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Salt Effects on Liquid−Liquid Equilibrium in Water + Ethanol + Alcohol + Salt Systems

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Liquid−liquid equilibrium data for the quaternary system (water + ethanol + alcohol + salt) were measured at 25 °C and 40 °C. The alcohols were 1-butanol, 1-pentanol, and 3-methyl-1-butanol. The salts were sodium chloride, sodium acetate, calcium chloride, potassium chloride, potassium sulfate, and potassium bromide. The results were compared with experimental liquid−liquid equilibrium data for the ternary, salt-free systems, both from the literature and determined in this work. In this way, the salt effect could be evaluated.

Introduction

Separation by solvent extraction becomes increasingly more difficult as the tie line becomes parallel to the solvent axis, as shown by a solutropic solution. The addition of a salt to such systems introduces ionic forces that affect the equilibrium, modifying the tie line, sometimes even to the extent of eliminating the solutrope. When the ions are solvated, some of the water becomes unavailable for the solution, and they are "salted out" from the aqueous phase. This salt effect may be used for removing organic components from water. On the other hand, when a polar solvent is added to an aqueous salt solution, it preferentially solvates the water that was solvating ions, to give a "salting in" effect. This effect may be used to recover salts from concentrated aqueous solutions. The salt effect is also important in biological separation processes such as purification of proteins, enzymes, nucleic acids, and others.

In recent years, some authors have studied the salt effect on the liquid−liquid equilibria of water + ethanol + alcohol systems.[1−5] In these systems, the solute is ethanol, and it is distributed between aqueous and organic phases. However, the amount of experimental data is still small. In this work, liquid−liquid equilibrium data were obtained for the systems water + ethanol + 1-butanol, water + ethanol + 3-methyl-1-butanol, and water + ethanol + 1-pentanol in the presence of sodium chloride, calcium chloride, sodium acetate, potassium chloride, potassium sulfate, and potassium bromide at 25 °C and 40 °C. The mixtures containing 1-butanol and 3-methyl-1-butanol were analyzed at 10 mass % salt in the overall mixture, while the systems with 1-pentanol were analyzed at 5 and 10 mass % salt in the overall mixture, except for the case of potassium sulfate, which precipitates at 10 mass %.

Experimental Section

Chemicals. All the reagents, ethanol, 1-butanol, 3-methyl-1-butanol, sodium chloride, sodium acetate, calcium chloride, potassium chloride, potassium sulfate, and potassium bromide, were of analytical grade (Merck) and were used without further purification.

Equilibrium Cell. For the determination of experimental liquid−liquid equilibrium data, equilibrium cells such those suggested by Stragevitch[6] were used. The cell temperature was regulated by a thermostatic bath (MLW MK-70, accurate to ±0.01 °C). The cell is shown in Figure 1.

Experimental Procedure. The overall mixture was prepared directly inside the cell, and the components were weighed on an analytical balance (Mettler H33AR, accurate to 0.0001 g). The mixture was vigorously agitated with a magnetic stirrer (Suprilab MAG-711) for 3 h, to allow an intimate contact between the phases, and the equilibrium was achieved by letting the mixture rest for 12 h. At equilibrium, the system split into two liquid phases, that become clear and transparent, with a well-defined interface. Separate samples of both phases were collected and analyzed.

Analytical Methods. Water, ethanol, 1-butanol, 3-methyl-1-butanol, and 1-pentanol were determined by gas chromatography using a Varian CX 300 Star gas chromatograph with a Porapak-Q packed column and a thermal conductivity detector; the hydrogen flow rate was 30 $cm^3 \cdot min^{-1}$, and the column temperature was 180 °C. The salt cannot be allowed in the packed column or in the detector. An empty column section of 30 cm was placed before the packed column. When the organic components were evaporated, the salt was deposited on the inner walls of this empty column, being eliminated from the gas stream. This section was then washed with distilled water and acetone, and further dried at 120 °C. The salt concentration can be determined by gravimetrical analysis, evaporating the solution at 120 °C, until constant mass. The same Mettler H33AR analytical balance was used to perform the gravimetrical analysis. Vianna et al.[7] validated this method when determining liquid−liquid equilibrium data of mixtures containing sodium acetate. All measures were performed in triplicate, with standard deviations of 0.2% for water, ethanol, 1-butanol, sodium acetate, and potassium chloride, 0.1% for 1-pentanol, 3-methyl-1-butanol, potassium sulfate, and sodium chloride, and 0.3% for potassium bromide and calcium chloride.

