J. Chem. Eng. Data 1980, 25, 271-273

Table V. Deviations for 2600 Common Points

combination of density correlation and mixing rule for T_{cm}	% av dev
i modified Rackett equation with Chueh-Prausnitz mixing rule	2.67
ii generalized Guggenheim equation with	
(a) Chiu et al. mixing rule	3.55
(b) Li mixing rule	3.32

Table VI. Summary of the Deviations for Polar Systems

	density model			
	generalized Guggenheim	Harmens	modified Rackett	Halm and Stiel
(a) Chueh-Prausnitz (824)[a]				
(i) % av dev	3.50	2.67	1.55	6.27
(ii) % max dev	−23.30	−26.63	−20.75	−70.50
(b) Harmens (830)[a]				
(i) % av dev		2.61		
(ii) % max dev		−17.88		
(c) Chiu et al. (826)[a]				
(i) % av dev	3.19			
(ii) % max dev	−28.39			

[a] Mixing rule for pseudocritical temperature. The numbers in parentheses indicate the number of points.

V	saturated liquid volume, cm^3/g-mol
x	mole fraction
Z_{RA}	constant in modified Rackett equation

Subscripts

c	ciritical value
i,j	components
ij	i–j binary interaction
m	mixture value
r	reduced value

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Vapor–Liquid Equilibrium Data for the Systems H_2O–H_2SO_4–HCl, H_2O–H_2SO_4–HBr, and H_2O–HBr at 780 mmHg Pressure

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With the help of a dynamic still made of tantalum, the liquid–vapor equilibria in the ternary systems H_2O–H_2SO_4–HCl and H_2O–H_2SO_4–HBr have been determined for the range of concentrations used in extractive distillation with sulfuric acid as solvent. Liquid–vapor equilibrium in the binary system H_2O–HBr has been determined for concentrations lower than that of the azeotrope. Hála's correlation is used to calculate the equilibrium compositions. Equilibrium temperatures are correlated with an empirical relation.

All the measurements found in the literature (*1*, *2*) relating to isobaric liquid–vapor equilibrium of the system H_2O–H_2SO–HCl cover a very small range of low hydrogen acid mole fractions only. For the system H_2O–H_2SO_4–HBr no result has been published at this date.

The importance of the knowledge of phase equilibria, particularly for the design of extractive distillation columns destined to completely recover the hydracid by removing the azeotrope H_2O–HCl or H_2O–HBr in the presence of sulfuric acid as solvent, has involved us in determining liquid–vapor equilibria in the two ternary systems H_2O–H_2SO_4–HBr and H_2O–H_2SO_4–HCl. The equilibrium of the binary H_2O–HBr has been also determined for concentrations lower than that of the azeotrope.

Experimental Method

Liquid–vapor equilibria are realized with the help of a dynamic Aubry-Gilot' pattern still (*3*). It consists of a tantalum coil mounted in a vessel through which circulates a thermoregulated fluid. The investigated solution passes continuously through the tantalum coil at a rate which permits sufficient contact time to establish thermal and phase equilibrium. At the outlet, the liquid

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Table I. Vapor-Liquid Equilibrium Data at 780 mmHg Pressure for the System H_2O-H_2SO_4-HCl

X_2	X_1	Y_1	t_b/°C
0.0813	0.0569	0.1922	112.2
0.0936	0.0314	0.0810	113.2
0.0965	0.0567	0.3143	110.9
0.1008	0.0325	0.1108	113.8
0.1067	0.0442	0.2664	113.5
0.1163	0.0430	0.3378	112.4
0.1181	0.0353	0.2590	115.8
0.1229	0.0330	0.2630	115.6
0.1253	0.0387	0.3521	113.2
0.1274	0.0278	0.2275	117.0
0.1292	0.0439	0.4707	106.6
0.1359	0.0328	0.3593	112.8
0.1363	0.0283	0.3018	116.9
0.1365	0.0472	0.6165	104.1
0.1391	0.0400	0.5240	105.9
0.1395	0.0364	0.4883	110.9
0.1406	0.0377	0.5126	107.7
0.1467	0.0211	0.2666	119.7
0.1489	0.0225	0.3005	119.0
0.1507	0.0294	0.4898	112.5
0.1532	0.0278	0.5003	112.7
0.1541	0.0244	0.3829	115.5
0.1543	0.0271	0.4939	112.8
0.1563	0.0335	0.6161	106.0
0.1569	0.0162	0.2657	121.0
0.1585	0.0355	0.7082	104.3
0.1607	0.0244	0.4891	114.5
0.1609	0.0212	0.4493	114.8
0.1696	0.0209	0.5281	113.6
0.1654	0.0255	0.5552	109.6
0.1674	0.0232	0.5371	111.0
0.1696	0.0153	0.3549	117.7
0.1743	0.0106	0.2958	121.3
0.1747	0.0177	0.5056	115.8
0.1775	0.0109	0.3141	121.0
0.1790	0.0134	0.4025	117.1
0.1818	0.0077	0.2368	123.1
0.1822	0.0112	0.3152	119.1
0.1827	0.0156	0.5075	115.0
0.1852	0.0271	0.8601	105.0
0.1866	0.0136	0.4409	116.7
0.1870	0.0199	0.6479	108.6
0.1891	0.0112	0.3189	118.4
0.1893	0.0200	0.7227	107.8
0.1903	0.0171	0.5931	110.0
0.1926	0.0146	0.5904	111.9

