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Vapor–Liquid Equilibria of the System Ethane + 2-Aminopropane

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Bubble and dew point pressures have been measured as a function of temperature for 19 mixtures of the binary system ethane + 2-aminopropane in the temperature range 278.15–368.15 K. It is shown that the data can be represented by using the Peng–Robinson equation of state.

Introduction

One of the main disadvantages of the production of sodium chloride by solution mining is the rather high energy demand per ton of salt produced as a result of the evaporization of water from the brine in multiple effect crystallizing evaporators.

Alternatively sodium chloride can be produced from brine by solventing out through the addition of a miscible organic solvent to the brine. The organic solvent should then be removed from the mother liquor by supercritical extraction with, for instance, ethane. One of the promising aspects of this route is the prospect of reduced energy consumption. 2-Aminopropane appears to be a very good solventing-out chemical.

In this context knowledge of vapor–liquid equilibria of the ternary system ethane + water + 2-aminopropane and its binary subsystems is required. Here we present experimentally determined vapor–liquid equilibrium data on the binary subsystem ethane + 2-aminopropane in the temperature range of interest. The Peng–Robinson equation of state (*1*) is used to describe the data.

Experimental Section

The measurements were carried out in a glass tube apparatus for use with pressures up to 20 MPa and temperatures up to 473 K described earlier by de Loos et al. (*2*). With this so-called Cailletet apparatus dew points and bubble points of mixtures of known composition can be determined visually. A sample of the binary mixture with known composition is present in a narrow glass tube, surrounded by a thermostat with circulating water, guaranteeing a constant temperature within 0.02 K. The temperature is measured with a Pt-100 resistance thermometer, calibrated against a standard thermometer. The uncertainty in the measured temperature is approximately 0.02 K. Mercury is used as a pressure intermediate between the sample and the oil in the pressure generating system. The pressure is measured with a dead-weight pressure gauge (Büdenberg) with an accuracy within 1 kPa.

Variation of the pressure at constant temperature, for a mixture with known composition in the apparatus, allows determination of the pressure where a gas bubble is about to (dis)appear, the so-called bubble point, and the pressure at which a liquid droplet is about to (dis)appear, the so-called dew point. The reproducibility of measured bubble and dew point pressures proved to be 10 kPa. The preparation of the mixtures is described elsewhere (*3*).

The mole fraction purity of the ethane used was greater than 0.9999 and that of the 2-aminopropane greater than 0.998. The ethane was a research grade gas supplied by Matheson Gas Products; 2-aminopropane was supplied by Merck.

Results

The p,T behavior of the 19 binary ethane + 2-aminopropane mixtures investigated is given in Table I. From plots of these p,T isopleths isothermal p,x sections can be obtained by interpolation. When at lower temperatures no dew point pressures can be measured because the volume of the gas phase is too large, approximate dew point pressures can be obtained by means of linear extrapolation of $\ln p$ against $1/T$. Although this procedure is only sound thermodynamically for pure substances at low reduced temperature, we found that in many cases it can be applied to binary mixtures too. The p,x sections at 298.15, 328.15, and 358.15 K are given in Figures 1–3. The vapor pressure of pure 2-aminopropane is taken from Boublik et al. (*4*) and the vapor pressure of pure ethane from Douslin and Harrison (*5*). The purity of the ethane used was

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Table I. Vapor–Liquid Equilibria for (1 – x)Ethane + (x)2-Aminopropane: Bubble and Dew Point Pressures p as a Function of Temperature T for a given Mole Fraction x[a]

