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Vapor Pressure of Solutions of Polar Aromatic Compounds in Cyclohexane at 298.15 and 323.15 K

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Vapor pressures measured by the static method at 298.15 or 323.15 K are reported for solutions in cyclohexane of polar aromatic compounds (2-methoxyphenol, 2-iodophenol, 2-benzoyl-1-naphthol, 2-chloronitrobenzene, 4-nitrotoluene, and 5-methyl-2-nitrophenol). The activity coefficients of cyclohexane have been calculated and analyzed in terms of an association model.

Introduction

This work is a continuation of our studies (*1-7*) on the thermodynamics of associated solutions and of the possibility of predicting the properties of solutions on the basis of the properties of pure compounds. The vapor pressures of the solutions of polar aromatic compounds in cyclohexane have been measured at 298.15 and 323.15 K. Among the substances investigated, 2-chloronitrobenzene and 4-nitrotoluene do not form hydrogen bonds, whereas 2-benzoyl-1-naphthol, 5-methyl-2-nitrophenol, 2-iodophenol, and 2-methoxyphenol form intramolecular hydrogen bonds.

Experimental Section

Materials. Spectroscopy grade cyclohexane (POCh Gliwice) was dried with sodium and distilled by using a column with 50 theoretical plates. The purity of cyclohexane used for the investigation was better than 99.9%. The polar compounds were purified by repeated crystallization followed by either distillation under reduced pressure or vacuum sublimation. The purities determined cryometrically by using a UNIPAN (Warsaw) type 605 differential scanning calorimeter are given in Table I.

Table I. Source and Purity of the Polar Compounds

compounds	source	purity
2-benzoyl-1-naphthol	synthesized	99.53%
2-chloronitrobenzene	Loba-Chemie, Wien, Austria	99.96%
2-iodophenol	Koch-Light	99.78%
2-methoxyphenol	Fluka A.G.	99.82%
4-nitrotoluene	Loba-Chemie, Wien, Austria	99.47%
5-methyl-2-nitrophenol	Koch-Light	99.91%

Apparatus and Procedure. Vapor pressure was measured in the apparatus shown in Figure 1. Three connected glass tubes (A_1, A_2, A_3) partly filled with mercury are the main part of the apparatus. In the side tubes A_1 and A_2 the samples (1-5 cm^3) of the solution and of the solvent are placed. The middle tube A_3 is connected with three lines: the pressure, evacuating, and high-vacuum ones. The pressure line includes a cylinder with compressed nitrogen, the pressure adjusting device R, the column M_2 containing molecular sieves type 4A, and a cutoff tap K_2. The evacuating line consists of a vacuum pump, a column M_1 filled with molecular sieves, a flow regulator, and a cutoff tap K_1. The pressure and evacuating lines are used to compress and expand vapors in the tubes A_1 and A_2. The high-vacuum line consists of a vacuum pump, a vacuum gauge G, and a cutoff tap K_4; it allows a vacuum of the order of 1 Pa to be maintained in tube A_3 so that the absolute vapor pressure measurements are possible. The temperature of the thermostating jacket surrounding the tubes is held constant to 0.005 K. Mixing of liquids is achieved by vibrating the rod to which the tubes and the jacket are attached. The differential method of vapor pressure measurement used in our study requires a high-purity solvent as a reference liquid. The purity criterion was the difference between dew and bubble point pressures (p_D and p_B). To avoid contamination of the solvent during its transfer from one container to another, a method was developed for its total degassing and dehydration within the measurement vessel. The degassing process consists of expanding the liquids to 150 cm^3 and compressing them rapidly to reach the initial volume. The remaining air bubble is then thoroughly removed. This procedure is repeated until no gas appears after compressing the sample. The dehydration process relies on the fact that the water content in the vapor phase is many times greater than in the liquid. Therefore, we remove water by several expansion-compression runs. The upper portion of the liquid, enriched with water, is then removed. The procedure is repeated until no changes in the vapor pressure of the sample are detected. The degree of dehydration is checked by measuring $p_D - p_B$. The measurements are carried out as follows. Both tubes are loaded with the same solvent taken in amounts permitting the simultaneous attainment of the dew point in tube A_2 and of the bubble point in tube A_1. The number of successive dehydration runs depends on the water content of the solvent and the type of solvent. For example, with cyclohexane and *n*-hexane, dehydration takes much less time than with benzene. If a sufficient number of dehydration runs is performed, a $p_D - p_B$ value of the solvent lower than 6 Pa may be achieved. The water-free solvent obtained in this way is subsequently used as a reference substance in the measurement of the difference Δp between the vapor pressures of solvent and mixture. The mixture is placed in tube A_2. The sample is degassed and dehydrated as described above. Tube A_3 is then opened to high vacuum, and the pressure is lowered until it reaches the value of the vapor pressure of mercury. The differences in mercury levels between tubes A_1 and A_2 (Δh_{12}) and A_1 and A_3 (Δh_{13}) are measured to 0.05 mm with a cathetometer. The Δh_{13} value is used to determine the vapor pressure of the pure solvent, $p°$. The Δp values are obtained from $\Delta h_{12}°$. This parameter is obtained by linear extrapolation of Δh_{12} with respect to the mercury level in the mixture tube to the mercury level for which the volume of the vapor is equal to zero. The hydrostatic pressure of the liquid under examination is taken into account while the absolute vapor pressures, as well as the vapor pressure differences, are calculated. The composition of the solution was determined after each experiment by measuring the refractive index using the Hilger-Chance precision refractometer in order to take into account the sample concentration changes during the degassing and dehydration process.