and vapor phases are separated and analyzed. The temperature and the pressure are measured in the separator. The temperature is read on a METRIX PX 2000 digital Pt resistance thermometer with an accuracy of ±0.1 °C. The pressure in the still is balanced by an external pressure of nitrogen by means of a differential U-tube manometer (precision ±0.5 mmHg) and measured with a Texas Instruments precision pressure gauge (Model 145) equipped with a fused quartz Bourdon capsule (precision ±0.1 mmHg). The accuracy of the pressure measured in the equilibrium still is therefore better than ±1 mmHg. The temperature of the thermoregulated fluid is adjusted to work under isobaric conditions; a pressure slightly higher than the atmospheric pressure is established in order to balance out variations in this quantity and pressure drops in the apparatus.

As regards the analyses, the total acid content was measured by titration with 0.1 N NaOH, and the concentration of Cl^- or Br^- was measured with a potentiometric system using a silver electrode. The mole fractions are so determined with an accuracy of $\pm 5 \times 10^{-4}$.

Results and Discussion

Table II. Vapor-Liquid Equilibrium Data at 780 mmHg Pressure for the System H_2O-H_2SO_4-HBr

X_2	X_1	Y_1	t_b/°C
0.1457	0.0491	0.1277	131.0
0.1514	0.0584	0.2642	130.7
0.1632	0.0210	0.0190	130.4
0.1689	0.0266	0.0306	132.6
0.1700	0.0200	0.0191	132.3
0.1733	0.0435	0.2243	132.7
0.1757	0.0399	0.1825	133.4
0.1777	0.0364	0.0196	133.7
0.1814	0.0584	0.4225	124.6
0.1849	0.0490	0.4038	129.7
0.1897	0.0150	0.0258	135.4
0.1903	0.0254	0.1203	136.7
0.1918	0.0412	0.4032	132.2
0.1984	0.0215	0.1205	137.9
0.2010	0.0201	0.1317	138.1
0.2033	0.0420	0.4630	128.9
0.2046	0.0367	0.4036	132.7
0.2074	0.0368	0.4310	131.7
0.2084	0.0362	0.4289	132.6
0.2113	0.0300	0.3458	135.6
0.2142	0.0467	0.6200	121.0
0.2197	0.0315	0.4472	133.3
0.2204	0.0169	0.1443	141.0
0.2176	0.0200	0.1824	140.0
0.2187	0.0119	0.1162	140.8
0.2219	0.0280	0.4223	135.4
0.2223	0.0423	0.5980	123.2
0.2225	0.0317	0.1381	141.8
0.2225	0.0315	0.4752	133.1
0.2248	0.0246	0.3870	136.9
0.2252	0.0313	0.4951	132.5
0.2269	0.0120	0.1343	143.2
0.2277	0.0206	0.2753	139.0
0.2280	0.0294	0.4898	133.5
0.2283	0.0167	0.1856	142.0
0.2310	0.0228	0.4162	137.0
0.2338	0.0157	0.2280	143.5
0.2356	0.0182	0.3459	138.8
0.2375	0.0098	0.1101	146.1
0.2419	0.0128	0.2267	146.2
0.2425	0.0141	0.2819	145.3
0.2438	0.0121	0.2229	146.3
0.2448	0.0157	0.4187	139.7
0.2483	0.0218	0.5196	134.4
0.2474	0.0091	0.1732	147.7
0.2508	0.0222	0.5698	131.5
0.2508	0.0210	0.5216	133.5
0.2504	0.0107	0.2119	146.7
0.2523	0.0185	0.5021	136.4
0.2524	0.0200	0.5215	134.6
0.2528	0.0159	0.4681	138.2
0.2556	0.0177	0.5028	135.7
0.2624	0.0159	0.5023	135.9
0.2639	0.0127	0.4584	139.0
0.2695	0.0069	0.2766	148.8
0.2867	0.0109	0.6382	136.6
0.2923	0.0057	0.2587	150.3

Table III. Coefficients of Equation 2

system	A	B	C	D
HCl-H_2SO_4-H_2O	43.073	−29.297	−39.163	35.826
HBr-H_2SO_4-H_2O	−63.187	108.28	30.784	−39.325

Ternaries H_2O-H_2SO_4-HCl and H_2O-H_2SO_4-HBr. By use of experimental points such as reported here (Tables I and II), the validity of Hála's model (*4*) has been examined for describing the liquid-vapor equilibria of electrolytic solutions. According to Hála, eq 1 defines the relative pseudovolatility β_{13} of the hydrochloric acid with regard to water in the presence of sulfuric acid (whose concentration in the vapor phase is negligible).

