(11) Butler, R. A.; Bates, R. G. In "Thermodynamics of Electrolytes in Mixed Solvents. II"; Furter, W. F., Ed.; American Chemical Society: Washington, 1979; Adv. Chem. Ser. No. 177, Chapter 16.
(12) Janz, G. J.; McIntyre, J. D. E. *J. Electrochem. Soc.* **1961**, *108*, 272.
(13) Klein, S. D. University of Florida, Chemistry Department Gainesville, FL, 1979; personal communication.
(14) Harned, H. S.; Ehlers, R. W. *J. Am. Chem. Soc.* **1932**, *54*, 1350.
(15) Bates, R. G.; Tanaka, K. *J. Solution Chem.* **1981**, *10*, 155.
(16) Vega, C. A.; Perez, B.; Torres, C. *J. Chem. Eng. Data* **1984**, *29*, 129.
(17) Bates , R. G.; Hetzer, H. B. *J. Phys. Chem.* **1961**, *65*, 667.
(18) Vega, C. A.; Delgado, S., submitted for publication in *J. Chem. Eng. Data*.

Received for review November 26, 1984. Accepted March 5, 1985.

# Isobaric Vapor–Liquid Equilibria for Systems Consisting of 2,4-Dimethylpentane, Cyclohexane, and *tert*-Butyl Alcohol

**Shri Krishna and B. S. Rawat***
*Indian Institute of Petroleum, Dehradun 248005, India*

**Vapor–liquid equilibrium data for 2,4-dimethylpentane–cyclohexane binary and 2,4-dimethylpentane–cyclohexane–*tert*-butyl alcohol ternary systems are measured at 760 mmHg pressure. The binary data are correlated by the Wilson equation. The ternary experimental vapor-phase compositions have been compared with those calculated from the binary constants determined for 2,4-dimethylpentane–cyclohexane system and reported earlier for 2,4-dimethylpentane–*tert*-butyl alcohol and cyclohexane–*tert*-butyl alcohol systems. The agreement between the two sets of data shows the ability of the Wilson equation to predict the ternary compositions from binary data alone for this system.**

## Introduction

2,4-Dimethylpentane (DMP) and cyclohexane (CH) are close-boiling components and form a minimum-boiling azeotrope (*1*) at 80.2 °C and therefore cannot be separated by ordinary distillation. Isobaric binary vapor–liquid equilibrium (VLE) data on these hydrocarbons and *tert*-butyl alcohol (TBA) have been reported earlier (*2*). With a view to try TBA as a suitable separating agent for these hydrocarbons, isobaric VLE have been determined for DMP–CH binary and DMP–CH–TBA ternary at 760 ± 1 mmHg. The binary data on DMP–CH have been correlated with a two-parameter Wilson equation. The binary Wilson parameters estimated for DMP–CH system and reported (*2*) earlier for the other two binaries have been used to calculate the ternary compositions by using a ternary form of the Wilson equation.

## Experimental Section

***Materials.*** Both the hydrocarbons were of minimum 99% purity, procured from Phillips, U.S.A., and used as such without further purification. *tert*-Butyl alcohol obtained from BDH, India, was dried and purified by fractional distillation with high reflux ratio in an Oldershaw column. The heart cut was collected discarding the first 10% and last 15%. The physical properties reported (*2*) earlier correspond to 99% purity.

***Apparatus.*** The VLE studies for the binary and the ternary system were carried out in the modified Fowler–Norris (*3*) still with provision for liquid and vapor circulation. The reboiler, Cottrell pump, and the equilibrium chambers were thoroughly lagged to avoid condensation which facilitated proper separation of liquid and vapor in the equilibrium chamber. Equilibriated liquid and vapor samples were collected separately after 4 h and were analyzed by gas chromatography.

