Effect of Some Inorganic Salts on the Ternary Liquid−Liquid Equilibria of the Water + 4-Methyl-2-pentanone + Propanoic or Butanoic Acid at 35 °C

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The effect of sodium chloride, sodium nitrate, sodium sulfate, zinc sulfate, and ammonium sulfate on the liquid−liquid equilibria (LLE) of water + 4-methyl-2-pentanone + propanoic or butanoic acid at 35 °C has been studied. The ternary LLE data of the systems have been predicted using the NRTL equation, the parameters of which were obtained from the infinite dilution activity coefficient values. The distribution data of the salt containing ternary liquid systems have been correlated through the use of the modified Campbell equation, and the constants obtained have been used to determine the extract phase solute concentrations and also to calculate the salt effect parameter. Results based on the modified Campbell equation show the following order of effectiveness of salts for systems containing propanoic acid: $Na_2SO_4 > ZnSO_4 > NaCl > (NH_4)_2SO_4 > NaNO_3$. And for systems with butanoic acid: $(NH_4)_2SO_4 > Na_2SO_4 > NaCl > ZnSO_4 > NaNO_3$.

Introduction

The solvent selection is of prime importance for successful separation by liquid−liquid extraction, and much of the process research is directed toward the evaluation of potential solvents. Among several solvent selection criteria, the distribution coefficient and selectivity are of considerable value since they measure the separating power of a solvent. To enhance the distribution coefficient and thereby the selectivity of a solvent, a salt is normally added. The presence of a salt in the liquid phase has substantial influence on the phase equilibria of the systems and can cause salting out or salting in. Dissolved salts either may increase the electrostriction of the aqueous solutions to such an extent that the nonelectrolyte is squeezed out (salting out) or may reduce the electrostriction of the solutions, enabling more of the nonelectrolyte to dissolve (salting in). However, only scant attention is given to apply this phenomenon in large scale operations. In fact, relatively little data have been compiled on salting out effects of the various salts on many nonelectrolytes, that lend themselves to solvent extraction from aqueous solutions. In the extraction of fatty acids, 4-methyl-2-pentanone (MIBK) is a frequently employed solvent. The present study deals with the effect of the five salts on the distribution of propanoic acid or butanoic acid between water and MIBK at 35 °C. The experimental data of the salt free systems were predicted using the NRTL model (Renon and Prausnitz, 1968).

Experimental Section

Materials. Analar grade propanoic acid and butanoic acid (M/s Reidel-De Haenag seelze, Hannover, Germany) and MIBK (M/s. S.D. Fine Chem Pvt. Ltd., India) were distilled, and heart cuts were collected and used immediately. The quality of the purified chemicals was ascertained by measuring their physical properties like boiling point, density, and refractive index. The measured values are compared with those of the literature (Weissberger, 1955) in Table 1. All the salts and the chemicals used for analytical purposes were of analar quality and used as such. Throughout this work double-distilled water was used.

Table 1. Physical Properties of Purified Chemicals

chemical	normal bp (°C) expt	normal bp (°C) lit.[a]	density at 35 °C expt	density at 35 °C lit.	refractive index at 35 °C expt	refractive index at 35 °C lit.
4-methyl-2-pentanone	115.5	115.65	0.7869	0.7871	1.3890	1.3893
propanoic acid	140.6	140.80	0.9775	0.9779	1.3800	1.3803
butanoic acid	163.2	163.25	0.9418	0.9427	1.3916	1.3918

[a] Literature (Weissberger, 1955).

Table 2. Equilibrium Data for the Water (1) + 4-Methyl-2-pentanone (2) + Propanoic Acid (3) System at 35 °C

w_{ij}: mass fraction of component i in phase j

aqueous phase (1) w_{11}	aqueous phase (1) w_{31}	organic phase (2) w_{12}	organic phase (2) w_{32}
0.9779	0.0121	0.0201	0.0279
0.9568	0.0327	0.0351	0.0869
0.9341	0.0539	0.0469	0.1450
0.8908	0.0942	0.0729	0.2396
0.8433	0.1347	0.1173	0.3267
0.8100	0.1700	0.1594	0.3756
0.7605	0.2045	0.2055	0.4155
0.7332	0.2268	0.2203	0.4297

Measurement of Solubility and Equilibrium Data. The experimental procedure on the salt effect on LLE described by Eisen and Joffe (1966) was followed in this investigation. The solubility and equilibrium data were measured at 35 °C and 1 atm pressure. The temperature was always maintained within ±0.05 °C of the experimental temperature. All weighings were carried out in a digital balance, with a readability of 0.0001 g. The solubility data of the salt free LLE systems were measured by titrating known masses of a heterogeneous mixture (MIBK + water) against the consolute component, propanoic or butanoic acid. The end point, given by the disappearance of turbidity, was noted. The same procedure was adopted in the salt-containing ternary liquid systems by replacing water with an aqueous salt solution. The salt concentration, w_s, was varied from 0.05 to 0.2, the mass fraction of salt in

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Table 3. Equilibrium Data for the Water (1) + 4-Methyl-2-pentanone (2) + Butanoic Acid (3) System at 35 °C

w_{ij}: mass fraction of component *i* in phase *j*			
aqueous phase (1)		organic phase (2)	
w_{11}	w_{31}	w_{12}	w_{32}
0.9796	0.0044	0.0230	0.0330
0.9677	0.0158	0.0321	0.1499
0.9554	0.0276	0.0495	0.2253
0.9421	0.0404	0.0651	0.3149
0.9296	0.0524	0.0820	0.3850
0.9241	0.0574	0.0930	0.4182
0.8424	0.0676	0.1090	0.4610
0.8770	0.1050	0.1500	0.5400

Table 4. Binary Interaction Parameters Obtained from Infinite Dilution Activity Coefficients

