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# Activity Coefficients in Cyclohexane–Alcohol Systems Near the Freezing Point of Cyclohexane

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**Activity coefficients of light alcohols and cyclohexane are determined by measuring freezing point lowering of solutions of alcohols in the cyclic hydrocarbon. Methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol were used as solutes. Fits to van Laar, Wilson, and some continuous association models showed that the latter models work much better, except when the solute is 2-methyl-2-propanol, which would be in the form of tetramers as the unique species in the low concentration range. The minor species in the remaining alcohols examined would be dimers. The magnitudes of the association equilibrium constants in the low concentration range indicate that athermal models of continuous association should be reformulated in order to interpret adequately the behavior of solutions in the whole range of composition.**

## Introduction

Measurements of freezing point depressions of a solvent have been widely used in the determination of molecular weights and activity coefficients in the region of high dilution of the solute.

Several properties of solutions of alcohols in hydrocarbons have been measured and examined by many authors from the standpoint of models for the excess Gibbs energy, especially those based on continuous association of alcohol molecules. One conclusion is that the region of low alcohol concentration does not fit as well as in other compositions (*1*). When the solvent is cyclohexane, there are peculiar circumstances, which make it particularly interesting for a comparative study of several models in order to have some basis for a better understanding of what really happens in the low concentration region of alcohol. It has been shown (*2*) from the determination of molecular weights that dimers are the preferred form of light alcohols in cyclohexane, but 2-methyl-2-propanol would be in the form of tetramers under the same conditions.

In this paper, the experimental data by Aguirre-Ode and Rojas (*2*) are used for the calculation of activity coefficients of both components near the freezing point of cyclohexane, in order to verify the interpretative capacity of different models. Besides 2-methyl-2-propanol (*tert*-butyl alcohol), the solutes considered are methyl, ethyl, 1-propyl, 2-propyl, 2-butyl, and isobutyl alcohol.

## Experimental Section

Cyclohexane and the alcohols were analytical grade reagents from Merck, most of them used without further purification after gas chromatography failed to show any significant impurity. The certified minimum purities were over 99.7%, except in the case of the butanols which reached only 99.0%. For this reason, the butanols were redistilled in a high-efficiency packed column. A heart cut was collected by discarding the first 20% of the distillate and the last 25% of the residue. The physical properties (density and refractive index) showed reasonable agreement with the values from literature. Mole fractions of the solutions were determined by weighing solvent and solute.

The experimental procedure was basically the described by Gillespie et al. (*3*). The solution was stirred by means of a mechanical device consisting of a helical stirrer connected through a fine flexible cord to a loose ring attached to an eccentric position on a rotating wheel. The cord was looped over a pulley in order to convert the circular motion of the wheel to the vertically oscillating motion required for the helical stirrer. The apparatus, shown in Figure 1, was placed in an ice-water bath.

A Beckmann thermometer was used to determine the temperature vs. time cooling curves for the solvent alone and for different concentrations of each one of the previously mentioned solutes in the solvent.

The freezing point depression, $\theta_m$, directly obtained from the experimental measurements, was corrected for the supercooling effect in the manner suggested by Gillespie et al. (*3*)

$$\hat{\theta} = \theta_m\left(1 - \frac{c_p}{\lambda_1}S\right) \qquad (1)$$

in which $c_p$ is the heat capacity of the liquid solvent, $\lambda_1$ is the heat of fusion of the solvent, $S = T - T_s$ is the extent of the supercooling, $T$ is the freezing point, and $T_s$ is the lowest temperature of the supercooled system. Figure 2 schematically shows the meaning of the different quantities.