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
$x = 0.037$					
278.73	2.607^{b}	299.10	4.007^{b}	312.45	5.107^{b}
278.77	0.925^{d}	299.79	2.422^{d}	314.38	5.227^{b}
286.80	3.107^{b}	305.16	3.071^{d}	315.35	5.247^{b}
288.85	1.407^{d}	306.54	4.617^{b}	315.97	4.859^{d}
292.71	3.507^{b}	311.20	3.942^{d}	316.01	5.267^{b}
296.30	2.053^{d}				
$x = 0.049$					
280.07	2.627^{b}	313.33	5.092^{b}	315.99	5.264^{b}
289.54	3.037^{b}	313.37	3.447^{d}	316.33	5.350^{b}
299.46	3.962^{b}	315.32	3.785^{d}	317.35	4.197^{d}
307.90	4.647^{b}	315.35	5.246^{b}	319.47	4.697^{b}
310.67	3.069^{d}	315.99	3.944^{d}		
$x = 0.063$					
278.76	2.527^{b}	305.88	1.864^{d}	319.60	5.447^{b}
284.14	2.847^{b}	306.43	4.427^{b}	321.37	5.507^{b}
285.82	0.826^{d}	312.22	2.472^{d}	322.74	3.947^{d}
288.84	3.147^{b}	312.92	4.987^{b}	323.36	5.547^{b}
293.59	1.061^{d}	316.21	5.247^{b}	324.12	4.469^{d}
298.34	3.807^{b}	317.92	5.337^{b}	325.61	4.698^{d}
300.02	1.427^{d}	318.11	3.185^{d}		
$x = 0.065$					
291.53	0.913^{d}	305.17	1.716^{d}	317.24	2.943^{d}
298.40	1.180^{d}	311.30	2.265^{d}	323.54	3.932^{d}
$x = 0.091$					
278.64	2.529^{b}	318.70	5.237^{b}	328.42	5.819^{b}
288.05	2.992^{b}	324.10	5.619^{b}	330.85	5.861^{b}
298.37	3.612^{b}	324.59	5.645^{b}	335.44	5.769^{b}
308.37	4.437^{b}	326.57	5.725^{b}		
$x = 0.095$					
296.32	0.763^{d}	311.10	1.529^{d}	332.10	3.533^{d}
301.37	0.985^{d}	321.89	2.435^{d}		
$x = 0.163$					
280.02	2.343^{b}	337.97	6.103^{b}	343.85	6.323^{b}
289.39	2.843^{b}	339.69	6.178^{b}	345.17	6.373^{b}
298.67	3.403^{b}	340.41	6.205^{b}	347.90	6.423^{b}
308.60	4.053^{b}	341.77	6.253^{b}	351.31	6.423^{b}
317.97	4.733^{b}	342.44	6.278^{b}	354.71	6.313^{b}
328.04	5.473^{b}	343.12	6.298^{b}	556.07	6.153^{b}
$x = 0.171$					
320.19	1.044^{d}	335.08	1.756^{d}	357.41	3.883^{d}
322.24	1.122^{d}	342.46	2.286^{d}	358.38	4.073^{d}
