J. Chem. Eng. Data **1999,** *44,* 1231−1234

Vapor−Liquid Equilibria of the Water + 1,3-Propanediol and Water + 1,3-Propanediol + Lithium Bromide Systems

SungYong Mun and Huen Lee*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea

Vapor−liquid equilibrium data of the water + 1,3-propanediol and water + 1,3-propanediol + lithium bromide systems were measured at 60, 160, 300, and 760 mmHg at temperatures ranging from 315 to 488 K. The apparatus used in this work is a modified still especially designed for the measurement of low-pressure VLE, in which both liquid and vapor are continuously recirculated. For the analysis of salt-containing solutions, a method incorporating refractometry and gravimetry was used. From the experimental measurements, the effect of lithium bromide on the VLE behavior of water + 1,3-propanediol was investigated. The experimental data of the salt-free system were successfully correlated using the Wilson, NRTL, and UNIQUAC models. In addition, the extended UNIQUAC model of Sander et al. was applied to the VLE calculation of salt-containing mixtures.

Introduction

A salt dissolved in a mixed solvent is capable of altering the composition of the equilibrium vapor phase through preferential association or other structure-related effects in the liquid phase. Hence, the salt effect on vapor−liquid equilibrium (VLE) behavior has been the subject of intense research for a long time. VLE behavior of a salt solution containing lithium bromide has been investigated in this study, emphasizing new knowledge of gas-phase compositions. This work could be very beneficial to the development of a new working fluid for an absorption chiller (Park et al., 1997; Kim et al., 1997). In addition, new experimental VLE data will be valuable in the development of a correlation which is based on a reliable model such as the extended UNIQUAC model of Sander et al. (1986) and simulation of an optimized absorption chiller cycle.

Experimental Section

Chemicals. The lithium bromide (+99 mol %) and 1,3-propanediol (98 mol %) were purchased from Aldrich Chemical Co. The HPLC-grade distilled water was supplied by Merck. All chemicals were used without any further purification.

Apparatus and Procedures. The experimental apparatus used in this work is a modified still (Park and Lee, 1997) especially designed for low-pressure VLE measurements. It is a recirculation-type apparatus, in which both liquid and vapor are continuously recirculated. It allows the determination of the equilibrium compositions of both phases. The temperature in the equilibrium cell was measured with a resistance thermometer (Normschliff Geratebau) having an accuracy of ±0.1 K. The pressure was determined by using a mercury U-tube manometer. When the pressure reached the desired value using a vacuum pump, the cell immersed in a silicone oil bath was then heated with a variable power source. Fine control of the system pressure could be obtained using two needle valves (KONCES Co.) attached to both sides of a small flask. In the middle part of equilibrium cell, two glass tubes causing the siphon effect were provided in order to recirculate the liquid phase. The vapor return branch was wrapped with an electrical heating tape in order to reduce the heat loss as much as possible. For the liquid solution in the cell to boil steadily, the temperature of silicone oil was kept 2−3 K higher than the mixture boiling point. When the equilibrium temperature was attained in the cell, the temperature was maintained for 1 h to ensure equilibrium conditions. A sample from each phase was taken in a short time while maintaining the same pressure inside the equilibrium cell. The vapor- and liquid-phase compositions were determined using an Abbe-type refractometer (ATAGO, 3T). Since the liquid phase contained a salt, the salt was separated using an evaporating apparatus (Yamamoto et al., 1996). The mole fraction of salt in this liquid phase was obtained from the mass of the separated salt.