Results and Discussion

The experimental liquid−liquid equilibrium data for the quaternary water + ethanol + alcohol + salt systems are

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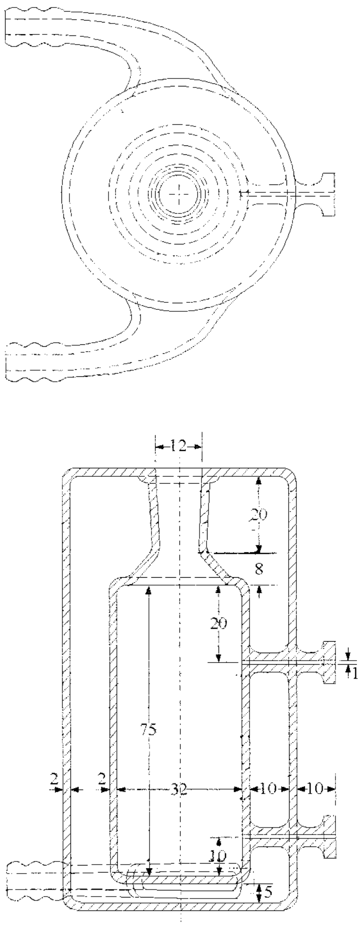

Figure 1. Equilibrium cell, dimensions in millimeters.

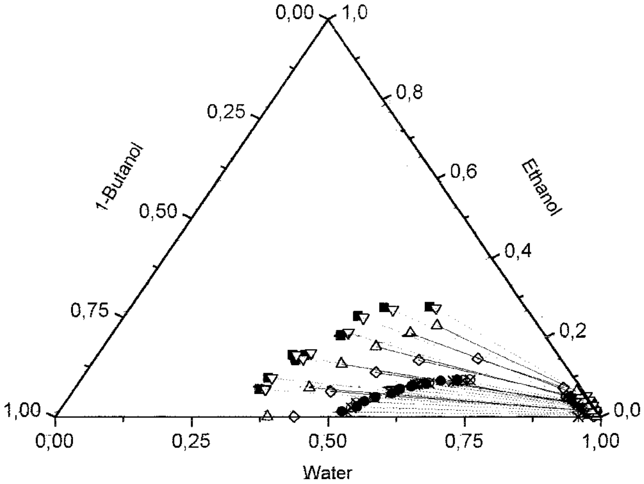

Figure 2. Liquid−liquid equilibrium of the water + ethanol + 1-butanol + sodium chloride system (■, 10 mass % NaCl, 25 °C; ▽, 10 mass % NaCl, 40 °C; ∗, salt-free, 25 °C; ●, Ruiz et al. (1984), salt-free, 25 °C; ⊗, Solomko et al. (1962), salt-free, 25 °C; ◇, Olaya et al. (1997), 9 mass % KCl, 25 °C; △, Olaya et al. (1997), 14 mass % KCl, 25 °C).

shown in Tables 1−6 as true mole fractions. Experimental data for the ternary, salt-free water + ethanol + alcohol systems are also shown in these tables.

Some of the experimental data can be seen in Figures 2−4, represented as salt-free mole fractions. In these figures also appear some data from the literature for the ternary basic, salt-free system, together with experimental data for the same ternary, salt-free system determined in this work.

Table 1. Mole Fractions of Water (1) + Ethanol (2) + 3-Methyl-1-butanol (3) + Salt (4) at 25 °C

aqueous phase				organic phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Salt-free							
0.9228	0.0072	0.0000		0.6000	0.1950	0.1970	
0.9668	0.0332	0.0000		0.4600	0.1800	0.3500	
0.9785	0.0215	0.0000		0.3900	0.1000	0.5000	
10 mass % Sodium Chloride in the Overall Mixture							
0.8638	0.0723	0.0000	0.0639	0.4640	0.3508	0.1722	0.0130
0.8633	0.0692	0.0000	0.0675	0.4481	0.3592	0.1803	0.0124
0.8742	0.0592	0.0000	0.0666	0.4138	0.3557	0.2210	0.0050
0.8873	0.0490	0.0000	0.0637	0.3661	0.3216	0.3087	0.0036
0.9032	0.0310	0.0000	0.0658	0.3066	0.2553	0.4367	0.0014
0.9010	0.0293	0.0000	0.0697	0.2958	0.2523	0.4496	0.0023
0.9100	0.0217	0.0000	0.0683	0.2709	0.1962	0.5319	0.0010
0.9135	0.0201	0.0000	0.0664	0.2709	0.1884	0.5402	0.0005
0.9209	0.0132	0.0000	0.0659	0.2530	0.1268	0.6199	0.0003
10 mass % Sodium Acetate in the Overall Mixture							
0.9329	0.0179	0.0000	0.0492	0.2749	0.1116	0.6128	0.0007
0.9258	0.0227	0.0000	0.0515	0.2843	0.1498	0.5645	0.0014
0.9215	0.0291	0.0000	0.0494	0.3134	0.1870	0.4978	0.0018
0.9092	0.0323	0.0000	0.0585	0.3123	0.2295	0.4549	0.0033
0.9035	0.0396	0.0000	0.0569	0.3444	0.2600	0.3912	0.0044
0.8988	0.0465	0.0000	0.0547	0.3751	0.2836	0.3357	0.0056
0.8679	0.0850	0.0000	0.0471	0.5154	0.2920	0.1770	0.0156
0.8314	0.1105	0.0132	0.0449	0.5888	0.2615	0.1261	0.0236
0.8216	0.1176	0.0196	0.0412	0.6132	0.2497	0.1101	0.0270
10 mass % Calcium Chloride in the Overall Mixture							
0.9109	0.0492	0.0000	0.0399	0.3599	0.2863	0.3485	0.0053
0.9160	0.0432	0.0000	0.0408	0.3130	0.2708	0.4121	0.0041
0.9158	0.0408	0.0000	0.0434	0.3097	0.2497	0.4373	0.0033
0.8966	0.0514	0.0000	0.0520	0.2787	0.2150	0.5043	0.0020
0.9029	0.0422	0.0000	0.0529	0.2621	0.1861	0.5501	0.0017
0.9023	0.0393	0.0000	0.0584	0.2541	0.1563	0.5887	0.0009

