Isothermal Vapor−Liquid Equilibrium Data for the Systems 1,4-Dioxane + Water + Tetrabutylammonium Nitrate and Acetonitrile + Water + Tetrabutylammonium Bromide

Alexander V. Kurzin,* Andrey N. Evdokimov, Gennadiy M. Poltoratskiy, Andrew Yu. Platonov, Vladimir E. Gusev, and Yulia M. Golubeva

Faculty of Chemical Technology, Saint-Petersburg State Technological University of Plant Polymers,
4, Ivana Chernykh, Saint-Petersburg, 198095 Russia

Isothermal vapor−liquid equilibrium data for the system 1,4-dioxane + water + tetrabutylammonium nitrate at 11 constant salt molalities ((0.1, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, and 4.00) mol·kg^{-1}) have been measured with the help of gas chromatography at (288, 298, and 308) K. Isothermal vapor−liquid equilibrium data for the system acetonitrile + water + tetrabutylammonium bromide at 5 constant salt molalities ((0.20, 0.40, 0.60, 0.80, and 1.00) mol·kg^{-1}) have also been measured with the help of gas chromatography at (298 and 323) K. The experimental data for these systems were correlated using the electrolyte nonrandom two-liquid model.

Introduction

Systems of mixed solvent electrolyte solutions, consisting of water, a nonelectrolyte, and a salt, have been the subject of many studies due both to their potential application to industrial unit operations[1] and to the frequent occurrence of these mixtures in natural systems. Electrolyte solutions have been the subject of a large number of experimental and theoretical studies aimed at prediction and correlation of the "salt effect" and its impact on fractional distillation.[1]

Owing to their complexity and the difficulty of predicting their thermodynamic properties, electrolyte solutions continue to represent an important area of theoretical interest as well. When the electrolyte species being studied contain apolar regions, such as hydrocarbon chains, their properties of solution show interesting behavior which can be attributed to a complex balance between long-ranged Coulombic and short-ranged intermolecular forces of the aqueous environment, and possibly conformational changes in the electrolyte.

The tetraalkylammonium salts provide a convenient model system in which to study the interplay of these forces. Correlation and prediction of the physical properties of these systems have proven to be difficult due to the complexity of the molecular interactions. Some years ago, there were a number of experimental studies of the vapor−liquid equilibrium (VLE) behavior of ternary solutions consisting of tetraalkylammonium salts in water + organic solvent mixtures.[2−7]

Several correlative and predictive models based on the local composition or group contribution concept have been proposed to calculate the VLE of systems formed by mixed solvents and electrolytes.

Slusher et al.[5] studied the vapor−liquid equilibrium behavior of ternary solutions consisting of either tetrapropylammonium bromide or tetrabutylammonium bromide in either aqueous 1-propanol or aqueous 2-propanol and correlated the experimental data using the electrolyte nonrandom two-liquid (NRTL) model.[8]

The aim of this work is to determine the effect of tetrabutylammonium salts on the vapor−liquid equilibrium of the 1,4-dioxane + water and acetonitrile + water systems at different conditions with the help of gas chromatography. Isothermal vapor−liquid equilibrium data for the system 1,4-dioxane + water + tetrabutylammonium nitrate at 11 constant salt molalities ((0.1, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, and 4.00) mol·kg^{-1}) have been measured at (288, 298, and 308) K. Isothermal vapor−liquid equilibrium data for the system acetonitrile + water + tetrabutylammonium bromide at 5 constant salt molalities ((0.20, 0.40, 0.60, 0.80, and 1.00) mol·kg^{-1}) have been measured at (298 and 323) K. The experimental data presented in this work were correlated using the electrolyte NRTL model of Mock et al.[8] Several new interaction parameters for this model were obtained and are presented in this work.