Results

The main source of errors in the measurement of vapor pressures in systems containing a polar compound and a hydrocarbon is the presence of traces of water (*8*). The small difference (<6 Pa) between the dew and bubble point pressures of cyclohexane proves the great efficiency of the dehydration procedure used for a pure solvent. The vapor pressures obtained for cyclohexane agree with those calculated from the

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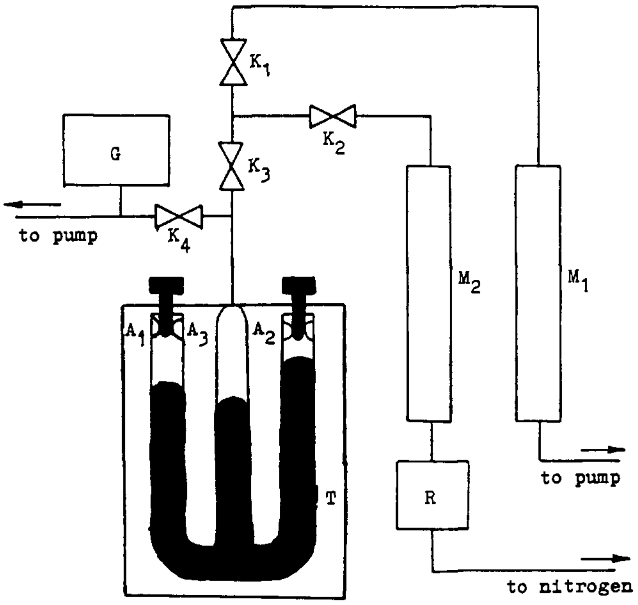

Figure 1. Schematic diagram of the apparatus.

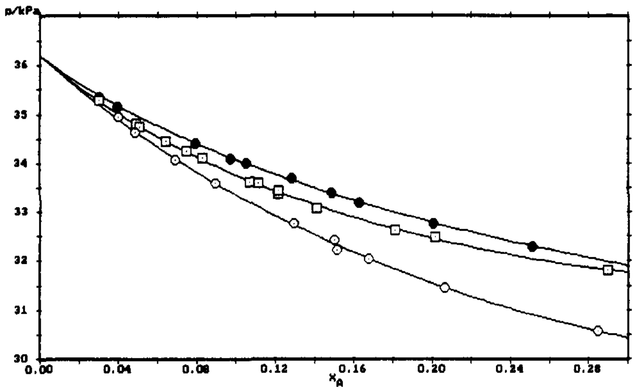

Figure 2. Vapor pressure p at 323.15 K of solutions in cyclohexane as a function of the mole fraction x_A of the polar solute. Points, experimental values: ○, 2-iodophenol; ●; 4-nitrotoluene; □, 5-methyl-2-nitrophenol; —, fit by the monomer–dimer association model using the parameters of Table IV.