328.32	1.400^{d}	349.94	2.915^{d}		
$x = 0.228$					
279.23	2.186^{b}	328.64	5.146^{b}	361.89	6.815^{b}
288.62	2.641^{b}	337.28	5.747^{b}	364.89	6.850^{b}
298.99	3.211^{b}	347.83	6.377^{b}	365.05	3.604^{d}
308.98	3.826^{b}	356.83	6.723^{b}	368.53	6.805^{b}
318.66	4.451^{b}	357.89	2.859^{d}	368.54	4.058^{d}
$x = 0.264$					
321.37	0.707^{d}	336.90	1.203^{d}	357.87	2.316^{d}
338.09	0.892^{d}	343.05	1.490^{d}		
$x = 0.344$					
280.07	2.013^{b}	318.36	3.873^{b}	348.87	5.723^{b}
289.46	2.403^{b}	328.74	4.483^{b}	358.69	6.303^{b}
298.63	2.823^{b}	338.73	5.093^{b}	368.14	6.783^{b}
308.98	3.353^{b}				
$x = 0.420$					
335.67	0.712^{d}	343.48	0.902^{d}	352.52	1.188^{d}
338.41	0.769^{d}	347.88	1.005^{d}	358.59	1.400^{d}
$x = 0.508$					
279.01	1.661^{b}	309.77	2.771^{b}	338.94	4.081^{b}
291.23	2.061^{b}	318.08	3.121^{b}	351.95	4.731^{b}
299.51	2.361^{b}	329.09	3.611^{b}	363.25	5.311^{b}
$x = 0.520$					
344.02	0.731^{d}	357.35	1.052^{d}	362.69	1.198^{d}
348.65	0.829^{d}	358.04	1.065^{d}	367.24	1.361^{d}
353.27	0.947^{d}	360.65	1.138^{d}		
$x = 0.655$					
278.77	1.286^{b}	318.62	2.392^{b}	348.25	3.432^{b}
288.51	1.522^{b}	328.14	2.702^{b}	357.89	3.802^{b}
299.13	1.812^{b}	338.26	3.052^{b}	372.13	4.222^{b}
309.05	2.092^{b}				
$x = 0.666$					
327.79	0.365^{d}	348.06	0.659^{d}	366.75	1.056^{d}
337.66	0.481^{d}	357.63	0.846^{d}		
$x = 0.745$					
278.55	1.027^{b}	318.01	1.882^{b}	348.19	2.717^{b}
288.82	1.228^{b}	328.35	2.144^{b}	357.35	3.003^{b}
298.95	1.432^{b}	338.45	2.432^{b}	367.94	3.388^{b}
309.22	1.655^{b}				
$x = 0.825$					
318.46	0.208^{d}	337.30	0.379^{d}	357.67	0.657^{d}
327.98	0.283^{d}	347.93	0.516^{d}	367.55	0.873^{d}
$x = 0.849$					
279.36	0.676^{b}	317.95	1.232^{b}	347.86	1.822^{b}
288.81	0.791^{b}	328.17	1.412^{b}	357.85	2.052^{b}
298.34	0.921^{b}	337.65	1.602^{b}	367.41	2.302^{b}
308.49	1.671^{b}				