Results and Discussion

The reliability of experimental procedures and apparatus was checked by measuring the vapor−liquid equilibria of the water−ethylene glycol system at 430 mmHg. Close agreement between the measured and literature data (Trimble and Potts, 1935) was found, as shown in Figure 1. The physical properties of water and 1,3-propanediol are listed in Table 1. Vapor−liquid equilibrium data for the water + 1,3-propanediol system were measured at 60, 160, 300, and 760 mmHg. These results are given in Table 2 and shown in Figure 2. A thermodynamic consistency test was applied to the experimental data by using the point test of Fredenslund et al. (1977). In the point test of Fredenslund, the mean deviation between the experimental and calculated values of the vapor-phase mole fractions should be less than 0.01 to satisfy the thermodynamic consistency. The result of the point test was 0.004 when the order of the Legendre polynomial was 5. The binary equilibrium data were correlated using the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) models for liquid-phase activity coefficients. The vapor phase was assumed to be ideal. The vapor pressures of pure solvents were calculated with equations given by Daubert and Danner (1989). The binary interaction parameters of each model were evalu-

10.1021/je990079r CCC: $18.00

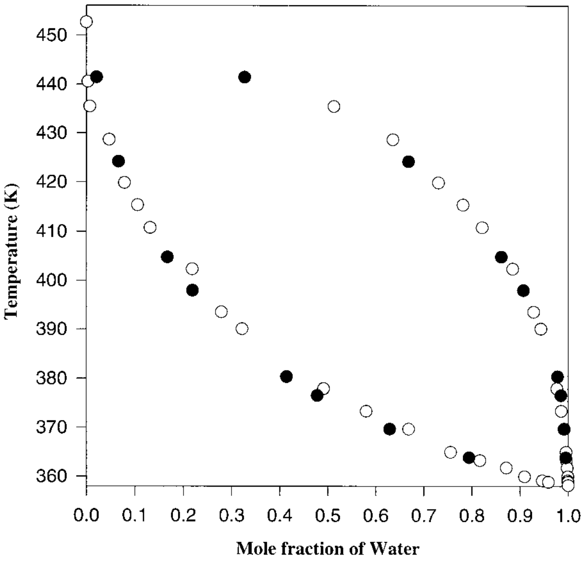

Figure 1. Vapor−liquid equilibria of the water (1) + ethylene glycol (2) system at 430 mmHg: (●) this work; (○) Trimble and Potts (1935).

Table 1. Boiling Points of Chemicals (T_b) and Constants for Antoine Equation[a]

name	T_b/K	A	B	C	region/K
water[b]	373.2	7.9361	1649.3	226.26	373−488
		7.9454	1655.7	226.92	314−460
1,3-propanediol[b]	487.6	9.3636	3118.9	266.66	373−488
		9.1950	2984.2	257.90	314−460

[a] $\log_{10}[P(\text{mmHg})] = A - B/[T(°\text{C}) + C]$. [b] Daubert and Danner (1989).

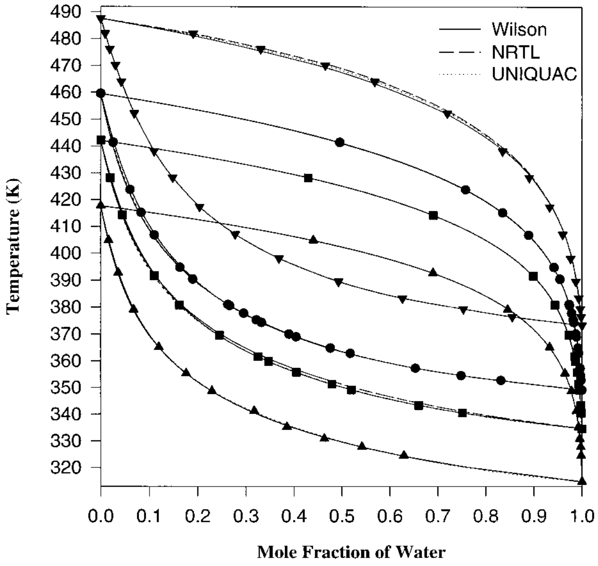

Figure 2. Vapor−liquid equilibria of the water (1) + 1,3-propanediol (2) system: (▲) 60 mmHg; (■) 160 mmHg; (●) 300 mmHg; (▼) 760 mmHg.

ated by a nonlinear regression method based on the maximum-likelihood principle (Kemeny and Manczinger, 1978) and are summarized in Table 3. The calculated equilibrium compositions of the water + 1,3-propanediol system are shown in Figure 1 along with the experimental data. For all the experimental data measured at four pressures, it is clear that the relative volatility of water increases as the pressure decreases. This trend is shown in Figure 3.

