

Isothermal Vapor–Liquid Equilibrium Data for the Ethanol + Ethyl Acetate + Sodium Iodide System at Five Temperatures

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Isothermal vapor–liquid equilibrium data at five temperatures (30.0, 40.3, 50.4, 61.2, and 70.2 °C) have been measured for the system ethanol + ethyl acetate + sodium iodide at constant salt molalities (0.000, 0.150, 0.300, 0.500, 0.700, 1.00, 1.50, 2.00 mol·kg⁻¹) with the help of headspace gas chromatography. The data were compared with the predicted results using the LIQUAC model published by Li et al.

1. Introduction

Phase equilibria for mixed-solvent electrolyte systems are of significant interest for the different separation processes in the chemical industry. Usually, even small amounts of salt have an appreciable effect on the relative volatility of the solvents through preferential solvation (Ohe, 1991). For solvent mixtures that exhibit an azeotrope, it is possible to use salts to eliminate the azeotrope entirely. Recently, this salt effect has been applied in industrial separations such as extractive distillation, where salts are used as an alternative to selective solvents as entrainer. Extractive distillation by adding one salt as a separating agent provides also an interesting alternative to conventional azeotropic distillation processes (Furter, 1977). Due to overhead products which are free of the separating agent, the energy consumption of the processes can be reduced. Furthermore, the problem of contamination of the distillate by separating agent is eliminated since the salt is nonvolatile.

The correlation and prediction of vapor–liquid behavior for electrolyte systems in mixed solvents have been examined by a number of investigators: Hala (1983); Mock and Chen (1986); Sander et al. (1986); Cardoso and O'Connell (1987); Tan (1990); Macedo et al. (1990); Li et al. (1994); Zeres and Prausnitz (1994); Kolker and de Pablo (1996). However, the data base for the development and thorough testing of these models is small. While many data exist for aqueous systems, much less data are available for salts in organic solvents or in mixed solvents.

In this work isothermal vapor–liquid equilibrium data at five temperatures (30.0, 40.3, 50.4, 61.2, and 70.2 °C) are presented for ethanol (1) + ethyl acetate (2) + sodium iodide (3) at constant salt molalities (0.000, 0.150, 0.300, 0.500, 0.700, 1.00, 1.50, 2.00 mol·kg⁻¹). The addition of sodium iodide to this solvent mixture decreases the amount of ethanol present in the vapor phase, shifting the azeotrope to the ethyl acetate rich region. This indicates a preferential solvation of the ions with the less volatile component ethanol.

The present data of vapor–liquid equilibria were correlated using the LIQUAC model published by Li et al. (1994).

2. Experimental Section

2.1. Materials. Ethyl acetate (HPLC grade) and ethanol were dehydrated with the help of molecular sieves. The

Table 1. Vapor–Liquid Equilibrium Data for Ethanol (1) + Ethyl Acetate (2) + Sodium Iodide (3) at 30.0 °C

x_1^a	y_1	Δy_1^b	$-\ln(a_1/a_0)^c$	x_1	y_1	Δy_1	$-\ln(a_1/a_0)$
				$m = 0.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.145	0.000		0.1021	0.124	-0.002	0.182
0.1499	0.186	-0.004		0.1499	0.171	0.001	0.106
0.1954	0.227	-0.000		0.1954	0.210	0.005	0.099
0.2544	0.274	0.007		0.2544	0.254	0.009	0.107
0.2947	0.299	0.008		0.2947	0.279	0.010	0.097
0.3500	0.325	0.005		0.3500	0.310	0.011	0.070
0.4001	0.345	0.000		0.4001	0.337	0.012	0.030
0.5006	0.395	0.003		0.5006	0.385	0.010	0.038
0.5956	0.439	0.000		0.5956	0.434	0.008	0.022
0.7002	0.500	-0.002		0.7002	0.496	0.004	0.017
0.7929	0.574	-0.006		0.7929	0.571	-0.003	0.013
0.9101	0.747	0.002		0.9101	0.745	0.002	0.012
				$m = 0.3 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.112	-0.004	0.295	0.1499	0.133	-0.012	0.398
0.1499	0.154	-0.004	0.230	0.1954	0.167	-0.012	0.387
0.1954	0.191	-0.001	0.220	0.2544	0.210	-0.007	0.354
0.2544	0.235	0.003	0.208	0.2947	0.233	-0.008	0.340
0.2947	0.260	0.005	0.193	0.3500	0.272	0.001	0.254
0.3500	0.294	0.008	0.145	0.4001	0.303	0.006	0.190
0.4001	0.318	0.006	0.119	0.5006	0.360	0.012	0.146
0.5006	0.375	0.013	0.082	0.5956	0.411	0.012	0.114
0.5956	0.424	0.011	0.061	0.7002	0.482	0.014	0.075
0.7002	0.488	0.008	0.050	0.7929	0.561	0.011	0.052
0.7929	0.566	0.004	0.033	0.9101	0.738	0.013	0.048
0.9101	0.742	0.008	0.026				
				$m = 0.7 \text{ mol}\cdot\text{kg}^{-1}$			
0.1954	0.144	-0.023	0.559	0.2544	0.161	-0.028	0.675
0.2544	0.187	-0.018	0.496	0.2947	0.185	-0.028	0.633
0.2947	0.202	-0.026	0.522	0.3500	0.218	-0.025	0.547
0.3500	0.240	-0.019	0.425	0.4001	0.244	-0.026	0.489
0.4001	0.270	-0.015	0.350	0.5006	0.304	-0.018	0.399
0.5006	0.327	-0.010	0.296	0.5956	0.375	0.000	0.264
0.5956	0.391	0.002	0.198	0.7002	0.454	0.008	0.185
0.7002	0.466	0.009	0.136	0.7929	0.550	0.018	0.098
0.7929	0.556	0.015	0.073	0.9101	0.731	0.019	0.083
0.9101	0.735	0.016	0.063				
				$m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.4001	0.216	-0.035	0.646	0.5956	0.331	-0.021	0.460
0.5006	0.281	-0.025	0.513	0.7002	0.418	-0.010	0.333
0.5956	0.343	-0.019	0.406	0.7929	0.530	0.012	0.178
0.7002	0.436	0.001	0.259	0.9101	0.719	0.013	0.145
0.7929	0.542	0.020	0.129				
0.9101	0.724	0.018	0.116				
				$m = 1.5 \text{ mol}\cdot\text{kg}^{-1}$			
0.4001	0.216	-0.035	0.646	0.5956	0.331	-0.021	0.460
0.5006	0.281	-0.025	0.513	0.7002	0.418	-0.010	0.333
0.5956	0.343	-0.019	0.406	0.7929	0.530	0.012	0.178
0.7002	0.436	0.001	0.259	0.9101	0.719	0.013	0.145
0.7929	0.542	0.020	0.129				
0.9101	0.724	0.018	0.116				
				$m = 2.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.4001	0.216	-0.035	0.646	0.5956	0.331	-0.021	0.460
0.5006	0.281	-0.025	0.513	0.7002	0.418	-0.010	0.333
0.5956	0.343	-0.019	0.406	0.7929	0.530	0.012	0.178
0.7002	0.436	0.001	0.259	0.9101	0.719	0.013	0.145
0.7929	0.542	0.020	0.129				
0.9101	0.724	0.018	0.116				

