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Phase Equilibria for Propan-1-ol + Water + Sodium Chloride and + Potassium Chloride and Propan-2-ol + Water + Lithium Chloride and + Lithium Bromide

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Measurements are reported on phase equilibria of the four mixtures propan-1-ol + water + sodium chloride, propan-1-ol + water + potassium chloride, propan-2-ol + water + lithium chloride, and propan-2-ol + water + lithium bromide at atmospheric pressure. The phase behavior of these mixtures exhibits three-phase equilibria, two liquids and one vapor, different from the previous reports that these only exhibit two phases. The phase diagrams for these mixtures are discussed.

Introduction

In a salt-containing mixture, the thermodynamic properties of the volatile components are different from those in a salt-free mixture. The relative volatilities of volatile components will be significantly altered even at low salt concentration. The increase of the relative volatility of a constituent component in a salt-containing solution is called "salting out"; a decrease is called "salting in". Systematic reviews of the salt effect in vapor–liquid equilibria (VLE) of such mixtures have been made (*1, 2*). Of the numerous vapor–liquid equilibrium studies of salt-containing mixtures, only a few (*3, 4*) had ever reported that the liquid phase will split into two immiscible phases near or at saturated salt concentrations. Though the phenomena of phase-splitting has been observed, the detailed compositions in each of the two immiscible liquid phases were not further analyzed. Instead, only the total composition of the liquid phase is reported and considered for VLE calculations which is not desirable in the design and operation of some important separation processes, such as extractive distillation.

Due to the different solubilities of a salt, as the composition of a binary mixture is varied it is possible for the liquid phase to split into two immiscible phases at certain salt concentrations depending on the solvents and the salt. Once the two immiscible liquid phases appear, the phase equilibrium should be considered as vapor–liquid–liquid equilibria (VLLE) instead of VLE. Some phase diagrams of liquid–liquid equilibria (LLE) (not VLLE) in salt-containing mixtures at a temperature of 25 °C have been published (*5, 6*). In order to observe the vapor–liquid–liquid equilibrium, and analyze the compositions of two liquid phases, a vapor–liquid equilibrium apparatus was designed. Four systems, propan-1-ol + H_2O + NaCl, propan-1-ol + H_2O + KCl, propan-2-ol + H_2O + LiCl, and propan-2-ol + H_2O + LiBr, were chosen to study. Vapor–liquid equilibria and vapor–liquid–liquid equilibria were measured at atmospheric pressure.

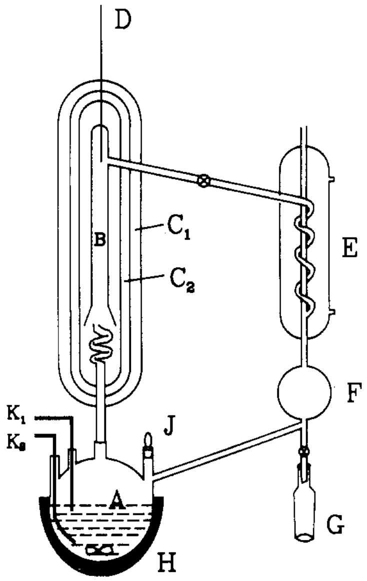

Figure 1. Scheme of vapor–liquid equilibrium apparatus: (A) liquid-phase bottle; (B) vapor-phase column; (C_1, C_2) insulating jackets; (D) thermometer; (E) condenser; (F) buffer; (G) vapor-phase sampling bottle; (H) electric heater with stirrer; (J) injection port; (K_1, K_2) liquid-phase sampling ports.

Experimental Work

Chemicals. The chemicals used were deionized distilled water, propan-1-ol (Kanto Chemical, 99 mass %), propan-2-ol (May & Baker, 99 mass %), LiBr, KCl, NaCl, and LiCl (Koch-Light, 99.95, 99.5, 99.5, and 99 mass %, respectively). All chemicals were used without further purification.