Experimental Section

Materials. 1,4-Dioxane (>99.8 mass %) and acetonitrile (AMD CHROMASOLV, ≥99.9 mass %) from Fluka were dehydrated and stored above 3 Å molecular sieves. Distilled and deionized water was used. Tetra-*n*-butylammonium bromide (TBAB) and tetra-*n*-butylammonium nitrate (TBAN) were obtained from Fluka (electrochemical grade, ≥99.0 mass %) and were previously dried at 75 °C in a vacuum oven until a constant mass was reached.

Procedure. Mixtures consisting of 1,4-dioxane, H_2O, and tetrabutylammonium nitrate or acetonitrile, H_2O, and tetrabutylammonium bromide were prepared gravimetrically with an analytical balance with an accuracy of ±0.1 mg. For each experiment, about 10 cm^3 of sample was charged into the 20 cm^3 heated sample vial. After the vial was closed by means of a special lid equipped with a washer, it was brought to the required temperature in a thermostatic cell that was controlled to within ±0.05 K. The mixtures were continuously agitated for 10 h at the target temperature ((288, 298, 308, and 323) K).

---

* To whom correspondence should be addressed. E-mail: zakora@mail.ru.

10.1021/je0301287 CCC: $27.50

Table 1. Vapor−Liquid Equilibrium Data for the System 1,4-Dioxane (1) + Water (2) + Tetrabutylammonium Nitrate (3)