			NRTL parameters ($\alpha = 0.3$)	
system	$\ln \tau_1^\infty$	$\ln \tau_2^\infty$	G_{12}	G_{21}
water (1) + 4-methyl-2-pentanone (2)	2.4310	7.0585	0.1595	0.6463
water (1) + propanoic acid (2)	1.2428	2.3577	0.5068	0.9720
water (1) + butanoic acid (2)	1.6686	3.7470	0.3650	0.8757
4-methyl-2-pentanone (1) + propanoic acid (2)	0.2900	0.2318	1.0623	0.8596
4-methyl-2-pentanone (1) + butanoic acid (2)	0.1969	0.1806	1.0133	0.9300

Table 5. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Propanoic Acid (3) + Sodium Chloride(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0509	0.9278	0.0136	0.0115	0.0235	0.9376	0.0345
	0.9066	0.0176	0.0298	0.0262	0.8652	0.1042
	0.8765	0.0231	0.0585	0.0781	0.7219	0.1910
	0.8525	0.0196	0.0877	0.0817	0.6271	0.2808
	0.8367	0.0198	0.1046	0.1146	0.5376	0.3364
	0.7977	0.0158	0.1404	0.1488	0.4374	0.4086
	0.7539	0.0329	0.1608	0.1880	0.3652	0.4447
0.1048	0.8769	0.0043	0.0098	0.0259	0.9383	0.0358
	0.8320	0.0104	0.0247	0.0243	0.8657	0.1100
	0.8458	0.0087	0.0459	0.0700	0.7218	0.2080
	0.8171	0.0130	0.0658	0.0958	0.6145	0.2896
	0.8105	0.0129	0.0816	0.1228	0.5337	0.3407
	0.7939	0.0084	0.0934	0.1137	0.5024	0.3822
	0.7813	0.0129	0.1015	0.1292	0.4504	0.4172
	0.7609	0.0134	0.1148	0.1486	0.3788	0.4702
0.1651	0.8130	0.0082	0.0182	0.0211	0.8491	0.1250
	0.7979	0.0078	0.0328	0.0475	0.7328	0.2161
	0.7804	0.0065	0.0480	0.0745	0.5993	0.3247
	0.7649	0.0102	0.0593	0.0952	0.5221	0.3796
	0.7567	0.0134	0.0619	0.0994	0.4952	0.4030
	0.7401	0.0144	0.0742	0.1228	0.4081	0.4656
	0.7337	0.0148	0.0774	0.1279	0.3611	0.5076
0.2001	0.7807	0.0073	0.0145	0.0267	0.8467	0.1236
	0.7749	0.0070	0.0270	0.0352	0.7169	0.2349
	0.7485	0.0142	0.0332	0.0710	0.5953	0.3337
	0.7417	0.0100	0.0485	0.0766	0.5132	0.4072
	0.7382	0.0056	0.0531	0.0831	0.4807	0.4340
	0.7343	0.0056	0.0550	0.0865	0.4505	0.4605
	0.7301	0.0058	0.0572	0.0951	0.4212	0.4814

Table 6. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Propanoic Acid (3) + Sodium Nitrate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0514	0.9231	0.0162	0.0125	0.0136	0.9512	0.0289
	0.8924	0.0192	0.0387	0.0641	0.8272	0.1074
	0.8688	0.0215	0.0631	0.0764	0.7436	0.1751
	0.8318	0.0198	0.0997	0.0935	0.6248	0.2737
	0.8009	0.0219	0.1309	0.1107	0.5366	0.3500
	0.7821	0.0249	0.1489	0.1426	0.4690	0.3824
	0.7701	0.0276	0.1587	0.1552	0.4512	0.3868
	0.7525	0.0267	0.1865	0.1719	0.3890	0.4245
0.1019	0.8713	0.0152	0.0123	0.0188	0.9463	0.0349
	0.8542	0.0142	0.0312	0.0338	0.8699	0.0951
	0.8302	0.0156	0.0592	0.0686	0.7370	0.1878
	0.7979	0.0168	0.0847	0.0816	0.6425	0.2688
	0.7880	0.0169	0.0971	0.0956	0.6018	0.2975
	0.7428	0.0225	0.1346	0.1396	0.4815	0.3783
	0.7302	0.0242	0.1441	0.1534	0.4475	0.3971
	0.7009	0.0294	0.1640	0.1753	0.3948	0.4298
0.1525	0.8307	0.0065	0.0097	0.0220	0.9350	0.0411
	0.8112	0.0086	0.0266	0.0424	0.8408	0.1159
	0.7963	0.0099	0.0426	0.0524	0.7611	0.1852
	0.7681	0.0088	0.0647	0.0742	0.6359	0.2899
	0.7517	0.0120	0.0838	0.1167	0.5312	0.3481
	0.7364	0.0130	0.0982	0.1201	0.4787	0.3979
	0.7233	0.0176	0.1065	0.1264	0.4362	0.4326
	0.6933	0.0215	0.1202	0.1612	0.3544	0.4829
0.2022	0.7811	0.0095	0.0091	0.0171	0.9447	0.0379
	0.7644	0.0095	0.0251	0.0529	0.8366	0.1038
	0.7531	0.0017	0.0433	0.0361	0.7719	0.1868
	0.7208	0.0032	0.0710	0.0638	0.6192	0.3086
	0.7166	0.0065	0.0738	0.0760	0.6096	0.3109
	0.6812	0.0094	0.1086	0.0371	0.5394	0.4190
	0.6810	0.0104	0.1153	0.1216	0.4339	0.4356
	0.6521	0.0114	0.1250	0.1455	0.3744	0.4741

