Isobaric Vapor-Liquid Equilibria for the Systems Glycerol-Water and Glycerol-Water Saturated with Sodium Chloride

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Vapor-liquid equilibrium data at atmospheric pressure for the systems glycerol-water and glycerol-water saturated with sodium chloride were determined in an improved Othmer still. The binary mixtures and salt-saturated solutions were analyzed by refractive index measurements. The equilibrium data for the glycerol-water system were thermodynamically consistent when tested by Herington's method.

Vapor-liquid equilibrium data for the systems glycerol-water and glycerol-water saturated with sodium chloride are of theoretical and industrial importance. Several industrial processes yield glycerol, sodium chloride, and water (*4*, *12*). Adequate knowledge of the vapor-liquid equilibrium data for these systems is useful. Although boiling point–composition data for both systems have been reported (*1*, *14*), it is difficult to predict their vapor-liquid equilibria because of the highly nonideal behavior of the systems, and experimental determinations are necessary.

EXPERIMENTAL

Chemicals. The glycerol and sodium chloride used were Fisher certified reagent grade. Glycerol containing about 4% of water was used as received throughout this investigation. The presence of water in the glycerol was not a cause for concern, as the other liquid component in this study was water. Demineralized water from a laboratory ion exchange unit (Bantam demineralizer by Barnstead) with a conductivity of less than 10^{-6} ohm^{-1} cm^{-1} was used. Both the glycerol and water were checked by refractive index as well as density measurements; the values thus determined were remarkedly consistent with literature data, as indicated in Table I.

Analytical Method. Refractive index measurement was used for analyzing the unknown binary liquid mixtures of both systems. This method afforded greater accuracy, less time required per sample, and the requirement of small samples only. Refractive index–composition data for the salt-free glycerol-water system are available (*7*). Measurements were made at 20.00° ± 0.02° C by means of an improved precision Valentine refractometer, with compensating prism, and an incandescent light source. Values were readily determined to 0.0001. To permit analysis of the ternary system, aqueous glycerol solutions of various concentrations by weight were carefully prepared and saturated with sodium chloride at 20° C. Salt content was determined by titration against standard silver nitrate (*14*). Refractive indices of the salt-saturated solutions were then determined at 20° C and a calibration curve for the system was prepared. Temperature measurement was made by a mercury-in-glass thermometer calibrated by the National Bureau of Standards. Table II shows the analytical data for the ternary system at 20° C.

Apparatus and Procedures. Equilibrium data were obtained by the use of an improved Othmer still (*9*). Temperature measurements were made to within ±0.2° C, using a copper-constantan thermocouple submerged in a thin-walled glass

Table I. Physical Properties of Liquids Used

	Density, G/Cc, 20° C		Refractive Index, 20° C	
Liquid	Exptl.	Lit.	Exptl.	Lit.
Water	0.9982	0.9982 (*8*)	1.3330	1.3330 (*8*)
Glycerol[a]	1.2546	1.2547 (*8*)	1.4680	1.4678 (7)

[a] Purity of glycerol used 96.30 weight %.

Table II. Refractive Index–Composition Data for Glycerol-Water Saturated with Sodium Chloride at 20° C

Weight % Glycerol[a]	Grams NaCl per 100 Grams Solution	Refractive Index, n_D, 20° C
0.00	36.0	1.3802
10.00	24.3	1.3868
20.00	22.4	1.3945
30.00	20.4	1.4026
40.00	18.3	1.4111
50.00	16.4	1.4204
60.00	14.3	1.4306
70.00	12.2	1.4412
80.00	10.4	1.4525
90.00	8.8	1.4640
100.00[b]	7.9	1.4759

[a] Salt-free basis. [b] Extrapolated.

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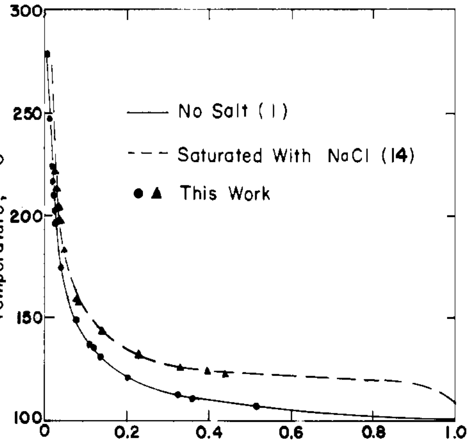

