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# Vapor–Liquid Equilibrium for the Binary Systems Ethylene Glycol–*n*-Amyl Alcohol and Ethylene Glycol–Isoamyl Alcohol

**Hyoek-Jong Joo[†] and Wolfgang Arlt[*]**

*Lehrstuhl für Technische Chemie B, Universität Dortmund, D-4600 Dortmund 50, Federal Republic of Germany*

**Vapor–liquid equilibrium data for the binary systems ethylene glycol (1,2-ethanediol) with *n*-amyl alcohol (1-pentanol) and ethylene glycol with isoamyl alcohol (3-methyl-1-butanol) have been measured at 100 mmHg (13.33 kPa) by using a recirculation still as proposed by Röck and Sieg. From these data, liquid-phase activity coefficients were fitted by using the Margules, van Laar, Wilson, and UNIQUAC equations. Vapor-pressure measurements of the pure substances were carried out, and the data were correlated with the Antoine equation. The binary data were used for the determination of UNIFAC parameters.**

## Introduction

Ethylene glycol and its ethers, diethers, esters, and polyglycols are industrially important solvents. With the development of the UNIFAC model (*1*), it was necessary to determine interaction parameters for glycols in order to describe important separation processes. Only little information is known about systems of alcohols with ethylene glycol (*2–7*). Because of lack of reliable data, we determined the vapor–liquid equilibria of ethylene glycol with the $C_5$ alcohols *n*- and isoamyl alcohol.

## Experimental Section

***Purification of the Components.*** Ethylene glycol (1,2-ethanediol) was obtained from Riedel-de-Haen (Seelze) and purified by fractional distillation at 1 kPa at a reflux ratio of 10:1 in a nitrogen-blanketed, adiabatically operated, packed column. The nitrogen was dried by phosphorus pentoxide ($P_2O_5$). The purity of the glycol was determined by gas chromatography using a conductivity detector to be 99.99%. *n*-Amyl alcohol (1-pentanol-1) and isoamyl alcohol (3-methyl-1-butanol) were obtained from Merck AG (Darmstadt). The raw materials were dried with anhydrous calcium sulfate ($CaSO_4$) and purified by fractional distillation. The purity and the content of isomers were tested by gas chromatography. No peak of impurities was found. Traces could be determined to less than 0.01%. In Table I, pure-compound properties are compared with values found in the literature.

***Appartus.*** Equilibrium was attained in an all-glass equilibrium still with circulation of both vapor and liquid phases. It has been described by Gmehling, Onken, and Schulte (*19*). Small modifications were carried out to take into account the differences in boiling points and viscosities; e.g., the liquid-phase stream had to be heated to 40 °C. For each data point, 30–45 min elapsed before the temperature reached a stable point and samples could be collected by syringes.

***Analysis.*** Liquid and vapor compositions were determined by using a precise digital densimeter (DMA02D by Heraeus/Paar). It was calibrated by using air and bidistilled water. Its precision is better than $10^{-4}$ g/mL. The measurements were carried out at 20 ± 0.01 °C. Weighed samples of ethylene glycol with alcohols were first measured to establish a calibration curve. The measurments of the equilibrium samples are repeated more than twice.

Table I. Physical Properties of Chemicals Used

| chemicals | $d_4^{20}$ exptl | $d_4^{20}$ lit. | $n_D^{20}$ exptl | $n_D^{20}$ lit. |
|---|---|---|---|---|
| ethylene glycol | 1.113 53 | 1.1135 (*16*) | 1.4312 | 1.4318 (*16*) |
| *n*-amyl alcohol | 0.814 50 | 0.8136 (*21*)<br>0.8146 (*22*) | 1.4097 | 1.4099 (*21*)<br>1.4102 (*22*) |
| isoamyl alcohol | 0.811 59 | 0.8117 (*21*)<br>0.8127 (*22*) | 1.4073 | 1.4073 (*21*)<br>1.4075 (*22*) |

Table II. Experimental Vapor Pressure, Calculated Antoine Constants (*A*, *B*, *C*), and Root Mean Squared Deviation (rmsd)

