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Isothermal Vapor–Liquid Equilibria of Binary and Ternary Mixtures Containing Alcohol, Alkanolamine, and Water with a New Static Device

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A new static device for the measurement of total-pressure vapor–liquid equilibria (VLE) data is described. The vapor pressures of pure substances and binary and ternary mixtures of alcohol, alkanolamine, and water in the temperature range from 60 to 95 °C are reported. The estimated data are the coefficients of the Wilson and UNIQUAC equations, the excess Gibbs energy, the activity coefficients, the vapor pressures, and the mole fractions in the vapor phase.

Introduction

Knowledge of the effect of pressure, temperature, and composition on vapor–liquid equilibria is important for designing separation units in the chemical industry. Vapor–liquid equilibrium data for alcohol–alkanolamine–water systems are rarely available in the literature. The increased industrial importance of these substances and their mixtures justifies this investigation.

The investigation systems show extreme differences between the vapor pressures of pure components, so that the y_1 vs. T curve rises steeply. Therefore, it is difficult to obtain a high accuracy in analyzing the gas phase and it is advisable to determine only the total pressure of the liquid with known composition at constant temperature. The p–T–x approach eliminates the major errors in VLE measurements and greatly reduces the cost of measurements. This paper reports the total-pressure isothermal vapor–liquid equilibria data of seven systems.

Experimental Section

***Apparatus*.** The apparatus, originally developed by A. Meier (*1*), is of the vapor-recycle type and is based on the static method. A complete description of the equipment is given by Nath (*2*). Here the apparatus is described in brief only.

Figure 1 shows a simplified drawing of the vapor pressure apparatus. The main part of the apparatus is an equilibrium cell (1) with a 50 cm long glass rod (2). A constant-temperature liquid bath (3) surrounds the cell where temperature is kept constant through a thermostat with a fluctuation below ±0.1 °C. The equilibrium cell has three openings. The first contains a platinum resistance thermometer Pt-100 (4) with suitable stopping which seals the opening. The second opening (12) is used for filling and draining the mixture. Further, it is used to clean the cell. The third opening connects the cell to a condenser over a built-in valve (5) on the glass rod. In the middle of the condenser zone (6) the glass rod has a hole (7) which connects the set vacuum zone (6) to the cell when the valve is closed. At the other end of the glass rod an iron stick (8) is attached. The upper end of the condenser zone is sealed with a glass stopper. The opening (9) at the left side near the iron stick is used for creating a vacuum in the cell. The iron stick serves the purpose of opening the valve (5) by raising the glass rod with a magnet.

Table I. Physical Properties of Chemicals

	density, g cm^{-3}		refractive index	
temp, °C	exptl	lit. (*9, 10*)	exptl	lit. (*9, 10*)
	Ethanolamine			
20	1.0155	1.015	1.4539	1.4541
25	1.0121		1.4526	
	Propanolamine			
20	0.9879	0.9871	1.4607	1.4617
25	0.9843	0.9824	1.4594	1.4591
	1-Propanol			
20	0.8031	0.8035	1.3850	1.3850
25	0.7996	0.7998	1.3834	1.3831
	Ethanol			
20	0.7892	0.7894	1.3611	1.3605
25	0.7855	0.7850	1.3596	1.3588
	Water			
20	0.9971	0.9972	1.3329	1.333
25	0.9970	0.9970	1.3324	1.3326
	Ethylene Glycol			
20	1.1102	1.1088	1.4312	1.4318
25	1.1089		1.4308	

Figure 2 gives the schematic layout plan of the experimental system.

***Procedure*.** The liquid solution of known composition is filled through the opening (12) in the equilibrium still. The liquid bath temperature is kept about 2 °C higher than the desired temperature. The condenser temperature is maintained at about 5–10 °C. The cell is then evacuated slowly. After some time the mixture begins bubbling. The glass valve is kept opened so that the mixture evaporates with inert gases and reaches the condenser zone. The vapors condense and fall back into the cell and the inert gases are withdrawn.

The vacuum is continuously increased and the mixture is evaporated and condensed for about 10 min.

Now the glass valve (5) is closed so that the liquid is withdrawn through the capillary because of the pressure difference between zones 8 and 9. Then again the valve is opened. This procedure is followed for a few minutes. Finally, the glass valve is closed and the liquid is withdrawn and about 1 cm of liquid is left above the valve in order to keep both zones isolated. The pressure is then so adjusted that the level in the capillary and in the still are alike. However, the temperature changes. The temperature of the liquid bath is again regulated in order to have the desired temperature in the cell. The level difference is subsequently corrected. The final adjustment of pressure requires 30–50 min.