[a] A superscript b denotes bubble point and a superscript d dew point.

Table II. Vapor–Liquid Equilibria for the System Ethane + 2-Aminopropane: Calculated Values of k_{12} and l_{12} for the Peng–Robinson Equation of State at Various Temperatures

	one parameter (l_{12}=0)	two parameters	
T/K	k_{12}	k_{12}	l_{12}
283.15	0.0572	0.0674	0.0177
298.15	0.0527	0.0543	0.0028
313.15	0.0486	0.0484	–0.0002
328.15	0.0417	0.0404	–0.0053
343.15	0.0403	0.0302	–0.0234
358.15	0.0409	0.0184	–0.0384

checked by measuring bubble points at various temperatures. The experimental bubble points agreed within the experimental uncertainty with literature (*5*).

Discussion

The Peng–Robinson equation of state (*1*) has proved to be well suited for the description and prediction of high-pressure vapor–liquid equilibria in hydrocarbon systems. Here this equation is applied for the representation of vapor–liquid equilibria in a system consisting of a hydrocarbon and a polar, hydrogen-bonding compound.

For the composition dependence of the a and b parameters of the Peng–Robinson equation we used the following mixing rules:

$$a = x_1^2 a_{11} + 2x_1x_2a_{12} + x_2^2 a_{22} \tag{1}$$

$$b = x_1^2 b_{11} + 2x_1x_2b_{12} + x_2^2 b_{22} \tag{2}$$

x_i is the mole fraction of component i and a_{ii} and b_{ii} are the a

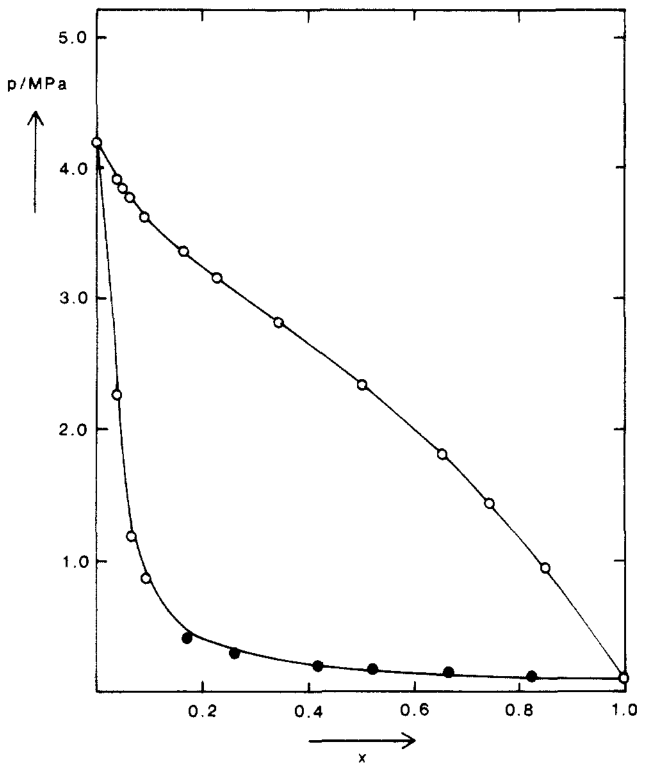

Figure 1. Vapor-liquid equilibria in the system (1 - x)ethane + (x)-2-aminopropane: isothermal p,x diagram at T = 298.15 K. ○, experiments; ●, extrapolated from experiments; —, calculated by using Peng-Robinson equation (*1*) with k_{12} = 0.0527 and l_{12} = 0.

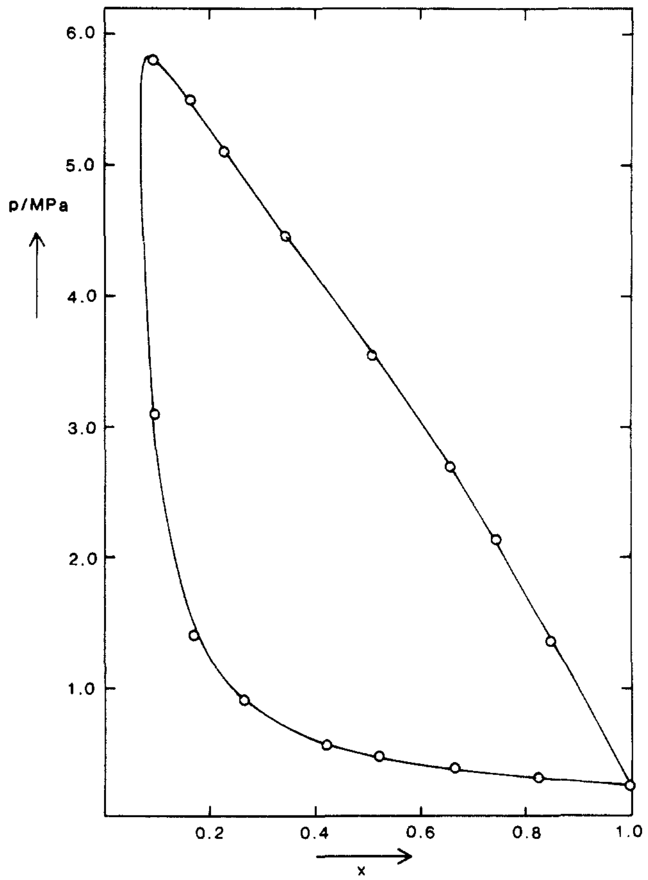

Figure 2. Vapor-liquid equilibria in the system (1 - x)ethane + (x)-2-aminopropane: isothermal p,x diagram at T = 328.15 K. ○, experiments; —, calculated by using Peng-Robinson equation (*1*) with k_{12} = 0.0417 and l_{12} = 0.