Mean Absolute Deviation (Δy_1): 0.010

^a Mole fraction on a salt-free basis: $x_1 = n_1/(n_1 + n_2)$, where n_1 and n_2 are the numbers of moles of solvents 1 and 2. ^b $\Delta y_1 = y_{1,\text{exp}} - y_{1,\text{calc}}$. ^c a is the relative volatility.

purity was checked by gas chromatography. The purity was greater than 99.9 mass % (ethyl acetate) and 99.8 mass

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Table 2. Vapor-Liquid Equilibrium Data for Ethanol (1) + Ethyl Acetate (2) + Sodium Iodide (3) at 40.3 °C^a

x_1^a	y_1	Δy_1	$-\ln(a_3/a_0)$	x_1	y_1	Δy_1	$-\ln(a_3/a_0)$
$m = 0.0 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.15 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.155	0.000		0.1021	0.135	0.002	0.158
0.1499	0.205	0.000		0.1499	0.183	0.002	0.146
0.1954	0.245	0.000		0.1954	0.221	0.003	0.131
0.2544	0.287	-0.002		0.2544	0.269	0.009	0.089
0.2947	0.312	-0.002		0.2947	0.293	0.007	0.090
0.3500	0.343	-0.002		0.3500	0.326	0.008	0.076
0.4001	0.370	-0.002		0.4001	0.355	0.010	0.063
0.5006	0.418	0.002		0.5006	0.408	0.010	0.043
0.5956	0.466	0.000		0.5956	0.459	0.009	0.028
0.7002	0.531	0.004		0.7002	0.526	0.008	0.019
0.7929	0.600	-0.003		0.7929	0.596	-0.003	0.016
0.9101	0.753	-0.003		0.9101	0.751	-0.0012	0.010
$m = 0.3 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.5 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.120	-0.004	0.298	0.1499	0.155	-0.005	0.437
0.1499	0.163	-0.005	0.282	0.1954	0.191	-0.012	0.406
0.1954	0.199	-0.006	0.263	0.2544	0.223	-0.013	0.340
0.2544	0.246	0.000	0.210	0.2947	0.250	-0.009	0.306
0.2947	0.272	0.000	0.192	0.3500	0.291	-0.006	0.241
0.3500	0.310	0.005	0.154	0.4001	0.320	0.002	0.222
0.4001	0.337	0.006	0.143	0.5006	0.383	0.003	0.149
0.5006	0.393	0.008	0.105	0.5956	0.439	0.012	0.109
0.5956	0.445	0.008	0.087	0.7002	0.514	0.020	0.071
0.7002	0.515	0.009	0.066	0.7929	0.585	0.009	0.060
0.7929	0.591	0.003	0.038	0.9101	0.744	-0.001	0.044
0.9101	0.748	-0.006	0.024		0.		
$m = 0.7 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.1954	0.157	0.000	0.553	0.2947	0.200	-0.028	0.595
0.2544	0.199	-0.013	0.482	0.3500	0.234	-0.026	0.538
0.2947	0.231	-0.013	0.410	0.4001	0.262	-0.026	0.500
0.3500	0.266	-0.010	0.364	0.5006	0.320	-0.024	0.423
0.4001	0.302	-0.002	0.305	0.5956	0.384	-0.015	0.338
0.5006	0.366	0.007	0.220	0.7002	0.485	0.013	0.187
0.5956	0.422	0.009	0.82	0.7929	0.567	0.009	0.137
0.7002	0.498	0.014	0.132	0.9101	0.735	0.001	0.095
0.7929	0.577	0.009	0.094				
0.9101	0.742	0.002	0.056				
$m = 1.5 \text{ mol}\cdot\text{kg}^{-1}$				$m = 2.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.4001	0.243	-0.026	0.602	0.5956	0.353	-0.021	0.472
0.5006	0.302	-0.025	0.508	0.7002	0.451	-0.002	0.324
0.5956	0.362	-0.022	0.432	0.7929	0.548	0.004	0.215
0.7002	0.477	0.018	0.216	0.9101	0.722	-0.004	0.159
0.7929	0.560	0.012	0.165				
0.9101	0.727	-0.001	0.136				

Mean Absolute Deviation (Δy_1): 0.008^a See footnotes a-c in Table 1.

(ethanol). For removing the moisture in the salt, sodium iodide (greater than 99.0%) was dried at 80 °C in a vacuum oven until constant weight was reached.

2.2. Apparatus. All liquid mixtures consisting of ethanol, ethyl acetate, and sodium iodide were prepared directly by using a Sartorius analytical balance, the accuracy of which was ± 0.1 mg. For each experimental point approximately 8 cm³ of sample solution was taken and put into the 22 cm³ sample vial. After the sample vials were tightly closed by means of a special aluminum lid, underneath which was a washer and a Teflon disk, they were brought to the appropriate temperature in the thermostatic bath controlled to within ± 0.1 deg. Measurements were commenced after they were kept at constant temperature at least 12 h to ensure equilibrium conditions.