The purest available chemicals supplied by Merck were used without further purification. The physical properties of these materials are summarized in Table I. Density was measured in a mechanical oscillator densimeter (Parr type).

***Uncertainties*.** The uncertainties in measuring temperature, pressure, and liquid composition which contribute to errors in

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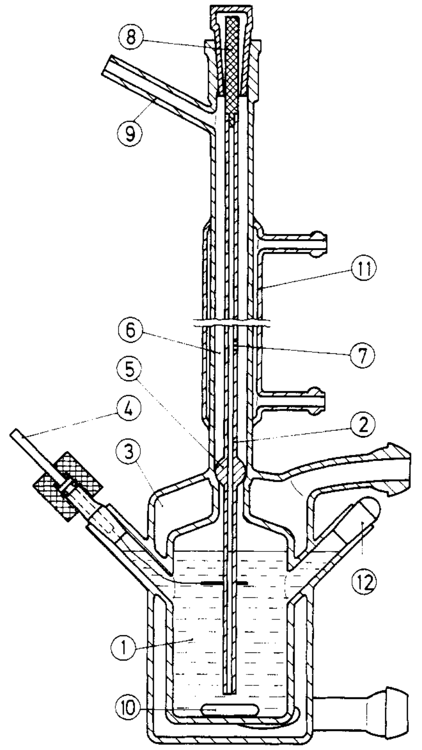

Figure 1. Vapor pressure apparatus: (1) equilibrium cell, (2) glass rod, (3) constant-temperature liquid bath, (4) four-wire resistance element Pt-100, (5) stop valve, (6) condenser zone, (7) hole in the glass rod, (8) iron stick, (9) vacuum connection, (10) magnet stirrer, (11) condenser, (12) feed and drain opening.

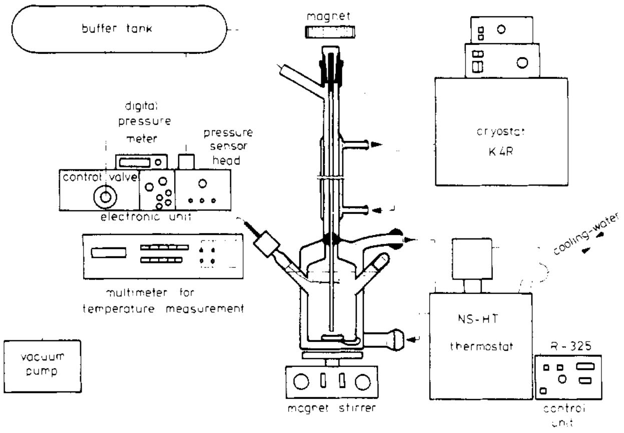

Figure 2. Layout plan of the cell with peripheral systems.

the equilibrium data are as follows.

The temperature of the liquid bath surrounding the equilibrium cell can be maintained within ±0.1 °C of the set temperature. For the bath we used the thermostat of Messgeräte-Werk Lauda Model NS-HT equipped with R-325 (PID) as a control device. The cell temperature was measured with a Pt-100 compensated (four-wire) resistance element connected with a multimeter Solatron 7055. The resistance vs. temperature table (DIN 43760) for Pt-100 was checked at several temperatures by using mercury thermometers with ±0.01 °C accuracy and a precision resistance bridge, Model H7, of Automatic Systems Laboratories. The temperature difference between the two was found to be below ±0.05 °C for all the checked points. Hence, for further use the above-mentioned DIN table with Pt-100 was used for temperature measurement.

The equilibrium cell was connected at the opening (9) to a vacuum pump through a compensation tank. A MKS Baratron type 170 capacitance manometer and control system was used for pressure measurement and control in the cell. The highest possible error altogether in the pressure measurement was below ±0.25% of the set value.

The desired composition in the liquid phase was weighed and filled in the cell after thorough mixing. The total volume of the filled mixture was about 150 mL in order to keep the vapor-phase volume quite small. Here we have neglected the change in the composition in the liquid phase when equilibrium exists.