Procedure. The recirculation still used is shown in Figure 1. The liquid sample, about 350 mL, was fed into bottle A

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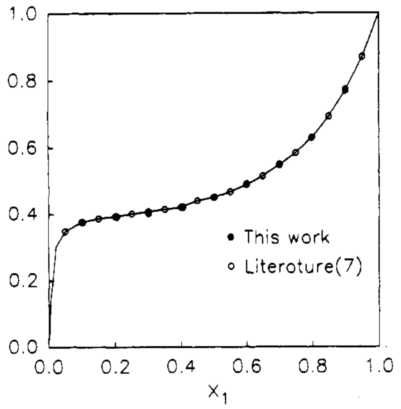

Figure 2. Comparison of these results with those of the literature for the propan-1-ol (1) + H_2O (2) system at atmospheric pressure.

Table I. Vapor–Liquid and Vapor–Liquid–Liquid Equilibria for Propan-1-ol (1) + H_2O (2) + NaCl (3)

(A) Vapor–Liquid Equilibrium

t/°C	x_3	x_1	y_1	α	x_1/x_2
88.0	0.0000	0.1030	0.3742	5.2068	0.1148
88.2	0.0105	0.0982	0.3882	5.8270	0.1102
88.3	0.0210	0.0941	0.4020	6.4717	0.1063
88.3	0.0313	0.0860	0.4253	7.8650	0.0974
88.4	0.0412	0.0843	0.4543	9.0430	0.0964
89.2	0.0532	0.0838	0.4599	9.3097	0.0971
89.8	0.0702	0.0782	0.4823	10.9820	0.0918
90.1	0.0842	0.0773	0.4922	11.5699	0.0922
87.7	0.0000	0.2052	0.3911	2.4878	0.2582
88.1	0.0102	0.2023	0.4203	2.8589	0.2569
88.4	0.0252	0.2011	0.4421	3.1481	0.2599
88.9	0.0302	0.1983	0.4623	3.4759	0.2570
89.6	0.0483	0.1862	0.4850	4.1160	0.2432
87.7	0.0000	0.3010	0.4012	1.5560	0.4306
87.8	0.0112	0.2984	0.4243	1.7329	0.4322
88.0	0.0245	0.2910	0.4406	1.9190	0.4251
88.5	0.0344	0.2873	0.4773	2.2652	0.4236
89.3	0.0499	0.2810	0.4936	2.4940	0.4200
90.0	0.0553	0.2760	0.5150	2.7854	0.4127
87.6	0.0000	0.4062	0.4205	1.0607	0.6841
87.8	0.0103	0.3996	0.4652	1.3070	0.6772
88.2	0.0243	0.3932	0.4865	1.4621	0.6750
88.6	0.0355	0.3882	0.5221	1.7218	0.6736
87.7	0.0000	0.5021	0.4500	0.8113	1.0084
87.9	0.0048	0.5019	0.4823	0.9246	1.0174
88.1	0.0073	0.5065	0.4897	0.9350	1.0418
88.7	0.0101	0.5113	0.5232	1.0488	1.0683
88.0	0.0000	0.6011	0.4897	0.6368	1.5069
88.6	0.0044	0.5823	0.4982	0.7122	1.4089
88.9	0.0086	0.5801	0.5123	0.7604	1.4104
88.8	0.0000	0.7010	0.5480	0.5171	2.3445
89.0	0.0046	0.6967	0.5523	0.5370	2.3324
89.9	0.0000	0.7988	0.6298	0.4285	3.9702
90.4	0.0030	0.7912	0.6422	0.4737	3.8445
92.3	0.0000	0.9012	0.7710	0.3691	9.1215
92.7	0.0012	0.9003	0.7833	0.4003	9.1401

(B) Vapor–Liquid–Liquid Equilibrium

	upper layer		lower layer		
t/°C	x_3	x_1	x_3	x_1	y_1
87.8	0.0134	0.3227	0.0603	0.0520	0.4356
87.9	0.0123	0.3812	0.0653	0.0497	0.4410
88.0	0.0111	0.4742	0.0756	0.0465	0.4499
88.0	0.0098	0.5003	0.0812	0.0443	0.4553
88.2	0.0084	0.5124	0.0899	0.0433	0.4587
88.5	0.0070	0.5370	0.1054	0.0422	0.4675 (satd)