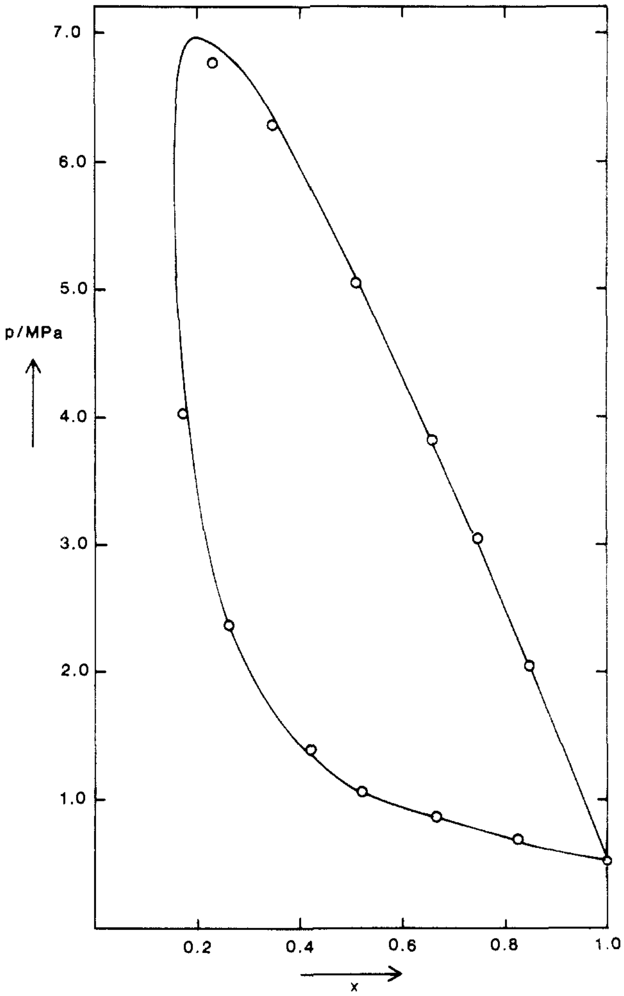

Figure 3. Vapor-liquid equilibria in the system (1 - x)ethane + (x)-2-aminopropane: Isothermal p,x diagram at T = 358.15 K. ○, experiments; —, calculated by using Peng-Robinson equation (*1*) with k_{12} = 0.0409 and l_{12} = 0.

and b values of pure i, which were calculated from the generalized equations given by Peng and Robinson (*1*). The binary constants a_{12} and b_{12} were calculated from

$$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2} \qquad (3)$$

$$b_{12} = (1 - l_{12})(b_{11} + b_{22})/2 \qquad (4)$$

k_{12} and l_{12} are adjustable binary interaction parameters which characterize the interaction of unlike molecules. Normally $l_{12} = 0$ is used and then eq 4 reduces to the conventional form $b = x_1b_{11} + x_2b_{22}$, but there is some evidence that with $l_{12} \neq 0$ eq 4 is improved significantly (*6*, *7*).

At each temperature the values of the binary interaction parameters were calculated from a best fit to the interpolated experimental data points by using the thermodynamic condition that the fugacity of either component is equal in the liquid and in the vapor phase. The expression for the fugacity from the Peng-Robinson equation of a component in a binary mixture by use of eq 1-4 is given by de Loos et al. (*7*). Values of k_{12} (one adjustable parameter, l_{12} = 0) and of k_{12} and l_{12} (two adjustable parameters) are given in Table II. For this system we found no significant improvement from the introduction of the second binary interaction parameter l_{12}.

In the Figures 1-3 a comparison is made between the experimental vapor-liquid equilibrium and the vapor-liquid equilibrium that was calculated with the Peng-Robinson equation of state (l_{12} = 0). The agreement is excellent.

Registry No. Ethane, 74-84-0; 2-aminopropane, 75-31-0.