$T = 288$ K				$T = 298$ K				$T = 308$ K			
x_1' [a]	y_1	γ_1	γ_2	x_1' [a]	y_1	γ_1	γ_2	x_1' [a]	y_1	γ_1	γ_2
					$m = 0.100$ mol·kg^{-1}						
0.0503	0.2740	4.4430	1.0621	0.0503	0.2641	4.5024	1.0263	0.0503	0.2514	4.5008	1.0116
0.1002	0.4316	4.0210	1.0132	0.1002	0.4273	4.3109	0.9978	0.1002	0.3906	4.1700	1.0367
0.1710	0.5144	3.1056	1.0277	0.1710	0.5085	3.3235	1.0253	0.1710	0.4974	3.5118	1.0410
0.5007	0.6287	1.5680	1.5883	0.5007	0.6167	1.5880	1.5380	0.5007	0.6103	1.6200	1.4820
0.7005	0.6747	1.2271	2.3756	0.7005	0.6647	1.2229	2.2433	0.7005	0.6487	1.2414	2.2503
0.9004	0.7940	1.0212	4.0834	0.9004	0.7674	1.0389	4.4101	0.9004	0.7410	1.0089	4.5404
					$m = 0.250$ mol·kg^{-1}						
0.0503	0.2816	4.6451	1.0610	0.0503	0.2708	4.6102	1.0274	0.0503	0.2569	4.5800	1.0011
0.1002	0.4364	4.0904	1.0055	0.1002	0.4349	4.3600	0.9822	0.1002	0.3964	4.2110	1.0200
0.1710	0.5186	3.1114	1.0144	0.1710	0.5166	3.3529	1.0145	0.1710	0.5035	3.5176	1.0193
0.5007	0.6315	1.5563	1.5564	0.5007	0.6204	1.5709	1.4960	0.5007	0.6154	1.6200	1.4500
0.7005	0.6787	1.2185	2.3102	0.7005	0.6675	1.2114	2.1933	0.7005	0.6511	1.2371	2.2133
0.9004	0.7942	1.0155	4.0702	0.9004	0.7640	1.0311	4.4502	0.9004	0.7370	1.0023	4.6007
					$m = 0.500$ mol·kg^{-1}						
0.0503	0.2904	4.7680	1.0473	0.0503	0.2786	4.6810	0.9958	0.0503	0.2623	4.6412	0.9853
0.1002	0.4426	4.1451	0.9922	0.1002	0.4405	4.3704	0.9633	0.1002	0.4032	4.2400	0.9989
0.1710	0.5281	3.1111	0.9759	0.1710	0.5226	3.3353	0.9723	0.1710	0.5107	3.5235	0.9928
0.5007	0.6363	1.5383	1.5083	0.5007	0.6230	1.5540	1.4608	0.5007	0.6210	1.6040	1.4010
0.7005	0.6837	1.2071	2.2367	0.7005	0.6724	1.2057	2.1333	0.7005	0.6517	1.2202	2.1833
0.9004	0.7920	1.0055	4.0680	0.9004	0.7615	1.0211	4.4912	0.9004	0.7326	0.9856	4.6501
					$m = 0.750$ mol·kg^{-1}						
0.0503	0.2960	4.8465	1.0347	0.0503	0.2855	4.7611	0.9768	0.0503	0.2677	4.6620	0.9611
0.1002	0.4504	4.1524	0.9656	0.1002	0.4463	4.3703	0.9378	0.1002	0.4094	4.1400	0.9767
0.1710	0.5379	3.1058	0.9385	0.1710	0.5315	3.3588	0.9434	0.1710	0.5205	3.5529	0.9614