Table 2. Mole Fractions of Water (1) + Ethanol (2) + 3-Methyl-1-butanol (3) + Salt (4) at 40 °C

aqueous phase				organic phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
10 mass % Sodium Chloride in the Overall Mixture							
0.8685	0.0665	0.0000	0.0650	0.4723	0.3490	0.1644	0.0143
0.8648	0.0639	0.0000	0.0713	0.4594	0.3584	0.1685	0.0137
0.8743	0.0575	0.0000	0.0682	0.4191	0.3502	0.2036	0.0271
0.8821	0.0460	0.0000	0.0719	0.3815	0.3252	0.2808	0.0125
0.8991	0.0315	0.0000	0.0694	0.3254	0.2673	0.3957	0.0116
0.9026	0.0266	0.0000	0.0708	0.3053	0.2505	0.4414	0.0028
0.9089	0.0260	0.0000	0.0651	0.3007	0.2175	0.4804	0.0014
0.9116	0.0178	0.0000	0.0706	0.2761	0.1905	0.5316	0.0018
0.9222	0.0113	0.0000	0.0665	0.2638	0.1276	0.6078	0.0008
10 mass % Sodium Acetate in the Overall Mixture							
0.8992	0.0459	0.0000	0.0549	0.3909	0.2810	0.3238	0.0043
0.9037	0.0386	0.0000	0.0577	0.3528	0.2614	0.3787	0.0071
0.9070	0.0329	0.0000	0.0601	0.3615	0.2189	0.4143	0.0053
0.9249	0.0256	0.0000	0.0495	0.3294	0.1833	0.4854	0.0019
0.9277	0.0206	0.0000	0.0517	0.3012	0.1516	0.5456	0.0016
0.9354	0.0153	0.0000	0.0493	0.2820	0.1125	0.6044	0.0011
10 mass % Calcium Chloride in the Overall Mixture							
0.9084	0.0500	0.0000	0.0416	0.3521	0.2974	0.3450	0.0055
0.9126	0.0453	0.0000	0.0421	0.3272	0.2689	0.3996	0.0043
0.9158	0.0406	0.0000	0.0436	0.3156	0.2550	0.4258	0.0036
0.9175	0.0369	0.0000	0.0456	0.2961	0.2155	0.4872	0.0012
0.9145	0.0337	0.0000	0.0518	0.2817	0.1870	0.5301	0.0012
0.9144	0.0330	0.0000	0.0526	0.2564	0.1598	0.5825	0.0013

In Figure 2 appears the salt effect of the addition of sodium chloride on the water + ethanol + 1-butanol ternary system. Experimental salt-free data for this system were also determined at 25 °C and found to be in good agreement with those reported by Ruiz et al.[8] and Solomko et al.,[9] both at 25 °C. From this figure, the effect of the salt addition can be seen. First, the size of the two-phase region greatly increases, because the organic phase points

Table 3. Mole Fractions of Water (1) + Ethanol (2) + 1-Butanol (3) + Salt (4) at 25 °C