Table II. Vapor–Liquid and Vapor–Liquid–Liquid Equilibria for Propan-1-ol (1) + H_2O (2) + KCl (3)

(A) Vapor–Liquid Equilibrium

t/°C	x_3	x_1	y_1	α	x_1/x_2
88.0	0.0000	0.1020	0.3722	5.2195	0.1136
88.3	0.0115	0.0972	0.3894	5.9233	0.1091
88.5	0.0262	0.0923	0.4133	6.9277	0.1047
88.7	0.0344	0.0872	0.4326	7.9810	0.0993
89.9	0.0774	0.0752	0.4943	12.0206	0.0887
90.3	0.0914	0.0743	0.5023	12.5740	0.0891
87.7	0.0000	0.2048	0.3903	2.4856	0.2575
88.3	0.0122	0.2012	0.4333	3.0356	0.2558
88.5	0.0262	0.2004	0.4536	3.3124	0.2591
89.1	0.0342	0.1953	0.4735	3.7056	0.2535
89.9	0.0583	0.1802	0.4935	4.4326	0.2366
90.6	0.0714	0.1583	0.5113	5.5630	0.2055
87.8	0.0000	0.3023	0.4034	1.5606	0.4333
88.0	0.0143	0.2965	0.4462	1.9117	0.4302
88.3	0.0225	0.2932	0.4621	2.0709	0.4285
88.5	0.0321	0.2893	0.4884	2.3152	0.4263
89.8	0.0512	0.2822	0.5056	2.6012	0.4233
90.2	0.0587	0.2742	0.5187	2.8527	0.4110
87.6	0.0000	0.4034	0.4187	1.0652	0.6762
87.8	0.0123	0.3976	0.4476	1.2277	0.6738
88.3	0.0252	0.3911	0.4887	1.4881	0.6700
88.7	0.0410	0.3823	0.5055	1.6517	0.6629
89.2	0.0505	0.3777	0.5234	1.8094	0.6605
87.7	0.0000	0.5034	0.4511	0.8107	1.0137
88.1	0.0052	0.5003	0.4914	0.9650	1.0117
88.5	0.0074	0.4952	0.5123	1.0708	0.9956
88.9	0.0113	0.4876	0.5334	1.2013	0.9731
89.6	0.0334	0.4776	0.5564	1.3719	0.9767
88.0	0.0000	0.6002	0.4875	0.6336	1.5013
88.5	0.0036	0.5863	0.5213	0.7684	1.4297
89.0	0.0066	0.5831	0.5403	0.8403	1.4212
89.5	0.0089	0.5776	0.5512	0.8982	1.3969
90.1	0.0102	0.5572	0.5734	1.0682	1.3343
88.8	0.0000	0.7021	0.5512	0.5211	2.3568
89.4	0.0056	0.6927	0.5724	0.5939	2.2960
90.4	0.0084	0.6823	0.5912	0.6734	2.2059
89.9	0.0000	0.7980	0.6292	0.4295	3.9505
90.3	0.0022	0.7963	0.6382	0.4512	3.9519
90.5	0.0031	0.7902	0.6554	0.5050	3.8229
92.4	0.0000	0.9022	0.7743	0.3719	9.2249
92.8	0.0015	0.8994	0.7982	0.4424	9.0757

(B) Vapor–Liquid–Liquid Equilibrium

	upper layer		lower layer		
t/°C	x_3	x_1	x_3	x_1	y_1
87.8	0.0155	0.3125	0.0556	0.0571	0.4245
87.8	0.0144	0.3623	0.0634	0.0562	0.4321
88.0	0.0138	0.4621	0.0721	0.0551	0.4398
87.9	0.0115	0.4876	0.0816	0.0540	0.4434
88.3	0.0101	0.5001	0.0854	0.0522	0.4501
88.4	0.0088	0.5126	0.0876	0.0512	0.4554 (satd)