Antoine equation (*9*). Temperature inside the apparatus, calculated from the measured vapor pressures of cyclohexane, differs from that measured in the thermostatic jacket by not more than 0.03 K.

The efficiency of removing water from the solution by the described method depends on the concentration of the polar component and its ability to hydrate (*10*). A rapid decrease of dehydration efficiency was observed for solutions with the mole fraction of the polar compound larger than 0.3. Therefore, most measurements have been performed in more dilute solutions. The results in concentrated solutions are less accurate. The vapor pressures of the pure polar compounds have not been measured for similar reasons.

The obtained vapor pressure data are presented in Table II. The mole fraction x_A of the polar compound in the liquid phase and the total vapor pressure p over the solution are given. The experimental data at 323.15 K are shown also on Figures 2 and 3.

Table II. Vapor Pressures p and Activity Coefficients γ_B of Cyclohexane in Polar Compound + Cyclohexane Solutions

x_A	p/kPa	γ_B	x_A	p/kPa	γ_B
2-Benzoyl-1-naphthol + Cyclohexane					
323.15 K					
0.0000	36.197	1.0000	0.0706	34.669	1.0315
0.0198	35.580	1.0032	0.0815	34.450	1.0373
0.0298	35.352	1.0071	0.0968	34.295	1.0501
0.0394	35.212	1.0133	0.1184	34.057	1.0686
0.0577	34.806	1.0213	0.1418	33.843	1.0909
0.0599	34.765	1.0225			
2-Chloronitrobenzene + Cyclohexane					
323.15 K					
0.0000	36.197	1.0000	0.1200	34.112	1.0722
0.0197	35.640	1.0047	0.1404	33.959	1.0928
0.0351	35.296	1.0111	0.1596	33.709	1.1097
0.0602	34.888	1.0264	0.1627	33.752	1.1152
0.0793	34.565	1.0382	0.1827	33.509	1.1345
0.0984	34.261	1.0510	0.2004	33.452	1.1576
0.1176	34.080	1.0683			
2-Iodophenol + Cyclohexane					
298.15 K					
0.0000	13.032	1.0000	0.1515	11.798	1.0680
0.0187	12.794	1.0006	0.1674	11.688	1.0784
0.0482	12.502	1.0083	0.2065	11.546	1.1178
0.0688	12.323	1.0160	0.2850	11.450	1.2303
0.0895	12.186	1.0276	0.5014	10.820	1.6682
0.1296	11.943	1.0538	0.8484	7.683	3.9057
0.1498	11.828	1.0686			
323.15 K					
0.0000	36.197	1.0000	0.1498	32.420	1.0558
0.0187	35.542	1.0010	0.1515	32.209	1.0512
0.0400	34.949	1.0065	0.1674	32.033	1.0655
0.0482	34.630	1.0061	0.2065	31.440	1.0977
0.0688	34.060	1.0117	0.2850	30.565	1.1849
0.0895	33.591	1.0208	0.5014	28.031	1.5606
0.1296	32.764	1.0420	0.8484	17.596	3.2416
2-Methoxyphenol + Cyclohexane					
298.15 K					
0.0000	13.032	1.0000	0.1206	12.222	1.0671
0.0385	12.647	1.0096	0.1514	12.151	1.0995
0.0608	12.483	1.0203	0.1675	12.146	1.1203
0.0808	12.382	1.0341	0.1954	12.124	1.1571
0.0982	12.322	1.0490	0.2127	12.059	1.1762
323.15 K					
0.0000	36.197	1.0000	0.1469	33.173	1.0762
0.0385	35.025	1.0071	0.1514	33.140	1.0808
0.0608	34.517	1.0163	0.1675	33.096	1.1003
0.0808	34.120	1.0267	0.1954	32.824	1.1293
0.0982	33.867	1.0389	0.2127	32.601	1.1464
0.1206	33.517	1.0546			
4-Nitrotoluene + Cyclohexane					
323.15 K					
0.0000	36.197	1.0000	0.1486	33.396	1.0854
0.0301	35.346	1.0073	0.1626	33.191	1.0969
0.0395	35.149	1.0116	0.2007	32.764	1.1347
0.0793	34.408	1.0335	0.2511	32.291	1.1939
0.0971	34.093	1.0445	0.3794	31.081	1.3878
0.1051	33.991	1.0507	0.5084	29.436	1.6608
0.1287	33.689	1.0698	0.6068	27.630	1.9510
5-Methyl-2-nitrophenol + Cyclohexane					
323.15 K					
0.0000	36.197	1.0000	0.1217	33.440	1.0535
0.0298	35.290	1.0054	0.1410	33.077	1.0658
0.0489	34.810	1.0120	0.1807	32.611	1.1019
0.0507	34.736	1.0117	0.2016	32.477	1.1262
0.0639	34.453	1.0178	0.2897	31.808	1.2403
0.0747	34.237	1.0234	0.4015	30.771	1.4249
0.0828	34.099	1.0283	0.4960	29.824	1.6409
0.1070	33.621	1.0417	0.6085	28.198	1.9991
0.1114	33.596	1.0461	0.7090	25.713	2.4561
0.1213	33.357	1.0505			