Figure 1. Boiling point data

well in the liquid. The thermocouple-potentiometer combination was calibrated against mercury-in-glass thermometers certified by the National Bureau of Standards. The boiling point–composition data agree rather well with the literature values (*1, 14*), as shown in Figure 1. An Emil Greiner Model 6 Cartesian manostat was used to maintain the system under a constant pressure of 760 ± 2.0 mm of Hg. The system was operated under a nitrogen atmosphere to avoid the possibility of the decomposition of glycerol due to the presence of oxygen in air. Atmospheric pressure was measured with a mercury column barometer. A surge tank between the still and the manostat served to damp out pressure fluctuations and thus to steady the readings of an oil manometer. Pressure was applied from a cylinder of compressed nitrogen, and vacuum, when required, was obtained by means of a water aspirator. The system was adjusted to a pressure of 760 mm of Hg and then sealed off from the atmosphere by the manostat. For the salt-saturated system, no attempt was made to control the pressure until after all salt additions had been completed and it was definitely established that an excess of solid salt was present. An external heater, rather than an internal one as in the original design, was employed for the same reason. The duration of a run was about 6 hours, as several preliminary runs indicated that this period was more than adequate to attain constancy of composition. The operating procedures of the equilibrium still are fairly standard (*2, 11*). Slow heating and boiling chips were employed to avoid bumping of the liquid during boiling.

RESULTS AND DISCUSSION

Tables III and IV and Figure 2 show the experimental and smoothed t-x-y data along with the activity coefficients

Table III. Vapor-Liquid Equilibrium Data for Glycerol-Water System

Experimental							Smoothed		
	Weight Fraction		Mole Fraction					Weight Fraction	
Temp., °C	x_1	y_1	x_1	y_1	γ_1	γ_2	Temp., °C	x_1	y_1
278.8	0.0055	0.7267	0.0275	0.9315	0.540	0.089	282.5	0.0050	0.4900
247.0	0.0095	0.7787	0.0467	0.9473	0.537	0.169	244.5	0.0100	0.7350
224.0	0.0143	0.8105	0.0690	0.9563	0.567	0.219	207.0	0.0200	0.9075
219.2	0.0160	0.8810	0.0767	0.9743	0.570	0.188	175.2	0.0400	0.9500
210.0	0.0190	0.8980	0.0901	0.9783	0.580	0.275	158.6	0.0600	0.9700
202.5	0.0220	0.8730	0.1031	0.9724	0.581	0.384	148.2	0.0800	0.9820
196.5	0.0250	0.9225	0.1159	0.9839	0.603	0.364	140.4	0.1000	0.9870
175.2	0.0400	0.9505	0.1756	0.9899	0.640	0.603	128.8	0.1500	0.9897
149.3	0.0775	0.9817	0.3004	0.9964	0.720	1.05	122.0	0.2000	0.9910
137.2	0.1090	0.9875	0.3847	0.9976	0.788	1.41	109.8	0.4000	0.9955
136.8	0.1110	0.9885	0.3895	0.9878	0.790	1.35	104.6	0.6000	0.9980
131.8	0.1313	0.9877	0.4358	0.9976	0.813	2.13	101.7	0.8000	0.9990
121.5	0.2015	0.9915	0.5633	0.9984	0.862	3.42	100.0	1.0000	1.0000
112.8	0.3205	0.9962	0.7068	0.9993	0.909	3.90			
111.3	0.3560	0.9970	0.7386	0.9994	0.916	4.15			
106.3	0.5145	0.9980	0.8442	0.9996	0.951	6.20			

Table IV. Vapor-Liquid Equilibrium Data for Glycerol-Water Saturated with Sodium Chloride

Experimental							Smoothed		
	Weight Fraction		Mole Fraction					Weight Fraction	
Temp., °C	$x_1{}^a$	y_1	$x_1{}^a$	y_1	γ_1	γ_2	Temp., °C	$x_1{}^a$	y_1
222.0	0.0200	0.9620	0.0944	0.9924	0.442	0.061	222.0	0.0200	0.9620
212.5	0.0250	0.9650	0.1159	0.9930	0.433	0.081	202.3	0.0300	0.9675
204.0	0.0290	0.9655	0.1324	0.9930	0.450	0.114	188.2	0.0400	0.9730
197.5	0.0330	0.9700	0.1485	0.9940	0.460	0.131	171.2	0.0600	0.9810
182.8	0.0455	0.9755	0.1959	0.9951	0.481	0.212	158.8	0.0800	0.9855
159.5	0.0785	0.9835	0.3038	0.9968	0.546	0.454	151.5	0.1000	0.9887
159.0	0.0797	0.9860	0.3068	0.9973	0.547	0.439	141.3	0.1500	0.9923
143.7	0.1385	0.9935	0.4510	0.9988	0.559	0.554	134.8	0.2000	0.9937
132.2	0.2290	0.9967	0.6029	0.9994	0.582	0.846	124.0	0.4000	0.9970
125.8	0.3300	0.9970	0.7157	0.9994	0.596	1.40	121.4	0.6000	0.9985
124.3	0.3960	0.9980	0.7702	0.9996	0.578	1.36	120.0	0.8000	0.9995
123.5	0.4375	0.9985	0.7990	0.9997	0.572	1.33	109.0	1.0000	1.0000

[a] Salt-free basis.