Results and Discussion

To correlate the vapor-liquid equilibrium data it is necessary to evaluate the liquid activity coefficient. The vapor-liquid equilibrium relation for the liquid activity coefficient γ_i of a component is given by

$$\gamma_i = y_i p \varphi_i / \{x_i p_{0i} \varphi_{0i} \exp[v_{0i}{}^{l}(p - p_{0i})/RT]\} \tag{1}$$

where y_i is the vapor-phase mole fraction, and φ_i the vapor-phase fugacity coefficient of component i at the total pressure p and temperature T. Further, φ_{0i} is the fugacity coefficient of pure component i at vapor pressure p_{0i} and $v_{0i}{}^{l}$, the liquid molar volume, all at temperature T. φ_i/φ_{0i} was taken here equal to 1. p_{0i} was calculated from Antoine parameters from Ohe (*3*). The molar volume v_{0i} can be calculated from the method given by Yen and Wood (*4*). We used the Wilson and UNIQUAC equations for determining the liquid-phase activity coefficients.

The excess Gibbs energy by the Wilson equation (*5*) is

$$g^{E}/RT = -\sum_{i=1}^{K} x_i \ln \left[\sum_{j=1}^{K} x_j \tau_{ij}\right] \tag{2}$$

with the liquid activity coefficient for component i

$$\ln \gamma_i = 1 - \ln \sum_{j=1}^{K} x_j \tau_{ij} - \sum_{k=1}^{K} \frac{x_k \tau_{ki}}{\sum_{j=1}^{K} x_j \tau_{kj}} \tag{3}$$

where

$$\tau_{ij} = (v_{0j}/v_{0i}) \exp[\Delta u_{ij}/RT] \tag{4}$$

$$\tau_{ij} \neq \tau_{ji} \qquad \Delta u_{ij} = u_{ij} - u_{jj} \tag{5}$$

The UNIQUAC equation for excess Gibbs energy is

$$g^{E}/RT = g^{E}{}_{\mathrm{comb}}/RT + g^{E}{}_{\mathrm{res}}/RT \tag{6}$$

with

$$\frac{g^{E}{}_{\mathrm{comb}}}{RT} = \sum_{i=1}^{K} x_i \ln \frac{\phi_i}{x_i} + (Z/2) \sum_{i=1}^{K} q_{0i} x_i \ln \frac{\theta_i}{\phi_i} \tag{6a}$$

$$g^{E}{}_{\mathrm{res}}/RT = -\sum_{i=1}^{K} q_{0i} x_i \ln \left(\sum_{j=1}^{K} \theta_j \tau_{ji}\right) \tag{6b}$$

The liquid activity coefficient is expressed in the form of

$$\ln \gamma_{i_{\mathrm{comb}}} = \ln \frac{\phi_i}{x_i} + (Z/2) q_{0i} \ln \frac{\theta_i}{\phi_i} + l_{0i} - \frac{\phi_i}{x_i} \sum_{j=1}^{K} x_j l_{0j} \tag{7a}$$

$$\ln \gamma_{i_{\mathrm{res}}} = q_{0i}\left[1 - \ln \left(\sum_{j=1}^{K} \theta_j \tau_{ji}\right) - \sum_{j=1}^{K} \left(\theta_j \tau_{ij} / \sum_{k=1}^{K} \theta_k \tau_{kj}\right)\right] \tag{7b}$$