Vapor pressure data of pure 2-methoxyphenol (*11*, *12*), 2-chloronitrobenzene (*13*), and 4-nitrotoluene (*11*) have been found in the literature. The vapor pressures are given at higher temperature, and, therefore, they had to be extrapolated to 323.15 and 298.15 K. The comparison of vapor pressures of 2-methoxyphenol, extrapolated by using the Antoine equation parameters given by different authors (*9*, *14*) and obtained from different data sets (*11*, *12*) shows that the extrapolation gives values that may differ by a factor of 2. The estimated vapor pressures of the polar compounds do not exceed 0.2 kPa at

Table III. Liquid Molar Volumes V of Pure Substances

substance	$V/(\text{cm}^3\ \text{mol}^{-1})$ 298.15 K	$V/(\text{cm}^3\ \text{mol}^{-1})$ 323.15 K
cyclohexane	108.76 (*18*)	112.96 (*18*)
2-benzoyl-1-naphthol		175.00[a]
2-chloronitrobenzene		117.68 (*13*)[b]
2-iodophenol	95.00[a]	95.00[a]
2-methoxyphenol	109.97 (*19*)	112.37 (*20*)
4-nitrotoluene		121.64 (*18*)[c]
5-methyl-2-nitrophenol		124.76 (*21*)

[a] Calculated from group contributions (*22*). [b] Interpolated. [c] Extrapolated.

323.15 K and 0.04 kPa at 298.15 K. In view of the uncertainty of extrapolation or the lack of data, the partial pressure of cyclohexane has been assumed to be equal to the total vapor pressure over the solution.

The activity coefficient γ_B of cyclohexane in the liquid phase (Table II) has been calculated by using following relation:

$$p = p^\circ\gamma_B(1 - x_A)\exp((B - V_B)(p^\circ - p)/RT) \quad (1)$$

where p° is the vapor pressure of cyclohexane, B, the second molar virial coefficient, V_B, the liquid molar volume of cyclohexane, R, the molar gas constant, and T, the equilibrium temperature. The values of the second molar virial coefficient of cyclohexane, $B = -1884$ cm^3 mol^{-1} at 298.15 K and $B = -1458$ cm^3 mol^{-1} at 323.15 K, were calculated from the Tsonopoulos correlation (*15*) by using the critical parameters and acentric factor given by Reid et al. (*16*).

Discussion

The vapor pressure of the investigated solutions may be represented by a model in which the solute is assumed to associate in part in the form of dimers. The solvent activity coefficient γ_B in this monomer–dimer association model can be expressed as

$$\gamma_B = \gamma_B^{\text{chem}}\gamma_B^{\text{phys}} \quad (2)$$

where γ_B^{chem} expresses the chemical effect of association and γ_B^{phys}, the effect of physical interactions.

The γ_B^{phys} term has been taken into account by using the Hildebrand regular solution model

$$\gamma_B^{\text{phys}} = \exp(D^2V_B\Phi_A^2/RT) \quad (3)$$

where $\Phi_A = x_AV_A/(x_AV_A + x_BV_B)$ is the solute volume fraction and D is a quantity related to the solubility parameters of the solute and solvent (*17*), treated here as an adjustable parameter. The values of liquid molar volumes of the components used in this work are given in Table III.