## Calculation of Activity Coefficients from Experimental Data

From the thermodynamic analysis of solid–liquid equilibrium, the following equation is derived

$$d \ln a_1 = -(\lambda_1/R)\, d(1/T) \qquad (2)$$

in which $a_1$ is the activity of the solvent, $\lambda_1$ is the heat of fusion of the solvent [J/mol], $R$ is the gas constant [J/(mol K)], and

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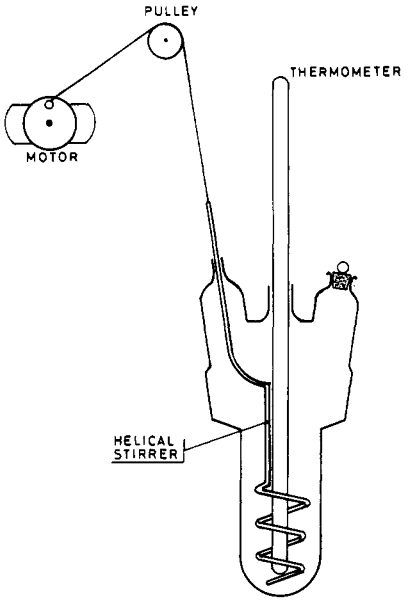

**Figure 1.** Apparatus for depression measurements.

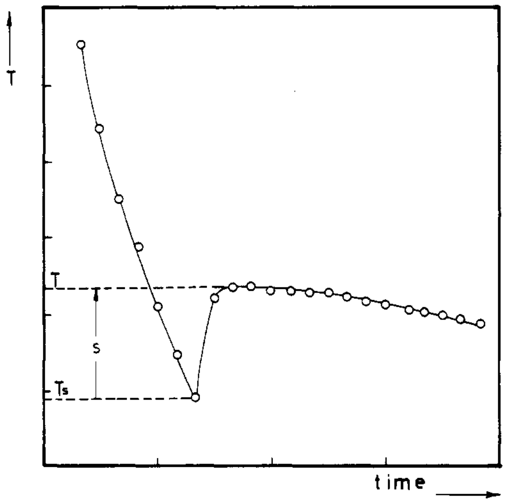

**Figure 2.** Supercooling effect.

$T$ is the absolute temperature [K].

As the heat of fusion is dependent of the temperature, a series expansion in terms of the freezing point lowering, $\theta$, allows us to write (*4*) after substitution and integration of eq 2

$$\ln a_1 = -\theta(A + B\theta + ...) \tag{3}$$

in which $A = \lambda_1/RT_0^2$; $B = (A - \Delta c_p/2RT_0)/T_0$; $T_0$ is the melting point of the solvent [K]; and $\Delta c_p$ is the specific heat capacity difference of liquid and solid solvent [J/(mol K)].

For cyclohexane, the following values were calculated from measured (*2*) or reference data (*5*): $\lambda_1$ = 2589 J/mol; $\Delta c_p$ = 19.5 J/(mol K); $T_0$ = 279.70 K; $A$ = 0.01691; $B = 2.25 \times 10^{-6}$. Since $B$ is so small compared to $A$, eq 3 can be linearized keeping only the first term in the series.

For the calculation of activity coefficient, it is common practice to use the osmotic coefficient, $\phi$, defined in the following manner:

$$\phi = (\ln a_1)/\ln x_1 \tag{4}$$

It can be shown by a series expansion that the following approximation is valid for low values of $x_2$, the mole fraction of the solute

$$\phi = -(\ln a_1)/z \tag{5}$$

in which $z = x_2/x_1$ is the mole fraction ratio.

**Table I. Parameters and Standard Deviations When Smoothing $\theta$ Data with Eq 8**

| solute | data points | $A_0$ | $A_1$ | $\sigma$, °C |
|---|---|---|---|---|
| methanol | 7 | 0.004 976 4 | 1.137 814 | 0.074 |
| ethanol | 8 | 0.014 856 0 | 1.135 240 | 0.064 |
| 1-propanol | 7 | 0.014 636 2 | 1.212 070 | 0.042 |
| 2-propanol | 8 | 0.014 314 5 | 1.357 694 | 0.043 |
| 2-butanol | 8 | 0.023 391 0 | 1.229 492 | 0.067 |
| isobutyl alcohol | 8 | 0.008 350 6 | 1.436 114 | 0.012 |
| *tert*-butyl alcohol | 8 | 0.062 894 3 | 5.763 086 | 0.013 |

On the other hand, it was empirically found that the ratio $z/(1 - \phi)$ behaved as a linear function of $z$ in all cases

$$z/(1 - \phi) = A_0 + A_1 z \tag{6}$$

in which $A_0$ and $A_1$ are the best parameters from the minimization of the objective function

$$\psi_\theta = \sum_k^N (\theta - \hat{\theta})_k^2 \tag{7}$$

$N$ is the number of experimental data points, $\hat{\theta}$ is the experimental freezing point lowering, and $\theta$ is the calculated freezing point lowering:

$$\theta = \frac{z[A_0 + (A_1 - 1)z]}{A[A_0 + A_1 z]} \tag{8}$$

Equation 8 is the result of combining the linear form of eq 3 with eq 5 and 6.