aqueous phase				organic phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Salt-free							
0.9587	0.0001	0.0413		0.5279	0.0131	0.4590	
0.9560	0.0234	0.0206		0.5843	0.0610	0.3547	
0.9262	0.0439	0.0299		0.6849	0.0892	0.2259	
10 mass % Sodium Chloride in the Overall Mixture							
0.9282	0.0066	0.0043	0.0609	0.3403	0.0682	0.5901	0.0014
0.9217	0.0100	0.0042	0.0641	0.3423	0.0960	0.5595	0.0022
0.9128	0.0173	0.0033	0.0666	0.3581	0.1535	0.4850	0.0034
0.9181	0.0173	0.0043	0.0603	0.3691	0.1402	0.4870	0.0037
0.9150	0.0204	0.0050	0.0596	0.3796	0.1541	0.4619	0.0044
0.9062	0.0299	0.0050	0.0589	0.4191	0.2033	0.3716	0.0060
0.9018	0.0285	0.0000	0.0697	0.4265	0.2501	0.3169	0.0065
0.9005	0.0316	0.0000	0.0679	0.4624	0.2709	0.2573	0.0094
0.8909	0.0414	0.0028	0.0649	0.5393	0.2717	0.1719	0.0171
10 mass % Sodium Acetate in the Overall Mixture							
0.9395	0.0090	0.0066	0.0449	0.4009	0.0591	0.5377	0.0023
0.9349	0.0137	0.0066	0.0448	0.4149	0.0920	0.4901	0.0030
0.9228	0.0192	0.0065	0.0515	0.4279	0.1289	0.4383	0.0049
0.9251	0.0237	0.0087	0.0425	0.4239	0.1234	0.4506	0.0021
0.9217	0.0268	0.0091	0.0424	0.4300	0.1364	0.4295	0.0041
0.9141	0.0344	0.0099	0.0416	0.4578	0.1595	0.3770	0.0057
0.8927	0.0441	0.0112	0.0520	0.5013	0.1945	0.2924	0.0118
0.8899	0.0481	0.0116	0.0504	0.5320	0.1948	0.2598	0.0134
0.8826	0.0542	0.0146	0.0486	0.5569	0.1975	0.2294	0.0162
10 mass % Calcium Chloride in the Overall Mixture							
0.9327	0.0190	0.0000	0.0483	0.3418	0.0778	0.5778	0.0026
0.9309	0.0209	0.0000	0.0482	0.3535	0.1134	0.5293	0.0038
0.9140	0.0329	0.0000	0.0531	0.3709	0.1509	0.4731	0.0051
0.9056	0.0429	0.0101	0.0414	0.4575	0.1938	0.3371	0.0116
0.8985	0.0495	0.0108	0.0412	0.4792	0.1994	0.3088	0.0126
0.8845	0.0609	0.0136	0.0410	0.5105	0.2061	0.2685	0.0149

Table 4. Mole Fractions of Water (1) + Ethanol (2) + 1-Butanol (3) + Salt (4) at 40 °C

aqueous phase				organic phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
10 mass % Sodium Chloride in the Overall Mixture							
0.9234	0.0085	0.0035	0.0637	0.3484	0.0970	0.5528	0.0018
0.9290	0.0058	0.0039	0.0613	0.3508	0.0691	0.5786	0.0015
0.9189	0.0122	0.0026	0.0663	0.3644	0.1539	0.4789	0.0028
0.9185	0.0165	0.0041	0.0609	0.3806	0.1446	0.4708	0.0040
0.9169	0.0188	0.0045	0.0598	0.3878	0.1596	0.4482	0.0044
0.9262	0.0290	0.0052	0.0396	0.4294	0.2096	0.3545	0.0065
0.9038	0.0252	0.000	0.0710	0.4373	0.2459	0.3081	0.0087
0.8976	0.0384	0.000	0.0640	0.4788	0.2658	0.2435	0.0119
0.8846	0.0484	0.000	0.0670	0.5510	0.2676	0.1629	0.0185
10 mass % Sodium Acetate in the Overall Mixture							
0.9477	0.0081	0.0000	0.0442	0.3721	0.0638	0.5600	0.0041
0.9410	0.0136	0.0000	0.0454	0.3942	0.0984	0.5027	0.0047
0.9320	0.0204	0.0000	0.0476	0.4096	0.1372	0.4461	0.0071
0.9267	0.0218	0.0084	0.0431	0.4232	0.1260	0.4449	0.0059
0.9241	0.0242	0.0087	0.0430	0.4336	0.1373	0.4222	0.0069
0.9183	0.0304	0.0090	0.0423	0.4626	0.1592	0.3699	0.0083
0.8905	0.0403	0.0121	0.0571	0.5283	0.1865	0.2694	0.0158
0.8805	0.0464	0.0153	0.0578	0.5583	0.1845	0.2386	0.0186
0.8623	0.0552	0.0204	0.0621	0.5969	0.1796	0.2006	0.0229
10 mass % Calcium Chloride in the Overall Mixture							
0.9255	0.0191	0.0000	0.0554	0.3475	0.0802	0.5695	0.0028
0.9232	0.0262	0.0000	0.0506	0.3682	0.1151	0.5130	0.0037
0.9229	0.0298	0.0000	0.0473	0.3834	0.1527	0.4590	0.0049
0.8976	0.0473	0.0108	0.0443	0.4583	0.1997	0.3348	0.0072
0.8938	0.0530	0.0126	0.0406	0.4752	0.2058	0.3103	0.0087
0.8701	0.0711	0.0169	0.0419	0.5028	0.2143	0.2718	0.0111

Table 5. Mole Fractions of Water (1) + Ethanol (2) + 1-Pentanol (3) + Salt (4) at 25 °C