The γ_B^{chem} term is given by the ideal monomer–dimer association model (*23*)

$$\gamma_B^{\text{chem}} = 1 + 2Kx_A^2/(1 + 2Kx_A(2 - x_A) + (1 + 4Kx_A(2 - x_A))^{1/2}) \quad (4)$$

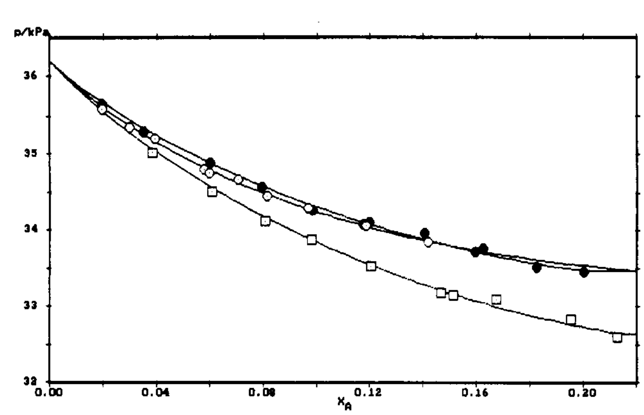

Figure 3. Vapor pressure p at 323.15 K of solutions in cyclohexane as a function of the mole fraction x_A of the polar solute. Points, experimental values: ○, 2-benzoyl-1-naphthol; ●, 2-chloronitrobenzene; □, 2-methoxyphenol; —, fit by the monomer–dimer association model using the parameters of Table IV.

where K is the thermodynamic equilibrium constant of dimerization.

Two model parameters, K and D, have been fitted to the experimental vapor pressure data by minimizing the objective function

$$f(K,D) = \sum(p(x_A)^{\text{exp}} - p(x_A,K,D))^2 \quad (5)$$

where $p(x_A)^{\text{exp}}$ is the vapor pressure measured for the solution with the solute's mole fraction x_A and $p(x_A,K,D)$ is the vapor pressure calculated from the association model for the same solute concentration.

The fitted values of the parameters K and D and the obtained deviations of vapor pressures are presented in Table IV. For systems for which the vapor pressures have also been measured at solute mole fraction greater than 0.3, those points have not been used. If the data for more concentrated solutions are used, the obtained deviations are greater than for other systems, probably due to the existence of traces of water in concentrated solutions. The dependence of vapor pressure on the solute mole fraction for the adjusted values of model parameters is shown in Figures 2 and 3 by solid lines.

The monomer–dimer association model with two adjustable parameters represents well the measured vapor pressure data, and the obtained deviations can be treated as estimates of the experimental errors. The small biases in comparison with the mean absolute deviations confirm the lack of any systematic deviations between model and data.

The investigated systems exhibit large positive deviations from ideality and the parameters obtained for 2-methoxyphenol + cyclohexane and 2-chloronitrobenzene + cyclohexane systems predict phase splitting at the limit of the experimental data range (see Figure 3). The existence of two liquid phases has not been observed experimentally, neither on the investigated isotherms nor on the solid–liquid equilibrium line (*3*). It was observed, however, that, for oversaturated solutions obtained by rapid cooling of the solution of 2-methoxyphenol in cyclo-

Table IV. Parameters K and D, equations 3 and 4, at Temperature T and Deviations between Experimental and Calculated Vapor Pressures Using the Monomer–Dimer Association Model

solute	T/K	K	D/MPa$^{1/2}$	RMSD[a]/kPa	Δp[b]/kPa	bias[c,d]/kPa
2-benzoyl-1-naphthol	323.15	16.3293	4.8509	0.030	0.024	−0.002
2-chloronitrobenzene	323.15	48.5968	5.8868	0.048	0.036	−0.005 L
2-iodophenol	298.15	3.9871	6.4518	0.020	0.015	−0.001 L
2-iodophenol	323.15	2.2114	6.3195	0.052	0.033	0.003
2-methoxyphenol	298.15	18.2778	6.1771	0.032	0.024	−0.002 L
2-methoxyphenol	323.15	7.8387	6.2139	0.056	0.042	−0.008 L
4-nitrotoluene	323.15	28.8744	5.0155	0.027	0.019	−0.004
5-methyl-2-nitrophenol	323.15	6.5678	5.4813	0.033	0.026	0.003

