of the mole fraction of cyclohexane, the $D_{AB}$ value at that point being the limiting mutual diffusion coefficient of the solutes in cyclohexane.

The graph for the binary systems comprising methylcyclohexane as one component and *n*-paraffinic alcohols as the other is given in Figure 3. The curvature of ethanol–methylcyclohexane is more, while that of the octanol–methylcyclohexane binary system is less, as expected. Further, this figure also shows an interesting feature in that all the curves meet around a single point (approximately at 36% of methylcyclohexane). To the left of the point of intersection the curves show the regular nature; that is, ethanol has a higher value of diffusion coefficient than the others and the gradation can be observed as in the cyclohexane–alcohol binary systems. However, on the right of the point of intersection, the trend is exactly opposite, with the diffusion coefficient values for higher alcohols more than that for the lower alcohols. The values for the diffusion coefficients of methylcyclohexane–alcohol binary systems are lower than those for cyclohexane–alcohol series at corresponding compositions. The present theories of liquid-state diffusion are inadequate to predict the nature of the graph or the values of the diffusion coefficients.

Two features of the present work are to be noted. Firstly, though all *n*-alkyl alcohols from ethanol to 1-octanol are completely miscible with cyclohexane and methylcyclohexane, methanol is not miscible in all proportions. Hence the binary systems methanol–cyclohexane and methanol–methylcyclohexane could not be studied in the present work. Secondly, the density of the binary systems ethanol–cyclohexane, propanol–cyclohexane, and ethanol–methylcyclohexane, for some of the compositions, is lower than either of the pure components. Thus for these systems, whenever the mixture density was lower than that of cyclohexane density, the experiment was conducted by keeping the pure solvent in the bottom compartment.

## Conclusion

The correlations given have limitations in that each correlation is applicable only to the system concerned. Further, they do not take care of the temperature effect and hence are applicable only at the temperature used in this work, and finally they cannot be applied to evaluate limiting mutual diffusion coefficients for $x_A \rightarrow 0$ and $x_B \rightarrow 0$, respectively.

## Glossary

| | |
|---|---|
| $A_1,A_2$ | coefficients in eq 3 |
| $B_1,B_2$ | coefficients in eq 3 |
| $C_1,C_2$ | coefficients in eq 3 |
| $\bar{C}_B,\bar{C}_T$ | average concentrations in the bottom and top compartments, g/cm$^3$ |
| $C_B^i,C_B^f$ | concentrations in the bottom compartment, initial and final, respectively, g/cm$^3$ |
| $C_T^i,C_T^f$ | concentrations in the top compartment, initial and final, respectively, g/cm$^3$ |
| $D_{AB}$ | mutual diffusion coefficient, cm$^2$/s |
| $D_{AB}^\infty$ | diffusion coefficient at infinite dilution, cm$^2$/s |
| $D_{C_B}$ | diffusion coefficient at the bottom compartment average concentration, cm$^2$/s |
| $D_{C_T}$ | diffusion coefficient at the top compartment average concentration, cm$^2$/s |
| $M_A$ | molecular weight of A |
| $P_i$ | property used in correlation defined by eq 4 |
| $V_A$ | molar volume, cm$^3$/g-mol |
| $x$ | mole fraction of the solvent |
| $\beta$ | cell constant, cm$^{-2}$ |
| $\eta_A$ | viscosity of component A, g/(cm·s) |
| $\eta_{expt}$ | experimentally determined viscosity for pure components, g/(cm·s) |
| $\eta_{lit.}$ | viscosity from literature for pure components, g/(cm·s) |
| $\rho_{expt}$ | experimentally determined density for pure components, g/cm$^3$ |
| $\rho_{lit.}$ | density from literature for pure components, g/cm$^3$ |

**Registry No.** Ethanol, 64-17-5; propanol, 71-23-8; butanol, 71-36-3; pentanol, 71-41-0; hexanol, 111-27-3; heptanol, 111-70-6; octanol, 111-87-5; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2.

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# Vapor–Liquid Equilibria for Four Binary Systems Made of Alcohol and Cyclohexylamine at 100 kPa

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**Boiling points for four binary systems made of an alcohol (methanol, ethanol, 1-propanol, or 2-propanol) and cyclohexylamine were measured with a flow-type ebulliometer at 100-kPa pressure, and their isobaric vapor–liquid equilibrium relations were determined.**

## Introduction

Vapor–liquid equilibria are required for an engineering application such as the design and operation of distillation equipment. Vapor–liquid equilibrium relations can be determined from boiling point curves, which are more easily obtained than conventional equilibrium measurements.