0.5007	0.6417	1.5345	1.4783	0.5007	0.6288	1.5300	1.4080	0.5007	0.6265	1.5860	1.3440
0.7005	0.6883	1.2021	2.1733	0.7005	0.6753	1.1886	2.0767	0.7005	0.6523	1.2014	2.1400
0.9004	0.7893	0.9944	4.0910	0.9004	0.7590	1.0044	4.4607	0.9004	0.7239	0.9767	4.6700
					$m = 1.000$ mol·kg^{-1}						
0.0503	0.3044	4.9326	1.0105	0.0503	0.2904	4.8220	0.9653	0.0503	0.2710	4.6403	0.9516
0.1002	0.4596	4.1907	0.9378	0.1002	0.4516	4.3504	0.9133	0.1002	0.4144	4.0800	0.9556
0.1710	0.5467	3.1325	0.9024	0.1710	0.5358	3.3294	0.9217	0.1710	0.5246	3.5471	0.9446
0.5007	0.6449	1.5187	1.4361	0.5007	0.6297	1.5020	1.3760	0.5007	0.6275	1.5700	1.3360
0.7005	0.6925	1.1928	2.1254	0.7005	0.6753	1.1686	2.0300	0.7005	0.6497	1.1829	2.1367
0.9004	0.7864	0.9866	4.1365	0.9004	0.7555	0.9889	4.4909	0.9004	0.7259	0.9644	4.7101
					$m = 1.500$ mol·kg^{-1}						
0.0503	0.3183	5.0432	0.9726	0.0503	0.2971	4.9002	0.9474	0.0503	0.2802	4.7600	0.9221
0.1002	0.4763	4.2108	0.8844	0.1002	0.4598	4.2800	0.8711	0.1002	0.4164	3.9906	0.9233
0.1710	0.5584	3.0223	0.8385	0.1710	0.5489	3.2941	0.8651	0.1710	0.5299	3.5353	0.9217
0.5007	0.6516	1.4923	1.3681	0.5007	0.6307	1.4540	1.3280	0.5007	0.6227	1.5200	1.3220
0.7005	0.6943	1.1628	2.0467	0.7005	0.6740	1.1300	1.9809	0.7005	0.6452	1.1500	2.1133
0.9004	0.7814	0.9711	4.1920	0.9004	0.7480	0.9589	4.5214	0.9004	0.7186	0.9389	4.7506
					$m = 2.000$ mol·kg^{-1}						
0.0503	0.3336	5.1610	0.9326	0.0503	0.3021	4.9220	0.9316	0.0503	0.2884	4.8612	0.9053
0.1002	0.4844	4.1709	0.8456	0.1002	0.4661	4.2090	0.8322	0.1002	0.4187	4.2020	0.9022
0.1710	0.5647	2.9823	0.8072	0.1710	0.5533	3.2294	0.8301	0.1710	0.5274	3.4706	0.9133
0.5007	0.6534	1.4583	1.3264	0.5007	0.6277	1.3960	1.2920	0.5007	0.6167	1.4780	1.3180
0.7005	0.6906	1.1285	2.0233	0.7005	0.6691	1.0943	1.9633	0.7005	0.6396	1.1157	2.1067
0.9004	0.7774	0.9522	4.2134	0.9004	0.7374	1.0344	4.6101	0.9004	0.7093	0.9144	4.8301
					$m = 2.500$ mol·kg^{-1}						
0.0503	0.3423	5.2018	0.9008	0.0503	0.3086	4.9603	0.9116	0.0503	0.2957	4.9400	0.8905