with

$$\tau_{ij} = \exp[-\Delta u_{ij}/RT] \tag{8a}$$

$$l_{0i} = (Z/2)(r_{0i} - q_{0i}) - (r_{0i} - 1) \tag{8b}$$

$$\theta_i = q_{0i} x_i / \sum_{j=1}^{K} q_{0j} x_j \tag{8c}$$

$$\phi_i = r_{0i} x_i / \sum_{j=1}^{K} r_{0j} x_j \tag{8d}$$

Table II. p-T-x Values for Different Binary Systems

$x_{1,\text{exptl}}$	P_{exptl}	$x_{1,\text{exptl}}$	P_{exptl}	$x_{1,\text{exptl}}$	P_{exptl}	$x_{1,\text{exptl}}$	P_{exptl}
Water (1)-Ethylene Glycol (2)							
T = 65.1 °C							
0.0		0.3	55.7	0.6	111.8	0.901	165.1
0.055	13.6	0.4	73.5	0.684	126.1	0.95	176.0
0.158	24.7	0.488	88.1	0.806	146.2	1.0	188.9
0.245	43.5	0.567	103.9				
T = 77.7 °C							
0.0		0.3	102.2	0.6	194.2	0.901	286.3
0.055	21.8	0.4	123.1	0.684	219.4	0.95	307.3
0.158	44.5	0.488	155.2	0.806	256.2	1.0	323.5
0.245	77.9	0.567	179.6				
T = 90.3 °C							
0.0		0.3	164.1	0.6	324.7	0.901	475.6
0.055	35.4	0.4	214.2	0.684	362.1	0.95	504.6
0.158	84.2	0.488	256.3	0.806	424.6	1.0	533.0
0.245	132.2	0.567	302.1				
Water (1)-Ethanolamine (2)							
T = 60.0 °C							
0.0		0.301	32.8	0.6	75.7	0.898	126.8
0.069	9.8	0.401	44.8	0.7	94.5	0.944	136.2
0.132	15.0	0.445	48.4	0.821	116.0	1.0	149.5
0.214	21.3	0.596	73.1				
T = 78.0 °C							
0.0	17.0	0.301	77.1	0.6	171.6	0.898	283.4
0.069	24.8	0.401	103.8	0.7	211.6	0.944	304.0
0.132	42.1	0.445	111.6	0.821	256.3	1.0	328.1
0.214	52.6	0.596	165.8				
T = 91.7 °C							
0.0	35.4	0.301	140.6	0.6	293.7	0.898	485.2
0.069	50.2	0.401	186.6	0.7	357.7	0.944	518.3
0.132	82.2	0.445	201.1	0.821	423.3	1.0	568.8
0.214	98.9	0.596	284.5				
Water (1)-Propanolamine (2)							
T = 75.0 °C							
0.0	8.0	0.287	66.2	0.615	151.6	0.918	256.7
0.053	14.9	0.392	85.7	0.714	187.4	0.966	273.7
0.148	33.1	0.480	115.0	0.806	222.9	1.0	289.2
T = 85.0 °C							
0.0	13.5	0.287	103.1	0.615	231.2	0.918	388.0
0.053	25.1	0.392	138.2	0.714	289.2	0.966	412.4
0.148	54.1	0.489	178.7	0.806	338.0	1.0	433.6
T = 95.0 °C							
0.0	24.0	0.287	155.1	0.615	350.9	0.918	566.2
0.053	40.9	0.392	210.0	0.714	425.0	0.966	601.2
0.148	81.9	0.480	263.4	0.806	494.7	1.0	635.5
Ethanol (1)-Ethanolamine (2)							
T = 65.0 °C							
0.0	7.2	0.3	141.6	0.589	263.3	0.9	403.9
0.05	33.3	0.4	180.7	0.6	270.6	0.932	412.4
0.12	62.1	0.5	224.5	0.7	313.3	1.0	439.3
0.216	105.0	0.551	248.9	0.8	357.3		
T = 75.0 °C							
0.0	13.8	0.3	214.1	0.589	407.8	0.9	611.8
0.05	50.8	0.4	275.2	0.6	410.1	0.932	634.1
0.12	97.1	0.5	342.4	0.7	473.6	1.0	667.6
0.216	158.2	0.551	376.2	0.8	543.8		
T = 85.0 °C							
0.0	23.9	0.216	237.4	0.5	506.2	0.6	608.4
0.05	78.2	0.3	321.4	0.551	563.2	0.7	704.0
0.12	146.7	0.4	409.5	0.589	599.4	1.0	
1-Propanol (1)-Propanolamine (2)							
T = 75.0 °C							
0.0	8.0	0.3	96.1	0.6	182.3	0.9	276.9
0.061	22.3	0.331	102.4	0.7	213.0	0.969	293.7
0.158	50.2	0.4	122.8	0.836	253.2	1.0	306.3
0.244	77.2	0.5	152.2				

Table II (*Continued*)

$x_{1,\text{exptl}}$	P_{exptl}	$x_{1,\text{exptl}}$	P_{exptl}	$x_{1,\text{exptl}}$	P_{exptl}	$x_{1,\text{exptl}}$	P_{exptl}
T = 85.0 °C							
0.0	13.5	0.3	150.2	0.6	279.8	0.9	423.3
0.061	34.9	0.331	158.0	0.7	327.1	0.969	456.3
0.158	81.7	0.4	189.6	0.836	392.2	1.0	470.3
0.244	121.4	0.5	233.6				
T = 95.0 °C							
0.0	24.0	0.3	224.5	0.6	419.5	0.9	634.2
0.061	57.4	0.331	238.9	0.7	490.5	0.969	672.2
0.158	121.9	0.4	286.6	0.836	580.1	1.0	698.4
0.244	183.8	0.5	349.7				