For the analysis of the vapor phase in equilibrium, the vapor was automatically withdrawn using a Perkin-Elmer F45 GLC vapor analyzer and it was analyzed by an F22 gas chromatograph with the help of a thermal conductivity detector and an integrator (Hewlett-Packard 3390A). A 1.2 m stainless steel column of Porapak Q 80/100 was used. The optimum operating conditions were the following:

Table 3. Vapor-Liquid Equilibrium Data for Ethanol (1) + Ethyl Acetate (2) + Sodium Iodide (3) at 50.40 °C^a

x_1	y_1	Δy_1	$-\ln(a_3/a_0)$	x_1	y_1	Δy_1	$-\ln(a_3/a_0)$
$m = 0.0 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.15 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.163	0.004		0.1021	0.142	-0.002	0.181
0.1499	0.210	-0.002		0.1499	0.189	-0.002	0.131
0.1954	0.254	0.000		0.1954	0.232	0.002	0.120
0.2544	0.298	-0.002		0.2544	0.280	0.005	0.089
0.2947	0.326	-0.002		0.2947	0.307	0.004	0.090
0.3500	0.360	-0.002		0.3500	0.341	0.005	0.082
0.4001	0.387	-0.003		0.4001	0.372	0.008	0.062
0.5006	0.439	-0.003		0.5006	0.429	0.009	0.043
0.5956	0.492	0.000		0.5956	0.485	0.012	0.027
0.7002	0.556	0.001		0.7002	0.550	0.007	0.025
0.7929	0.626	-0.003		0.7929	0.622	-0.001	0.019
0.9101	0.777	-0.001		0.9101	0.775	-0.005	0.009
$m = 0.3 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.5 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.122	-0.009	0.338	0.1954	0.189	-0.014	0.381
0.1499	0.169	-0.009	0.267	0.2544	0.232	-0.014	0.342
0.1954	0.209	-0.008	0.256	0.2947	0.259	-0.013	0.325
0.2544	0.257	-0.004	0.208	0.3500	0.297	-0.009	0.286
0.2947	0.284	-0.004	0.201	0.4001	0.328	-0.007	0.258
0.3500	0.319	-0.003	0.186	0.5006	0.395	0.004	0.183
0.4001	0.352	0.002	0.148	0.5956	0.454	0.008	0.151
0.5006	0.411	0.006	0.114	0.7002	0.522	0.004	0.138
0.5956	0.468	0.008	0.097	0.7929	0.609	0.009	0.072
0.7002	0.534	0.005	0.087	0.9101	0.771	0.007	0.030
0.7929	0.614	0.003	0.050				
0.9101	0.773	0.001	0.021				
$m = 0.7 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.1954	0.169	-0.021	0.515	0.2947	0.220	-0.023	0.543
0.2544	0.214	-0.019	0.448	0.3500	0.254	-0.022	0.500
0.2947	0.240	-0.019	0.428	0.4001	0.284	-0.023	0.466
0.3500	0.278	-0.015	0.380	0.5006	0.348	-0.016	0.384
0.4001	0.315	-0.008	0.319	0.5956	0.421	-0.001	0.288
0.5006	0.380	0.001	0.246	0.7002	0.498	0.002	0.233
0.5956	0.447	0.012	0.179	0.7929	0.591	0.010	0.145
0.7002	0.520	0.013	0.145	0.9101	0.764	0.012	0.069
0.7929	0.598	0.007	0.117				
0.9101	0.768	0.009	0.050				
$m = 1.5 \text{ mol}\cdot\text{kg}^{-1}$				$m = 2.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.4001	0.254	-0.032	0.619	0.5956	0.376	-0.019	0.474
0.5006	0.321	-0.025	0.506	0.7002	0.455	-0.020	0.404
0.5956	0.396	-0.010	0.390	0.7929	0.561	-0.005	0.268
0.7002	0.467	-0.016	0.357	0.9101	0.759	0.013	0.101
0.7929	0.574	0.003	0.217				
0.9101	0.759	0.013	0.101				

Mean Absolute Deviation (Δy_1): 0.008^a See footnotes a-c in Table 1.

injection temperature, 190 °C; oven temperature, 170 °C; detector temperature, 190 °C; carrier gas, helium (the purity of 99.9%) with a flow rate of 0.41 cm³·s⁻¹. Some experimental details have been already described elsewhere (Weidlich and Gmehling, 1985).

Calibration was necessary before the peak areas could be used to determine the vapor-phase composition. To obtain the calibration curve, various mixtures of ethanol + ethyl acetate were prepared. Then these mixtures were injected, and the peak area fractions were obtained. The mole fractions and area fractions were correlated using a sixth-order polynomial. The vapor-phase composition was determined with the help of the calibration curve. The average error in the measurement of the mole fraction is ± 0.0018 , which was obtained by comparing the known composition of the made-up sample to the composition calculated from the calibration curve.

Because of the negligible amounts evaporated (small vapor volume, moderate pressure), it was assumed that the liquid-phase composition was the same as that initially fed in the sample vial.