the binary aqueous salt solution (grams of salt per grams of binary aqueous salt solution), well below the saturation limit. In the systems containing propanoic acid, addition of a few salts of this study resulted in precipitation beyond a certain salt concentration and hindered the determination of the solubility data. Similarly, in the systems with butanoic acid, precipitation occurred with all salts except for sodium nitrate ($w_s = 0.05$). The solubility data for the ternary systems as well as for the salt-containing systems are available elsewhere (Govindarajan, 1993). To obtain equilibrium data, a heterogeneous mixture of known composition was prepared, agitated for 2 h, and allowed to stand in a separating tube for 4 h to 6 h to attain equilibrium. The layers were separated and weighed; each of the layers was subjected to the determination of acid content by titrating against standard sodium hydroxide (carbondioxide free) solution using phenolphthalein as indicator. These acid concentrations fix the ends of the tie lines on the already determined solubility curve, thereby indicating mass fractions of all the components. The tie line data are given in Tables 2 and 3. In salt-containing systems also, the equilibrium layers were separated and weighed. The concentrations of three of the four components of the aqueous phase were determined: the ketone concentration was determined by converting it into iodoform and titrating against sodium thiosulfate and the acid content as previously described. The salt content was determined by evaporation, keeping the oven temperature around 80 °C. Knowing the mass of the entire aqueous phase and mass of the three components, the mass and hence mass fraction of the fourth component, namely water, was obtained by difference. The mass fractions of the individual components in the organic phase were obtained by a material balance as the quantities of each of the components of the (initial) heterogeneous mixture were known. In systems containing zinc sulfate and ammonium sulfate, the organic phase was subjected to determination for its contents and the aqueous phase contents were determined by a material balance. The estimated relative error in the mass fraction of propanoic acid, butanoic acid, and MIBK was (0.01 to 0.02), and the error in the determination of the salt content was (0.0005 to 0.002).

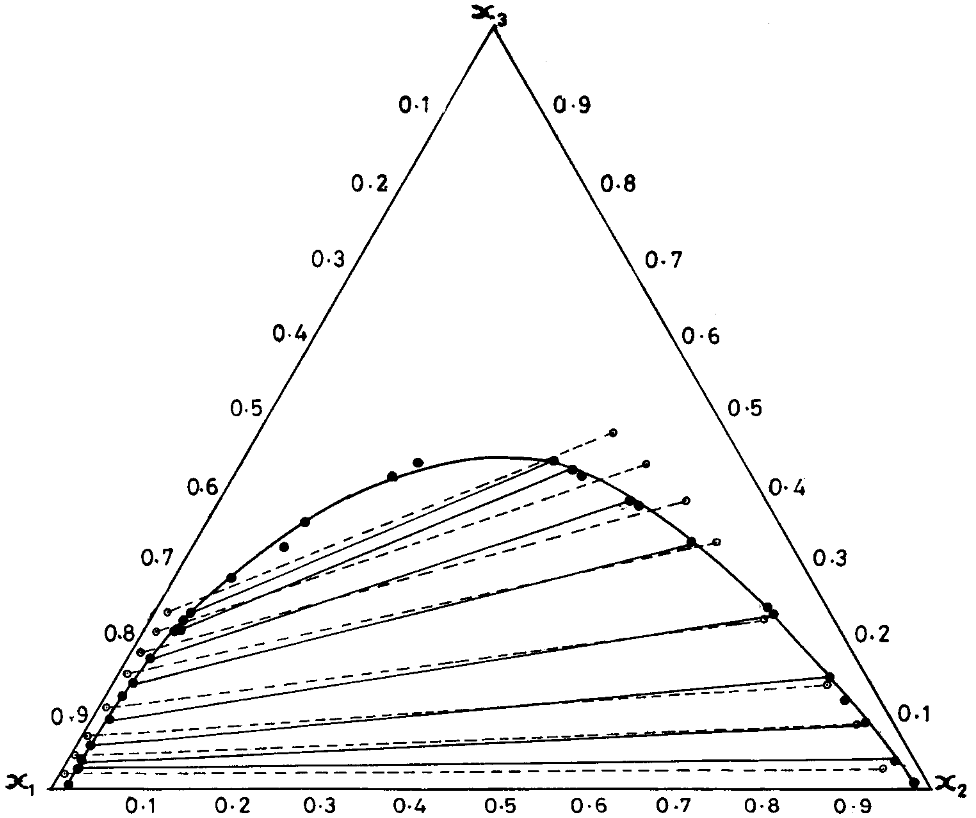

Figure 1. Liquid−liquid equilibrium data for water (1) + 4-methyl-2-pentanone (2) + propanoic acid (3) at 35 °C and experimental and predicted tie lines by fitting the NRTL equation: (●) experimental; (⊙) NRTL.