Table III. List of Reduced Parameters (J mol^{-1}) for Systems in Table II

temp, °C	Wilson eq		UNIQUAC eq	
	Δu_{12}	Δu_{21}	Δu_{12}	Δu_{21}
Water-Ethylene Glycol				
65.1	2416.8	-2398.6	993.1	-2168.5
77.7	1824.9	-1307.8	172.3	-1669.3
90.3	1546.8	-473.5	-37.6	-1553.5
Water-Ethanolamine				
60.0	426.5	-429.4	-714.4	-4754.5
78.0	-188.0	262.8	-1366.4	-4790.5
91.7	-114.6	248.1	-1238.1	-5060.6
Water-Propanolamine				
75.0	314.9	234.8	-1260.1	-4771.2
85.0	519.1	263.1	-1234.2	-4876.9
95.0	575.2	275.1	-1297.2	-4983.0
Ethanol-Ethanolamine				
65.0	3406.7	-2032.2	237.2	-67.4
75.0	10.5	215.6	248.2	-120.0
85.0	25.4	218.9	244.8	-107.8
1-Propanol-Propanolamine				
75.0	-628.7	281.9	-864.9	859.6
85.0	-612.0	326.6	-818.7	821.1
95.0	-583.9	306.3	-747.0	732.0

Two parameters were fitted to the isothermal VLE data, namely, Δu_{ij} and Δu_{ji}. We fitted these parameters to the isothermal p-x_i data using the Simplex method described by Nelder and Mead (*7*). The objective function used is

$$Q = \sum_{j=1}^{N} (1 - p_{\text{calcd}}/p_{\text{exptl}})_j^2 \tag{9}$$

to assess the fit, where Q is the sum of the mean square deviations, and N the number of data points.

First the apparatus was tested by measuring the vapor pressures of pure ethanol and water. The experimental vapor pressures were compared with those calculated by using Antoine constants from Ohe (*3*). The arithmetic mean deviations for ethanol and water were found under the tolerance limit of ±0.25%.

Table II contains the experimental isothermal p-x_1 data at different temperatures for the following systems: (1) water-ethylene glycol at 65.1, 77.7, and 90.3 °C; (2) water-ethanolamine at 60.0, 78.0, and 91.7 °C; (3) water-propanolamine at 75.0, 85.0, and 95.0 °C; (4) ethanol-ethanolamine at 65.0, 75.0, and 85.0 °C; (5) 1-propanol-propanolamine at 75.0, 85.0, and 95.0 °C. The calculated pressure, the composition of the vapor phase, the activity coefficient of both components, and the excess Gibbs energy using the Wilson and UNIQUAC equations are available as supplementary material (see paragraph at the end of text regarding supplementary material). Table III contains the reduced parameters Δu_{12} and Δu_{21}. The systems ethanol-water at 70 °C and 1-propanol-water at 60 °C are taken from ref *8*.

Figure 3 gives the bubble lines for the systems water-ethylene glycol and ethanol-ethanolamine. Both of these systems show nearly pseudoideal behavior. The activity coefficients and the equilibrium curve of the system water-ethylene glycol calculated with the Wilson and UNIQUAC equations can be seen in Figure 4. The activity coefficients from the Wilson equation show a symmetrical negative deviation from the ideal solution. However, the UNIQUAC equation produces concen-

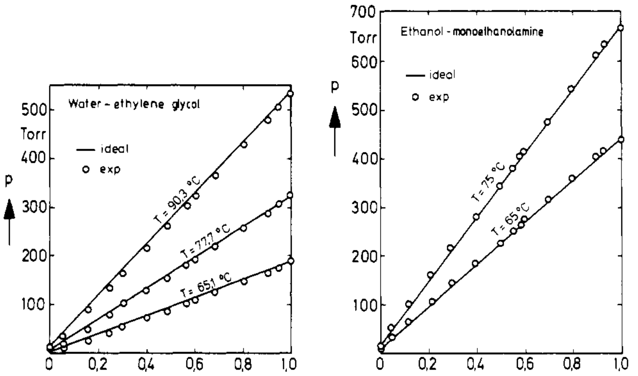

Figure 3. *p*-*T*-*x* values for the systems water-ethylene glycol and ethanol-ethanolamine.