0.1002	0.4920	4.1354	0.8111	0.1002	0.4685	4.1200	0.8089	0.1002	0.4193	4.1204	0.8806
0.1710	0.5705	2.9176	0.7710	0.1710	0.5506	3.1059	0.8096	0.1710	0.5248	3.3882	0.9036
0.5007	0.6527	1.4282	1.3045	0.5007	0.6227	1.3480	1.2740	0.5007	0.6106	1.4380	1.3160
0.7005	0.6866	1.0942	1.9933	0.7005	0.6634	1.0671	1.9667	0.7005	0.6320	1.0871	2.1133
0.9004	0.7717	0.9289	4.2504	0.9004	0.7253	1.0044	4.7411	0.9004	0.6985	0.8833	4.9207
					$m = 3.000$ mol·kg^{-1}						
0.0503	0.3497	5.2168	0.8726	0.0503	0.3126	4.9801	0.8968	0.0503	0.3030	5.0417	0.8737
0.1002	0.5014	4.1745	0.7767	0.1002	0.4695	4.0321	0.7889	0.1002	0.4225	3.9403	0.8578
0.1710	0.5723	2.8352	0.7421	0.1710	0.5485	3.0059	0.7880	0.1710	0.5167	3.2824	0.9024
0.5007	0.6502	1.3922	1.2816	0.5007	0.6164	1.3010	1.2580	0.5007	0.6055	1.4080	1.3160
0.7005	0.6831	1.0712	1.9833	0.7005	0.6585	1.0429	1.9667	0.7005	0.6259	1.0586	2.1233
0.9004	0.7640	0.9044	4.3006	0.9004	0.7139	0.8611	4.8505	0.9004	0.6853	0.8556	5.0701
					$m = 3.500$ mol·kg^{-1}						
0.0503	0.3547	5.1812	0.8515	0.0503	0.3143	4.9602	0.9189	0.0503	0.2986	4.9204	0.8747
0.1002	0.5072	4.0369	0.7378	0.1002	0.4704	3.9500	0.7701	0.1002	0.4184	3.8300	0.8478
0.1710	0.5747	2.7176	0.7072	0.1710	0.5453	2.8941	0.7687	0.1710	0.5125	3.1882	0.8904
0.5007	0.6481	1.3527	1.2564	0.5007	0.6128	1.2660	1.2480	0.5007	0.5987	1.3720	1.3200
0.7005	0.6781	1.0485	1.9867	0.7005	0.6537	1.0229	1.9733	0.7005	0.6204	1.0386	2.1267
0.9004	0.7566	0.8833	4.3917	0.9004	0.7056	0.8411	4.9209	0.9004	0.6730	0.8310	5.1902
					$m = 4.000$ mol·kg^{-1}						
0.0503	0.3611	5.2210	0.8315	0.0503	0.3164	4.9420	0.8747	0.0503	0.2964	4.8600	0.8705
0.1002	0.5143	3.9619	0.7214	0.1002	0.4695	3.8800	0.7589	0.1002	0.4160	3.7320	0.8333
0.1710	0.5725	2.6529	0.6951	0.1710	0.5417	2.8059	0.7566	0.1710	0.4971	3.0353	0.9090
0.5007	0.6456	1.3123	1.2360	0.5007	0.6065	1.2320	1.2440	0.5007	0.5923	1.3380	1.3205
0.7005	0.6727	1.0157	1.9801	0.7005	0.6470	1.0014	1.9833	0.7005	0.6148	1.0171	2.1367
0.9004	0.7474	0.8622	4.5201	0.9004	0.6983	0.8267	5.0013	0.9004	0.6667	0.8111	5.2303