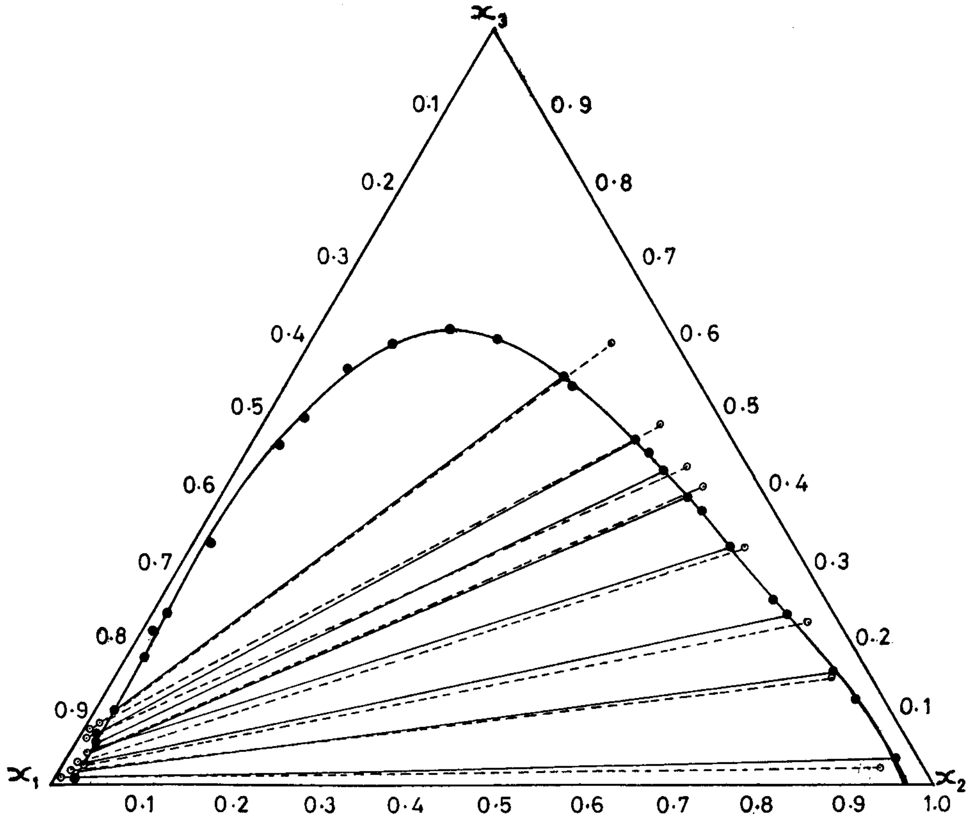

Figure 2. Liquid−liquid equilibrium data for water (1) + 4-methyl-2-pentanone (2) + butanoic acid (3) at 35 °C and experimental and predicted tie lines by fitting the NRTL equation: (●) experimental; (⊙) NRTL.

Results and Discussion

Prediction of LLE Data. The NRTL equation (Renon and Prausnitz, 1968) was used to predict the ternary LLE data of the systems water + MIBK + propanoic or butanoic acid. The constituent binary interaction parameters, listed in Table 4, were obtained by using infinite dilution activity coefficient values. For the partially miscible water + MIBK system, the van Laar constants, characterizing the infinite

Table 7. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Propanoic Acid (3) + Sodium Sulfate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0561	0.9314	0.0077	0.0074	0.0000	0.9753	0.0213
	0.9053	0.0095	0.0352	0.0281	0.8459	0.1182
	0.8793	0.0107	0.0608	0.0596	0.7252	0.2070
	0.8529	0.0129	0.0857	0.0898	0.6156	0.2864
	0.8222	0.0157	0.1077	0.1255	0.5170	0.3558
	0.8002	0.0165	0.1268	0.1507	0.4469	0.4013
	0.7732	0.0173	0.1482	0.1801	0.3710	0.4483
	0.7625	0.0178	0.1554	0.2008	0.3470	0.4516
0.1042	0.8805	0.0058	0.0059	0.0030	0.9740	0.0230
	0.8650	0.0058	0.0257	0.0406	0.8433	0.1161
	0.8487	0.0057	0.0400	0.0610	0.7397	0.1993
	0.8206	0.0058	0.0646	0.0946	0.5991	0.3058
	0.8023	0.0089	0.0800	0.1272	0.5049	0.3672
	0.7833	0.0106	0.0918	0.1471	0.4417	0.4101
	0.7710	0.0114	0.0982	0.1749	0.3793	0.4446
	0.7659	0.0118	0.1023	0.1929	0.3208	0.4789
0.1562	0.8363	0.0010	0.0071	0.0048	0.9500	0.0452
	0.8177	0.0014	0.0251	0.0373	0.7833	0.1794
	0.8116	0.0016	0.0308	0.0451	0.7266	0.2283
	0.7964	0.0025	0.0441	0.0881	0.6073	0.3044
	0.7803	0.0067	0.0514	0.1002	0.5294	0.3699
	0.7662	0.0070	0.0586	0.1254	0.4492	0.4244
	0.7553	0.0074	0.0619	0.1505	0.3881	0.4602
	0.7389	0.0081	0.0644	0.1699	0.3352	0.4935
0.2180	0.7836	0.0018	0.0029	0.0057	0.9693	0.0264
	0.7709	0.0034	0.0136	0.0380	0.8104	0.1516
	0.7623	0.0048	0.0214	0.0692	0.6612	0.2696
	0.7393	0.0050	0.0276	0.0987	0.5733	0.3280
	0.7337	0.0054	0.0312	0.1198	0.4834	0.3968
	0.7178	0.0058	0.0341	0.1341	0.4202	0.4449
	0.7096	0.0062	0.0342	0.1413	0.3661	0.4924
	0.6988	0.0064	0.0342	0.1523	0.3426	0.5045