Table 2. Experimental Vapor−Liquid Equilibrium Data of the Water (1) + 1,3-Propanediol (2) System at Pressures of 60, 160, 300, and 760 mmHg

T/K	x_1	y_1	T/K	x_1	y_1
		760 mmHgT/K			
487.55	0.0000	0.0000	417.25	0.2040	0.9326
481.95	0.0089	0.1908	407.05	0.2778	0.9598
476.25	0.0184	0.0035	398.05	0.3685	0.9763
470.15	0.0299	0.4653	389.45	0.4929	0.9873
463.95	0.0420	0.5685	383.25	0.6263	0.9932
452.15	0.0690	0.7196	379.25	0.7535	0.9964
438.15	0.1100	0.8439	376.35	0.8551	0.9982
428.25	0.1482	0.8902	373.15	1.0000	1.0000
		300 mmHg			
459.45	0.0000	0.0000	375.25	0.3218	0.9818
441.35	0.0254	0.4957	374.25	0.3324	0.9830
423.65	0.0603	0.7580	369.95	0.3896	0.9876
415.15	0.0831	0.8348	368.95	0.4045	0.9885
406.75	0.1103	0.8893	364.75	0.4759	0.9918
394.65	0.1633	0.9420	362.75	0.5176	0.9930
390.25	0.1898	0.9542	357.15	0.6532	0.9962
380.95	0.2624	0.9733	354.35	0.7487	0.9973
380.55	0.2663	0.9740	352.65	0.8315	0.9982
377.65	0.2955	0.9786	349.05	1.0000	1.0000
	60 mmHg			160 mmHg	
417.65	0.0000	0.0000	442.15	0.0000	0.0000
404.85	0.0160	0.4404	428.15	0.0193	0.4298
392.65	0.0359	0.6901	417.25	0.0447	0.6904
379.05	0.0676	0.8455	391.45	0.1108	0.8987
365.15	0.1198	0.9326	380.75	0.1623	0.9436
355.25	0.1763	0.9646	369.55	0.2450	0.9724
348.75	0.2296	0.9784	361.55	0.3251	0.9842
341.25	0.3171	0.9885	359.75	0.3472	0.9862
335.25	0.3851	0.9928	355.65	0.4050	0.9902
330.85	0.4633	0.9954	351.25	0.4791	0.9935
327.85	0.5416	0.9975	349.15	0.5195	0.9948
324.55	0.6293	0.9985	343.35	0.6600	0.9975
314.75	1.0000	1.0000	340.55	0.7511	0.9985
			334.65	1.0000	1.0000

Table 3. Correlations with Wilson, NRTL, and UNIQUAC Models for the Water (1) + 1,3-Propanediol (2) System

pressure (mmHg)	model	parameters[a]	Δy	ΔT/K
760	Wilson	$\Delta\lambda_{12} = 2651.40$, $\Delta\lambda_{21} = 744.92$	0.0061	0.17
	NRTL	$\Delta g_{12} = 7552.0$, $\Delta g_{21} = -3640.6$, $\alpha = 0.3$	0.0048	0.70
	UNIQUAC	$\Delta\mu_{12} = -401.56$, $\Delta\mu_{21} = 1175.0$	0.0040	0.40
300	Wilson	$\Delta\lambda_{12} = 2365.6$, $\Delta\lambda_{21} = 539.06$	0.0026	0.33
	NRTL	$\Delta g_{12} = 6978.1$, $\Delta g_{21} = -3521.9$, $\alpha = 0.3$	0.0036	0.37
	UNIQUAC	$\Delta\mu_{12} = -368.36$, $\Delta\mu_{21} = 976.76$	0.0008	0.37
160	Wilson	$\Delta\lambda_{12} = 1862.5$, $\Delta\lambda_{21} = -251.56$	0.0031	0.28
	NRTL	$\Delta g_{12} = -1762.5$, $\Delta g_{21} = 1625.0$, $\alpha = 0.3$	0.0016	0.78
	UNIQUAC	$\Delta\mu_{12} = -677.73$, $\Delta\mu_{21} = 903.71$	0.0011	0.17
60	Wilson	$\Delta\lambda_{12} = 1625.0$, $\Delta\lambda_{21} = -1014.1$	0.0021	0.31
	NRTL	$\Delta g_{12} = -1890.6$, $\Delta g_{21} = 1487.5$, $\alpha = 0.3$	0.0022	0.34
	UNIQUAC	$\Delta\mu_{12} = -317.58$, $\Delta\mu_{21} = 183.79$	0.0024	0.37