**Table I. Isobaric VLE Data for 2,4-Dimethylpentane (1)–Cyclohexane (2) Systems**

| | | $Y_1$ | | exptl | | calcd | |
|---|---|---|---|---|---|---|---|
| temp, °C | $X_1$ | exptl | calcd | $\gamma_1$ | $\gamma_2$ | $\gamma_1$ | $\gamma_2$ |
| 80.67 | 0.040 | 0.046 | 0.042 | 1.144 | 0.992 | 1.047 | 1.000 |
| 80.60 | 0.095 | 0.105 | 0.099 | 1.102 | 0.993 | 1.041 | 1.000 |
| 80.50 | 0.157 | 0.168 | 0.162 | 1.070 | 0.994 | 1.034 | 1.001 |
| 80.38 | 0.254 | 0.266 | 0.260 | 1.051 | 0.995 | 1.026 | 1.004 |
| 80.31 | 0.331 | 0.340 | 0.336 | 1.033 | 0.999 | 1.020 | 1.006 |
| 80.25 | 0.398 | 0.404 | 0.401 | 1.022 | 1.004 | 1.016 | 1.008 |
| 80.22 | 0.430 | 0.435 | 0.432 | 1.020 | 1.006 | 1.014 | 1.010 |
| 80.20 | 0.471 | 0.471 | 0.472 | 1.009 | 1.016 | 1.012 | 1.011 |
| 80.22 | 0.581 | 0.577 | 0.580 | 1.001 | 1.025 | 1.007 | 1.016 |
| 80.27 | 0.685 | 0.679 | 0.683 | 0.998 | 1.033 | 1.004 | 1.022 |
| 80.35 | 0.797 | 0.791 | 0.795 | 0.997 | 1.042 | 1.001 | 1.029 |
| 80.42 | 0.895 | 0.888 | 0.893 | 0.995 | 1.077 | 1.000 | 1.035 |
| 80.46 | 0.950 | 0.945 | 0.949 | 0.996 | 1.109 | 1.000 | 1.039 |

Since the binary DMP–CH is a close-boiling system, the equilibrium boiling temperatures were repeatedly verified in an ebulliometer with the synthetic blends in the whole range of compositions by using a calibrated Beckmann thermometer. The temperatures were measured within ±0.01 °C. The accuracy of the chromatographic method used for analysis of the equilibrium phase was ±3.0%.

## Results and Discussion

The VLE data on DMP–CH and DMP–CH–TBA are presented in Tables I and II, respectively. From these data the liquid-phase activity coefficients were calculated by using the following equation (*4*).

$$\gamma_i = \frac{PY_i}{P_i^0 X_i} Z_i \tag{1}$$

However, the values of vapor-phase imperfection, $Z_i$, were found to be almost equal to unity and as such was ignored in eq 1.

The pure component vapor pressures were calculated from the Antoine constants reported in the literature (*5–7*).

The values of activity coefficients calculated as above are presented in Table I. The data for binary DMP–CH system were tested for the thermodynamic consistency by Heringtons's (*8*) area method. The values of $D$ and $J$ for this system were 0.0364 and 1.010, respectively, which show that the data are consistent as the value of $D$ is less than the value of $J$.

**Table II. Isobaric Ternary VLE Data for 2,4-Dimethylpentane (1)–Cyclohexane (2)–*tert*-Butyl Alcohol (3) System at 760 mmHg**