Table 8. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Propanoic Acid (3) + Zinc Sulfate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0543	0.9308	0.0145	0.0092	0.0101	0.9438	0.0309
	0.8879	0.0143	0.0444	0.0342	0.7891	0.1596
	0.8456	0.0178	0.0828	0.0812	0.5947	0.3024
	0.8204	0.0171	0.1011	0.1047	0.5266	0.3535
	0.8134	0.0202	0.1104	0.1466	0.4679	0.3853
	0.7672	0.0455	0.1286	0.2103	0.3545	0.4323
0.1039	0.8145	0.0694	0.0134	0.1417	0.8003	0.0580
	0.7981	0.0757	0.0234	0.0680	0.8194	0.1126
	0.7629	0.0870	0.0469	0.0728	0.6996	0.2276
	0.7682	0.0563	0.0724	0.1518	0.5362	0.3120
	0.7266	0.0885	0.0771	0.2115	0.4205	0.3670
	0.7059	0.0726	0.1181	0.2186	0.3547	0.4267
0.1381	0.8445	0.0073	0.0113	0.0184	0.9188	0.0628
	0.8362	0.0044	0.0218	0.0385	0.8356	0.1259
	0.8157	0.0057	0.0400	0.0742	0.6924	0.2327
	0.8078	0.0058	0.0442	0.0930	0.6063	0.3007
	0.7893	0.0058	0.0591	0.1216	0.5139	0.3645
	0.7783	0.0059	0.0602	0.1497	0.4337	0.4166
0.2061	0.7841	0.0027	0.0051	0.0463	0.9051	0.0420
	0.7664	0.0041	0.0125	0.0342	0.8429	0.1229
	0.7631	0.0040	0.0233	0.0671	0.7037	0.2292
	0.7528	0.0054	0.0254	0.0977	0.5616	0.3407
	0.7346	0.0053	0.0334	0.1341	0.4653	0.3996
	0.7175	0.0058	0.0356	0.1556	0.4016	0.4406

Table 9. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Propanoic Acid (3) + Ammonium Sulfate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0442	0.9012	0.0097	0.0466	0.0362	0.8759	0.0879
	0.8692	0.0109	0.0769	0.0753	0.7388	0.1859
	0.8455	0.0153	0.0966	0.1121	0.6300	0.2571
	0.8346	0.0118	0.1141	0.1091	0.5939	0.2927
	0.7920	0.0143	0.1490	0.1579	0.4642	0.3779
	0.7616	0.0128	0.1785	0.1868	0.3993	0.4137
	0.7365	0.0217	0.1930	0.2035	0.3599	0.4366
0.0940	0.8605	0.0079	0.0415	0.0622	0.8270	0.1057
	0.8332	0.0105	0.0663	0.0891	0.7049	0.2018
	0.8161	0.0108	0.0846	0.1232	0.5977	0.2791
	0.7650	0.0295	0.1125	0.1550	0.4843	0.3582
	0.7582	0.0133	0.1334	0.1643	0.4370	0.3952
	0.7282	0.0154	0.1535	0.1964	0.3480	0.4524
	0.7153	0.0140	0.1584	0.2129	0.3137	0.4712
0.1574	0.7969	0.0045	0.0474	0.0206	0.7774	0.2020
	0.7610	0.0046	0.0746	0.1134	0.5745	0.3121
	0.7401	0.0069	0.0894	0.1374	0.4904	0.3715
	0.7252	0.0078	0.0975	0.1504	0.4302	0.4194
	0.6982	0.0107	0.1136	0.1748	0.3671	0.4581
	0.6974	0.0115	0.1143	0.1296	0.3335	0.5369
0.2185	0.7440	0.0043	0.0339	0.0647	0.8254	0.1084
	0.7341	0.0043	0.0445	0.0845	0.7074	0.2023
	0.7231	0.0060	0.0512	0.0983	0.5915	0.3024
	0.6994	0.0060	0.0638	0.1280	0.5078	0.3631
	0.6807	0.0065	0.0742	0.1454	0.4272	0.4248
	0.6726	0.0056	0.0798	0.1521	0.3776	0.4680
	0.6412	0.0073	0.0806	0.1610	0.3509	0.4859

dilution activity coefficients, were determined by using the experimentally determined mutual solubility data through the van Laar equations reported by Null (1970). The activity coefficient end values in the water−propanoic acid binary were obtained by using the VLE data of Ito and Yoshida (1963). For the remaining three binaries the Erdos equation (Erdos, 1956) was employed to estimate the activity coefficient end values. The binary interaction parameters were obtained by solving simultaneously the NRTL equations for infinite dilution activity coefficients through the Newton−Raphson technique. In this work, the indirect method was employed to predict the LLE data. The indirect method, commonly known as the isothermal flash calculation enables the determination of tie line ends from a given feed composition in the heterogeneous region and the calculation procedure is similar to the one given in the literature (Null, 1970). Figures 1 and 2 show the experimental and predicted data for the water + 4-methyl + 2-pentanone + propanoic or butanoic acid system at 35 °C, respectively. The F is the absolute mole percentage deviation in mole fraction (x is experimental and $\hat{x}$ is calculated) of component i of the tie line k in phase j.

$$F = 100[\sum^{k}\sum^{i}\sum^{j}(x_{ijk} - \hat{x}_{ijk})^2/6M]^{1/2} \tag{1}$$

ΔD is the mean error in the solute distribution ratio

$$\Delta D = 100\{\sum^{k}/[(D_k - \hat{D}_k)/D_k]^2/M\}^{1/2} \tag{2}$$

where D_k and $\hat{D}_k$ are respectively the experimental and predicted solute distribution ratios for the kth tie line and M is the number of tie lines. The F and ΔD values for the system containing propanoic acid are 3.48 and 15.35, and for the system containing butanoic acid, they are 3.25 and 31.07, respectively. These values of F and ΔD are comparable with those reported by Arce et al. (1993).