[a] All energy parameters are expressed in J·mol^{-1}.

Isobaric VLE data were also measured at pressures of 160, 300, and 760 mmHg for the water + 1,3-propanediol + lithium bromide system. The results are presented in Tables 4 and 5. The liquid concentration is presented on a salt-free basis x' ($x' = n_1/(n_1 + n_2)$, where n_1 and n_2 represent the number of moles of solvents 1 and 2). This makes it easy to investigate the effect of salt on the VLE behavior of the salt-free system. As shown in Figure 4, the salt investigated in this work exhibits a salting-out effect on 1,3-propanediol. In other words, addition of lithium bromide to this solvent mixture increases the amount of 1,3-propanediol in the vapor phase at equilibrium. This

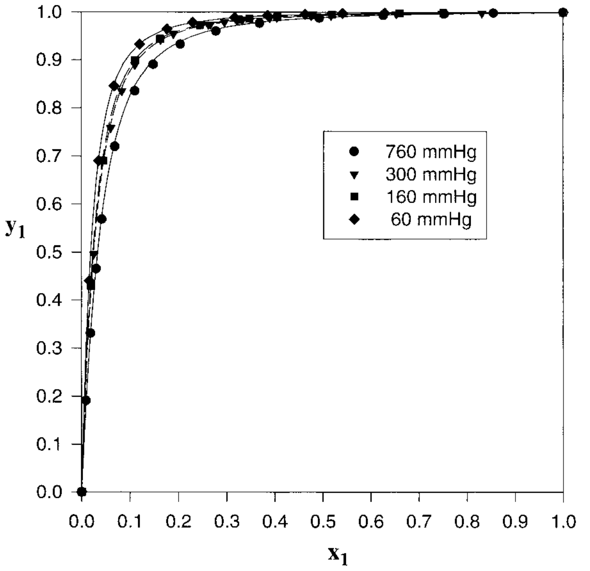

Figure 3. *X*−*Y* plots of all the experimental data of the water (1) + 1,3-propanediol (2) system measured at pressures of 60, 160, 300, and 760 mmHg.

Table 4. Experimental Vapor−Liquid Equilibrium Data of the Water (1) + 1,3-Propanediol (2) + Lithium Bromide (3) System at 760 mmHg

T/K	x_1'	x_3	y_1	T/K	x_1'	x_3	y_1
391.15	0.484	0.007	0.983	438.25	0.140	0.039	0.858
389.35	0.520	0.008	0.986	382.55	0.781	0.038	0.994
399.35	0.372	0.008	0.970	443.45	0.121	0.039	0.831
403.25	0.330	0.009	0.962	379.45	0.880	0.039	0.998
396.45	0.419	0.012	0.973	426.35	0.219	0.055	0.912
416.85	0.221	0.010	0.932	420.95	0.259	0.057	0.931
409.15	0.280	0.011	0.949	430.25	0.203	0.059	0.903
385.15	0.627	0.014	0.992	401.25	0.466	0.060	0.972
443.15	0.101	0.015	0.797	405.25	0.416	0.061	0.962
382.75	0.702	0.016	0.994	399.05	0.504	0.064	0.976
431.45	0.152	0.019	0.881	393.65	0.603	0.066	0.986
381.05	0.773	0.024	0.995	387.45	0.743	0.068	0.994
408.65	0.308	0.026	0.950	441.25	0.160	0.069	0.865
425.25	0.191	0.028	0.902	391.15	0.667	0.073	0.992
388.85	0.585	0.027	0.988	429.35	0.230	0.078	0.905
449.35	0.090	0.027	0.765	407.15	0.450	0.090	0.963
399.25	0.420	0.029	0.968	423.25	0.297	0.092	0.926
431.35	0.163	0.031	0.879	405.85	0.479	0.094	0.965
380.35	0.810	0.028	0.996	417.25	0.353	0.093	0.944
418.15	0.240	0.031	0.927	472.65	0.065	0.118	0.538
386.75	0.643	0.030	0.992	483.25	0.048	0.142	0.408
383.55	0.729	0.032	0.994	487.95	0.030	0.168	0.267
380.85	0.820	0.036	0.995				