| equilib temp, °C | $X_1$ | $X_2$ | exptl $Y_1$ | exptl $Y_2$ | calcd $Y_1$ | calcd $Y_2$ |
|---|---|---|---|---|---|---|
| 79.8 | 0.321 | 0.186 | 0.350 | 0.209 | 0.335 | 0.179 |
| 79.8 | 0.607 | 0.189 | 0.536 | 0.171 | 0.541 | 0.164 |
| 79.6 | 0.461 | 0.016 | 0.485 | 0.016 | 0.474 | 0.015 |
| 79.6 | 0.443 | 0.037 | 0.470 | 0.041 | 0.457 | 0.035 |
| 79.6 | 0.403 | 0.070 | 0.431 | 0.081 | 0.422 | 0.068 |
| 79.5 | 0.437 | 0.045 | 0.455 | 0.049 | 0.451 | 0.044 |
| 79.4 | 0.470 | 0.038 | 0.495 | 0.040 | 0.473 | 0.036 |
| 79.4 | 0.433 | 0.048 | 0.467 | 0.051 | 0.448 | 0.046 |
| 78.8 | 0.301 | 0.201 | 0.334 | 0.216 | 0.319 | 0.196 |
| 77.6 | 0.281 | 0.221 | 0.311 | 0.241 | 0.301 | 0.219 |
| 77.6 | 0.040 | 0.185 | 0.064 | 0.226 | 0.063 | 0.257 |
| 77.6 | 0.468 | 0.025 | 0.491 | 0.026 | 0.480 | 0.024 |
| 76.4 | 0.113 | 0.489 | 0.125 | 0.521 | 0.120 | 0.477 |
| 76.0 | 0.302 | 0.232 | 0.331 | 0.264 | 0.318 | 0.225 |
| 75.8 | 0.461 | 0.039 | 0.481 | 0.403 | 0.476 | 0.038 |
| 74.8 | 0.131 | 0.422 | 0.151 | 0.443 | 0.143 | 0.424 |
| 74.5 | 0.099 | 0.195 | 0.141 | 0.238 | 0.141 | 0.248 |
| 74.4 | 0.445 | 0.037 | 0.479 | 0.042 | 0.471 | 0.036 |
| 74.0 | 0.340 | 0.170 | 0.359 | 0.181 | 0.363 | 0.168 |
| 73.8 | 0.437 | 0.049 | 0.479 | 0.051 | 0.463 | 0.048 |
| 73.5 | 0.302 | 0.220 | 0.326 | 0.239 | 0.325 | 0.218 |
| 73.4 | 0.284 | 0.121 | 0.315 | 0.138 | 0.337 | 0.131 |
| 73.2 | 0.242 | 0.160 | 0.277 | 0.176 | 0.292 | 0.176 |
| 73.0 | 0.143 | 0.232 | 0.180 | 0.265 | 0.183 | 0.269 |
| 72.9 | 0.154 | 0.251 | 0.184 | 0.273 | 0.192 | 0.282 |
| 72.6 | 0.450 | 0.061 | 0.475 | 0.065 | 0.470 | 0.059 |
| 72.1 | 0.075 | 0.498 | 0.090 | 0.515 | 0.084 | 0.507 |
| 72.0 | 0.062 | 0.470 | 0.070 | 0.487 | 0.072 | 0.493 |
| 72.0 | 0.279 | 0.224 | 0.310 | 0.231 | 0.308 | 0.227 |
| 71.9 | 0.335 | 0.195 | 0.356 | 0.207 | 0.358 | 0.192 |
| 71.8 | 0.282 | 0.224 | 0.299 | 0.232 | 0.311 | 0.228 |
| 71.7 | 0.066 | 0.519 | 0.073 | 0.521 | 0.073 | 0.527 |
| 71.6 | 0.124 | 0.413 | 0.140 | 0.426 | 0.140 | 0.426 |
| 71.6 | 0.292 | 0.229 | 0.318 | 0.240 | 0.317 | 0.230 |
| 71.5 | 0.290 | 0.259 | 0.314 | 0.276 | 0.310 | 0.255 |
| 71.4 | 0.261 | 0.292 | 0.271 | 0.312 | 0.280 | 0.290 |
| 71.0 | 0.245 | 0.338 | 0.248 | 0.337 | 0.260 | 0.331 |

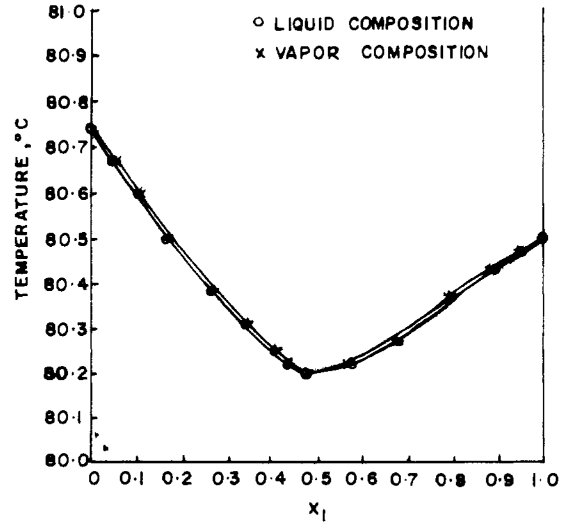

**Figure 1.** $t$-$x$,$y$ plot for DMP (1)–CH (2) system at 760.0 mmHg.

The experimental data for the binary DMP–CH system presented in Figure 1 were correlated with a two-constant Wilson (*9*) equation using the nonlinear least-squares technique (*10*) by minimizing the $\Sigma(Q_{\text{exptl}} - Q_{\text{calcd}})^2$ function. The calculated activity coefficients and vapor-phase compositions are compared with those of the experimental values in Table I. As can be seen from this data the agreement between the experimental and calculated data is good. The percentage deviation of $Y$ values is of the order of about 1.9%.