[a] Liquid phase mole fraction on a salt-free basis.

Table 2. Vapor−Liquid Equilibrium Data for the System Acetonitrile (1) + Water (2) + Tetrabutylammonium Bromide (3)

$T = 298$ K								$T = 323$ K							
x_1' [a]	y_1	γ_1	γ_2	x_1' [a]	y_1	γ_1	γ_2	x_1' [a]	y_1	γ_1	γ_2	x_1' [a]	y_1	γ_1	γ_2
$m = 0.200$ mol·kg^{-1}															
0.0207	0.2937	5.1554	0.9259	0.4987	0.7737	1.6320	1.7467	0.0207	0.3199	6.5003	0.8756	0.4987	0.7241	1.5510	1.2451
0.0514	0.4951	5.3915	1.0591	0.6546	0.7820	1.3141	2.4899	0.0514	0.4455	5.6884	0.8381	0.6546	0.7379	1.3010	1.8489
0.1008	0.6068	4.1871	1.1032	0.7531	0.7903	1.1356	3.3088	0.1008	0.6027	4.2151	0.8330	0.7531	0.7572	1.1635	2.5429
0.2011	0.6993	3.2863	1.2933	0.8496	0.8648	1.1183	3.6265	0.2011	0.6744	2.9305	0.8650	0.8496	0.8606	1.0814	2.6302
0.2968	0.7186	2.3621	1.4512	0.9503	0.9379	1.0332	4.7567	0.2968	0.6896	2.1129	0.9736	0.9503	0.9324	1.0144	3.5026
0.4024	0.7503	1.9365	1.5726					0.4024	0.7089	1.7536	1.0681				
$m = 0.400$ mol·kg^{-1}															
0.0207	0.2441	4.054227	0.9378	0.4987	0.7558	1.5321	1.8117	0.0207	0.2689	4.8651	0.8441	0.4987	0.6744	1.4265	1.2652
0.0514	0.4193	4.0056	1.0689	0.6546	0.7641	1.2377	2.5977	0.0514	0.3848	4.3254	0.8657	0.6546	0.6924	1.2126	1.9089
0.1008	0.5586	3.4422	1.1066	0.7531	0.7765	1.0918	3.4503	0.1008	0.5337	3.3233	0.8011	0.7531	0.7172	1.1005	2.6087
0.2011	0.6703	2.8575	1.2862	0.8496	0.8441	1.0678	4.0906	0.2011	0.6248	2.4064	0.8124	0.8496	0.8468	1.0116	2.9064
0.2968	0.6924	2.0942	1.4597	0.9503	0.9144	0.9921	6.4538	0.2968	0.6439	1.7856	0.9335	0.9503	0.9186	0.9492	4.6312
0.4024	0.7268	1.7546	1.6090					0.4024	0.6565	1.5550	1.0695				
$m = 0.600$ mol·kg^{-1}															
0.0207	0.2248	3.4833	0.8973	0.4987	0.7351	1.4197	1.8723	0.0207	0.2179	4.2167	0.8147	0.4987	0.6248	1.3056	1.2914
0.0514	0.3696	3.1389	1.0314	0.6546	0.7475	1.1538	2.6489	0.0514	0.3365	3.5748	0.8810	0.6546	0.6468	1.1257	1.9384
0.1008	0.5048	2.8174	1.1242	0.7531	0.7586	1.0449	3.6517	0.1008	0.4882	2.7665	0.8279	0.7531	0.6799	1.0245	2.6850
0.2011	0.6206	2.3696	1.3254	0.8496	0.8193	1.0111	4.6263	0.2011	0.5724	1.9281	0.8088	0.8496	0.8317	0.9476	3.2522
0.2968	0.6606	1.8323	1.4765	0.9503	0.8924	0.9524	7.9874	0.2968	0.5889	1.5424	0.9322	0.9503	0.9020	0.9014	5.6698
0.4024	0.6924	1.5617	1.6933					0.4024	0.6068	1.3696	1.1138				
$m = 0.800$ mol·kg^{-1}															
0.0207	0.1944	2.9129	0.9014	0.4987	0.7199	1.3065	1.8603	0.0207	0.1627	3.1347	0.7276	0.4987	0.5779	1.2069	1.2888
0.0514	0.3186	2.4655	1.0160	0.6546	0.7337	1.0900	2.6887	0.0514	0.2965	2.8198	0.8715	0.6546	0.6013	1.0586	1.9586
0.1008	0.4662	2.2986	1.0706	0.7531	0.7475	1.0073	3.7361	0.1008	0.4537	2.3226	0.8113	0.7531	0.6400	0.9682	2.6931
0.2011	0.5931	2.0104	1.2624	0.8496	0.8013	0.9649	4.9617	0.2011	0.5241	1.7555	0.8267	0.8496	0.8165	0.8879	3.4246
0.2968	0.6275	1.6044	1.4939	0.9503	0.8772	0.9222	8.9777	0.2968	0.5420	1.3303	0.9290	0.9503	0.8910	0.8397	6.1310
0.4024	0.6772	1.3971	1.6251					0.4024	0.5544	1.2801	1.1168				
$m = 1.000$ mol·kg^{-1}															
0.0207	0.1558	2.1880	0.8853	0.4987	0.6993	1.2115	1.9073	0.0207	0.1337	2.3295	0.7073	0.4987	0.5310	1.1148	1.3163
0.0514	0.2537	1.8248	1.0339	0.6546	0.7172	1.0276	2.7546	0.0514	0.2648	2.0081	0.8533	0.6546	0.5572	0.9862	1.9828
0.1008	0.4262	1.9190	1.0509	0.7531	0.7324	0.9659	3.8764	0.1008	0.4165	1.9859	0.8157	0.7531	0.6027	0.9053	2.7249
0.2011	0.5558	1.6653	1.2176	0.8496	0.7779	0.9126	5.4048	0.2011	0.4731	1.4905	0.8175	0.8496	0.8082	0.8214	3.6489
0.2968	0.6055	1.4097	1.4410	0.9503	0.8606	0.8904	10.0256	0.2968	0.4937	1.1948	0.9165	0.9503	0.8772	0.7917	6.6865
0.4024	0.6468	1.2376	1.6488					0.4024	0.5144	1.1753	1.1742				