aqueous phase				organic phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
Salt-free							
0.9869	0.0131	0.0000		0.3980	0.0454	0.5567	
0.9305	0.0695	0.0000		0.5268	0.1963	0.2769	
0.8888	0.0970	0.0142		0.6598	0.1878	0.1524	
5 mass % Potassium Chloride in the Overall Mixture							
0.9669	0.0082	0.0000	0.0249	0.3339	0.0403	0.6253	0.0005
0.9580	0.0173	0.0000	0.0247	0.3435	0.0792	0.5771	0.0002
0.9484	0.0260	0.0000	0.0256	0.3531	0.1121	0.5344	0.0004
0.9431	0.0308	0.0000	0.0261	0.3695	0.1383	0.4917	0.0005
0.9338	0.0396	0.0000	0.0266	0.3899	0.1668	0.4426	0.0007
0.9248	0.0482	0.0000	0.0270	0.4011	0.1896	0.4084	0.0009
0.9216	0.0516	0.0000	0.0268	0.4210	0.2138	0.3643	0.0009
0.9124	0.0608	0.0000	0.0268	0.4424	0.2332	0.3230	0.0014
0.9020	0.0712	0.0000	0.0268	0.4640	0.2449	0.2888	0.0023
0.8948	0.0784	0.0000	0.0268	0.4772	0.2538	0.2512	0.0178
10 mass % Potassium Chloride in the Overall Mixture							
0.9353	0.0075	0.0000	0.0572	0.2794	0.0445	0.6516	0.0245
0.9414	0.0093	0.0000	0.0493	0.2929	0.0836	0.6223	0.0012
0.9270	0.0218	0.0000	0.0512	0.3080	0.1227	0.5675	0.0018
0.9259	0.0230	0.0000	0.0511	0.3230	0.1527	0.5235	0.0008
0.9230	0.0259	0.0000	0.0511	0.3285	0.1830	0.4878	0.0007
0.9184	0.0308	0.0000	0.0508	0.3314	0.2081	0.4592	0.0013
0.8950	0.0497	0.0000	0.0553	0.3879	0.2883	0.3194	0.0044
0.8871	0.0576	0.0000	0.0553	0.4084	0.3031	0.2825	0.0060
0.9019	0.0467	0.0000	0.0514	0.3717	0.2562	0.3717	0.0004
5 mass % Potassium Sulfate in the Overall Mixture							
0.9794	0.0051	0.0000	0.0155	0.3839	0.0398	0.5763	0.0000
0.9775	0.0112	0.0000	0.0113	0.4012	0.0732	0.5256	0.0000
0.9721	0.0183	0.0000	0.0096	0.4220	0.1021	0.4759	0.0000
0.9584	0.0359	0.0000	0.0057	0.4166	0.1350	0.4473	0.0011
0.9529	0.0422	0.0000	0.0049	0.4456	0.1595	0.3942	0.0007
0.9416	0.0543	0.0000	0.0041	0.4549	0.1735	0.3710	0.0006
0.9391	0.0575	0.0000	0.0034	0.5049	0.1906	0.3040	0.0005
0.9298	0.0672	0.0000	0.0030	0.5330	0.2004	0.2660	0.0006
0.9268	0.0707	0.0000	0.0025	0.5623	0.2056	0.2317	0.0004
0.9089	0.0889	0.0000	0.0022	0.5957	0.2114	0.1919	0.0010
5 mass % Potassium Bromide in the Overall Mixture							
0.9700	0.0054	0.0000	0.0246	0.3782	0.0359	0.5857	0.0002
0.9611	0.0139	0.0000	0.0250	0.3865	0.0679	0.5451	0.0005
0.9530	0.0215	0.0000	0.0255	0.4006	0.0970	0.5020	0.0004
0.9308	0.0430	0.0000	0.0262	0.4141	0.1317	0.4535	0.0007
0.9228	0.0510	0.0000	0.0262	0.4349	0.1575	0.4060	0.0016
0.9109	0.0625	0.0000	0.0266	0.4552	0.1761	0.3665	0.0022
0.8976	0.0755	0.0000	0.0269	0.4832	0.1937	0.3197	0.0034
0.8939	0.0797	0.0000	0.0264	0.5033	0.2088	0.2835	0.0044
0.8830	0.0908	0.0000	0.0262	0.5343	0.2160	0.2444	0.0053
0.8900	0.0853	0.0000	0.0247	0.5532	0.2251	0.2159	0.0058
10 mass % Potassium Bromide in the Overall Mixture							
0.9407	0.0086	0.0000	0.0507	0.3174	0.0430	0.6391	0.0005
0.9320	0.0161	0.0000	0.0519	0.3356	0.0798	0.5841	0.0005
0.9229	0.0249	0.0000	0.0522	0.3456	0.1117	0.5414	0.0013
0.9160	0.0312	0.0000	0.0528	0.3653	0.1447	0.4876	0.0024
0.9095	0.0376	0.0000	0.0529	0.3839	0.1720	0.4413	0.0028
0.9001	0.0463	0.0000	0.0536	0.4009	0.1941	0.4011	0.0039
0.8729	0.0714	0.0000	0.0557	0.4215	0.2178	0.3551	0.0056
0.8754	0.0699	0.0000	0.0547	0.4323	0.2340	0.3262	0.0075
0.8669	0.0788	0.0000	0.0543	0.4670	0.2455	0.2782	0.0093
0.8715	0.0767	0.0000	0.0518	0.4910	0.2538	0.2419	0.0133

are moved in the direction of a greater concentration of 1-butanol. It was also observed that the temperature, apparently, has little effect on the electrolyte liquid−liquid equilibrium. The experimental points corresponding to temperatures of 25 °C and 40 °C are placed over the same trajectory, and sometimes, they are almost equal. In these figures also appear two sets of salt effect data reported by Olaya et al.[5] for the same system, using 7 mass % and 14 mass % potassium chloride, both at 25 °C. The experimental data have shown that the salt effect of potassium chloride is less important than those of sodium chloride, sodium acetate, and calcium chloride, although the two latter do not appear in the figure.