**Table III. Wilson Constants**

| system | constants $\Lambda_{12}$ | constants $\Lambda_{21}$ |
|---|---|---|
| CH-TBA | 0.7177 | 0.6826 |
| DMP-TBA | 0.7552 | 0.5246 |
| DMP-CH | 0.8155 | 1.1138 |

The binary Wilson constants evaluated above for the DMP–CH system and reported in the literature (*2*) for the CH–TBA and DMP–TBA systems were used for calculating the ternary compositions from these binary data by using the ternary form of Wilson equation

$$\ln \gamma_i = 1.0 - \ln \left[\sum_{j=1}^{3} X_j \Lambda_{ij}\right] - \sum_{k=1}^{3} \left[ \frac{X_k \Lambda_{ki}}{\sum_{j=1}^{3} X_j \Lambda_{kj}} \right] \quad (2)$$

where

$$\Lambda_{ij} = \frac{V_j^{\text{L}}}{V_i^{\text{L}}} \exp\left( -\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (3)$$

The values of the constants used in the above equation are given in Table III. The ternary vapor-phase compositions calculated from the binary data alone have been compared with experimental values in Table II. From these data the average percent deviations $[100(Y_{\text{exptl}} - Y_{\text{calcd}})/Y_{\text{exptl}}]$ between the experimental and calculated ternary compositions of $Y_1$, $Y_2$, and $Y_3$ are of the order of 1.0, 5.5, and 2.8, respectively. These deviations are not large considering the limitations of the correlating equations. The agreement between experimental and calculated values shows the capability of the Wilson equation to predict the ternary compositions from the binary data for DMP–CH–TBA system.

The ternary system forms a minimum-boiling azeotrope at 71 ± 0.2 °C consisting of 0.2450, 0.3377, and 0.4173 mole fraction of DMP, CH, and TBA, respectively (Table II).

## Acknowledgment

We are thankful to Dr. I. B. Gulati, Director, Indian Institute of Petroleum, for his keen interest and permission to publish the work.

## Glossary

| | |
|---|---|
| $\Lambda_{ij}$, $\Lambda_{ji}$, $\Lambda_{ki}$ | Wilson parameters |
| $D$, $J$ | Herington's parameters |
| $P$ | total pressure, atm |
| $P_i^0$ | saturated vapor pressure of pure component $i$, atm |
| $R$ | gas constant, cm$^3$ atm/(deg mol) |
| $T$ | temperature, K |
| $V_i^{\text{L}}$ | liquid molar volume of $i$, cm$^3$/mol |
| $X_i$ | liquid molar composition of $i$ |
| $Y_i$ | vapor molar composition of $i$ |
| $Z_i$ | vapor-phase imperfection factor for $i$ |
| $Q_{\text{exptl}}$ | $X_1 \ln \gamma_1 + X_2 \ln \gamma_2$ |
| $Q_{\text{calcd}}$ | $-X_1 \ln (X_1 + \Lambda_{12}X_2) - X_2 \ln (\Lambda_{21}X_1 + X_2)$ |

*Greek Letters*

| | |
|---|---|
| $\gamma_i$ | liquid-phase activity coefficient of component $i$ |
| $\lambda_{ij} - \lambda_{ii}$ | energy parameters of Wilson equation, cal/mol |

*Subscripts*

| | |
|---|---|
| 1, 2, and 3 | 2,4-DMP, cyclohexane, and *tert*-butyl alcohol, respectively |

**Registry No.** DMP, 108-08-7; CH, 110-82-7; TBA, 75-65-0.

**Literature Cited**

(1) Horsley, L. H. "Azeotropic Data"; American Chemical Society: Washington, DC, 1952.
(2) Tripathi, R. P.; Krishna, S.; Gulati, I. B. *J. Chem. Eng. Data* **1976**, *21*, 44.
(3) Hala, E.; Fried, V.; Vilim, O. "Vapour-Liquid Equilibrium"; Pergamon Press: London, 1967.
(4) Van Ness, H. C. "Classical Thermodynamics of Non-electrolyte Solutions"; MacMillan: New York, 1964; p 136.
(5) Dreisbach, R. R. *Adv. Chem. Ser.* **1959**, *22*.
(6) Dreisbach, R. R. *Adv. Chem. Ser.* **1955**, *15*.
(7) Hala, E.; Wichterle, I.; Polak, J.; Boublik, T. "Vapour-Liquid Equilibrium at Normal Pressures"; Pergamon Press: London, 1968.
(8) Herington, E. C. G. *J. Inst. Pet.* **1951**, *37*, 457.
(9) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(10) Nagahama, K.; Suzuki, I.; Hirata, M. *J. Chem. Eng. Jpn.* **1971**, *4*, 1.

Received for review August 4, 1983. Revised manuscript received March 7, 1985. Accepted April 16, 1985.