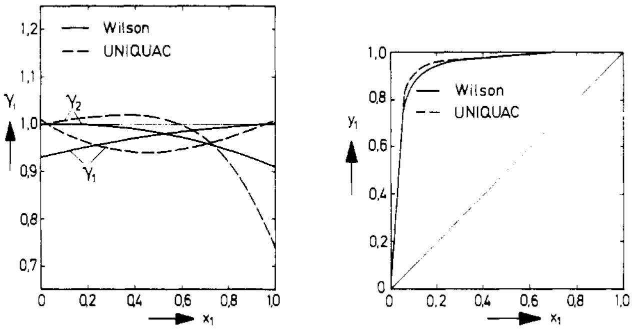

Figure 4. γ-*x* and *y*-*x* behavior for the system water-ethylene glycol at 65.1 °C.

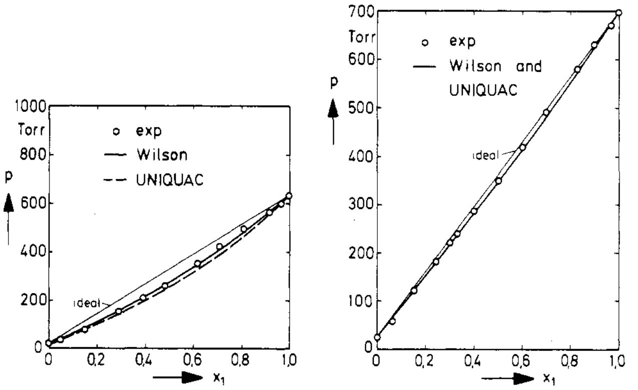

Figure 5. *p*-*x* behavior of the systems water-propanolamine and 1-propanol-propanolamine at 95 °C.

Table IV. Vapor-Liquid Equilibria for Ternary Systems

$x_{1,\mathrm{exptl}}$	$x_{2,\mathrm{exptl}}$	P_{exptl}	$x_{1,\mathrm{exptl}}$	$x_{2,\mathrm{exptl}}$	P_{exptl}
Ethanol (1)-Ethanolamine (2)-Water (3)					
T = 65.0 °C					
0.05	0.052	268.8	0.115	0.746	86.9
0.099	0.036	304.2	0.115	0.844	68.2
0.045	0.068	248.8	0.679	0.104	445.6
0.0459	0.122	235.5	0.637	0.139	398.7
0.070	0.181	235.3	0.540	0.236	331.2
0.058	0.233	200.6	0.460	0.277	310.5
0.078	0.321	198.2	0.372	0.364	267.8
0.074	0.345	188.7	0.278	0.439	217.8
0.086	0.447	151.4	0.203	0.536	166.3
0.109	0.635	109.8	0.150	0.595	121.6
0.108	0.753	84.6			
T = 75.0 °C					
0.05	0.052	392.5	0.115	0.746	135.4
0.099	0.036	496.2	0.115	0.844	109.2
0.045	0.068	377.5	0.679	0.104	624.5
0.059	0.122	365.9	0.637	0.139	569.6
0.07	0.181	361.2	0.540	0.236	518.1
0.058	0.233	317.2	0.460	0.277	470.2
0.078	0.321	281.8	0.372	0.364	406.9
0.074	0.345	267.5	0.278	0.439	336.2
0.086	0.447	245.7	0.203	0.536	252.9
0.109	0.635	194.3	0.150	0.595	210.4
0.108	0.753	129.2			
T = 85.0 °C					
0.05	0.052	593.2	0.109	0.635	256.7
0.099	0.036	731.5	0.108	0.753	191.7
0.045	0.068	574.6	0.115	0.746	208.2
0.059	0.122	556.4	0.115	0.844	161.4
0.070	0.181	552.3	0.460	0.277	696.2
0.058	0.233	484.8	0.372	0.364	598.3
0.078	0.321	433.1	0.278	0.439	517.5
0.074	0.345	428.3	0.203	0.536	378.3
0.086	0.447	355.5	0.150	0.595	335.7
1-Propanol (1)-Propanolamine (2)-Water (3)					
T = 55.0 °C					
0.123	0.124	156.8	0.120	0.370	92.9
0.248	0.124	155.6	0.250	0.375	93.8
0.374	0.124	154.6	0.375	0.375	77.9
0.500	0.125	152.0	0.500	0.370	85.0
0.625	0.125	145.3	0.125	0.500	65.7
0.750	0.125	129.1	0.250	0.500	71.7
0.122	0.252	116.5	0.370	0.500	66.4
0.250	0.250	121.6	0.125	0.625	53.6
0.375	0.250	125.4	0.250	0.625	56.8
0.500	0.250	118.5	0.125	0.750	39.7
0.625	0.250	102.4			
T = 65.0 °C					
0.123	0.124	250.4	0.120	0.370	142.8
0.248	0.124	248.9	0.250	0.375	147.7
0.374	0.124	248.1	0.375	0.375	128.5
0.500	0.125	245.1	0.500	0.370	140.5
0.625	0.125	233.6	0.125	0.500	107.0
0.750	0.125	209.8	0.250	0.500	113.9
0.122	0.252	191.5	0.370	0.500	111.0
0.250	0.250	199.7	0.125	0.625	79.5
0.375	0.250	199.8	0.250	0.625	82.5
0.500	0.250	191.6	0.125	0.750	56.7
0.625	0.250	166.0			
T = 75.0 °C					
0.123	0.124	379.8	0.120	0.370	235.2
0.248	0.124	386.2	0.250	0.375	240.9
0.374	0.124	386.8	0.375	0.375	202.6
0.500	0.125	384.3	0.500	0.370	244.3
0.625	0.125	365.9	0.125	0.500	164.5
0.750	0.125	330.1	0.250	0.500	179.8
0.122	0.252	297.9	0.370	0.500	175.4
0.250	0.250	311.6	0.125	0.625	120.2
0.375	0.250	311.9	0.250	0.625	130.2
0.500	0.250	299.3	0.125	0.750	84.8
0.625	0.250	268.8			