Comment on Previous Experimental Works. Two methodologies are found in the literature on the experimental procedure on the salt effect on LLE. In the first approach, a quaternary (three liquid + one salt) was considered as a pseudoternary (two liquid + one aqueous salt solution) system and the experimental procedure

Table 10. Correlation Constants Obtained by the Application of the Modified Campbell Equation (Eq 3) to the Experimental Data of the Water + 4-Methyl-2-pentanone + Propanoic Acid or Butanoic Acid + Salt Systems at 35 °C

solute	salt	a	$10^{-2}b$	r	c	$10^{-2}d$	r
propanoic acid	sodium chloride	0.3160	0.0232	0.9861	0.9621	0.0003	0.0655
	sodium nitrate	0.3188	0.0097	0.8836	0.9636	0.0008	0.2319
	sodium sulfate	0.2616	0.0410	0.9929	0.9418	0.0089	0.9700
	zinc sulfate	0.2377	0.0447	0.9596	0.9092	0.0123	0.8770
	ammonium sulfate	0.2992	0.0217	0.9468	0.9786	0.0074	0.6477
butanoic acid	sodium chloride	0.7876	0.0294	0.9459	0.9361	0.0003	0.0584
	sodium nitrate	0.6965	0.0139	0.9451	0.8842	0.0016	0.4134
	sodium sulfate	0.7771	0.0442	0.9859	0.9519	0.0056	0.6718
	zinc sulfate	0.8089	0.0185	0.8281	0.8984	−0.0029	−0.4859
	ammonium sulfate	1.3183	−0.0136	−0.0560	1.2896	−0.0297	−0.2480

Table 11. Salt Effect Parameter Obtained from the Modified Campbell Constants for the Water + 4-Methyl-2-pentanone + Propanoic Acid or Butanoic Acid + Salt Systems at 35 °C

	k_s values from eq 4 at $w'_{32} = 0.5$				
solute	Na_2SO_4	$ZnSO_4$	NaCl	$(NH_4)_2SO_4$	$NaNO_3$
propanoic acid	5.07	5.04	4.35	2.24	1.66
butanoic acid	6.10	5.13	5.60	8.78	2.26

Table 12. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Butanoic Acid (3) + Sodium Chloride(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0500	0.9305	0.0085	0.0112	0.0231	0.8441	0.1328
	0.9226	0.0088	0.0201	0.0470	0.7071	0.2433
	0.9105	0.0089	0.0292	0.0710	0.5890	0.3400
	0.9022	0.0103	0.0344	0.0961	0.5036	0.4003
	0.8954	0.0103	0.0400	0.1042	0.4500	0.4458
	0.8832	0.0107	0.0487	0.1217	0.3503	0.5280
0.1050	0.8809	0.0054	0.0086	0.0248	0.8254	0.1498
	0.8771	0.0081	0.0139	0.0412	0.7197	0.2315
	0.8657	0.0080	0.0185	0.0653	0.6066	0.3271
	0.8606	0.0082	0.0231	0.0740	0.5154	0.4087
	0.8527	0.0093	0.0266	0.0828	0.4495	0.4667
	0.8482	0.0108	0.0297	0.0950	0.3894	0.5128
	0.8402	0.0097	0.0298	0.0980	0.3552	0.5468
0.1552	0.8351	0.0034	0.0053	0.0242	0.8288	0.1470
	0.8297	0.0037	0.0088	0.0407	0.6989	0.2604
	0.8251	0.0038	0.0120	0.0478	0.5978	0.3544
	0.8184	0.0038	0.0152	0.0652	0.5053	0.4295
	0.8143	0.0019	0.0183	0.0727	0.4462	0.4811
	0.8090	0.0038	0.0191	0.0773	0.3961	0.5266
	0.8041	0.0055	0.0203	0.0868	0.3714	0.5418
0.2078	0.7805	0.0000	0.0066	0.0274	0.6949	0.2777
	0.7718	0.0018	0.0083	0.0402	0.6031	0.3567
	0.7696	0.0019	0.0103	0.0456	0.5189	0.4355
	0.7647	0.0038	0.0123	0.0569	0.4598	0.4833
	0.7584	0.0073	0.0102	0.0491	0.5654	0.3855
	0.7557	0.0037	0.0140	0.0712	0.3546	0.5742

Table 13. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Butanoic Acid (3) + Sodium Nitrate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component *i* in phase *j*					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	2_2	w_{32}
0.0525	0.9147	0.0184	0.0144	0.0459	0.8190	0.1351
	0.9066	0.0156	0.0251	0.0640	0.6954	0.2403
	0.9012	0.0078	0.0357	0.0796	0.5927	0.3267
	0.8979	0.0125	0.0447	0.0880	0.5005	0.4023
	0.8797	0.0122	0.0520	0.1134	0.4494	0.4372
	0.8769	0.0081	0.0590	0.1128	0.4008	0.4853
	0.8640	0.0121	0.0640	0.1326	0.3625	0.5049
0.1047	0.8697	0.0139	0.0116	0.0435	0.8254	0.1311
	0.8624	0.0157	0.0202	0.0574	0.7043	0.2327
	0.8514	0.0125	0.0284	0.0786	0.6000	0.3214
	0.8405	0.0121	0.0381	0.0894	0.5064	0.4037
	0.8302	0.0143	0.0449	0.1021	0.4312	0.4657
	0.8282	0.0120	0.0462	0.1059	0.4206	0.4726
	0.8195	0.0127	0.0511	0.1133	0.3643	0.5224
0.1537	0.8174	0.0074	0.0186	0.0512	0.6918	0.2570
	0.8053	0.0074	0.0246	0.0669	0.5879	0.3452
	0.7960	0.0101	0.0321	0.0874	0.4906	0.4220
	0.7969	0.0045	0.0352	0.0900	0.4544	0.4551
	0.7924	0.0045	0.0384	0.0947	0.4075	0.4965
	0.7844	0.0032	0.0418	0.1039	0.3669	0.5284
0.2070	0.7794	0.0049	0.0076	0.0218	0.8476	0.1306
	0.7736	0.0032	0.0144	0.0406	0.7243	0.2351
	0.7532	0.0048	0.0258	0.0790	0.5047	0.4161
	0.7460	0.0064	0.0296	0.0827	0.4482	0.4685
	0.7428	0.0050	0.0308	0.0877	0.4174	0.4934
	0.7241	0.0062	0.0319	0.0811	0.3798	0.5313