| | ethylene glycol | | isoamyl alcohol | | *n*-amyl alcohol | |
|---|---|---|---|---|---|---|
| | *t*, °C | *P*, mmHg | *t*, °C | *P*, mmHg | *t*, °C | *P*, mmHg |
| | 62.20 | 1.20 | 31.32 | 4.86 | 30.03 | 2.84 |
| | 65.50 | 1.63 | 42.36 | 10.86 | 36.08 | 4.68 |
| | 68.65 | 1.92 | 46.70 | 14.47 | 41.20 | 6.81 |
| | 72.13 | 2.70 | 51.57 | 19.78 | 46.34 | 9.86 |
| | 78.34 | 4.30 | 57.64 | 28.62 | 52.40 | 14.62 |
| | 84.60 | 6.35 | 68.33 | 52.09 | 58.90 | 21.97 |
| | 92.18 | 10.09 | 74.12 | 70.87 | 64.64 | 30.88 |
| | 97.61 | 13.90 | 79.47 | 92.51 | 70.70 | 43.14 |
| | 103.20 | 18.65 | 86.93 | 132.33 | 76.41 | 58.63 |
| | 108.82 | 24.28 | 92.55 | 170.80 | 83.84 | 85.49 |
| | 113.45 | 30.65 | 99.03 | 227.08 | 90.60 | 118.60 |
| | 118.20 | 38.78 | 105.90 | 300.20 | 96.57 | 155.52 |
| | 123.09 | 48.69 | 119.57 | 503.41 | 102.60 | 201.40 |
| | 128.00 | 60.54 | 126.76 | 650.01 | 107.43 | 246.50 |
| | 132.62 | 74.00 | 131.39 | 760.00 | 122.45 | 440.28 |
| | 137.65 | 92.39 | | | 138.19 | 760.00 |
| | 141.86 | 109.10 | | | | |
| | 146.84 | 133.19 | | | | |
| *A* | 6.46430 | | 7.17731 | | 7.15206 | |
| *B* | 1157.499 | | 1272.107 | | 1278.223 | |
| *C* | 119.489 | | 164.712 | | 161.075 | |
| rmsd, mmHg | 0.68 | | 0.47 | | 0.17 | |

## Vapor-Pressure Measurements of the Pure Substances

For the three pure compounds (ethylene glycol, *n*-amyl alcohol, isoamyl alcohol) vapor-pressure measurements were carried out by using the equilibrium still. Pressures were measured up to 0.02 mmHg with a precision mercury manometer (Wallace and Tiernan). The temperature in the equilibrium still was determined by calibrated mercury-in-glass thermometers within 0.03 °C, and the experimental data obtained are given in Table II together with calculated constants of the Antoine equation

$$\log P_i^\circ(\text{mmHg}) = A - B/(t(^\circ\text{C}) + C)$$

## Treatment of VLE Data

Vapor–liquid equilibrium measurements were performed for the two binary systems *n*-amyl alcohol–ethylene glycol and isoamyl alcohol–ethylene glycol at 100 mmHg (13.33 kPa). The

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[†] Chungnam National University 300-01 Dae-jon, South Korea.

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Table III. Experimental VLE Data[a] and Optimized Constants for the Most Common Models for the Description of the Activity Coefficient

| | n-amyl alcohol (1)–ethylene glycol (2)<br>$P = 100$ mmHg (13.33 kPa)<br>$A_{12}$ | <br><br>$A_{12}$ | isoamyl alcohol (1)–ethylene glycol (2)<br>$P = 100$ mmHg (13.33 kPa)<br>$A_{12}$ | <br><br>$A_{12}$ |
|---|---|---|---|---|
| Margules | 1.3778 | 1.3608 | 1.2677 | 1.4717 |
| van Laar | 1.3787 | 1.3598 | 1.2777 | 1.4687 |
| Wilson | 214.952 | 1039.49 | 71.7094 | 1164.79 |
| UNIQUAC | 496.203 | −33.5089 | 590.752 | −102.053 |

| $t$, °C | $x_1$ | $y_1$ | $t$, °C | $x_1$ | $y_1$ |
|---|---|---|---|---|---|
| 137.69 | 0.0024 | 0.0705 | 133.94 | 0.0096 | 0.2199 |
| 134.25 | 0.0073 | 0.1831 | 114.46 | 0.0502 | 0.6602 |
| 127.62 | 0.0191 | 0.3926 | 103.91 | 0.0945 | 0.8088 |
| 117.52 | 0.0452 | 0.6134 | 97.52 | 0.1751 | 0.8695 |
| 108.76 | 0.0928 | 0.7615 | 93.82 | 0.2580 | 0.8987 |
| 103.02 | 0.1648 | 0.8310 | 91.51 | 0.3543 | 0.9165 |
| 99.37 | 0.2562 | 0.8719 | 91.18 | 0.3693 | 0.9225 |
| 96.99 | 0.3611 | 0.8906 | 89.54 | 0.4568 | 0.9269 |
| 94.87 | 0.4843 | 0.9148 | 89.08 | 0.4835 | 0.9354 |
| 93.21 | 0.5902 | 0.9265 | 87.94 | 0.5634 | 0.9415 |
| 91.81 | 0.6908 | 0.9380 | 87.39 | 0.5940 | 0.9453 |
| 90.57 | 0.7726 | 0.9533 | 86.52 | 0.6518 | 0.9505 |
| 89.54 | 0.8412 | 0.9659 | 86.04 | 0.6840 | 0.9540 |
| 88.67 | 0.8982 | 0.9768 | 85.39 | 0.7220 | 0.9596 |
| 88.09 | 0.9336 | 0.9861 | 84.96 | 0.7541 | 0.9629 |
| 87.55 | 0.9635 | 0.9897 | 84.46 | 0.7824 | 0.9657 |
| 89.33 | 0.9823 | 0.9940 | 83.60 | 0.8308 | 0.9702 |
| 87.05 | 0.9940 | 0.9969 | 83.09 | 0.8695 | 0.9768 |
| | | | 82.64 | 0.8973 | 0.9807 |
| | | | 81.91 | 0.9403 | 0.9879 |