tration-dependent extrema which seem to be unrealistic.

Figure 5 shows the bubble lines for the systems water-propanolamine and 1-propanol-propanolamine at 95 °C. Here the calculated p values with both agree quite well.

Finally, the ternary systems ethanol-ethanolamine-water and 1-propanol-propanolamine-water were measured at different temperatures. Table IV contains the experimental vapor pressures with liquid-phase composition for these systems. The predicted vapor pressure and vapor-phase compositions for given liquid-phase composition and temperatures from the Wilson and UNIQUAC equations are available as supplementary material. The differences between measured and predicted vapor pressures are significant and much greater than Δp in the binary systems. The prediction becomes worse with ascending temperature. In most cases the experimental pressure is higher than the predicted one. In general, the Wilson equation predicts the ternary equilibria more accurately than the UNIQUAC equation, but both fail because of the association effects in these ternary systems with highly associating components. Another reason for the greater differences in Δp may be the temperature-independent parameters of the systems ethanol-water at 70 °C and 1-propanol-water at 60 °C as mentioned before.

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Glossary

A	Antoine constant
B	Antoine constant
C	Antoine constant
g	Gibbs energy, J mol^{-1}
N	number of data points
p	pressure, mmHg
q	pure-component area parameter
Q	sum of mean square deviations
r	pure-component volume parameter
R	universal gas constant, 62.361 mmHg L mol^{-1} K^{-1}
T	temperature, °C or K
Δu_{ij}	binary interaction parameter ($u_{ij} - u_{jj}$), J mol^{-1}
v	molar volume, L mol^{-1}
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	coordination number, 10
γ_i	activity coefficient of component i
ϕ_i	volume fraction of component i
θ_i	area fraction of component i
τ_{ij}	$\exp[-(u_{ij} - u_{jj})/RT]$
φ_i	fugacity coefficient of component i

Superscripts

E	excess
l	liquid

Subscripts

calcd	calculated
comb	combinatorial
i, j, k	component i, j or k
0	pure component

Registry No. Ethanolamine, 141-43-5; propanolamine, 156-87-6; 1-propanol, 71-23-8; ethanol, 64-17-5; ethylene glycol, 107-21-1.

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Supplementary Material Available: Complete tables of experimental and calculated VLE data of binary and two ternary systems (16 pages). Ordering information is given on any current masthead page.