The flow-type ebulliometer was previously proposed for measuring isobaric bubble points (*1*). In the present study, boiling points were measured with the flow-type ebulliometer for the four binary systems made of an alcohol (methanol, ethanol, 1-propanol, or 2-propanol) and cyclohexylamine, and their vapor-phase compositions were determined by the successive calculation method of Tao (*2*) with vapor-phase corrections of Hayden–O'Connell (*3*). Vapor–liquid equilibrium data

**Table I. Densities $\rho$, Normal Boiling Points $T_b$, and Refractive Indexes $n_D$ of the Materials Used**

| | $\rho$(298.15 K)/(g cm$^{-3}$) | | $T_b$/K | | $n_D$(298.15 K) | |
|---|---|---|---|---|---|---|
| material | exptl | lit. | exptl | lit. | exptl | lit. |
| methanol | 0.7866 | 0.786 55 (*15*) | 337.69 | 337.659 (*15*) | 1.3271 | |
| ethanol | 0.7852 | 0.785 08 (*15*) | 351.48 | 351.475 (*15*) | 1.3599 | 1.3596 (*15*) |
| 1-propanol | 0.7809 | 0.780 87 (*15*) | 370.28 | 370.359 (*15*) | 1.3833 | |
| 2-propanol | 0.7999 | 0.799 85 (*15*) | 355.42 | 355.44 (*15*) | 1.3753 | |
| cyclohexylamine | 0.8623 | 0.862 3 (*19*) | 407.57 | 407.65 (*10*) | 1.4572 | 1.4565 (*16*) |

**Table II. Experimental Boiling Point $T$ and Equilibrium Vapor-Phase Mole Fraction $Y$ of Alcohol Calculated by the Method of Tao (*2*) for Four Binary Systems[a] at 100 kPa as a Function of the Liquid-Phase Mole Fraction $X$ of the Alcohol**

| | I | | II | | III | | IV | |
|---|---|---|---|---|---|---|---|---|
| $X$ | $Y$ | $T$/K | $Y$ | $T$/K | $Y$ | $T$/K | $Y$ | $T$/K |
| 0.000 | 0.000 | 407.10 | 0.000 | 407.10 | 0.000 | 407.10 | 0.000 | 407.10 |
| 0.100 | 0.404 | 392.17 | 0.326 | 396.40 | 0.198 | 402.74 | 0.306 | 397.31 |
| 0.200 | 0.620 | 381.16 | 0.527 | 388.22 | 0.367 | 398.64 | 0.496 | 390.11 |
| 0.300 | 0.741 | 373.19 | 0.669 | 381.21 | 0.512 | 394.62 | 0.641 | 383.62 |
| 0.400 | 0.829 | 365.99 | 0.766 | 375.47 | 0.631 | 390.87 | 0.744 | 378.15 |
| 0.500 | 0.883 | 360.46 | 0.840 | 370.32 | 0.734 | 387.16 | 0.831 | 372.59 |
| 0.600 | 0.925 | 355.23 | 0.893 | 365.89 | 0.821 | 383.42 | 0.883 | 368.59 |
| 0.700 | 0.960 | 349.67 | 0.937 | 361.45[b] | 0.891 | 379.71 | 0.926 | 364.82 |
| 0.800 | 0.982 | 344.66 | 0.967 | 357.59 | 0.944 | 376.06 | 0.961 | 361.16 |
| 0.900 | 0.994 | 340.53 | 0.988 | 354.08 | 0.980 | 372.76 | 0.985 | 357.93 |
| 1.000 | 1.000 | 337.35 | 1.000 | 351.15 | 1.000 | 369.93 | 1.000 | 355.09 |

[a] Systems: I, methanol–cyclohexylamine; II, ethanol–cyclohexylamine; III, 1-propanol–cyclohexylamine; IV, 2-propanol–cyclohexylamine. [b] Experimental dew point, 378.98 K.