2.3. Consistency of the Experimental Data. The consistency of the composition measurement by GC was

Table 4. Vapor–Liquid Equilibrium Data for Ethanol (1) + Ethyl Acetate (2) + Sodium Iodide (3) at 61.2 °C^a

x_1	y_1	Δy_1	$-\ln(a_2/a_0)$	x_1	y_1	Δy_1	$-\ln(a_3/a_0)$
$m = 0.0 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.15 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.167	0.000		0.1021	0.145	-0.005	0.169
0.1499	0.221	0.000		0.1499	0.193	-0.008	0.173
0.1954	0.264	0.001		0.1954	0.236	-0.007	0.154
0.2544	0.312	0.000		0.2544	0.285	-0.005	0.133
0.2947	0.341	0.000		0.2947	0.316	-0.002	0.112
0.3500	0.376	-0.001		0.3500	0.355	0.001	0.088
0.4001	0.406	0.001		0.4001	0.385	0.001	0.089
0.5006	0.459	-0.001		0.5006	0.446	0.005	0.053
0.5956	0.511	-0.001		0.5956	0.503	0.007	0.035
0.7002	0.577	-0.002		0.7002	0.571	0.005	0.026
0.7929	0.646	-0.008		0.7929	0.643	-0.002	0.015
0.9101	0.796	-0.005		0.9101	0.794	-0.003	0.014
$m = 0.3 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.5 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.137	-0.002	0.235	0.1954	0.199	-0.016	0.372
0.1499	0.178	-0.010	0.271	0.2544	0.248	-0.012	0.320
0.1954	0.220	-0.009	0.242	0.2947	0.280	-0.008	0.286
0.2544	0.272	-0.004	0.196	0.3500	0.320	-0.003	0.243
0.2947	0.300	-0.004	0.191	0.4001	0.355	0.002	0.215
0.3500	0.341	0.001	0.152	0.5006	0.422	0.010	0.149
0.4001	0.374	0.005	0.135	0.5956	0.482	0.013	0.118
0.5006	0.433	0.006	0.107	0.7002	0.559	0.019	0.073
0.5956	0.490	0.007	0.085	0.7929	0.639	0.016	0.031
0.7002	0.563	0.010	0.058	0.9101	0.792	0.010	0.026
0.7929	0.641	0.007	0.021				
0.9101	0.793	0.004	0.019				
$m = 0.7 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.2544	0.227	-0.019	0.434	0.2947	0.232	-0.025	0.535
0.2947	0.257	-0.018	0.405	0.3500	0.267	-0.026	0.503
0.3500	0.299	-0.011	0.343	0.4001	0.297	-0.027	0.481
0.4001	0.334	-0.007	0.311	0.5006	0.363	-0.022	0.399
0.5006	0.404	0.004	0.225	0.5956	0.432	-0.011	0.317
0.5956	0.469	0.012	0.169	0.7002	0.519	0.001	0.235
0.7002	0.548	0.018	0.117	0.7929	0.622	0.018	0.105
0.7929	0.633	0.019	0.059	0.9101	0.782	0.012	0.087
0.9101	0.788	0.012	0.049				
$m = 1.5 \text{ mol}\cdot\text{kg}^{-1}$				$m = 2.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.5006	0.352	-0.013	0.444	0.7002	0.489	-0.008	0.355
0.5956	0.408	-0.019	0.418	0.7929	0.606	0.017	0.171
0.7002	0.507	0.002	0.284	0.9101	0.772	0.009	0.144
0.7929	0.615	0.002	0.132				
0.9101	0.776	0.012	0.122				

Mean Absolute Deviation (Δy_1): 0.008^a See footnotes a–c in Table 1.

checked by comparison of the observed mole fraction of ethanol with test mixtures of exactly known composition. To check the reproducibility of the experimental data, samples of the same compositions were measured twice. The experimental data show satisfactory agreement with the prepared data. The accuracy is $\pm 0.38\%$, and the reproducibility was within $\pm 0.31\%$.

To confirm the reliability of the experimental vapor phase equilibrium data, also the salt-free system ethanol (1) + ethyl acetate (2) was measured at five temperatures. The experimental data obtained are given in Tables 1–5 and in Figures 1–5, where they are compared with the literature data using UNIQUAC (parameters taken from Gmehling et al., 1977). Mean relative deviations are 1.01% (30.0 °C), 0.35% (40.3 °C), 0.64% (50.4 °C), 0.29% (61.2 °C), and 0.80% (70.2 °C) in mole fraction. The thermodynamic consistency of the experimental data was examined with the help of the Redlich–Kister area test (Redlich and Kister, 1948). The area deviations found are 0.0% (30.0 °C), 0.5% (40.3 °C), 0.4% (50.4 °C), 2.4% (61.2 °C), and 0.6% (70.2 °C), respectively. This means that the VLE data measured for ethanol (1) + ethyl acetate (2) can be considered as thermodynamically consistent.

Table 5. Vapor–Liquid Equilibrium Data for Ethanol (1) + Ethyl Acetate (2) + Sodium Iodide (3) at 70.2 °C^a

x_1	y_1	Δy_1	$-\ln(a_2/a_0)$	x_1	y_1	Δy_1	$-\ln(a_3/a_0)$
$m = 0.0 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.15 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.176	0.000		0.1021	0.165	0.009	0.087
0.1499	0.235	0.002		0.1499	0.213	0.009	0.145
0.1954	0.276	-0.002		0.1954	0.255	0.003	0.105
0.2544	0.328	0.001		0.2544	0.305	0.001	0.105
0.2947	0.362	0.005		0.2947	0.338	0.003	0.106
0.3500	0.396	0.003		0.3500	0.375	0.003	0.087
0.4001	0.422	0.000		0.4001	0.406	0.006	0.065
0.5006	0.469	-0.009		0.5006	0.457	0.006	0.048
0.5956	0.516	-0.015		0.5956	0.507	0.007	0.034
0.7002	0.598	0.002		0.7002	0.583	-0.001	0.028
0.7929	0.673	0.003		0.7929	0.666	-0.003	0.020
0.9101	0.815	0.000		0.9101	0.813	0.003	0.017
$m = 0.3 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.5 \text{ mol}\cdot\text{kg}^{-1}$			
0.1021	0.155	0.010	0.158	0.2544	0.260	-0.012	0.329
0.1499	0.197	0.000	0.241	0.2947	0.293	-0.008	0.313
0.1954	0.242	0.002	0.177	0.3500	0.336	-0.002	0.260
0.2544	0.292	0.004	0.170	0.4001	0.373	0.003	0.207
0.2947	0.321	0.004	0.180	0.5006	0.440	0.010	0.118
0.3500	0.360	0.006	0.153	0.5956	0.493	0.006	0.091
0.4001	0.393	0.009	0.119	0.7002	0.572	0.012	0.076
0.5006	0.450	0.006	0.077	0.7929	0.658	0.017	0.056
0.5956	0.502	0.002	0.052	0.9101	0.807	0.012	0.052
0.7002	0.581	0.009	0.037				
0.7929	0.663	0.011	0.034				
0.9101	0.810	0.008	0.031				
$m = 0.7 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.2544	0.249	-0.009	0.384	0.3500	0.297	-0.010	0.438
0.2947	0.279	-0.008	0.381	0.4001	0.327	-0.012	0.408
0.3500	0.321	-0.004	0.327	0.5006	0.396	-0.005	0.299
0.4001	0.356	0.000	0.278	0.5956	0.451	-0.010	0.257
0.5006	0.422	0.005	0.193	0.7002	0.535	-0.002	0.225
0.5956	0.477	0.001	0.155	0.7929	0.636	0.014	0.154
0.7002	0.554	0.004	0.148	0.9101	0.795	0.012	0.128
0.7929	0.644	0.012	0.117				
0.9101	0.800	0.011	0.097				
$m = 1.5 \text{ mol}\cdot\text{kg}^{-1}$				$m = 2.0 \text{ mol}\cdot\text{kg}^{-1}$			
0.5006	0.370	-0.012	0.408	0.7002	0.509	-0.007	0.326
0.5956	0.428	-0.016	0.350	0.7929	0.607	0.001	0.270
0.7002	0.522	-0.001	0.274	0.9101	0.776	0.001	0.238
0.7929	0.623	0.011	0.207				
0.9101	0.785	0.008	0.187				