[a] Liquid phase mole fraction on a salt-free basis.

Analysis Method. Water and solvent (1,4-dioxane or acetonitrile) mole fractions (on a salt-free basis) in the vapor (y_i) phase can be analyzed by gas chromatography. To analyze the vapor phase, a gas syringe (1 mL) is used. A gas chromatograph (Chrom-5, Laboratorni Pristroje, Praha, Czech Republic) was used with a thermal conductivity detector (the electric current was 80 mA) and 1.5 m glass column (Chromosorb W HP) and an integrator. The injector temperatures were 220 °C for the system 1,4-dioxane + water + TBAB and 200 °C for the system acetonitrile + water + TBAN. The chamber temperatures were 150 °C for the system 1,4-dioxane + water + TBAB and 135 °C for the system acetonitrile + water + TBAN. The carrier gas was helium (purity = 99.9%) flowing at 0.5 cm^3·s^{-1}.

Calibrations were necessary before the peak areas could be used to determine the composition of the vapor phase. A calibration curve was made by injecting a mixture of solvent and water, prepared gravimetrically by using an analytical balance with an accuracy of ±0.1 mg. Because of negligible amounts in the vapor phase (small vapor volume, moderate pressure), it was reasonable to assume that the liquid phase composition is the same as the feed composition. To prepare the calibration samples for the vapor phase, various solvent and water mixtures were completely evaporated in a 1000 ± 0.1 cm^3 vessel at 298 K and injected. To obtain the calibration equation, the required mass fractions and area fractions were correlated with a third-order polynomial with the least-squares method (mean deviation = 0.1%). The average uncertainty in the measurement of the mole fraction is ±0.002, which was obtained by comparing the known composition of the prepared liquid samples with the composition calculated from the calibration equation.

Results and Discussion

The experimental isothermal vapor−liquid equilibrium data are given in Table 1 and Table 2. To describe the observed VLE behavior, the experimental data are correlated using the electrolyte NRTL model of Mock et al.[8] The electrolyte NRTL model used to correlate the VLE data is an extension of the Chen model (for single-solvent electrolyte systems) to mixed solvent electrolyte systems.[8] The model parameters are specific for the solvent−solvent and solvent−salt pairs. For each system, six energy parameters (Δg_{ij}, Δg_{ji}) and three nonrandomness factors (α_{ij}) are required. Binary solvent−solvent parameters were directly taken from published data.[8,9] The nonrandomness factors ($\alpha_{\mathrm{TBAN,water}}$, $\alpha_{\mathrm{TBAN,dioxane}}$, $\alpha_{\mathrm{TBAB,water}}$, and $\alpha_{\mathrm{TBAB,acetonitrile}}$) were set arbitrarily to 0.2, 0.1, 0.2, and 0.05, respectively, as pointed out by Mock et al.[8] The remaining model parameters were fitted to the experimental data by minimization of the following objective function F using the Simplex−Nelder−Mead method:[10]

$$F(\Delta g_{ij}, \Delta g_{ji}, \alpha_{ij}) = \sum_{nt} \sum_{np} (y_{i,1(\mathrm{exptl})} - y_{i,1(\mathrm{calcd})})^2 = \min \quad (1)$$

where y represents the vapor phase mole fraction, and nt and np are the number of data sets and the number of data

Table 3. Energy Parameters (Δg_{ij} and Δg_{ji}/J·mol^{-1}) and Nonrandomness Factors (α_{ij}) for the Electrolyte NRTL Model[a]

i	j	α_{ij}	Δg_{ij}	Δg_{ji}
1,4-dioxane	water	0.3	2874.334	2024.935
1,4-dioxane	TBAN	0.1	3369.516 (f)[b]	−822.603 (f)
water	TBAN	0.2	2613.158 (f)	−134.126 (f)
acetonitrile	water	0.2858	1528.665	5538.057
acetonitrile	TBAB	0.05	3957.233 (f)	−1150.710 (f)
water	TBAB	0.2	2491.527 (f)	−47.094 (f)

[a] Reference 8. [b] (f) means that these interaction parameters have been fitted in this work.

Table 4. Mean Absolute Deviations of Vapor Phase Compositions for the Electrolyte NRTL Model for the Studied Systems

	$\lvert\Delta y\rvert$[a]	
T/K	data points	NRTL
1,4-Dioxane + Water + Tetrabutylammonium Nitrate		
288	66	0.005
298	66	0.006
308	66	0.005
av deviation		0.005
Acetonitrile + Water + Tetrabutylammonium Bromide		
298	55	0.006
323	55	0.006
av deviation		0.006

[a] $\lvert\Delta y\rvert = (1/n)\sum_1^n \lvert y_{i,1}(\text{exptl}) - y_{i,1}(\text{calcd})\rvert$, where n represents the number of data points.