through port J. Energy was supplied from an electrical heater (H) to evaporate the liquid. Once the liquid was boiling, the heater temperature was kept 20 °C higher than the boiling point in order to maintain steady boiling. To reduce heat loss as little as possible, column B was insulated with twofold jackets being vacuated to 10^{-5} Torr. For each run, the time needed to reach equilibrium was 40 min or so; then the system temperature was recorded by a calibrated thermometer (D) with 0.1 K accuracy. All the experiments were run at atmospheric pressure which was 760 ± 3 mmHg. The vapor-phase sample was collected in bottle G. The liquid-phase samples must be collected from ports K_1 and K_2 separately, and then mixed together immediately and placed in a constant-temperature bath which is kept at the same temperature as the system. This method of liquid-phase sampling ensures that both the immiscible liquid-phase samples are collected with minimum error. Placing the liquid-phase samples into the bath was essential to avoid the equilibrium state of the two immiscible liquid phases being altered because the solubilities of the salt in solvents are dependent on temperature.

For each system, the experiment began with a salt-free mixture of solvents with the appropriate composition. After measurement on this mixture, the heater power was turned off and the stopper of port J was removed to add more salt. After the preparation of a new liquid sample, the power of

Table III. Vapor–Liquid and Vapor–Liquid–Liquid Equilibria for Propan-2-ol (1) + H_2O (2) + LiCl (3)

(A) Vapor–Liquid Equilibrium

t/°C	x_3	x_1	y_1	α	x_1/x_2
83.0	0.0000	0.1011	0.5034	9.0129	0.1125
84.1	0.0082	0.0952	0.5112	9.9397	0.1062
84.6	0.0252	0.0864	0.5203	11.4690	0.0973
82.5	0.0410	0.0680	0.5564	17.1910	0.0763
82.6	0.0811	0.0521	0.6750	37.7872	0.0601
83.1	0.1200	0.0350	0.7412	78.9642	0.0414
81.7	0.0000	0.1923	0.5345	4.8228	0.2381
81.7	0.0110	0.1745	0.5482	5.7400	0.2142
81.8	0.0200	0.1652	0.5898	7.2658	0.2027
82.0	0.0451	0.1421	0.6110	9.4827	0.1748
80.9	0.0652	0.1320	0.6448	11.9371	0.1644
81.8	0.1101	0.1208	0.7532	22.2119	0.1571
81.2	0.0000	0.3133	0.5600	2.7896	0.4562
81.5	0.0092	0.3120	0.5713	2.9386	0.4596
81.3	0.0281	0.2911	0.5980	3.6226	0.4276
80.8	0.0520	0.2560	0.6327	5.0062	0.3699
80.4	0.0701	0.2465	0.6833	6.5952	0.3607
82.2	0.0840	0.2503	0.7201	7.7058	0.3760
80.8	0.0000	0.4110	0.5898	2.0605	0.6978
81.1	0.0102	0.4003	0.6089	2.3324	0.6791
80.8	0.0276	0.3903	0.6223	2.5738	0.6705
80.8	0.0530	0.3454	0.6644	3.7520	0.5741
82.0	0.0901	0.3387	0.7324	5.3437	0.5430
80.3	0.0000	0.5330	0.6135	1.3908	1.1413
81.0	0.0111	0.5214	0.6541	1.7358	1.1153
80.6	0.0350	0.5021	0.6804	2.1111	1.0847
81.8	0.0650	0.4972	0.7412	2.8962	1.1357
80.2	0.0000	0.5910	0.6265	1.1608	1.4450
80.6	0.0121	0.5897	0.6373	1.2226	1.4809
80.8	0.0220	0.5712	0.6522	1.4077	1.4041
80.7	0.0360	0.5630	0.7510	2.3411	1.4040
80.5	0.0000	0.7440	0.7371	0.9647	2.9063
80.9	0.0130	0.7360	0.7723	1.2166	2.9323
80.9	0.0000	0.8321	0.7840	0.7324	4.9559
81.2	0.0071	0.8210	0.8444	1.1832	4.7760
81.1	0.0000	0.9101	0.8901	0.8000	10.1235
81.3	0.0030	0.9060	0.9210	1.2096	9.9560