| | mean deviation in $y$ | mean deviation in $y$ |
|---|---|---|
| Margules | 0.0061 | 0.0125 |
| van Laar | 0.0061 | 0.0126 |
| Wilson | 0.0052 | 0.0123 |
| UNIQUAC | 0.0056 | 0.0122 |

[a] Concentrations in mole fraction.

Table IV. Pure-Compound Parameters

| compound i | $\nu_i$, mL/mol | $r_i$ | $q_i$ |
|---|---|---|---|
| ethylene glycol | 55.92 | 2.4088 | 2.248 |
| isoamyl alcohol | 109.22 | 4.1279 | 3.588 |
| n-amyl alcohol | 108.63 | 4.1287 | 3.592 |

data were checked for thermodynamic consistency by using the integral test described by Redlich and Kister (*9*) and Herington (*10*) plus the point-to-point test developed by van Ness, Byer, and Gibbs (*11*) and modified by Christiansen and Fredenslund (1, 12). The consistency checking procedure was described by Gmehling and Onken in ref 8. Both data sets passed the consistency tests with good results (sign "+").

Then the data were fitted to the most common models for the excess Gibbs energy i.e., Margules (*13*), van Laar (*14*), Wilson (*15*), and UNIQUAC (*17*) equations. For fitting activity coefficients, $\gamma_i$, we chose the nonlinear Simplex method modified by Nelder and Mead (*18*). For calculating the pure-compound vapor pressures, the Antoine equation constants given in Table II were used. The procedure is described in Volume 1 of ref *8*.

## Results

The experimental data and the computed parameters are given in Table III. The parameters of the different expressions for the excess Gibbs energy were determined by using the pure-compound properties given in Tables II and IV, assuming vapor-phase ideality. As an objective function, we used the squared relative $\gamma$ deviations described in ref *8*. The nomenclature used in Table III (Wilson: $A_{ij} = \lambda_{ij} - \lambda_{ii}$; UNIQUAC: $A_{ij} = u_{ij} - u_{jj}$) is taken from the same reference. Values are expressed in cal/(K mol) for the UNIQUAC and Wilson equa-

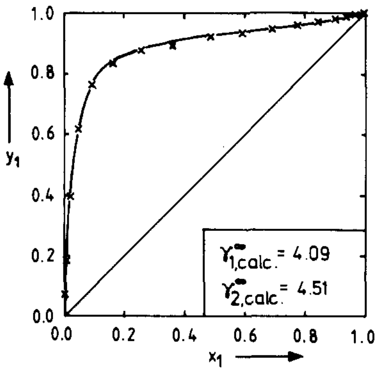

**Figure 1.** $X$–$Y$ diagram for the system n-amyl alcohol–ethylene glycol at 100 mmHg (line calculated with Wilson equation).

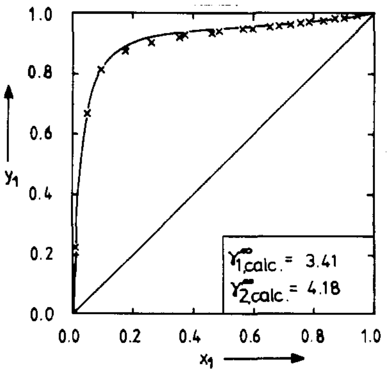

**Figure 2.** $X$–$Y$ diagram for the system isoamyl alcohol–ethylene glycol at 100 mmHg (line calculated with Wilson equation).

tions. As the gas constant, 1.98721 cal/mol has been used.

Plots of the experimental data are provided in Figures 1 and 2. Azeotropic behavior was not found.

As a private communication, our measurements were used by Skjold-Jørgensen et al. (*20*) for the data base of the determination of the interaction between the glycol group "DOH" and the alcohol group "OH" in the UNIFAC method.