**Table III. Antoine Constants[a] of the Materials Used**

| material | $A$ | $B$ | $C$ | 100($\Delta P/P$)[b] |
|---|---|---|---|---|
| methanol (*11*) | 7.223 44 | 1597.40 | −31.54 | 0.08 |
| ethanol (*11*) | 7.001 67 | 1454.74 | −60.29 | 0.10 |
| 1-propanol (*10, 12*) | 6.642 67 | 1306.20 | −88.58 | 0.14 |
| 2-propanol (*10, 12*) | 6.501 87 | 1158.87 | −97.67 | 0.17 |
| cyclohexylamine (*10*) | 5.786 40 | 1223.36 | −83.98 | 0.56 |

[a] $\log (P/\text{kPa}) = A - B/((T/\text{K}) + C)$. [b] $\Delta P/P = \sum |(P_{\text{calc}} - P_{\text{expt}})/P_{\text{calc}}|/N$ ($N$, number of data points).

for these systems are not available in the literature.

Applications of a three-parameter pseudocubic equation of state previously proposed (*4*) and the Wilson equation (*5*) with vapor-phase corrections for those systems are discussed.

## Experimental Section

The experimental apparatus and procedures are the same as those described previously (*1*). The atmospheric pressures were obtained from the boiling point temperatures of water. Special grade reagents of the alcohols and cyclohexylamine were supplied by Wako Pure Chemical Industry Co., Ltd. Methanol, ethanol, and 2-propanol were used without further purification. Cyclohexylamine and 1-propanol were further purified with use of an Oldershaw column with 30 plates. The physical properties of the materials used are listed in Table I.

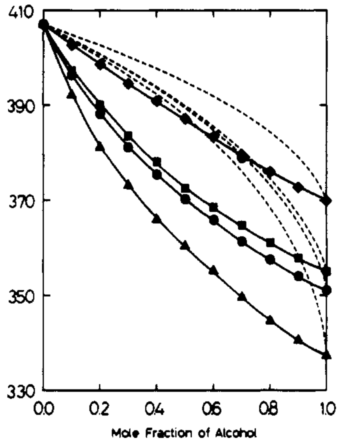

**Figure 1.** Vapor–liquid equilibria for four binary systems made of alcohol and cyclohexylamine at 100 kPa. Curves: (—) experimental boiling point curve; (- -) calculated dew point curve by method of Tao (*2*). Experimental points: (▲) methanol–cyclohexylamine; (●, ○) ethanol–cyclohexylamine; (◇) 1-propanol–cyclohexylamine; (■) 2-propanol–cyclohexylamine.

## Results and Discussion

The experimental boiling points were corrected from the raw data to those at 100 kPa, as described previously (*1, 6–9*). The boiling points at 100 kPa are given in Table II and shown in Figure 1. The Antoine constants of the pure components (Table III) were fitted to the present experimental boiling points and the vapor pressures given in the literature (*10–12*). The vapor-phase corrections were made with the Hayden–O'Connell method (*3*), using the parameters shown in Table IV. The association parameter $\eta_{12}$ of unlike molecules was estimated with the equation in Table IV (given in footnote *e*) in which the value $\Delta\eta$ was evaluated from the experimental second virial coefficient data of Millen and Mines (*13*) for the methanol–trimethylamine system. The heat of mixing was neglected in the present calculations. The activity coefficients in the liquid phase

**Table IV. Parameters Used for Vapor-Phase Correction: Critical Pressure $P_c$, Critical Temperature $T_c$, Molar Volume $V$, Mean Radius of Gyration $R'$, Molecular Dipole Moment $\mu$, and Association Parameter $\eta$**

| material | $P_c$/MPa | $T_c$/K | $V$/(10$^{-3}$ m$^3$ mol$^{-1}$) | $R'$/Å | $\mu$/D | $\eta$[a] |
|---|---|---|---|---|---|---|
| methanol (*17*) | 7.954 | 513.2 | 0.0407[b] | 1.536 | 1.66 | 1.63 |
| ethanol (*17*) | 6.383 | 516.3 | 0.0587[b] | 2.250 | 1.69 | 1.40 |
| 1-propanol (*17*) | 5.168 | 536.7 | 0.0770[b] | 2.736 | 1.68 | 1.40 |
| 2-propanol (*17*) | 4.762 | 508.4 | 0.0751[b] | 2.726 | 1.66 | 1.32 |
| cyclohexylamine (*19*) | 4.199[c] | 614.9[c] | 0.1150[b] | 3.707[d] | 1.26 | 0.20[e] |

[a] $\eta_{12} = (\eta_{11} + \eta_{22})/2 + \Delta\eta$, $\Delta\eta = 1.60$. [b] This work. [c] Estimated by the Lydersen method (*18*). [d] Evaluated from its parachor. [e] Assumed as 0.20.