Ternary System Methane-Carbon Dioxide-Hydrogen Sulfide. Excess Enthalpy Data by Flow Calorimetry

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Excess enthalpy measurements for the ternary system methane-carbon dioxide-hydrogen sulfide in gaseous phase were performed utilizing an isothermal flow calorimeter. The investigation was conducted at three temperatures, 293.15, 305.15, and 313.15 K, and pressures of 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively). The determination of the excess enthalpies for the binary systems methane-carbon dioxide and methane-hydrogen sulfide has been the object of two previous articles. The binary interaction constants, k_{ij}, obtained for these binary systems by nonlinear regression, have been utilized as initial values for an analogous iteration procedure applied in the treatment of the experimental data obtained for the ternary system. Two series of binary interaction constants, k_{ij}, have been determined from the experimental data: coefficients k_{ij} independent of temperature and pressure, and k_{ij}'s adjusted as a function of temperature and pressure. A better prediction of the excess enthalpy experimental data was obtained from the latter series of binary interaction coefficients.

Introduction

A complete literature review of excess enthalpy measurements for binary systems in gaseous phase was presented in preceding articles (*1*, *2*). The importance of excess enthalpy data, from both the scientific point of view as well as that related to equipment design, was also discussed in these articles.

Experimental data of excess enthalpy for the binary systems methane-carbon dioxide (*1*) and methane-hydrogen sulfide (*2*) were reported. The binary interaction constants k_{ij} computed for optimal portrayal of the experimental data were also presented.

Following a logical sequence in our investigation program, this article presents excess enthalpy data for the ternary system methane-carbon dioxide-hydrogen sulfide.

The flow calorimeter utilized throughout this entire program possesses only two independent inlets for gaseous streams. Consequently, one series of cylinders containing a binary mixture of 86.8% methane and 13.2% hydrogen sulfide was prepared for this investigation. A second series of cylinders of 99.8% pure carbon dioxide, containing 100 ppm of CO, 50 ppm of H_2, 100 ppm of H_2O, and approximately 0.2% of N_2 as impurities, was utilized in conjunction with the series of cylinders of binary mixtures methane-hydrogen sulfide. The experimental measurements reported in this article encompass only excess enthalpy data within the range of ternary compositions obtained by mixing the gaseous contents of these two series of cylinders.

Experimental Method

A detailed description of the equipment and experimental method has been presented in previous articles (*1-5*). As indicated in the introductory section of this article, like in the case of the study of binary systems, two gaseous streams arrive independently at the calorimeter inlet, under temperature and pressure conditions T_1, P_1 and T_2, P_2, respectively. For the case of the ternary system methane-carbon dioxide-hydrogen sulfide, which is reported in this article, one of the gas streams is a binary mixture of methane and hydrogen sulfide. The choice of the percentages of 86.8% methane to 13.2% hydrogen sulfide was guided by the intention of utilizing a proportion within the range of typical compositions for natural gas.

The other stream is 99.8% pure carbon dioxide. These two gaseous streams arrive by independent lines to the calorimeter under temperature and pressure conditions which are nearly identical, i.e., $T_1 \approx T_2$ and $P_1 \approx P_2$. Then the two streams are mixed thoroughly. Since the mixture is endothermic, the process is accompanied by a temperature drop. To compensate for this temperature drop, a measured quantity of energy is supplied to the system by a power supply, so that the temperature of the exit gas mixture, T_0, at the calorimeter outlet is very nearly the same as the inlet temperatures (T_1, T_2) of the two entering gas streams.

The main objective of the investigation reported in this article is to verify the possibility of utilization of results obtained from the binary systems, in particular the binary interaction coefficients k_{ij}, for prediction of experimental data for the ternary system. In order to direct this study in a rational manner, the same nominal temperature and pressure conditions utilized in the study of the binary systems have been selected for the present study of the ternary system. The nominal temperatures were 293.15, 305.15, and 313.15 K. For each of these isotherms experiments were conducted at pressures of 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively).

Experimental Results

As previously found for the two binary systems methane-carbon dioxide (*1*) and methane-hydrogen sulfide (*2*), the pressure drops across the calorimeter, i.e., $\Delta P_1 = P_1 - P_0$ and $\Delta P_2 = P_2 - P_0$ are below 7×10^{-4} MPa, and therefore negligible. The temperature differences, i.e., $\Delta T_1 = T_1 - T_0$ and $\Delta T_2 = T_2 - T_0$, are below 0.05 K. Consequently, it is justifiable

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