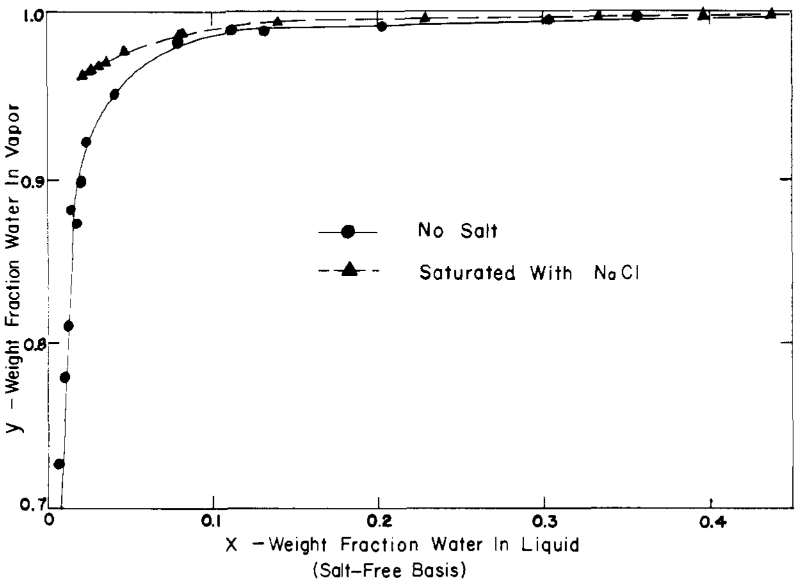

Figure 2. Vapor-liquid equilibrium data

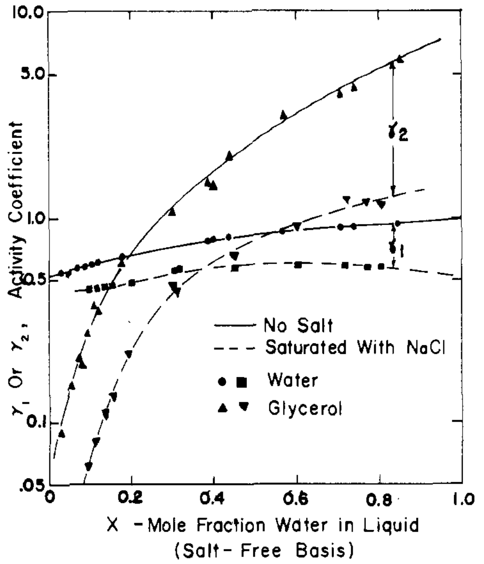

Figure 3. Activity coefficients

(Figure 3) for the systems studied. The solubilities of sodium chloride in the binary liquid mixtures at their boiling points have been reported (*14*) and are not included here. The activity coefficients were calculated by the equation

$$\gamma_i = \frac{\pi y_i}{p_i x_i} \tag{1}$$

The vapor pressure data for pure liquid water (*8*) and glycerol (*10, 13*) are available in the literature. For the ternary system, the activity coefficients were calculated for the two liquids by using the vapor pressures at the boiling points of the solution saturated with sodium chloride.

It can be seen, by comparing Tables III and IV and the lines on Figure 3, that the activity coefficients of both water and glycerol for the ternary system are decreased over the entire range by the presence of the salt. This is as would be expected, as the salt has a marked solubility in both liquids which would tend to reduce the escaping tendency of both water and glycerol. The salt effect is more pronounced in the case of glycerol, as sodium chloride is more soluble in glycerol than in water on the basis of moles of solute per mole of solvent. Simultaneous positive and negative deviations from Raoult's law are observed for the systems studied. This is not unexpected for the salt-saturated system. For the salt-free system, this behavior is apparently caused by the formation of strong hydrogen bonds between glycerol and water (*3*).