---

# Solubilities of Various Nitroanilines in Water–Pyridine, Water–Acetonitrile, and Water–Ethylene Glycol Solvents

**Jean-Louis Brisset**[†]

*Laboratoire de Chimie Analytique des Processus Industriels, E.S.P.C.I., 75231 Paris Cedex, France*

**The solubilities of various nitroanilines have been determined in aqueous solutions of pyridine, acetonitrile, or ethylene glycol in a large range of composition, and the corresponding transfer free energies calculated. The solubilities increase with the amount of organic cosolvent in the mixtures. Besides, under their logarithm form, they are linear functions of that of a particular species, ferrocene. This result is independent of the nature of the organic solvent and may be considered as an argument in favor of the use of a solvent function based on the solubility of molecular species.**

## Introduction

Many attempts have been made to characterize a given nonaqueous solvent (or a solvent mixture) by means of a "solvent parameter". The solubility parameters have been recently reviewed in the literature (*1*). In this paper we are concerned with the solubilities of several mono-, di-, and trinitroanilines in aqueous solutions of pyridine (PY), acetonitrile (AN), or 1,2-ethanediol (ethylene glycol, ETG) in a great range of compositions. The selection of a new series of binary mixtures as the solvents allows us to develop previously reported values (*2*–*4*) of the solubilities of the nitroanilines. Besides, our data match the solubilities of some electrolytes in the same media which have been already determined (*5*). They improve also our knowledge of the considered mixtures which have been otherwise examined electrochemically by Kalidas et al. (*6*) or by us (*7*, *8*) since they allow the determination of the transfer free enthalpy of a given solute i from water (W) to a particular mixture (S). The relevant $\Delta G_t^\circ(i)$ value is defined for one molecule of i taken in the standard state in water and in the mixture S by the change of the standard Gibbs energy:

$$\Delta G_t^\circ(i) = {}^sG^\circ(i) - {}^wG^\circ(i) \qquad (1)$$

$\Delta G_t^\circ(i)$ can be determined experimentally from solubility measurements of i in water and in the mixture S, if one assumes that the solubilities are low enough to allow one to consider the concentrations $C_{sat}(i)$ instead of the activities:

$$\Delta G_t^\circ(i) = RT \ln ({}^wC_{sat}(i)/{}^sC_{sat}(i)) \qquad (2)$$

$\Delta G_t^\circ(i)$ is also related to the transfer activity coefficient $\gamma_t(i)$ by

$$\Delta G_t^\circ(i) = RT \ln \gamma_t(i) \qquad (3)$$

which is the usual parameter to evaluate the medium effects.

## Experimental Section

Ferrocene (E) and most of the selected nitroanilines are commercially available chemicals: 4-nitroaniline (A), 2,4-dinitroaniline (B), 2,6-dinitroaniline (H), 2,4,6-trinitroaniline or picramine (C), 3-nitroaniline (F). The 2,4,6-trinitrodiphenylamine or picrylaniline (D) was prepared by slowly adding freshly distilled aniline (0.2 mol) to a methanolic solution of picryl chloride (0.2 mol). The mixture was heated at 60 °C for 2 h. D precipitated on cooling.

All the solutes were recrystallized several times before use. Pure solvents were freshly distilled and stored under $N_2$.

The general procedure for the solubility measurements which were performed spectrophotometrically has been reported (*5*). A similar precision for the values of $-\log C_{sat}(i)$ (i.e., 0.05 log unit) can then be expected.

## Results and Discussion

The solubility data for the nitroanilines in W–PY, W–AN, and W–ETG mixtures are listed in Tables I–III, respectively, while Table IV is devoted to the corresponding values in $CH_3OH$–AN mixtures.

Tables I–III illustrate a general trend of the $C_{sat}(i)$ values which are very low in pure water and increase with the proportion of the organic compound in the solvent mixture. Such a behavior has already been observed for molecular species in other aquoorganic mixtures (*2*–*4*) as well as for various picrates in the same solvents (*5*).

If one assumes that the solubility of i in a particular mixture S (water and organic cosolvent OS in a given ratio) is due to the solvation by water or by OS molecules, the following equilibria are involved:

$$i_{solid} + pH_2O \rightleftharpoons i_{aq} \qquad (4)$$

$$i_{solid} + qOS \rightleftharpoons i_{solv} \qquad (5)$$

Then

$${}^sC_{sat}(i) = (i_{aq}) + (i_{solv}) \qquad (6)$$

Experimental data relevant to pure water or pure organic solvent show that $(i_{aq})$ is much lower than $(i_{solv})$. Equilibrium 4 can thus be discarded as a first approximation. The equilibrium

---

[†] Present address: Laboratoire des Réacteurs en Phase Plasma, E.N.S.C.P., 75005 Paris, France.

0021-9568/85/1730-0381$01.50/0