(B) Vapor–Liquid–Liquid Equilibrium

	upper layer		lower layer		
t/°C	x_3	x_1	x_3	x_1	y_1
81.0	0.0154	0.3427	0.0596	0.0526	0.6323
81.2	0.0146	0.3765	0.0665	0.0435	0.6373
81.1	0.0134	0.4431	0.0762	0.0404	0.6412
81.2	0.0122	0.4825	0.0824	0.0378	0.6486
81.2	0.0102	0.5023	0.0903	0.0334	0.6552
81.3	0.0090	0.5470	0.0988	0.0318	0.6615 (satd)

Table IV. Vapor–Liquid and Vapor–Liquid–Liquid Equilibria for Propan-2-ol (1) + H_2O (2) + LiBr (3)

(A) Vapor–Liquid Equilibrium

t/°C	x_3	x_1	y_1	α	x_1/x_2
84.4	0.0000	0.0801	0.5110	12.0011	0.0871
84.2	0.0102	0.0723	0.5232	13.8933	0.0788
84.1	0.0250	0.0621	0.5343	17.3278	0.0680
84.0	0.0430	0.0534	0.5640	22.9307	0.0591
82.7	0.0730	0.0444	0.5933	31.3974	0.0503
82.6	0.1030	0.0383	0.7234	65.6700	0.0446
81.8	0.0000	0.1921	0.5332	4.8039	0.2378
81.8	0.0111	0.1703	0.5448	5.8310	0.2080
82.0	0.0340	0.1497	0.5712	7.5603	0.1797
81.1	0.0503	0.1400	0.6021	9.2953	0.1729
81.0	0.0689	0.1343	0.6423	11.5747	0.1685
81.3	0.0903	0.1203	0.6844	15.8578	0.1524
81.2	0.0000	0.3123	0.5594	2.7958	0.4541
81.6	0.0099	0.3073	0.5712	3.0027	0.4507
81.8	0.0230	0.2902	0.5930	3.5637	0.4225
80.8	0.0503	0.2687	0.6220	4.4784	0.3946
80.4	0.0703	0.2586	0.6643	5.6733	0.3853
82.2	0.0856	0.2521	0.6911	6.6373	0.3806
80.9	0.0000	0.4202	0.5892	1.9790	0.7247
81.1	0.0101	0.4012	0.6020	2.2775	0.6815
80.8	0.0303	0.3812	0.6334	2.8047	0.6477
80.8	0.0532	0.3573	0.6654	3.5771	0.6061
82.1	0.0820	0.3410	0.6889	4.2794	0.5910
80.4	0.0000	0.5110	0.6035	1.4565	1.0450
81.1	0.0121	0.5222	0.6231	1.5127	1.1213
80.6	0.0460	0.4998	0.6956	2.2870	1.1004
81.7	0.0702	0.4811	0.7223	2.8054	1.0722
80.2	0.0000	0.6158	0.6430	1.1237	1.6028
80.5	0.0102	0.6133	0.6633	1.2421	1.6290
80.9	0.0255	0.6003	0.6983	1.5411	1.6042
80.8	0.0388	0.5921	0.7244	1.8107	1.6042
80.2	0.0000	0.7142	0.7030	0.9472	2.4990
80.5	0.0188	0.7132	0.7443	1.1705	2.6612
80.4	0.0000	0.8023	0.7721	0.8348	4.0582
80.6	0.0085	0.8012	0.8021	1.0057	4.2102
81.1	0.0000	0.9020	0.8733	0.7489	9.2041
81.4	0.0021	0.9013	0.8902	0.8878	9.3302

(B) Vapor–Liquid–Liquid Equilibrium

	upper layer		lower layer		
t/°C	x_3	x_1	x_3	x_1	y_1
81.1	0.0167	0.3214	0.0564	0.0526	0.6298
81.1	0.0152	0.3522	0.0653	0.0501	0.6354
81.1	0.0145	0.4214	0.0756	0.0476	0.6398
81.2	0.0134	0.4633	0.0812	0.0452	0.6420
81.2	0.0112	0.4965	0.0886	0.0442	0.6456
81.4	0.0101	0.5254	0.0954	0.0432	0.6543 (satd)