applicable to a true ternary (three liquid) system was merely followed. That is, solubility data were measured first and then equilibrium data were determined by measuring one of the constituent's concentration in each of the two conjugate phases and by fixing the tie line end points on the already determined solubility curve. This procedure is erroneous because of two reasons: (i) According to the phase rule, a three-component two-phase system is univarient at a given temperature (T) and pressure (P), enabling one to fix the ends of the tie lines by analyzing a single component. That is, at a given T and P there exists only one solubility curve. However, a four-component two-phase system can have many solubility envelopes (Nagata, 1986) and it is a bivarient system. Consideration of a quaternary as a pseudoternary is therefore wrong, as the distribution of salt is different in different phases and a single pseudosolubility curve cannot exist. (ii) Moreover, precipitation of salt in the organic phase region normally hinders the complete determination of a pseudosolubility curve; in some instances a type I system transforms into a type II system upon addition of salt. Further comments on this erroneous practice were reported elsewhere (Ruiz and Marcilla Gomis, 1993; Govindarajan and Sabarathinam, 1995). In the second approach, equilibrium data alone were determined by measuring the concentration of all four components in one phase and calculating their concentrations in the other phase by a material balance (Eisen and Joffe, 1966). The latter procedure, a correct one, was followed in this work.

Water + 4-Methyl-2-pentanone + Propanoic Acid + Salt Systems at 35 °C. The distribution data of the system in the presence of sodium chloride are presented in Table 5. The distribution of propanoic acid into the organic phase increases with the increase of salt concentration. This trend is also observed with other salts, namely, sodium nitrate, sodium sulfate, zinc sulfate, and ammonium sulfate whose distribution results are given in Tables 6−9. The values in Tables 5−9 indicate that most of the salt remains only in the aqueous phase. The distribution data of these systems were correlated by the modified Campbell equation (Govindarajan and Sabarathinam, 1995):

$$\log(w'_{32}) = (a + bw_s) + (c + dw_s)\log(w'_{31}) \qquad (3)$$

Table 14. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Butanoic Acid (3) + Sodium Sulfate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component i in phase j					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0521	0.9367	0.0073	0.0044	0.0148	0.9405	0.0440
	0.9255	0.0108	0.0120	0.0382	0.8179	0.1430
	0.9121	0.0141	0.0203	0.0665	0.6908	0.2427
	0.9017	0.0114	0.0307	0.0867	0.5556	0.3577
	0.8976	0.0109	0.0359	0.0988	0.4912	0.4100
	0.8946	0.0100	0.0400	0.1060	0.4538	0.4394
	0.8918	0.0074	0.0435	0.1150	0.4057	0.4787
	0.8821	0.0068	0.0491	0.1365	0.3305	0.5327
0.1027	0.8845	0.0081	0.0032	0.0243	0.9240	0.0517
	0.8767	0.0079	0.0099	0.0489	0.7914	0.1597
	0.8727	0.0066	0.0143	0.0626	0.6821	0.2553
	0.8655	0.0016	0.0191	0.0784	0.5738	0.3478
	0.8612	0.0047	0.0235	0.0833	0.5055	0.4112
	0.8585	0.0034	0.0262	0.0978	0.4450	0.4572
	0.8515	0.0049	0.0285	0.1110	0.4007	0.4883
	0.8426	0.0047	0.0298	0.1263	0.3463	0.5274
0.1548	0.8343	0.0031	0.0047	0.0269	0.8498	0.1233
	0.8276	0.0045	0.0091	0.0573	0.6961	0.2458
	0.8116	0.0047	0.0125	0.0803	0.5473	0.3724
	0.8125	0.0059	0.0144	0.0935	0.4787	0.4276
	0.8115	0.0034	0.0162	0.0997	0.4251	0.4730
	0.8041	0.0046	0.0176	0.1042	0.3803	0.5149
	0.7929	0.0046	0.0183	0.1202	0.3305	0.5493
0.2044	0.7807	0.0043	0.0054	0.0568	0.6919	0.2500
	0.7626	0.0042	0.0060	0.0706	0.5626	0.3668
	0.7670	0.0073	0.0083	0.0851	0.4930	0.4202
	0.7624	0.0045	0.0097	0.0905	0.4299	0.4796
	0.7553	0.0075	0.0103	0.0929	0.3817	0.5254
	0.7316	0.0098	0.0106	0.1101	0.3442	0.5457

Table 15. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Butanoic Acid (3) + Zinc Sulfate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component i in phase j					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0542	0.9254	0.0130	0.0074	0.0259	0.8329	0.1412
	0.9172	0.0145	0.0139	0.0491	0.6830	0.2679
	0.9094	0.0142	0.0180	0.0621	0.5644	0.3735
	0.9050	0.0179	0.0195	0.0950	0.4953	0.4093
	0.8898	0.0140	0.0344	0.1177	0.3876	0.4914
0.1058	0.8797	0.0063	0.0089	0.0327	0.8123	0.1528
	0.8726	0.0080	0.0122	0.0595	0.6737	0.2649
	0.8617	0.0064	0.0184	0.0844	0.5587	0.3569
	0.8737	0.0085	0.0208	0.1009	0.4885	0.4090
	0.8528	0.0048	0.0275	0.1069	0.4303	0.4611
	0.8436	0.0062	0.0301	0.1212	0.3707	0.5066
	0.8418	0.0032	0.0304	0.1261	0.3330	0.5398
0.1535	0.8402	0.0049	0.0050	0.0298	0.8173	0.1434
	0.8201	0.0046	0.0128	0.0802	0.5600	0.3598
	0.8066	0.0122	0.0132	0.0988	0.4700	0.4312
	0.8000	0.0109	0.0174	0.1142	0.4195	0.4663
	0.7887	0.0120	0.0219	0.1247	0.3696	0.5057
	0.7745	0.0118	0.0166	0.1279	0.3309	0.5412
0.1969	0.7944	0.0106	0.0018	0.0153	0.9307	0.0471
	0.7859	0.0088	0.0037	0.0614	0.6669	0.2684
	0.7697	0.0086	0.0065	0.0786	0.5601	0.3613
	0.7546	0.0085	0.0231	0.1022	0.4702	0.4276
	0.7320	0.0072	0.0140	0.1230	0.3360	0.5410