In Figure 3 appears the salt effect of the addition of calcium chloride on the water + ethanol + 3-methyl-1-

Table 6. Mole Fractions of Water (1) + Ethanol (2) + 1-Pentanol (3) + Salt (4) at 40 °C

aqueous phase				organic phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
5 mass % Potassium Chloride in the Overall Mixture							
0.9680	0.0068	0.0000	0.0252	0.3539	0.0427	0.6022	0.0012
0.9603	0.0141	0.0000	0.0256	0.3700	0.0803	0.5490	0.0007
0.9529	0.0212	0.0000	0.0259	0.3867	0.1133	0.4989	0.0011
0.9463	0.0271	0.0000	0.0266	0.4019	0.1409	0.4565	0.0007
0.9411	0.0322	0.0000	0.0267	0.4199	0.1680	0.4112	0.0009
0.9341	0.0385	0.0000	0.0274	0.4397	0.1908	0.3682	0.0013
0.9284	0.0445	0.0000	0.0271	0.4496	0.2142	0.3347	0.0015
0.9185	0.0540	0.0000	0.0275	0.4672	0.2292	0.3010	0.0026
0.9124	0.0603	0.0000	0.0273	0.4946	0.2398	0.2622	0.0034
0.8983	0.0743	0.0000	0.0274	0.5178	0.2495	0.2284	0.0043
10 mass % Potassium Chloride in the Overall Mixture							
0.9449	0.0041	0.0000	0.0510	0.3093	0.0505	0.6396	0.0006
0.9359	0.0117	0.0000	0.0524	0.3235	0.0949	0.5802	0.0014
0.9332	0.0142	0.0000	0.0526	0.3322	0.1319	0.5344	0.0015
0.9220	0.0246	0.0000	0.0534	0.3395	0.1730	0.4866	0.0009
0.9143	0.0314	0.0000	0.0543	0.3425	0.2011	0.4543	0.0021
0.9020	0.0427	0.0000	0.0553	0.3611	0.2264	0.4107	0.0018
0.9027	0.0417	0.0000	0.0556	0.3755	0.2531	0.3687	0.0027
0.8936	0.0506	0.0000	0.0558	0.3952	0.2673	0.3338	0.0037
0.8940	0.0503	0.0000	0.0557	0.4147	0.2833	0.2979	0.0041
0.8850	0.0588	0.0000	0.0562	0.4358	0.2975	0.2611	0.0056
5 mass % Potassium Sulfate in the Overall Mixture							
0.9828	0.0062	0.0000	0.0110	0.3714	0.0440	0.5846	0.0000
0.9720	0.0170	0.0000	0.0110	0.3879	0.0823	0.5298	0.0000
0.9677	0.0227	0.0000	0.0096	0.4086	0.1098	0.4816	0.0000
0.9675	0.0250	0.0000	0.0075	0.4604	0.1586	0.3750	0.0060
0.9599	0.0336	0.0000	0.0065	0.4752	0.1739	0.3509	0.0000
0.9512	0.0430	0.0000	0.0058	0.4970	0.1864	0.3161	0.0005
0.9476	0.0468	0.0000	0.0056	0.4996	0.1924	0.3076	0.0004
0.9318	0.0633	0.0000	0.0049	0.5265	0.2021	0.2706	0.0008
0.9272	0.0684	0.0000	0.0044	0.5562	0.2079	0.2353	0.0006
0.8943	0.1019	0.0000	0.0038	0.5909	0.2107	0.1980	0.0004
10 mass % Potassium Sulfate in the Overall Mixture							
0.9820	0.0046	0.0000	0.0134	0.3829	0.0472	0.5699	0.0000
0.9797	0.0095	0.0000	0.0108	0.4013	0.0847	0.5139	0.0001
0.9775	0.0131	0.0000	0.0094	0.4216	0.1132	0.4649	0.0003
0.9679	0.0239	0.0000	0.0082	0.4329	0.1434	0.4236	0.0001
0.9553	0.0375	0.0000	0.0072	0.4639	0.1656	0.3704	0.0001
0.9504	0.0433	0.0000	0.0063	0.4758	0.1752	0.3489	0.0001
0.9446	0.0498	0.0000	0.0056	0.5050	0.1907	0.3041	0.0002
0.9254	0.0697	0.0000	0.0049	0.5332	0.2005	0.2661	0.0002
0.9220	0.0736	0.0000	0.0044	0.5624	0.2056	0.2318	0.0002
0.9271	0.0697	0.0000	0.0032	0.5960	0.2116	0.1920	0.0004
5 mass % Potassium Bromide in the Overall Mixture							
0.9683	0.0071	0.0000	0.0246	0.3843	0.0395	0.5761	0.0001
0.9524	0.0219	0.0000	0.0257	0.3942	0.0717	0.5341	0.0000
0.9703	0.0044	0.0000	0.0253	0.4064	0.1011	0.4925	0.0000
0.8881	0.0834	0.0000	0.0285	0.4959	0.1915	0.3099	0.0027
0.8926	0.0795	0.0000	0.0279	0.5145	0.2038	0.2774	0.0043
10 mass % Potassium Bromide in the Overall Mixture							
0.9435	0.0070	0.0000	0.0495	0.3300	0.0430	0.6251	0.0019
0.9324	0.0148	0.0000	0.0528	0.3432	0.0822	0.5723	0.0023
0.9266	0.0203	0.0000	0.0531	0.3573	0.1153	0.5242	0.0032
0.9230	0.0240	0.0000	0.0530	0.3811	0.1475	0.4686	0.0028
0.9171	0.0295	0.0000	0.0534	0.3957	0.1758	0.4248	0.0037
0.8953	0.0489	0.0000	0.0429	0.4305	0.2194	0.3428	0.0073
0.8820	0.0618	0.0000	0.0562	0.4534	0.2334	0.3042	0.0090
0.8797	0.0652	0.0000	0.0551	0.4798	0.2425	0.2670	0.0107