Table 5. Experimental Vapor−Liquid Equilibrium Data of the Water (1) + 1,3-Propanediol (2) + Lithium Bromide (3) System at 160 and 300 mmHg

T/K	x_1'	x_3	y_1	T/K	x_1'	x_3	y_1
	160 mmHg				300 mmHg		
377.35	0.247	0.051	0.961	392.35	0.241	0.052	0.954
388.85	0.168	0.048	0.928	397.95	0.203	0.051	0.938
398.75	0.120	0.050	0.878	408.35	0.145	0.051	0.894
404.45	0.097	0.052	0.825	414.15	0.120	0.052	0.866
414.45	0.065	0.049	0.732	429.45	0.068	0.049	0.726
376.85	0.309	0.102	0.961	400.05	0.239	0.102	0.924
385.95	0.235	0.101	0.939	409.05	0.184	0.102	0.895
402.45	0.136	0.098	0.852	422.25	0.117	0.101	0.802
411.35	0.096	0.102	0.759	429.25	0.091	0.102	0.711
417.55	0.071	0.099	0.665	433.55	0.076	0.100	0.683

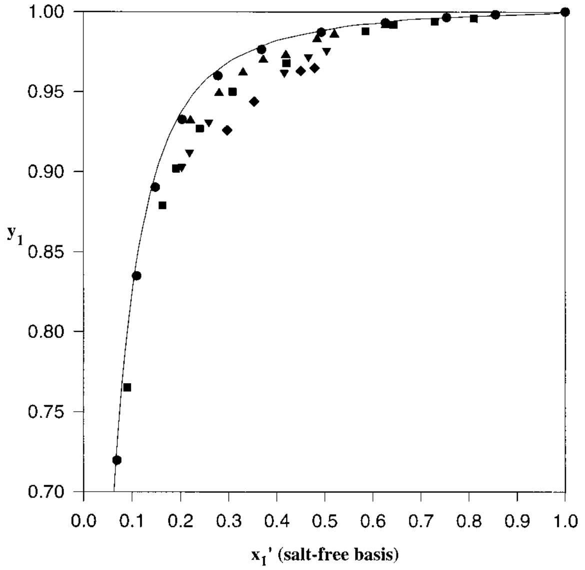

Figure 4. Vapor−liquid equilibria of the water (1) + 1,3-propanediol (2) + lithium bromide (3) system at 760 mmHg: (●) salt-free system; (▲) x_3 = 0.007−0.014; (■) x_3 = 0.026−0.032; (▼) x_3 = 0.055−0.064; (◆) x_3 = 0.090−0.093.

Table 6. UNIQUAC Reference Interaction Parameters (a^*_{kl}/K)

	H_2O	$C_3H_8O_2$	Li^+	Br^-
H_2O	0.0	−48.3[a]	−59.2[b]	−43.5[b]
$C_3H_8O_2$	141.33[a]	0.0	1756.73[c]	1084.64[c]
Li^+	−484.2[b]	885.93[c]	0.0	10.0[c]
Br^-	−128.8[b]	868.96[c]	−903.96[c]	0.0

[a] Binary interaction parameter for the salt-free system. [b] Sander et al. (1986). [c] Estimated from the data of this work.