Mean Absolute Deviation (Δy_1): 0.006^a See footnotes a–c in Table 1.

3. Results and Discussion

In Tables 1–5 the experimental vapor-phase equilibrium data for the system ethanol + ethyl acetate + sodium iodide system at five temperatures are listed. In Figures 1–5 these experimental data are plotted in the form of an x – y diagram. In these figures the salt effect on the vapor–liquid equilibrium of the ethanol–ethyl acetate system can be seen qualitatively. It was observed that the presence of sodium iodide decreases the ethanol mole fraction in the vapor phase and this effect increases with increasing salt concentration but decreases with increasing temperature.

To describe the observed VLE behavior, the experimental data are correlated using the LIQUAC model proposed by Li et al. (1994), which is based on an expression of the excess Gibbs energy, consisting of three terms:

$$G^E = G_{LR}^E + G_{MR}^E + G_{SR}^E \quad (1)$$

The G_{LR}^E term represents the long-range (LR) interaction contribution caused by the Coulomb electrostatic forces. Corresponding activity coefficients of solvent and

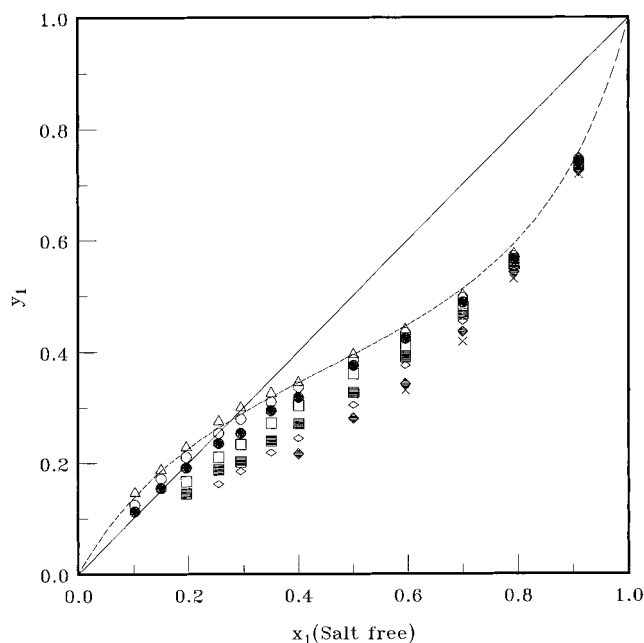


Figure 1. x - y vapor-liquid equilibrium diagram for the system ethanol-ethyl acetate-NaI at 30.0 °C: (Δ) $m = 0.0$, (\circ) $m = 0.15$, (\bullet) $m = 0.3$, (\square) $m = 0.5$, (\blacksquare) $m = 0.7$, (\diamond) $m = 1.0$, (\blacklozenge) $m = 1.5$, (\times) $m = 2.0$ mol·kg⁻¹; (---) ($m = 0.0$ mol·kg⁻¹) calculated by the UNIQUAC model (parameters taken from Gmehling et al., 1977).

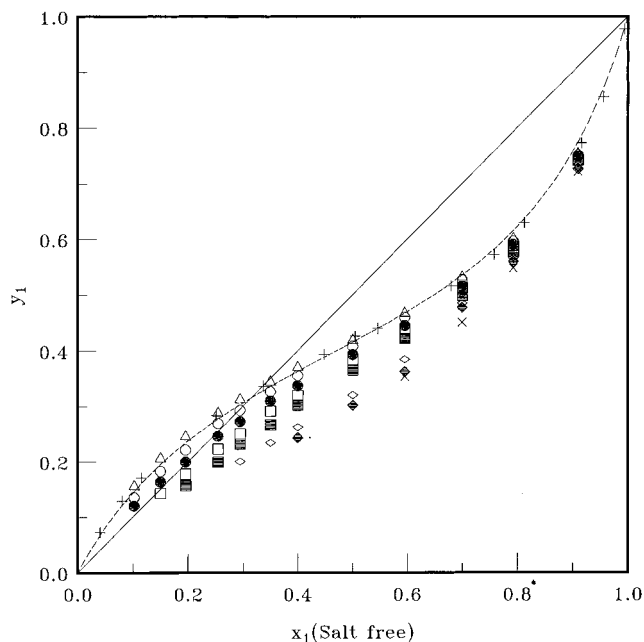


Figure 2. x - y vapor-liquid equilibrium diagram for the system ethanol-ethyl acetate-NaI at 40.3 °C: (Δ) $m = 0.0$, (\circ) $m = 0.15$, (\bullet) $m = 0.3$, (\square) $m = 0.5$, (\blacksquare) $m = 0.7$, (\diamond) $m = 1.0$, (\blacklozenge) $m = 1.5$, (\times) $m = 2.0$ mol·kg⁻¹; (---) ($m = 0.0$ mol·kg⁻¹) calculated by the UNIQUAC model (parameters taken from Gmehling et al., 1977); (+) $m = 0.0$ mol·kg⁻¹ 40.0 °C (Murthi and van Winkle, 1958).