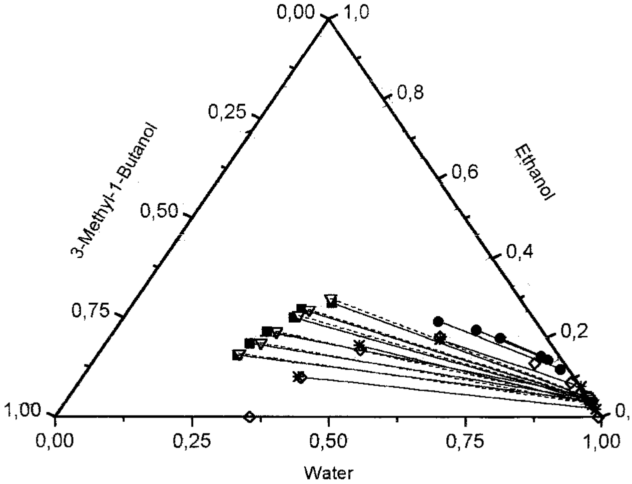

Figure 3. Liquid−liquid equilibrium of the water + ethanol + 3-methyl-1-butanol + calcium chloride system (■, 10 mass % $CaCl_2$, 25 °C; ▽, 10 mass % $CaCl_2$, 40 °C; ∗, salt-free, 25 °C; ●, Bonner (1910), salt-free, 0 °C; ◇, Tegtmeier and Misselhorn (1981), salt-free, 30 °C).

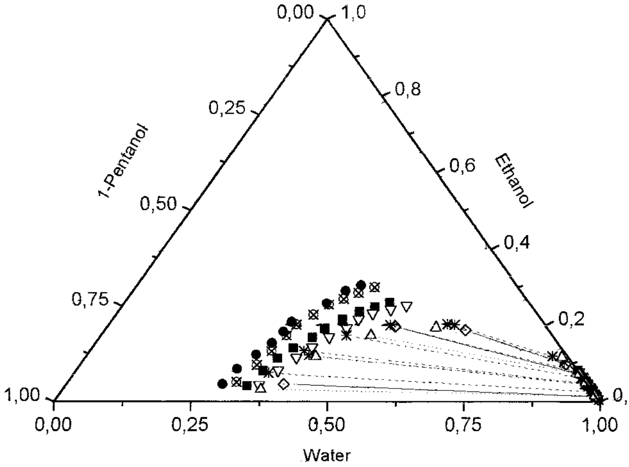

Figure 4. Liquid−liquid equilibrium of the water + ethanol + 1-pentanol + potassium chloride system (■, 5 mass % KCl, 25 °C; ▽, 5 mass % KCl, 40 °C; ●, 10 mass % KCl, 25 °C; ⊗, 10 mass % KCl, 40 °C; ◇, salt-free, 25 °C; ∗, Galán et al. (1989), salt-free, 20 °C; △, Othmer et al. (1941), salt-free, 25.5 °C).

butanol ternary system. Experimental salt-free data for this system were also determined in this work, and the results were found to be in agreement with those reported by Tegtmeier and Misselhorn[10] at 30 °C. It is important to point out that the data from Tegtmeier and Misselhorn are not experimental tie lines but just two sides of the binodal curve. Experimental tie lines for this system determined by Bonner[11] at 0 °C appear also in this figure. The salt effects, including those of sodium chloride and sodium acetate, are similar to those obtained for the water + ethanol + 1-butanol system, although these salts are not shown in the figure. The size of the biphasic region increases, and the slope of the tie lines is slightly changed. Again, the temperature, apparently, has little effect on the electrolyte liquid−liquid equilibrium.