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Physical Behavior of Some Reaction Media. Density, Viscosity, Dielectric Constant, and Refractive Index Changes of Ethanol–Dioxane Mixtures at Several Temperatures

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Viscosities, densities, dielectric constants, and refractive indexes were determined for ethanol–dioxane mixtures at 15, 20, 25, 30, and 35 °C. These properties are represented by means of empirical relations wherein the composition and temperature effects are involved. The analysis of the dielectric constant data revealed experimental evidence of molecular interactions between the components of the system.

Introduction

This paper is part of our research concerning the kinetics of S_N2 reactions between ions and dipolar molecules in solvents where the ionic reactant associates to form ion pairs (*1–6*).

In the progress of these investigations we decided to extend our studies to binary solvent systems, where the mixture of the two organic cosolvents, in various proportions, could enable us to change the physical properties of the reaction media.

Thus, in a first attempt we studied the kinetics of the reaction of sodium ethoxide and methyl iodide in ethanol–dioxane mixtures (*6*). In this investigation, in agreement with analogous literature kinetic data (*7*, *8*), we observed that the corresponding reaction is markedly accelerated as the dioxane content is progressively increased. This effect has been attributed to changes in the reactant-solvating ability of the medium. Consequently, taking into account this behavior, the ethanol–dioxane mixtures can be considered as very important reaction media for various studies of nucleophilic substitution reactions.

One problem, generally encountered in such studies, is to correlate reaction rate data with the physical properties of the corresponding media.

However, among the many intensive physical properties of liquids the dielectric constant (ϵ), viscosity (η), and index of refraction (n) remain the common solvent parameters used to interpret medium effects upon mechanisms of reactions for polar and ionic species (*9*), as well as upon electrochemical data and ionic equilibria (*10*, *11*).

Although extensive tabulation of values of these properties for pure solvents are generally available, literature data for various binary solvent systems are often incomplete and may be reported only as empirical graphs.

This situation has encouraged us to make a series of systematic measurements of density, viscosity, dielectric constant, and refractive index of ethanol–dioxane mixtures over the whole composition range and temperatures from 15 to 35 °C.

Because plots of Y values (where $Y = \epsilon, \eta, \rho, n$) vs. solvent composition are nonlinear, an attempt has been made to express these properties by means of single equations wherein the temperature and composition effects are involved.

It is noted that these equations can be used as interpolation formulas allowing prediction of the data at any temperature and composition.

Experimental Section

Reagents. Absolute ethanol (Fluka, p.a.) was further purified according to a recommended method (*12*).

Carlo Erba 1,4-dioxane (99%, bp 101 °C) was further purified by refluxing with sodium metal for several days and redistilling; the whole procedure was repeated until the sodium remained bright after several hours. In all distillations only the middle fraction coming over at the reported boiling point and comprising about 75% was retained. Pure-component physical properties are listed and compared to average literature data in Table I. Mixtures were gravimetrically prepared on a Mettler analytical balance just before their use. The probable error in the dioxane mole fraction X_2 is estimated to be less than 10^{-4}.

Measurements. Dielectric constant measurements were carried out at 2.0 MHz by the heterodyne beat method with a Wissenschaftliche-Technische Werkstäten DM 01 Dipolmeter. The thermostated measuring cells (MFL 1/S and MFL 2/S type) were adequate to cover the dielectric constant range of ethanol–dioxane mixtures at the temperatures used. The overall experimental uncertainty in ϵ values (standard deviation) was approximately equal to ±0.2%. The cells were previously calibrated with standard pure liquids in accordance with the manufacturer's specifications and with National Bureau of Standards Circular 514 (*13*).

Density measurements were made in a capillary pycnometer of approximately 25 cm^3 capacity. The pycnometer was calibrated with distilled water at each temperature. The standard deviations of the densities of the solutions used were less than 0.01%.

Viscosities were measured with an Ubbelohde capillary viscosimeter (Schott Mainz Jena Glas C 2023). In all determina-

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