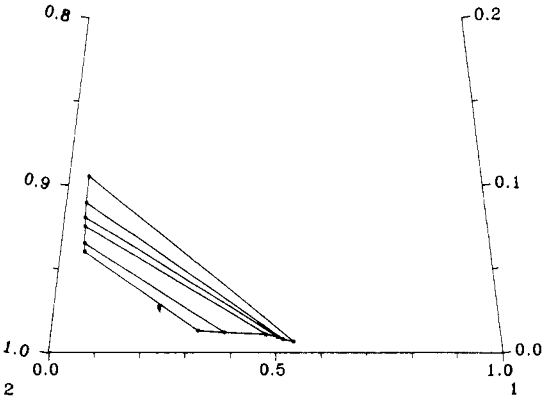

Figure 3. Phase diagram of the propan-1-ol (1) + H_2O (2) + NaCl (3) system at atmospheric pressure and boiling points.

the heater was restarted to proceed with another new experiment. These steps were repeated until the liquid was saturated with salt. The whole liquid sample remaining in bottle A was then discarded, bottle A was washed with distilled water, and a new salt-free mixture with a different composition was prepared for the next experiment run.

Methods of Analysis. The compositions of solvent in the vapor and liquid phases were analyzed by GC with a TCD detector (China Chromatography Co., 8700T). A column of Propak Q was used. The optimum operating conditions were the following: injection temperature, 170 °C; oven temperature, 160 °C; detector temperature, 160 °C; carrier gas, helium with a flow rate of 0.5 $cm^3\ s^{-1}$. To avoid the nonvolatile salt being accumulated in the column, a piece of filter column was placed before the analyzing column. A calibration curve was obtained by measuring a set of standard solutions with known mole fractions of alcohol in the alcohol + H_2O mixtures, and the curve was used to calculate the mole fraction of alcohol in unknown samples. The average error in the measurement of the mole fraction is ±0.0005 which was obtained by comparing the known composition of the made-up sample to the composition calculated from the calibration curve. The mass of salt in the sample was measured, after removal of the solvent, by using a Mettler balance with a precision of ±0.0001 g.

Results and Discussion

To test the reliability of the equilibrium still designed in this study, a vapor–liquid equilibrium experiment of the

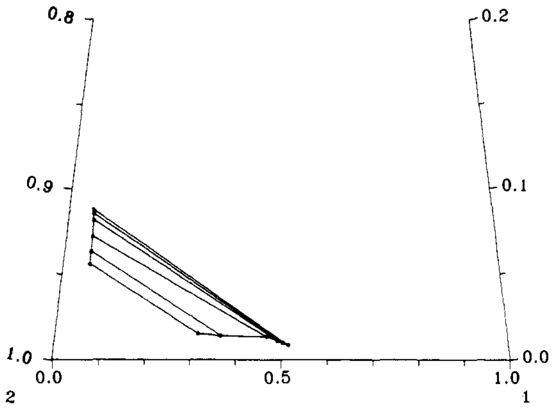

Figure 4. Phase diagram of the propan-1-ol (1) + H_2O (2) + KCl (3) system at atmospheric pressure and boiling points.

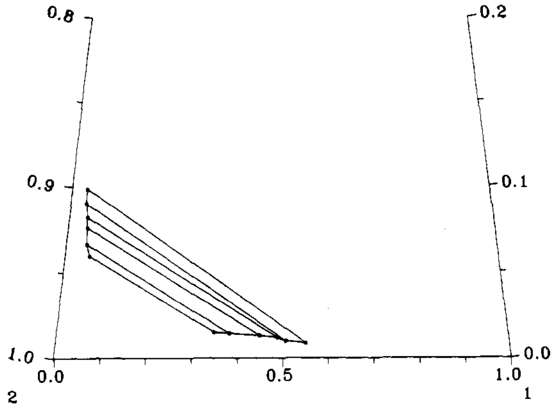

Figure 5. Phase diagram of the propan-2-ol (1) + H_2O (2) + LiCl (3) system at atmospheric pressure and boiling points.