In Figure 4 appears the salt effect due to the addition of potassium chloride to the system water + ethanol + 1-pentanol. Experimental data for the ternary system without salt were also determined at 25 °C and found to be in good agreement with those reported by Galán et al.[12] at 20 °C and Othmer et al.[13] at 25.5 °C. The effect of potassium chloride on the water + ethanol + 1-pentanol system is, again, easily noticed, as the organic phase points are moved toward a greater concentration of 1-pentanol. The effect is quite similar for the addition of potassium bromide, but the addition of potassium sulfate has little effect on the original liquid−liquid equilibrium, although, once again, these salt effects are not shown in the figure. Again, the temperature appears to also have little effect.

Conclusions

Liquid−liquid equilibrium data of quaternary water +

ethanol + 1-butanol + salt, water + ethanol + 3-methyl-1-butanol + salt, and water + ethanol + 1-pentanol + salt systems were determined at 25 °C and 40 °C by chromatographic and gravimetric analysis. The salts used were sodium chloride, sodium acetate, and calcium chloride, for the systems with 1-butanol and 3-methyl-1-butanol, and potassium chloride, potassium bromide, and potassium sulfate, for the systems with 1-pentanol. The effect of the salt addition on the original ternary systems was observed by the increase of the two-phase region and the changes in the slopes of the experimental tie lines. Experimental data for the ternary systems without salt were also determined and compared with those previously published, showing good agreement. In a general form, all salts have caused a "salting out" effect. In appearance, sodium salts have more effect on the original liquid−liquid equilibrium data than potassium salts, especially potassium sulfate, which has an extremely little effect. The effect of temperature is also very little, while the effect of salt concentration is considerably more important.

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Literature Cited

(1) Malinowski, J. J.; Daugulis, A. J. Salt Effects in Extraction of Ethanol, 1-Butanol and Acetone from Aqueous Solutions. *AIChE J.* **1994**, *40*, 1459−1465.

(2) Ruiz, F.; Gomis, V.; Botella, R. F. Extraction of Ethanol from Aqueous Solution 1. Solvent Less Volatile than Ethanol: 2-Ethylhexanol. *Ind. Eng. Chem. Res.* **1987**, *26*, 696.

(3) Ruiz, F.; Gomis, V.; Botella, R. F. Extraction of Ethanol from Aqueous Solution 2. Solvent More Volatile than Ethanol: Dichloromethane. *Ind. Eng. Chem. Res.* **1988**, *27*, 648.

(4) Gomis, V.; Ruiz, F.; Boluda, N.; Saquete, M. D. Salt Effects in Extraction of Ethanol from Aqueous Solution: 2-Ethylhexanol + Sodium Chloride as the Solvent. *Ind. Eng. Chem. Res.* **1998**, *37*, 599−603.

(5) Olaya, M. M.; Conesa, J. A.; Marcilla, A. Salt Effect in the Quaternary System Water + Ethanol + 1-Butanol + Potassium Chloride at 25 °C. *J. Chem. Eng. Data* **1997**, *42*, 858−864.

(6) Stragevitch, L. Liquid−Liquid Equilibrium in Non Electrolyte Mixtures. D. Sc. Thesis (in portuguese), FEQ/UNICAMP, Campinas, 1997.

(7) Vianna, R. F.; d'Ávila, S. G.; Marinho, R. L. Liquid−Liquid Equilibrium in Mixtures containing Electrolytes. *IX Brazilian Congress of Chemical Engineering—COBEQ* (in portuguese); ABEQ, Brazilian Association of Chemical Engineering: Salvador, 1992; Vol. 3, pp 531−539.

(8) Ruiz, F.; Prats, D.; Gomis, V. Quaternary Liquid−Liquid Equilibrium. Water−Ethanol−1-Butanol−Chloroform at 25 °C. Experimental Determination and Graphical Representation of Equilibrium Data. *J. Chem. Eng. Data* **1984**, *29*, 147−151.

(9) Solomko, V. P.; Panasyuk, V. D.; Selenskaya, A. M. Mutual Solubility of Four-component System Water-Acetone-Ethyl Alcohol-Butyl Alcohol. *Zh. Prikl. Khim.* **1962**, *35*, 628−633.

(10) Tegtmeier, U.; Misselhorn, K. Use of the UNIFAC Method for the Precalculation of Extraction Parameters. *Chem. Ing. Tech.* **1981**, *53*, 542−546.

(11) Bonner, W. Experimental Determination of Binodal Curves, Plait Points and Tie Lines in Fifty Systems, each consisting in Water and Two Organic Liquids. *J. Phys. Chem.* **1910**, *14*, 738−789.

(12) Galán, J. C.; Moreno, J. M. M.; Valle, R. T.; Segado, A. R. Equilibrio Líquido-Líquido de Mezclas Ternarias Ethanol/Agua/Alcoholes. *Anales de Química* **1989**, *A85*, 273−279.

(13) Othmer, D. F.; White, R. E.; Trueger, E. Liquid−Liquid Extraction Data. *Ind. Eng. Chem.* **1941**, *33*, 1240−1248.

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