indicates a preferential association of lithium bromide with water. Experimental results for the salt-containing system were correlated using the extended UNIQUAC model of Sander et al.(1986). The UNIQUAC volume (r_k) and surface area (q_k) parameters were taken from the original paper of Sander et al. (1986). The model parameters are ion-specific values, and no ternary parameters are required. For a binary solvent−salt system, the following 14 parameters were needed to calculate the VLE: two solvent−solvent interaction parameters; two ion−ion interaction parameters; eight ion−solvent interaction parameters; and two salt−solvent interaction parameters. The interaction parameters between water and ions studied in this work were presented by Sander et al. (1986), and the solvent−solvent interaction parameters were obtained by the salt-free system correlation. The other model parameters were estimated by minimization of the following objective function:

$$F = \sum^{N} [(\ln \gamma_{1,\mathrm{exptl}} - \ln \gamma_{1,\mathrm{calcd}})^2 + (\ln \gamma_{2,\mathrm{exptl}} - \ln \gamma_{2,\mathrm{calcd}})^2]$$

where γ_{exptl} and γ_{calcd} refer to the experimental and calculated activity coefficients, respectively, and N is the number of data points. The calculated and experimental activity coefficients were obtained assuming that the vapor phase is ideal. Since the pressure is low and there are other sources of uncertainties in the experimental measurements, this assumption is acceptable. The UNIQUAC reference interaction parameters a^*_{kl} and the $\delta_{ij,m}$ parameters are presented in Tables 6 and 7. The model represented experimental data with high accuracy, especially at a low salt concentration. At pressures of 160, 300, and 760 mmHg, the mean absolute deviations in the vapor phase were 0.0342, 0.0338, and 0.0130 mole fractions, respectively. A comparison between the experimental and

Table 7. $\delta_{ij,m}$/K Parameters ($\delta_{ij,m} = \delta_{ji,m}$)

	$m = H_2O$	$m = C_3H_8O_2$
LiBr	35098.93[a]	197995.8[a]

[a] Estimated from the data of this work.

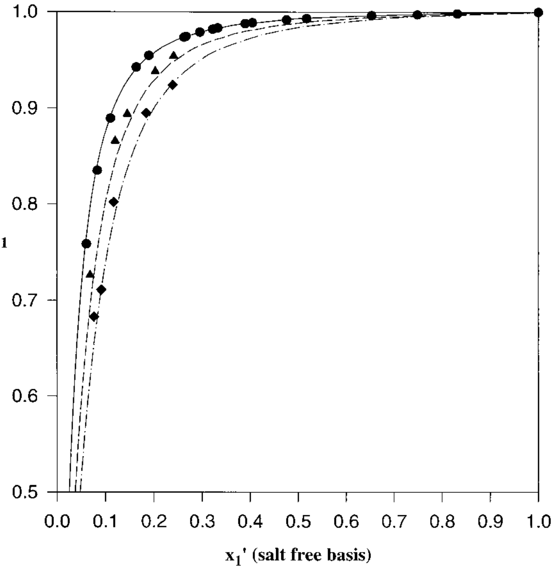

Figure 5. Vapor−liquid equilibria of the water (1) + 1,3-propanediol (2) + lithium bromide (3) system at 300 mmHg: (●, —) experimental and calculated results for the salt-free system; (▲, − −) experimental and calculated results at $x_3 = 0.05$; (◆, − · − · −) experimental and calculated results at $x_3 = 0.10$.