Table 16. Equilibrium Data for the System Water (1) + 4-Methyl-2-pentanone (2) + Butanoic Acid (3) + Ammonium Sulfate(s) at 35 °C

salt concn in the initial salt soln (w_s)	mass fraction of component i in phase j					
	aqueous phase (1)			organic phase (2)		
	w_{11}	w_{21}	w_{31}	w_{12}	w_{22}	w_{32}
0.0504	0.9339	0.0093	0.0069	0.0163	0.9415	0.0416
	0.9204	0.0099	0.0167	0.0517	0.8227	0.1251
	0.9108	0.0125	0.0261	0.0692	0.6842	0.2457
	0.9012	0.0096	0.0376	0.0893	0.5770	0.3330
	0.8944	0.0071	0.0451	0.1122	0.4976	0.3900
	0.8847	0.0075	0.0492	0.1175	0.4336	0.4485
	0.8833	0.0073	0.0543	0.1246	0.3778	0.4972
	0.8751	0.0073	0.0589	0.1386	0.3419	0.5190
0.1043	0.8683	0.0061	0.0133	0.0483	0.8116	0.1401
	0.8663	0.0061	0.0219	0.0633	0.6834	0.2533
	0.8544	0.0044	0.0308	0.0889	0.5577	0.3534
	0.8442	0.0041	0.0374	0.1056	0.4941	0.4003
	0.8206	0.0156	0.0409	0.1192	0.4154	0.4654
	0.8190	0.0170	0.0458	0.1279	0.3706	0.5015
	0.8129	0.0189	0.0458	0.1300	0.3353	0.5347
0.1561	0.8340	0.0059	0.0029	0.0249	0.9288	0.0463
	0.8288	0.0059	0.0067	0.0352	0.8025	0.1623
	0.8227	0.0063	0.0069	0.0687	0.5559	0.3754
	0.8139	0.0103	0.0071	0.0800	0.4812	0.4388
	0.8136	0.0087	0.0077	0.0835	0.4288	0.4877
0.2041	0.7697	0.0041	0.0072	0.0823	0.4990	0.4187
	0.7657	0.0038	0.0071	0.0769	0.4154	0.5077
	0.7595	0.0071	0.0046	0.0901	0.3641	0.5458
	0.7551	0.0058	0.0049	0.0944	0.3431	0.5625

where $w'_{32} = w_{32}/(w_{12} + w_{22} + w_{32})$ and $w'_{31} = w_{31}/(w_{11} + w_{21} + w_{31})$ are mass fractions on a salt free basis. The "salt free basis" should not be mistaken for "pseudoternary"; while the salt free basis refers to the basis of a calculation procedure and utilizes the actual quaternary system's (with salt) data, the pseudoternary treats a quaternary as a (pseudo)ternary system on certain assumptions.

In eq 3, a, b, c, and d are constants which depend upon the nature of the system components, including that of the salt and temperature, but are independent of salt concentration. The constants a, b, c, and d computed by the method of least squares along with the correlation coefficient, r, are presented in Table 10. The average absolute deviation in the predicted extract phase solute concentrations using the modified Campbell equation is 0.0204. The effectiveness of a salt in bringing the nonelectrolyte out of a solution is quantitatively measured by a parameter, popularly known as the salt effect parameter. In other words, the salt effect parameter, k_s, is a measure of the effectiveness of salt in salting out the nonelectrolytes from their solution. Following Govindarajan and Sabarathinam (1995), the salting out parameter, k_s, has been related to the constants of eq 3:

$$k_s = A(1 - w_s)/(c + dw_s) \tag{4}$$

where

$$A = b - (ad/c) + (d/c)\log(w'_{32})$$

The values of k_s at $w_s = 0.2$ are given in Table 11. Thus the order of effectiveness of salts is

$$Na_2SO_4 > ZnSO_4 > NaCl > (NH_4)_2SO_4 > NaNO_3$$

Water + 4-Methyl-2-pentanone + Butanoic Acid + Salt Systems at 35 °C. The addition of salt significantly alters the distribution coefficient, as butanoic acid prefers the organic phase only even in the absence of salt. The distribution data of the system in the presence of sodium chloride, sodium nitrate, sodium sulfate, zinc sulfate, and ammonium sulfate are shown in Tables 12−16, respectively. The data in Tables 12−16 also show that most of the initial salt remains in the aqueous phase. Even the least effective sodium nitrate has a profound effect in extracting butanoic acid. The correlation constants a, b, c, and d of the modified Campbell correlation for the five salts are also provided in Table 10, and the values of salting out parameter at $w_s = 0.2$ are given in Table 11. When the constants are used to predict the extract phase solute concentrations, the average absolute deviation is found to be 0.0529. The order of effectiveness of salts is

$$(NH_4)_2SO_4 > Na_2SO_4 > NaCl > ZnSO_4 > NaNO_3$$

Conclusions

The experimentally determined liquid−liquid equilibria of the systems water + 4-methyl-2-pentanone + propanoic acid or butanoic acid were predicted using the NRTL equation.

Among the five salts tried, sodium nitrate is found to be least effective in salting out the fatty acid. As the number of carbon atoms in the fatty acid increases, more ionic species are required to salt out the fatty acid, and hence ammonium sulfate is more effective in extracting butanoic acid rather than propanoic acid.

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