ion, γ_s^{LR} and γ_j^{LR} , can be expressed using the extended Debye-Hückel theory

$$\ln \gamma_s^{\text{LR}} = [2AM_s d/b^3 d_s][1 + bI^{1/2} - (1 + bI^{1/2})^{-1} - 2 \ln(1 + bI^{1/2})] \quad (2)$$

$$\ln \gamma_j^{\text{LR}} = -Z_j^2 A I^{1/2} / (1 + bI^{1/2}) \quad (3)$$

where A and b are the Debye-Hückel parameters. The relations to absolute temperature T , density d of mixed

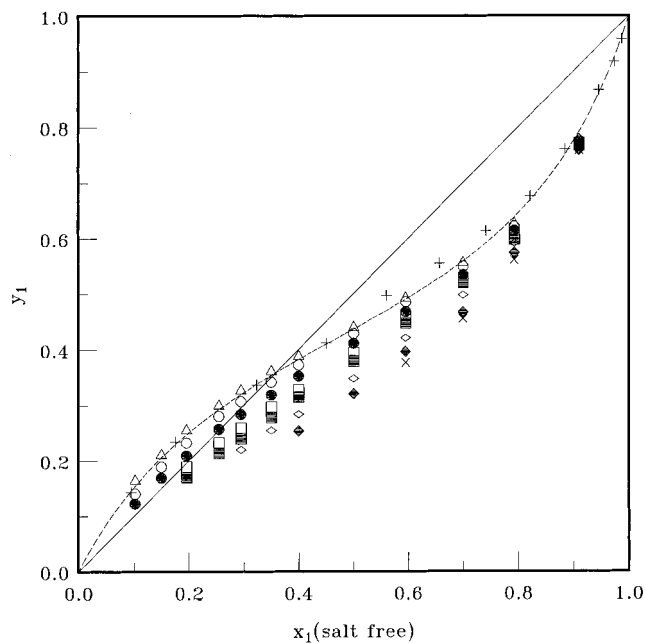


Figure 3. x - y vapor-liquid equilibrium diagram for the system ethanol-ethyl acetate-NaI at 50.4 °C: (Δ) $m = 0.0$, (\circ) $m = 0.15$, (\bullet) $m = 0.3$, (\square) $m = 0.5$, (\blacksquare) $m = 0.7$, (\diamond) $m = 1.0$, (\blacklozenge) $m = 1.5$, (\times) $m = 2.0$ mol·kg⁻¹; (---) ($m = 0.0$ mol·kg⁻¹) calculated by the UNIQUAC model (parameters taken from Gmehling et al., 1977); (+) $m = 0.0$ mol·kg⁻¹ 50.0 °C (Kharin et al., 1968).

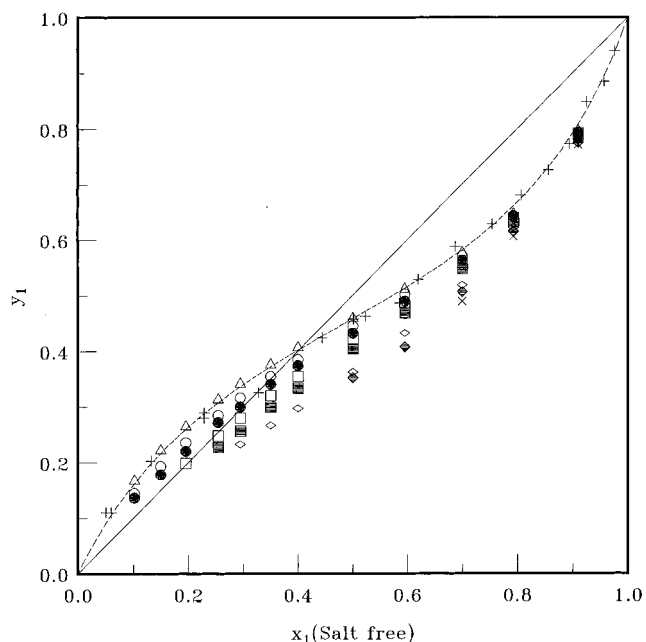


Figure 4. x - y vapor-liquid equilibrium diagram for the system ethanol-ethyl acetate-NaI at 61.2 °C: (Δ) $m = 0.0$, (\circ) $m = 0.15$, (\bullet) $m = 0.3$, (\square) $m = 0.5$, (\blacksquare) $m = 0.7$, (\diamond) $m = 1.0$, (\blacklozenge) $m = 1.5$, (\times) $m = 2.0$ mol·kg⁻¹; (---) ($m = 0.0$ mol·kg⁻¹) calculated by the UNIQUAC model (parameters taken from Gmehling et al., 1977); (+) $m = 0.0$ mol·kg⁻¹ 60.0 °C (Murthi and van Winkle, 1958).

solvent, and relative permittivity ϵ of mixed solvent are

$$A = 1.327757 \times 10^5 d^{1/2} / (\epsilon T)^{3/2} \quad (4)$$

$$b = 6.359696 d^{1/2} / (\epsilon T)^{1/2} \quad (5)$$

The G_{MR}^{E} term, which accounts for the middle-range (MR) interactions represents the ion-dipole effects. The middle-range interaction contribution to the activity coefficients of solvent and ion can be described using the Pitzer

