TOA (B) + Cyclohexane (D) + Propionic Acid (A)									
0.0000	0.1988	0.8012	0.788 52	0.4203	0.2002	0.1565	0.6433	0.816 50	−1.2931
0.0068	0.1950	0.7982	0.789 22	0.3723	0.2341	0.1533	0.6125	0.822 03	−1.5818
0.0180	0.1901	0.7919	0.790 56	0.2584	0.2678	0.1400	0.5922	0.827 63	−1.8175
0.0548	0.1887	0.7566	0.795 52	−0.0456	0.3207	0.1355	0.5439	0.837 27	−2.2930
0.0775	0.1805	0.7421	0.798 37	−0.2359	0.3650	0.1206	0.5144	0.844 66	−2.3958
0.0913	0.1784	0.7303	0.800 39	−0.3744	0.4350	0.1085	0.4565	0.855 37	−2.3573
0.1183	0.1811	0.7007	0.804 31	−0.5871	0.5726	0.0822	0.3452	0.870 65	−1.7306
0.1260	0.1668	0.7072	0.805 19	−0.6765	0.7905	0.0398	0.1697	0.919 58	−0.6477
0.1710	0.1657	0.6633	0.811 92	−1.0354	1.0000	0.0000	0.0000	0.987 98	0.0000

containing diluent V^E are calculated from the observed density. The excess molar volumes of TOA + propionic acid + diluent (benzene, toluene, *p*-xylene, hexane, cyclohexane, or ethanol) systems are measured in this work. Figure 7 shows the excess molar volume for ternary systems, and observed data were listed in Table 5. This figure indicates that all curves of the excess molar volume have a minimum point at a certain mole fraction of propionic acid as well as in the case of TOA + propionic acid. The values of V^E at $x_A = 0$ in Figure 7 are the values of V^E of the TOP + diluent system where the volume ratio is TOP:diluent = 1:1; that is, the mass percent of TOA for the diluent in the ternary system is kept constant as TOA + benzen, 48.02; TOA + toluene, 48.34; TOA + *p*-xylene, 48.51; TOA + ethanol, 50.57; TOA + hexane, 55.16, and TOA + cyclohexane, 51.04 mass %, respectively. The maximum value of excess molar

volume $|V^E_{MAX}|$ of all ternary systems shows a smaller value than that of the TOA + propionic acid system. When diluent is added to the TOA + propionic acid system, the mole fraction (x_A) with the maximum value of $|V^E_{MAX}|$ is shifted to the lower composition of propionic acid.

Conclusion

The measurement of excess molar volume for TOA + propionic acid at 298.15 K was carried out. The diluent effect on excess molar volume for TOA + propionic acid was examined by the measurement of densities for TOA + propionic acid + diluent (benzene, toluene, *p*-xylene, hexane, cyclohexane, or ethanol) systems.

Literature Cited

Asfour, A. A.; Dullien, A. Viscosities and Densities of Four Binary Liquid Systems at 25.00 °C. *J. Chem. Eng. Data* **1981**, *26*, 312−316.

Chen, F.; Tanaka, H.; Naka, Y.; Oshima, E. Studies of the Association Mechanism and Diluent Effect Using Excess Volume-System of Tri-octylamine and Lower Calboxylic Acids. *Kagaku Kougaku Ronbunshu* **1988**, *14*, 779−785.

Chen, F.; Naka, Y.; Tanaka, H.; Oshima, E. Effect of Diluent on Extraction Equilibrium of Acetic Acid with Tri-octylamine. *Kagaku Kougaku Ronbunshu* **1989**, *15*, 1057−1063.

Juan, O.; Angulo, M. C. Excess Volume of Benzene + 1-Hexanol and 3-Methyl-3-Pentanol at three Different Temperatures. *J. Chem. Eng. Data* **1984**, *29*, 340−343.

Kawano, Y.; Kusano, K.; Takahashi, T.; Kondo, K.; Nakasio, F. Extraction Equilibrium of Lower Carboxylic Acids with Long-Chain Alkylamine. *Kagaku Kougaku Ronbunshu* **1982**, *8*, 404−409.

Kohler, F.; Gopal, R.; Gotze, G.; Atrops, H.; Demiriz, M. A. Molecular Instruction in Mixtures of carboxylic acids with Amines. 2. Volumetric Cunductimetric, and NMR Properties. *J. Phys. Chem.* **1981**, *85*, 2524−2529.

Noda, K.; Aono, Y.; Ishida, K. Viscosity and Density of Ethanol-acetic Acid-Water mixtures. *Kagaku Kougaku Ronbunshu* **1983**, *9*, 237−240.

Petrino, P. J.; Gaston-Bonhomme, Y. H.; Chevalier, J. L. E. Viscosity and Density of Binary Liquid Mixtures of Hydrocarbons, Esters, Ketones and Normal Chloroalkanes. *J. Chem. Eng. Data* **1995**, *40*, 136−140.

Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier Publishing Co.: London, 1965; Vol. 2, pp 99−102.

Yamamoto, H.; Nishi, Y.; Shibata, J. Association Model in Tri-n-Octylamine(TOA)-Carboxylic Acid-Diluent Systems. *Solvent Extr. Res. Dev. Jpn.* **1995**, *2*, 171−185.

Wei, I.; Rowley, R. L. Binary Liquid mixture Vicosities and Densities. *J. Chem. Eng. Data* **1984**, *29*, 332−335.

Yu, C.; Tsai, F. Excess Volume of Binary Mixtures of Benzene + 1-Alkanols at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1994**, *39*, 441−443.

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