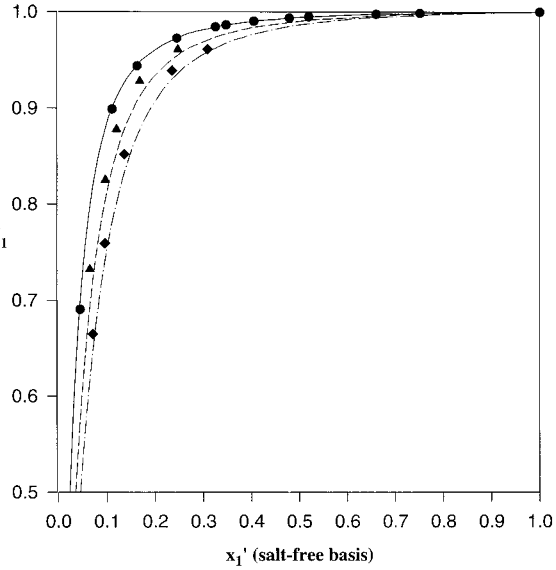

Figure 6. Vapor−liquid equilibria of the water (1) + 1,3-propanediol (2) + lithium bromide (3) system at 160 mmHg: (●, —) experimental and calculated results for the salt-free system; (▲, − −) experimental and calculated results at $x_3 = 0.05$; (◆, − · − · −) experimental and calculated results at $x_3 = 0.10$.

calculated values is shown in Figures 5 and 6. As Sander mentioned in his work, the predicted values are expected to be the most reliable at atmospheric pressure because most of the experimental data used to find out the parameter values were measured under atmospheric pressure conditions.

Nomenclature

a^*_{im} = reference interaction parameter
F = objective function
Δg_{ij} = interaction energy parameter of NRTL model
k_{ij} = binary interaction parameter
N = the number of data points
P = pressure
r_k = UNIQUAC volume parameter
q_k = UNIQUAC surface area parameter
T = temperature
T_b = boiling point
ΔT = mean absolute deviation in bubble point temperature
x_i = liquid-phase mole fraction of component i
x_i' = liquid-phase mole fraction of component i on a salt-free basis
y_i = vapor-phase mole fraction of component i
Δy = mean absolute deviation in vapor phase composition

Greek Letters

α = nonrandomness factor
$\delta_{ij,m}$ = interaction parameter between salt and solvent
γ_{calcd} = calculated activity coefficient
γ_{exptl} = experimental activity coefficient
$\Delta\lambda_{ij}$ = interaction energy parameter of Wilson model
$\Delta\mu_{ij}$ = interaction energy parameter of UNIQUAC model

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

Daubert, T. E.; Danner, R. P. *Physical And Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere Publishing Co.: New York, 1989.

Fredenslund, A.; Gemhling, J.; Rasenmussen, P. *Vapor-Liquid Equilibria using UNIFAC*; Elsvier: Amsterdam, 1977.

Kemeny, S.; Manczinger, J. Treatment of Binary Vapor-Liquid Equilibrium Data. *Chem. Eng. Sci.* **1978**, *33*, 71−76.

Kim, J. S.; Park, Y.; Lee, H.; Yu, S. I. Heat Capacities of the Water + Lithium Bromide + Ethanolamine and Water + Lithium Bromide + 1,3-propanediol Systems. *J. Chem. Eng. Data* **1997**, *42*, 371−373.

Park, S. B.; Lee, H. Vapor-Liquid Equilibria for the Binary Monoethanolamine+Water and Monoethanolamine+Ethanol Systems. *Korean J. Chem. Eng.* **1997**, *14* (2), 146−148.

Park, Y.; Kim, J. S.; Lee, H. Physical Properties of the Lithium Bromide + 1,3-Propanediol + Water System. *Int. J. Refrig.* **1997**, *20*, 319−325.

Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

Sander, B.; Fredenslund, A.; Rasmussen, P. Calculation of Vapor-Liquid Equilibria in Mixed Solvent/Salt System Using an Extended UNIQUAC Equation. *Chem. Eng. Sci.* **1986**, *41*, 1171−1183.

Trimble, H. M.; Potts, W. Glycol-Water Mixtures Vapor Pressure-Boiling Point-Composition Relations. *Ind. Eng. Chem.* **1935**, *27*, 66−68.

Wilson, G. M. Vapor-liquid equilibrium XI: A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−134.

Yamamoto, H.; Fukase, K.; Shibata, J. Vapor-Liquid Equilibria for Alcohol + Alcohol + Sodium Iodide at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1066−1070.

Received for review March 16, 1999. Accepted July 12, 1999. This work was supported by Grant No. 97-2-10-0301-3 from the Basic Research Program of the KOSEF.

JE990079R