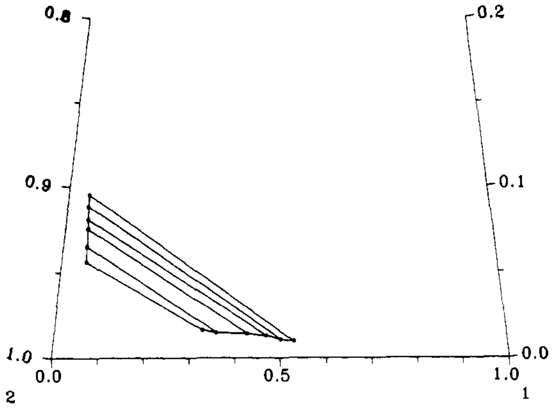

Figure 6. Phase diagram of the propan-2-ol (1) + H_2O (2) + LiBr (3) system at atmospheric pressure and boiling points.

propan-1-ol + H_2O system at atmospheric pressure was done, and the result is shown in Figure 2. The average deviation in the vapor-phase composition between the experimental data and that found in the literature (7) was 0.35%.

The experimental data of the four systems propan-1-ol + H_2O + NaCl, propan-1-ol + H_2O + KCl, propan-2-ol + H_2O + LiCl, and propan-2-ol + H_2O + LiBr at atmospheric pressure are listed in Tables I–IV, respectively. In each system, the subscripts 1–3 represent alcohol, water, and salt, respectively.

The relative volatility α was usually used to reflect the salt effect in a salt-containing mixture. Here, α is defined as

$$\alpha = \frac{y_1/x_1}{y_2/x_2} \qquad (1)$$

where x_1 and y_1 are the mole fractions of alcohol in the liquid and vapor phases, respectively, and x_2 and y_2 are the mole fractions of water in the liquid and vapor phases, respectively. Part A of each table lists the vapor–liquid equilibrium data and is divided into nine subsets. In each subset, the mole ratio x_1/x_2 is nearly constant while the amount of salt is increased. The more salt dissolved in the mixture, the greater the relative volatility. So for each system, alcohol was the salting-out component and water was the salting-in component.

In each system, the liquid phase split into two immiscible phases. Analyzing the compositions of these two equilibrium liquid phases, it was found that the upper layer was the alcohol-rich, salt-poor phase, and the lower layer was the water-rich, salt-rich phase. This was due to the large difference between the solubility of the salt in alcohol and that in water. The salts are perhaps all "structure makers" in the sense of enhancing the structure of water. Therefore, the alcohol tends to become less soluble in water and ultimately forms a second, more stable liquid phase. Once the liquid phase splits, any addition of salt will alter the compositions of both immiscible phases. When the system is saturated with salt, the compositions of each phase will no longer change, even though the relative amount of the two solvents may change as predicted by the phase rule.

The vapor–liquid–liquid equilibrium results are summarized in part B of Tables I–IV. Figures 3–6 are the phase diagrams for the four systems studied. They indicate the regions in which the liquid phase will split.

Conclusion

Vapor–liquid equilibrium measurements were made on four systems consisting of two solvents and one salt at atmospheric pressure. For each mixture, the alcohol was the salting-out component. The reported experimental data included two parts, the vapor–liquid equilibrium data and the vapor–liquid–liquid equilibrium data. It is important to note that when the liquid phase splits into two immiscible liquid phases, the compositions of the two liquid phases should not be treated as a total composition for the reason of better design and operation of some important separation processes.

Glossary

x_1	mole fraction of alcohol in the liquid phase
x_2	mole fraction of water in the liquid phase
x_3	mole fraction of salt in the liquid phase
y_1	mole fraction of alcohol in the vapor phase
y_2	mole fraction of water in the vapor phase
α	relative volatility of alcohol to water

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