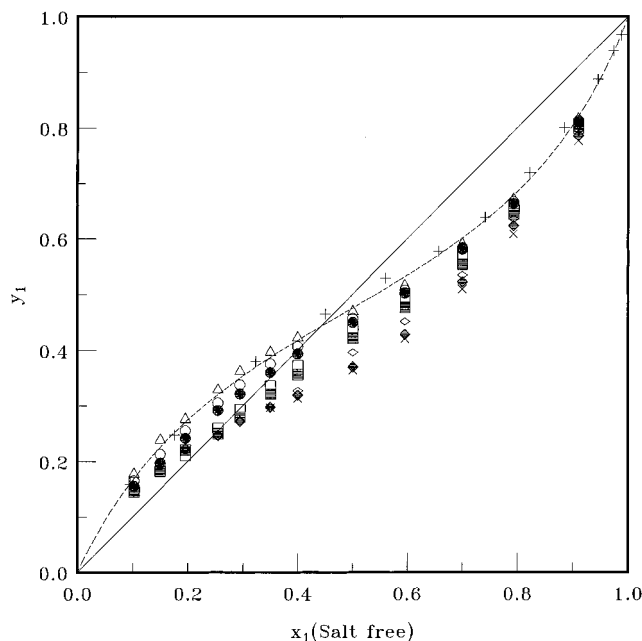


Figure 5. x - y vapor-liquid equilibrium diagram for the system ethanol-ethyl acetate-NaI at 70.2 °C: (Δ) $m = 0.0$, (\circ) $m = 0.15$, (\bullet) $m = 0.3$, (\square) $m = 0.5$, (\blacksquare) $m = 0.7$, (\diamond) $m = 1.0$, (\blacklozenge) $m = 1.5$, (\times) $m = 2.0$ mol·kg $^{-1}$; (---) ($m = 0.0$ mol·kg $^{-1}$) calculated by the UNIQUAC model (parameters taken from Gmehling et al., 1977); (+) $m = 0.0$ mol·kg $^{-1}$ 70.0 °C (Kharin et al., 1968).

model. But in the LIQUAC model it is a little different from the Pitzer equation in that the ion-solvent interaction parameters are introduced into this model and three species interactions are ignored. They are expressed by

$$\ln \gamma_s^{\text{MR}} = \sum_{\text{ion}} B_{s,\text{ion}}(I) m_{\text{ion}} - (M_s/M_m) \sum_s \sum_{\text{ion}} [B_{s,\text{ion}}(I) + IB'_{s,\text{ion}}(I)] x'_s m_{\text{ion}} - M_s \sum_c \sum_a [B_{c,a}(I) + IB'_{c,a}(I)] m_c m_a \quad (6)$$

$$\ln \gamma_j^{\text{MR}} = (M_m)^{-1} \sum_s B_{j,s}(I) x'_s + [Z_j^2/(2M_m)] \sum_s \sum_{\text{ion}} B'_{s,\text{ion}}(I) x'_s m_{\text{ion}} + \sum_a B_{j,a}(I) m_a + (Z_j^2/2) \sum_c \sum_a B'_{c,a}(I) m_c m_a - B_{s,j}(I)/M_s \quad (7)$$

where x'_s is the salt-free mole fraction of solvent, s , and $B'(I)$ is equal to $dB(I)/dI$. The ion-ion interaction parameter $B_{c,a}$ and ion-solvent interaction $B_{s,\text{ion}}$ parameter are described by

$$B_{c,a} = b_{c,a} + c_{c,a} \exp(-I^{1/2} + 0.13I) \quad (8)$$

$$B_{s,\text{ion}} = b_{s,\text{ion}} + c_{s,\text{ion}} \exp(-1.2I^{1/2} + 0.13I) \quad (9)$$

where b_{ij} and c_{ij} are the middle-range interaction parameters between species i and j ($b_{ij} = b_{j,i}$, $c_{ij} = c_{j,i}$, $c_{i,i} = 0$, and $c_{s,s} = b_{s,s} = 0$), where i and j denote ion or solvent.

The G_{SR}^E term expresses the contribution of the short-range (SR) interactions to excess Gibbs energy and can be described using the UNIQUAC equation. The expressions for activity coefficients of solvent, s , and ion, j , are written as

$$\ln \gamma_s^{\text{SR}} = \ln \gamma_s^{\text{C}} + \ln \gamma_s^{\text{R}} \quad (10)$$

$$\ln \gamma_j^{\text{SR}} = \ln \gamma_j^{\text{C}} + \ln \gamma_j^{\text{R}} - (\ln \gamma_{j(\text{B})}^{\text{C}} + \ln \gamma_{j(\text{B})}^{\text{R}}) \quad (11)$$

where γ_k^{C} and γ_k^{R} are called the combinatorial activity coefficient and the residual activity coefficient of ion or solvent and can be expressed respectively as

$$\ln \gamma_k^{\text{C}} = 1 - V_k + \ln V_k - 5q_k[1 - V_k/F_k + \ln(V_k/F_k)] \quad (12)$$

$$\ln \gamma_k^{\text{R}} = q_k \{ 1 - \ln[\sum_i q_i x_i \Psi_{ik} / (\sum_i q_i x_i)] - \sum_i [\sum_i q_i x_i \Psi_{ki} / \sum_l (q_l x_l \Psi_{il})] \} \quad (13)$$

$$V_k = r_k / \sum_i r_i x_i \quad (14)$$

$$F_k = q_k / \sum_i q_i x_i \quad (15)$$

$$\Psi_{ik} = \exp(-a_{ik}/T) \quad (16)$$

In eqs 13–15 i and l cover all species (ions and solvents) and r_k and q_k are the van der Waals volumes and surface areas of species k . In eq 16 a_{ik} ($a_{ik} \neq a_{ki}$) is the UNIQUAC interaction parameter between species i and k .

The term in parenthesis on the right side of eq 11 can be obtained from normalizing the activity coefficient of ion j to the infinite dilution reference state ($x'_s \rightarrow 1$, $I \rightarrow 0$, $\gamma_j \rightarrow 1$).