**Table V. Activity Coefficients $\gamma_i^\infty$ in the Liquid Phase at Infinite Dilution at Temperature $T$**

| system | $T$/K | $\gamma_1^\infty$ | $T$/K | $\gamma_2^\infty$ |
|---|---|---|---|---|
| methanol (1)–cyclohexylamine (2) | 407.10 | 0.638 | 337.35 | 0.306 |
| ethanol (1)–cyclohexylamine (2) | 407.10 | 0.687 | 351.15 | 0.409 |
| 1-propanol (1)–cyclohexylamine (2) | 407.10 | 0.643 | 369.93 | 0.352 |
| 2-propanol (1)–cyclohexylamine (2) | 407.10 | 0.784 | 355.09 | 0.438 |

at infinite dilution $\gamma_i^\infty$ were calculated from the experimental boiling point curves by the procedures of Gautreaux and Coates (*14*) (Table V). The vapor-phase compositions were estimated from the experimental boiling point data by the successive-calculation method of Tao (*2*) and are shown in Table II and Figure 1. To confirm the reliability of the present calculations, one dew point temperature was measured, as shown in Table II and Figure 1, for ethanol–cyclohexylamine by using the dew point–bubble point apparatus previously proposed (*8*). The accuracy of the calculated vapor-phase mole fractions given in Table II seems to be within 0.010.

Applications of the pseudocubic equation of state previously proposed (*4*) and the Wilson equation (*5*) with vapor-phase corrections were considered for these systems. The equation of state used in the present study is given as follows:

$$P = \frac{RT}{V^* - b} - \frac{a}{(V^*)^2} \tag{1}$$

where

$$V^* = (V - \epsilon b)(V + \sigma b)/V \tag{2}$$

$$a_0 = \frac{27}{64}\frac{(RT_c)^2}{P_c}, \quad b = \frac{RT_c}{8P_c} \tag{3}$$

$$\epsilon = (1 - \theta)(\xi - 2), \quad \sigma = (1 - \theta)(\xi + 2) \tag{4}$$

$$\xi = [(4 - \theta)/(1 - \theta)]^{1/2} \tag{5}$$

$$\theta = 8Z_c/3, \quad Z_c = P_cV_c/RT_c \tag{6}$$

in which $P$, $V$, $T$, $R$, and $Z$ respectively denote the pressure, molar volume, temperature, gas constant, and compressibility factor. $V^*$ represents the apparent volume. The subscript "c" means the critical value. The equation of state has three parameters, $a$, $b$, and $\theta$. The parameters $a_0$, $b$, and $\theta$ can be evaluated solely from the critical values $P_c$, $V_c$, and $T_c$. Almost similar to the previous work (*4*), the temperature dependence on parameter $a$ was introduced as follows:

$$a = Ka_0, \quad \ln K = S(1 - T_r^{1/2}), \quad T_r = T/T_c \tag{7}$$

In the present paper, the parameter $S$ was computed from the experimental boiling point data at 100 kPa for each substance.

To apply the equation of state to mixtures, the following mixing rules were used in the present study.

$$a = \sum\sum x_i x_j a_{ij}, \quad a_{ij} = (1 - k_{ij})[a_i a_j]^{1/2} \tag{8}$$

$$b = \sum\sum x_i x_j b_{ij}, \quad b_{ij} = (1 - l_{ij})(b_i + b_j)/2 \tag{9}$$

$$\theta = \sum x_i \theta_i \tag{10}$$

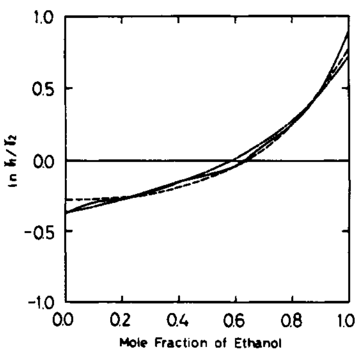

**Figure 2.** Activity coefficient curves calculated for the ethanol (1)–cyclohexylamine (2) system at 100 kPa: (—) calculated by the method of Tao (*2*); (---) calculated by the Wilson equation (*5*); (--) calculated by the pseudocubic equation of state (*4*).

where, $k$ and $l$ denote the binary interaction parameters. Subscripts $i$ and $j$ represent the components.