Herington proposed a method of testing isobaric equilibrium data for thermodynamic consistency (*5, 6*). This involves plotting log (γ_1/γ_2) *vs.* x_1, as shown in Figure 4. The algebraic sum of areas *A* and *B* is evaluated by graphical integration as follows:

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = \mathrm{I} \tag{2}$$

A percentage deviation, *D*, is calculated by

$$D = \frac{100|I|}{\Sigma} \tag{3}$$

where $|I|$ is the absolute value of *I*. The percentage deviation is then compared with another value, *J*, defined by

$$J = \frac{150|\theta|}{T_{\min}} \tag{4}$$

On the basis of the treatment of a large amount of experimental data, Herington showed thermodynamically that if the condition

$$D < J \tag{5}$$

is fulfilled, the data are considered to be consistent. Applying Herington's method to the glycerol-water system yields values for $\Sigma = 0.504$, $D = 65.0$, and $J = 76.4$. Therefore, we may conclude that the experimental data of the binary system are indeed thermodynamically consistent. The inconsistencies indicated by the activity coefficients are apparently due to the assumption of ideal behavior of the vapor phase in calculating the coefficients as implied in Equation 1.

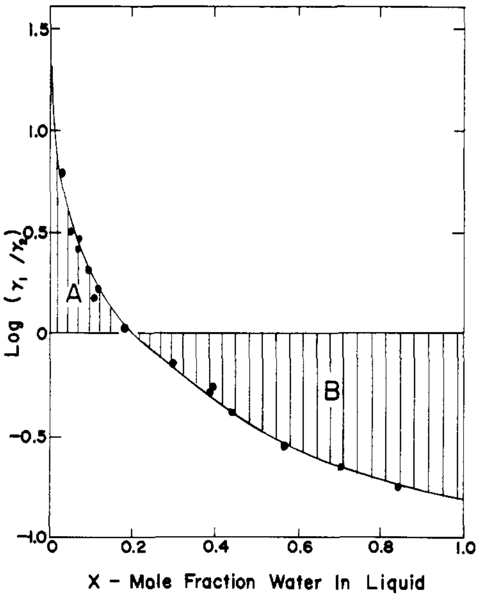

Figure 4. Consistency of glycerol-water system by Herington's method

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NOMENCLATURE

D = percentage deviation defined by Equation 3
I = algebraic sum of areas in Figure 4, defined by Equation 2
J = parameter defined by Herington, Equation 4
p = vapor pressure of pure component, mm Hg
$T_{\min}$ = lowest boiling point of system, ° K
x = mole fraction or weight fraction in liquid phase as indicated
y = mole fraction or weight fraction in vapor phase as indicated
γ = activity coefficient
θ = difference in boiling points of system at given pressure, ° C or ° K
π = total pressure, mm of Hg
Σ = sum of areas A and B in Figure 4 without regard to sign

Subscripts

1, 2 = components water and glycerol, respectively
i = component 1 or 2

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Enthalpies of Tetralin and Mixtures of Tetralin and *n*-Pentane

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Enthalpy measurements for Tetralin and five mixtures of Tetralin with *n*-pentane are presented for the temperature range 120° to 660° F., with pressures up to 1400 p.s.i.a.

A FLOW CALORIMETER has been used to measure the enthalpy of Tetralin (1,2,3,4-tetrahydronaphthalene) and mixtures containing 19.7, 39.9, 58.8, 79.5, and 89.3 mole % *n*-pentane. The temperature ranged from 120° to 688° F., with pressures up to 1400 p.s.i.a. The flow calorimeter has been described (*4*). Comparison with the literature values for pentane (*2*) and water (*7*) shows that the apparatus measures enthalpy differences with an average deviation of 1.5 B.t.u. per pound.

The *n*-pentane used was of very high purity, and by chromatographic analysis had only a trace of isopentane. The Tetralin was purified by fractional distillation, using a laboratory-packed column with about 20 theoretical stages and a reflux ratio of 40 to 1. The selected pure Tetralin portion had a refractive index of 1.5410 n_D^{20}, and a density of 0.9691 at 60° F.

The calorimeter measures the enthalpy of the hydro-

Table I. Properties of Liquid Phase Tetralin Systems with *n*-Pentane at 75° F and 1 Atm

Material	Wt. % *n*-Pentane	Liquid Density, G./Cm.^{3}	Heat of Mixing, B.t.u./Lb.	Enthalpy to Add, B.t.u./Lb.
100% Tetralin	0	0.9619	0	91.7
19.7 mole % pentane	11.8	0.9133	1.53	97.4
39.9 mole % pentane	26.6	0.8527	1.92	103.5
58.8 mole % pentane	43.7	0.7867	1.81	109.8
79.5 mole % pentane	67.9	0.7113	1.11	118.2
89.3 mole % pentane	82.0	0.6681	0.64	122.4
100 mole % pentane	100.0	0.6219	0	129.4