The general expressions for the activity coefficient of solvent s and ion j are

$$\ln \gamma_s = \ln \gamma_s^{\text{LR}} + \ln \gamma_s^{\text{MR}} + \ln \gamma_s^{\text{SR}} \quad (17)$$

$$\ln \gamma_j = (\ln \gamma_j^{\text{LR}} + \ln \gamma_j^{\text{MR}} + \ln \gamma_j^{\text{SR}}) - \ln(M_s/M_m + M_s \sum_i m_i) \quad (18)$$

where the last term of eq 18 was obtained due to conversion of concentration scale from mole fraction to the molality for the activity coefficient.

This model is suitable for the description of both single and mixed solvent systems and is especially successful in the region of high electrolyte concentration (Polka et al., 1994). The model includes only binary interaction parameters, and a large number of parameters have been already fitted with the help of a large data base. In this work a few parameters were directly taken from the model parameter matrix (Li et al., 1994), shown in Table 6. The other parameters were fitted to the experimental data using the Simplex-Nelder-Mead method (Nelder and Mead, 1965) with the following objective function:

$$F(a_{ij}, a_{jp}, b_{ij}, c_{ij}) = \sum_{\text{nt}} \sum_{\text{np}} g_y (y_{\text{exp}} - y_{\text{calc}})^2 = \min \quad (19)$$

where y represents the vapor-phase mole fraction, g_y is a weighting factor. nt and np are the number of data sets in the data base and the number of data points for each data set. The subscripts, exp and calc , denote experimental data and calculated values. When fitting, y_i can be calculated from

$$P = x_1 \gamma_1 P_1^{\text{f}} + x_2 \gamma_2 P_2^{\text{f}} \quad (20)$$

and

$$y_i = x_i \gamma_i P_i^{\text{f}} / P \quad (21)$$

where x_i is the liquid-phase mole fraction of the solvent i

Table 6. Binary Interaction Parameters, Volume, and Surface Area Parameters for the LIQUAC Model (Li et al., 1994)

<i>i</i>	<i>j</i>	a_{if}^a	a_{ji}^a	b_{if}^a	c_{ji}^a	r_i	q_i
ethanol	ethyl acetate	-58.671	230.14				
ethanol	Na ⁺	-172.2	-304.8	3.811	1.435		
ethanol	I ⁻	314.32	194.5	-3.434	-1.340		
ethyl acetate	Na ⁺	333.68 (f)	-262.80 (f)	2.253 (f)	1.944 (f)		
ethyl acetate	I ⁻	339.78 (f)	410.31 (f)	-1.595 (f)	-0.923 (f)		
Na ⁺	I ⁻	-220.4	563.5	0.2591	-0.0367		
ethanol						2.1055	1.9720
ethyl acetate						3.4786	3.1160
Na ⁺						1.0	1.0
I ⁻						1.0	1.0

^a (f) means that these interaction parameters have been fitted in this work.

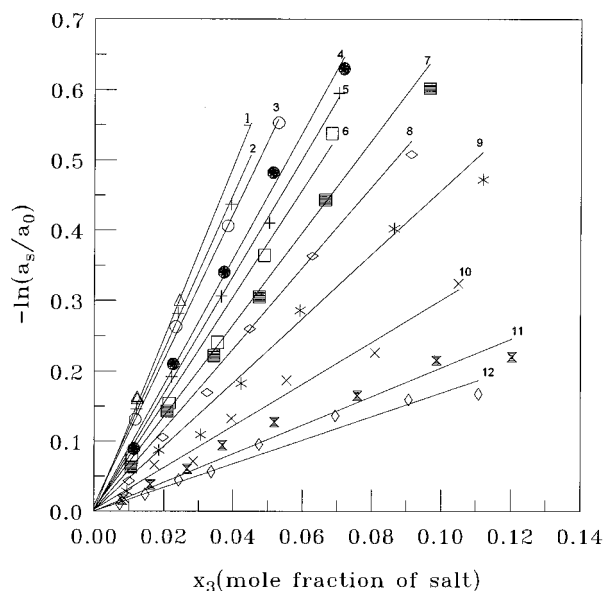


Figure 6. Salt effects of sodium iodide on the ethanol (1) + ethyl acetate (2) system at different solvent compositions (40.3 °C): (1) $x_1 = 0.1021$; (2) $x_1 = 0.1499$; (3) $x_1 = 0.1954$; (4) $x_1 = 0.2544$; (5) $x_1 = 0.2942$; (6) $x_1 = 0.3500$; (7) $x_1 = 0.4001$; (8) $x_1 = 0.5006$; (9) $x_1 = 0.5956$; (10) $x_1 = 0.7002$; (11) $x_1 = 0.7929$; (12) $x_1 = 0.9101$.

based on the assumption of total dissociation of the salt. The saturation vapor pressure of the pure solvent *i*, P_i^s , at system temperature was calculated by the Antoine equation using Antoine constants from the literature (Gmehling et al., 1977). The activity coefficient of the solvent *i* was calculated by eq 11. The fitted interaction parameters are listed in Table 6, together with the parameters taken from the literature (Li et al., 1994). Mean absolute deviations between experimental and calculated vapor-phase mole fractions are listed in Tables 1–5. The calculated vapor-phase mole fractions show satisfactory agreement with the experimental values.

The salt effect on the VLE can be seen more easily from the ratio of the relative volatilities (Johnson and Furter, 1960)

$$\ln\left(\frac{a_s}{a_0}\right) = \ln\left[\frac{(y_1/x_1)/(y_2/x_2)_s}{(y_1/x_1)/(y_2/x_2)_0}\right] = kx_3 \quad (22)$$

where the subscripts *s* and 0 denote the salt-containing and salt-free systems, respectively. *k* is a salt effect parameter that depends on the system and the solvent composition and x_3 is the mole fraction of the salt. The values of $-\ln(a_s/a_0)$ are listed in Tables 1–5. As a typical example, Figure 6 shows $-\ln(a_s/a_0)$ as a function of x_3 . From this figure it is observed that the salt effect parameter, *k*, decreases with increasing ethanol concentration. When the solvent com-

position is fixed, the salt effect is proportional to the salt concentration.

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