$$\beta_{13} = \frac{Y_1}{1 - Y_1} \frac{X_3(1 + X_1 + X_2)}{X_1(X_1 + X_2)} \qquad (1)$$

Assuming that the excess Gibbs energy of the solution can

Table IV. Vapor-Liquid Equilibrium Data at 780 mmHg Pressure for the System H_2O-HBr

X_1	Y_1	t_b/°C
0.0866	0.0006	110.5
0.0957	0.0014	112.2
0.1037	0.0034	114.7
0.1134	0.0099	116.7
0.1193	0.0113	117.6
0.1245	0.0187	118.8
0.1273	0.0243	119.7
0.1351	0.0348	121.1
0.1421	0.0424	121.9
0.1460	0.0659	122.9
0.1551	0.1173	124.2
0.1676	0.1676	124.7

be expressed with a series expansion in terms of the ionic strength of the solution and keeping only the first three terms of the series, one obtains the relation

$$\ln \beta_{13} = A + BI^{1/2} + C(1 - 2X_1 - X_2) + DX_2 \qquad (2)$$

where $I = X_1 + X_2$.

The coefficients of eq 2, determined by linear regression, are given in Table III.

For these calculations, only the first dissociation of the sulfuric acid is taken into account since the concentration of SO_4^{2-} ions is completely negligible in view of the high acidity of the solution.

In addition, it should be observed that small errors in the experimental determination of the compositions lead to very important relative error for the coefficient of relative volatility β_{13} in the range of low concentrations (although in theory, Hâla's correlation has to be restricted to dilute solutions only). On the other hand, for high concentrations, the equilibrium is not as well represented by Hâla's correlation, but the relative error of β_{13} is much lower.

Table V. Coefficients of Equation 3

system	*a*	*b*	*c*	*d*	*e*	*f*	std dev (°C)
H_2O-H_2SO_4-HCl	63.740	1126.1	−3183.2	642.89	−1582.7	−9909.8	3.0
H_2O-H_2SO_4-HBr	−74.292	3668.9	−12059	1666.8	−3069.3	−16556	1.5

Binary H_2O-HBr. As regards the binary system H_2O-HBr, the comparison between the results of the present work (Table IV) and that of Carriere and Cerveau (*5*) shows a good agreement on the boiling curve (Figure 1), however with slight deviation for the azeotropic temperature. As to the dew-point curve, higher values are obtained in the range of lower concentrations.

Boiling Temperatures. The experimental boiling temperatures were correlated with a multilinear regression giving the coefficients of the equation

$$t_b/°C = a + bX_1 + cX_1^2 + dX_2 + eX_2^2 + fX_1X_2 \qquad (3)$$

The coefficients obtained are given in Table V for the two ternary systems.

The ranges of validity are the following: with HCl, $0 < X_1 < 0.06$, $0.10 < X_2 < 0.22$; with HBr, $0 < X_1 < 0.05$, $0.18 < X_2 < 0.27$.

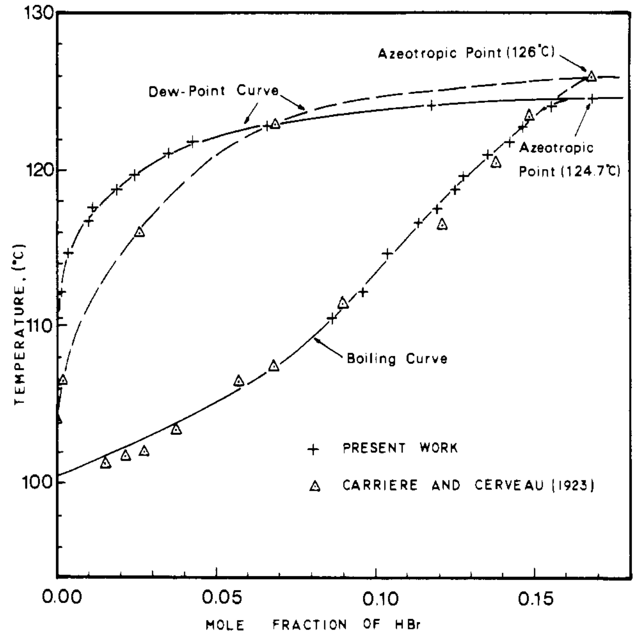

Figure 1. Temperature-composition diagram for the H_2O-HBr system at 780 mmHg pressure.

Nevertheless, the values obtained remain correct even outside the range of validity given above. These equations have no theoretical background but are very useful for computer programs.

Glossary

β	Hâla coefficient
I	ionic strength
X	mole fraction in liquid
Y	mole fraction in vapor
t_b	boiling temperature, °C

Subscripts

1	hydrochloric acid or hydrobromic acid
2	sulfuric acid
3	water

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