Those calculated results using the pseudocubic equation of state and Wilson equation with vapor-phase corrections are shown in Table VI. The parameters in Table VI were evaluated to minimize the sum of squares in the difference between the calculated boiling point and the experimental one. The value of $\Delta Y$ indicates the average difference between the calculated vapor composition and the one obtained by the method of Tao (*2*). The values of $\Delta T$ and $\Delta Y$ are negligible, as shown in Table VI. Figure 2 shows the activity coefficient curves calculated in three ways, using the method of Tao, the Wilson equation, and the pseudocubic equation of state for the ethanol–cyclohexylamine system. The difference among them is negligible.

For the pseudocubic equation of state, the activity coefficient $\gamma_i$ was evaluated with the following equation.

$$\gamma_i = \hat{\phi}_i/\phi^\circ_i \tag{11}$$

where, the fugacity coefficients $\hat{\phi}_i$ in a mixture and $\phi^\circ_i$ in a pure substance were calculated with the equation of state. The fugacity coefficient of the present pseudocubic equation of state for a mixture is given in the Appendix.

## Conclusions

In the present study, boiling points for the four binary systems made of alcohol (methanol, ethanol, 1-propanol, or 2-propanol) and cyclohexylamine were measured with a flow-type ebulliometer at 100 kPa. The isobaric vapor–liquid equilibrium relations were calculated from the experimental boiling point curves. The vapor–liquid equilibrium data obtained in the present study were successfully correlated with the pseudocubic equation of state and with the Wilson equation.

**Table VI. Wilson Parameters $\Lambda_{ij}$, Interaction Parameters of Pseudocubic Equation of State $k_{ij}$, $l_{ij}$, Mean Absolute Deviations in Temperature $\Delta T$, and Vapor-Phase Composition $\Delta Y$ Obtained from the VLE Data[a]**

| | Wilson equation | | | | pseudocubic equation of state | | | |
|---|---|---|---|---|---|---|---|---|
| system | $\Lambda_{12}$ | $\Lambda_{21}$ | $\Delta Y$ | $\Delta T$/K | $k_{12}$ | $l_{12}$ | $\Delta Y$ | $\Delta T$/K |
| I | 3.0765 | 0.3250 | 0.005 | 0.50 | −0.251 | −0.175 | 0.008 | 0.16 |
| II | 2.7227 | 0.3669 | 0.002 | 0.21 | −0.148 | −0.106 | 0.008 | 0.10 |
| III | 3.0596 | 0.3265 | 0.002 | 0.08 | −0.240 | −0.219 | 0.004 | 0.05 |
| IV | 2.5795 | 0.3874 | 0.003 | 0.18 | −0.092 | −0.062 | 0.009 | 0.16 |

[a] Systems: I, methanol (1) + cyclohexylamine (2) ; II, ethanol (1) + cyclohexylamine (2); III, 1-propanol (1) + cyclohexylamine (2); IV, 2-propanol (1) + cyclohexylamine (2). $\Delta Y = \sum|Y_{\text{calc}} - Y_{\text{ref}}|/N$. $\Delta T = \sum|T_{\text{calc}} - T_{\text{exptl}}|/N$ ($N$, number of experimental points; $Y_{\text{ref}}$, calculated by the method of ref 2).

**Acknowledgment**

We thank Messrs. Kazuhiro Sugaya, Haruhisa Inoue, and Tsuneo Sakuma for their help on the present experiment.

**Appendix: Fugacity Coefficient of the Three-Parameter Pseudocubic Equation of State**

The fugacity coefficient of component $k$ in a mixture, $\hat{\phi}_k$, is given as follows:

$$RT \ln \hat{\phi}_k = I_1 + I_2 + I_3 + I_4 + I_5 + I_6 + I_7 \quad \text{(A1)}$$

where

$$I_1 = RT\left[\left(\frac{\theta}{\theta+\lambda}\right)\ln\left(\frac{V}{V-\theta b}\right) + \left(\frac{\lambda}{\theta+\lambda}\right)\ln\left(\frac{V}{V+\lambda b}\right)\right] \quad \text{(A2)}$$