points for each data set, respectively. The subscripts exptl and calcd denote experimental data and calculated values, respectively. The vapor phase composition can be calculated by solving iteratively the equilibrium condition

$$y_i P = x_i \gamma_i P_i^{\,s} \Phi_i \tag{2}$$

where

$$P = x_1 \gamma_1 P_1^{\,s} \Phi_1 + x_2 \gamma_2 P_2^{\,s} \Phi_2 \tag{3}$$

$$\Phi_i = \varphi_i^{\,s} PF_i / \varphi_i^{\,v} \tag{4}$$

The saturation vapor pressure of pure solvent i, P_i^{s}, at system temperature was calculated with the published Antoine constants.[9] φ_i^{v} is the fugacity coefficient of solvent i in the vapor phase, φ_i^{s} is the fugacity coefficient of pure solvent i at saturation pressure, and PF_i is the Poynting factor. x_i is the liquid phase mole fraction of solvent i based on the assumption of total dissociation of salt. φ_i^{s} is approximately equal to φ_i^{v}, and PF_i is approximately equal to 1 at atmosphere pressure, and so Φ_i is equal to 1.

All model binary energy parameters (τ_{ij}, G_{ij}) and activity coefficients of solvents γ_i were calculated as described by Mock at al.[8] The NRTL energy parameters and nonrandomness factors are given in Table 3.

Conclusion

The VLE behavior of the systems 1,4-dioxane + water + tetrabutylammonium nitrate and acetonitrile + water + tetrabutylammonium bromide have been investigated at different salt concentrations. The electrolyte NRTL model was used to correlate the VLE behavior of both the 1,4-dioxane + water + tetrabutylammonium nitrate and acetonitrile + water + tetrabutylammonium bromide systems. This model represents the experimental data with the required accuracy which is represented in Table 4.

Literature Cited

(1) Furter, W. F. Salt Effect in Distillation: A Literature Review II. *Can. J. Chem. Eng.* **1977**, *55*, 229−239.

(2) David-Auslaender, J.; Gutmann, H.; Kertes, A. S.; Zangen, M. Nonideal Behavior of Alkylammonium Salts in Organic Solvents at Elevated Temperatures. *J. Solution Chem.* **1974**, *3*, 251−260.

(3) Treiner, C.; Tzias, P. Standard Gibbs Free Energy of Transfer of n-Bu$_4$NBr from Water to Water−Solvent Mixtures as Deduced from Precise Vapor Pressure Measurements at 298.15 K. *Adv. Chem. Ser.* **1976**, *155*, 303−317.

(4) Slusher, J. T.; Decker, K. J.; Liu, H.; Vega, C. A.; Cummings, P. T.; O'Connell, J. P. Vapor−Liquid Equilibria and Salt Apparent Molar Volumes of the Water + 2-Propanol + Tetrabutylammonium Bromide System. *J. Chem. Eng. Data* **1994**, *39*, 506−509.

(5) Slusher, J. T.; Cummings, P. T.; Hu, Y.; Vega, C. A.; O'Connell, J. P. Vapor−Liquid Equilibrium and Density Measurements of Tetraalkylammonium Bromide + Propanol + Water Systems. *J. Chem. Eng. Data* **1995**, *40*, 792−798.

(6) Treiner, C.; Tzias, P.; Chemla, M.; Poltoratskii, G. M. Solvation of Tetrabutylammonium Bromide in Water + Acetonitrile Mixtures at 298.15 K from Vapor Pressure Measurements of Dilute Solutions. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2007−2015.

(7) Burns, J. A.; Furter, W. F. Effects of Salts Having Large Organic Ions on Vapor−Liquid Equilibrium. *Adv. Chem. Ser.* **1976**, *155*, 99−127.

(8) Mock, B.; Evans, L. B.; Chen, C.-C. Thermodynamic Representation of Phase Equilibria of Mixed Solvents−Electrolyte Systems. *AIChE J.* **1986**, *32*, 1655−1664.

(9) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt, Germany, 1977.

(10) Nelder, J. A.; Mead, R. A. A Simplex Method for Function Minimization. *Comput. J.* **1965**, *7*, 308−313.

Received for review February 7, 2003. Accepted November 1, 2003.

JE0301287