[a] RMSD = $(\sum(p(x_A)^{\text{exp}} - p(x_A,K,D))^2/(N - 2))^{1/2}$, where N is the number of experimental points and 2 is the number of adjustable parameters. [b] $\Delta p = \sum p|(x_A)^{\text{exp}} - p(x_A,K,D)|/N$. [c] Bias $= \sum(p(x_A)^{\text{exp}} - p(x_A,K,D))/N$. [d] L denotes prediction of liquid–liquid equilibrium.

hexane below the solid–liquid equilibrium temperature, two liquid phases appeared at a temperature of about 290 K (*24*).

The possibility of describing the properties of investigated systems by the monomer–dimer model is consistent with the results of our previous papers (*3*, *4*, *6*), where the suggestion is made that the polar compounds incapable of forming intermolecular hydrogen bonds dimerize as a result of dipole interactions. The presented results confirm also that the effect of association on the thermodynamic properties of the solutions of polar compounds in inert solvent is very important. The model taking self-association explicitly into account leads to a satisfactory representation of experimental data with adjustable parameters with defined physicochemical meaning. The model parameters K and D can be predicted on the basis of the properties of pure substances using the homomorph concept (*6*, *7*).

Acknowledgment

We thank Professor A. Bylicki for his comments.

Glossary

B	second molar virial coefficient of cyclohexane, $cm^3\ mol^{-1}$
D	parameter in eq 3, $MPa^{1/2}$
K	thermodynamic association constant
p	total vapor pressure over the solution, kPa
p_B	bubble point pressure
p_D	dew point pressure
p°	vapor pressure of pure cyclohexane, kPa
R	molar gas constant (=8314.31), $cm^3\ kPa\ K^{-1}\ mol^{-1}$
T	equilibrium temperature, K
V_A	molar volume of solute, $cm^3\ mol^{-1}$
V_B	liquid molar volume of cyclohexane, $cm^3\ mol^{-1}$
x_A	mole fraction of solute in the liquid phase
x_B	mole fraction of cyclohexane in the liquid phase
γ_B	activity coefficient of cyclohexane in the liquid phase
Δp	difference between the vapor pressures of pure cyclohexane and mixture

Registry No. 2-Methoxyphenol, 90-05-1; 2-iodophenol, 533-58-4; 2-benzoyl-1-naphthol, 21009-99-4; 2-chloronitrobenzene, 88-73-3; 4-nitrotoluene, 99-99-0; 5-methyl-2-nitrophenol, 700-38-9; cyclohexane, 110-82-7.

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Liquid–Liquid Mutual Solubilities of Binary Mixtures of Ammonia with *n*-Heptane, *n*-Decane, *n*-Undecane, and *n*-Dodecane up to Upper Critical Solution Temperature

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Liquid–liquid mutual solubilities for binary mixtures of ammonia with *n*-heptane, *n*-decane, *n*-undecane, and *n*-dodecane have been measured between 317 K and the upper critical solution temperatures. The liquid–liquid equilibrium curves were expressed with the scaled equation of state. The upper critical solution temperature is a linear function of the number of carbon atoms in the *n*-alkane.

Introduction

Accurate liquid–liquid equilibrium data in the critical region are important not only for the theoretical study of critical phenomena but also for the development of semiempirical correlations near the critical region. In our previous study (*1*), we reported liquid–liquid mutual solubility data for binary mixtures of ammonia with *n*-pentane, *n*-hexane, and *n*-octane up to the upper critical solution temperatures. In this study, we report similar data for ammonia with *n*-heptane, *n*-decane, *n*-undecane, and *n*-dodecane.

Experimental Section

***Apparatus and Procedure*.** The experimental measurements were performed in a pressurized Pyrex-glass cell. Miscibility temperature was determined by observing turbidity changes during heating and cooling of solutions. The apparatus and the procedures were essentially the same as those described in our previous study (*1*). We measured the mutual solubility both at the vapor–liquid–liquid equilibrium (VLLE) pressure and under pressure at the liquid–liquid equilibrium (LLE) pressure in the previous study. Figure 1 shows the comparison between the VLLE pressures reported in the previous study with the vapor pressure of pure ammonia. It can be seen that the VLLE

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