$$I_2 = -RT[3(2\sum X_l b_{lk} - b) - 4(\theta_k b + 2\theta(\sum X_l b_{lk} - b))] \times \left[\left(\frac{\theta}{\theta+\lambda}\right)^2 \frac{1}{V-\theta b} + \left(\frac{\lambda}{\theta+\lambda}\right)^2 \frac{1}{V+\lambda b} + \frac{2\theta\lambda}{(\theta+\lambda)^3 b} \ln\left(\frac{V+\lambda b}{V-\theta b}\right)\right] \quad \text{(A3)}$$

$$I_3 = -3RT[\theta b(1 - \theta_k) + \theta_k b(1-\theta) + 4\theta(1-\theta) \times (\sum X_l b_{lk} - b)]\left[\frac{\lambda}{(\theta+\lambda)^2}\frac{1}{V+\lambda b} - \frac{\theta}{(\theta+\lambda)^2}\frac{1}{V-\theta b} + \frac{\theta-\lambda}{(\theta+\lambda)^3 b}\ln\left(\frac{V+\lambda b}{V-\theta b}\right)\right] \quad \text{(A4)}$$

$$I_4 = -2(\sum X_l a_{lk})\left[\left(\frac{\epsilon}{\epsilon+\sigma}\right)^2\frac{1}{V-\epsilon b} + \left(\frac{\epsilon}{\epsilon+\sigma}\right)^2\frac{1}{V+\sigma b} + \frac{2\epsilon\sigma}{(\epsilon+\sigma)^3 b}\ln\left(\frac{V+\sigma b}{V-\epsilon b}\right)\right] \quad \text{(A5)}$$

$$I_5 = 8a[(1-\theta_k)b + 2(1-\theta)(\sum X_l b_{lk} - b)]\left[\left(\frac{\epsilon^3}{2(\epsilon+\sigma)^3}\right)\frac{1}{(V-\epsilon b)^2} + \left(\frac{3\epsilon^2\sigma}{(\epsilon+\sigma)^4 b}\right)\frac{1}{(V-\epsilon b)} + \left(\frac{\sigma^3}{2(\epsilon+\sigma)^3}\right)\frac{1}{(V+\sigma b)^2} - \left(\frac{3\epsilon\sigma^2}{(\epsilon+\sigma)^4 b}\right)\frac{1}{(V+\sigma b)} - \frac{3\epsilon\sigma(\epsilon-\sigma)}{(\theta+\lambda)^5 b^2}\ln\left(\frac{V+\sigma b}{V-\epsilon b}\right)\right] \quad \text{(A6)}$$

$$I_6 = -6a[\theta b(1-\theta_k) + \theta_k b(1-\theta) + 4\theta(1-\theta) \times (\sum X_l b_{lk} - b)]\left[\left(\frac{\epsilon^2}{2(\epsilon+\sigma)^3}\right)\frac{1}{(V-\epsilon b)^2} + \left(\frac{\epsilon(2\sigma-\epsilon)}{(\epsilon+\sigma)^4 b}\right)\frac{1}{V-\epsilon b} + \left(\frac{\sigma(2\epsilon-\sigma)}{(\epsilon+\sigma)^4 b}\right)\frac{1}{V+\sigma b} - \left(\frac{\sigma^2}{2(\epsilon+\sigma)^3}\right)\frac{1}{(V+\sigma b)^2} + \left(\frac{\epsilon^2 - 4\epsilon\sigma + \sigma^2}{(\epsilon+\sigma)^5 b^2}\right)\ln\left(\frac{V+\sigma b}{V-\epsilon b}\right)\right] \quad \text{(A7)}$$

$$I_7 = -RT \ln Z \quad \text{(A8)}$$

in which

$$\lambda = 3(1-\theta) \quad \text{(A9)}$$

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# Solubility of Hydrogen in Aqueous Ethanolamine Solutions at Temperatures between 323 and 423 K

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**The solubility of hydrogen in aqueous ethanolamine solutions was measured at temperatures between 323 and 423 K at pressures up to 20 MPa. Henry's coefficients derived from the experimental results are successfully predicted by the scaled particle theory.**

## Introduction

The solubility of hydrogen in aqueous amine solutions is of industrial, as well as of scientific, interest. For example, in the synthesis of ethylenediamine from ethanolamine and ammonia, the degree of conversion is controlled by the hydrogen content of the liquid phase. In the thermodynamics of phase equilibria, the prediction of gas solubility in mixed solvents is still an un-

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