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## Glossary

| | |
|---|---|
| $A, B, C$ | constants of the Antoine equation |
| $A_{ij}$ | parameter used in Margules, van Laar, Wilson, and UNIQUAC equations |
| $P_i^s$ | vapor pressure of pure component i, mmHg |
| $d$ | density, g/mL |
| $n_D$ | refraction index |
| $q_i$ | pure-component area parameter of component i |
| $r_i$ | pure-component volume parameter of component i |
| $t$ | temperature, °C |
| $u_{ij}$ | interaction energy parameter in UNIQUAC equation |
| $v_i$ | molar liquid volume of component i, mL/mol |
| $x_i$ | liquid-phase mole fraction of component i |
| $y_i$ | vapor-phase mole fraction of component i |

*Greek Letters*

| | |
|---|---|
| $\gamma_i$ | activity coefficient of component i |

## Literature Cited

(1) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibria Using UNIFAC"; Elsevier: Amsterdam, 1977.
(2) Deitert, P. MS Thesis, Dortmund, 1978.
(3) Chandramouli, V. V.; Laddha G. S. *J. Sci. Ind. Res. Sect. D* **1962**, *21*, 269.
(4) Mainkar, S. V.; Mene, P. S. *Indian J. Technol.* **1970**, *8*, 320.
(5) Surovy, J.; Dojcansky, J. *Chem. Zvesti* **1974**, *28*, 313.
(6) Shokla, N. P. *Indian Chem. Eng.* **1968**, *10*, 48.
(7) Sedletskaya, I. S.; Kogan, V. B. *Zh. Prikl. Khim.* (*Leningrad*) **1969**, *42*, 2551.
(8) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt/M., 1977; 12 volumes.
(9) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 341, 345.
(10) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(11) van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238.
(12) Christiansen, L. J.; Fredenslund, Aa. *AIChE J.* **1975**, *21*, 49.
(13) Margules, M. *Sitzungsber. Akad. Wiss. Wien* **1895**, *104*, 1243.
(14) van Laar, J. J. *Z. Phys. Chem. Abt. A* **1928**, *137*, 421.
(15) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(16) "Selected Values of Properties of Chemical Compounds"; Thermodynamic Research Center Data Project A-42, Table 23-2-1-(1.1036)-a; Texas A & M University: College Station, TX, 1980.
(17) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(18) Nelder, J.; Mead, R. *Comput. J.* **1962**, *7*, 308.
(19) Gmehling, J.; Onken, U.; Schulte, H.-W. *J. Chem. Eng. Data* **1980**, *25*, 29.
(20) Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem., Process Des. Dev.* **1979**, *18*, 714.
(21) Vogel, A. I. *J. Chem. Soc.* **1948**, *1814*.
(22) Addison, C. C. *J. Chem. Soc.* **1945**, 98.

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# Density, Viscosity, Surface Tension, and Carbon Dioxide Solubility and Diffusivity of Methanol, Ethanol, Aqueous Propanol, and Aqueous Ethylene Glycol at 25 °C

**Yong S. Won, Dong K. Chung, and Anthony F. Mills***

*School of Engineering and Applied Science, University of California, Los Angeles, California 90024*

**Density, viscosity, surface tension, and carbon dioxide solubility and diffusivity, at 25 °C, are reported for methanol, ethanol, and aqueous propanol solutions over the complete composition range and for aqueous ethylene glycol solutions for glycol mole fractions between 0 and 0.2. Where comparisons were possible, the agreement with previous data is satisfactory.**

In recent studies of mass transfer in turbulent falling liquid films (*1*, 2), test liquids having a wide range of pertinent thermodynamic and transport properties were required. In particular it was desired to conveniently achieve a range of viscosity and surface tension, for which aqueous ethylene glycol and aqueous propanol solutions at 25 °C were chosen; methanol and ethanol were also utilized. The relevant properties were density, viscosity, surface tension, and carbon dioxide solubility and diffusivity, for which the data in the literature were incomplete. Thus a comprehensive set of independent measurements was obtained in our laboratory and is reported here. Useful prior work includes that of Hayduk and Malik (*3*) and Mikhail and Kimmel (*4*).

## Experimental Procedures

***Carbon Dioxide Solubilities.*** The $CO_2$ solubility was determined by saturating the test liquids in a gas bubbler immersed in an isothermal bath. Liquid-phase $CO_2$ concentrations were determined by using a standard wet chemistry technique (*1*). The partial pressures of $CO_2$ over the liquids were calculated by subtracting the vapor pressures of the liquids from the measured total pressures. Special care was taken to minimize the net evaporation rate from the bath, so that bubbling for an extended period of time did not cause a significant composition change of the test solution.

***Molecular Diffusivity of Carbon Dioxide.*** The "sphere cell" method was used to measure liquid-phase diffusivities, which involved absorbing $CO_2$ into a laminar ripple free liquid film formed on the surface of a 3.78-cm o.d. sphere. The con-

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