The quality of the smoothing of the experimental data can be appreciated from Table I, in which optimum values of $A_0$ and $A_1$, together with the respective standard deviations of the fits, are shown for each system. Standard deviations are low enough as to support the applicability of the empirical eq 6.

The following step should be the calculation of the activity coefficients as a function of the stoichiometric mole fraction, i.e., those which come up from considering monomers of alcohol as the solute. However, the behavior of the osmotic coefficient was such that the quantity $(1 - \phi)$ did not approach naturally to zero when extrapolated for $z = 0$. The basis of calculation was changed, by assuming successively only dimers, trimers, tetramers, etc., as the unique real species of alcohol in solution until a clear trend, consistent with the limiting condition $(1 - \phi) \rightarrow 0$ for $z \rightarrow 0$, was observed. The results were quite convincing and showed that all alcohols studied, except *tert*-butyl alcohol, complied with the limiting condition when considering dimers as the species of alcohol present in solution. *tert*-Butyl alcohol behaved consistently when tetramers were selected.

The results are not surprising, since they correspond to the molecular weight data obtained from another extrapolation procedure (*2*).

Consequently, the activity coefficients of the solvent were calculated with the following equation

$$\hat{\gamma}_1^{(n)} = \frac{\exp(A\theta z^{(n)})}{x_1^{(n)}} \tag{9}$$

in which the superscript $(n)$ denotes the use of dimers or tetramers instead of monomers as the stoichiometric species. For the calculation on the basis of monomers, the following conversion is made:

$$\hat{\gamma}_1 = \hat{\gamma}_1^{(n)} x_1^{(n)}/x_1 \tag{10}$$

**Table II. Mole Fractions, Experimental Freezing Point Lowering, and Activity Coefficients from Experimental Data**

| $x$ | $\hat{\theta}$, °C | $\hat{\gamma}_1$ | $\hat{\gamma}_2$ |
|---|---|---|---|
| Cyclohexane (1)–Methanol (2) | | | |
| 0.01286 | 0.777 | 1.0099 | 0.2685 |
| 0.01290 | 0.797 | 1.0099 | 0.2685 |
| 0.02540 | 1.043 | 1.0215 | 0.1577 |
| 0.02542 | 1.129 | 1.0215 | 0.1577 |
| 0.03760 | 1.238 | 1.0334 | 0.1137 |
| 0.03762 | 1.473 | 1.0334 | 0.1137 |
| 0.06116 | 1.824 | 1.0574 | 0.0752 |
| Cyclohexane (1)–Ethanol (2) | | | |
| 0.00900 | 0.973 | 1.0056 | 0.6178 |
| 0.00904 | 0.992 | 1.0056 | 0.6178 |
| 0.01788 | 1.429 | 1.0123 | 0.4452 |
| 0.01790 | 1.437 | 1.0123 | 0.4452 |
| 0.03513 | 2.162 | 1.0273 | 0.2878 |
| 0.04353 | 2.441 | 1.0351 | 0.2458 |
| 0.05990 | 2.962 | 1.0511 | 0.1919 |
| 0.07572 | 3.380 | 1.0673 | 0.1589 |
| Cyclohexane (1)–1-Propanol (2) | | | |
| 0.00705 | 0.800 | 1.0042 | 0.6747 |
| 0.01400 | 1.256 | 1.0092 | 0.5099 |
| 0.02086 | 1.615 | 1.0147 | 0.4114 |
| 0.02762 | 1.931 | 1.0203 | 0.3463 |
| 0.03429 | 2.208 | 1.0262 | 0.3002 |
| 0.04736 | 2.713 | 1.0382 | 0.2393 |
| 0.06008 | 3.190 | 1.0504 | 0.2008 |
| Cyclohexane (1)–2-Propanol (2) | | | |
| 0.00699 | 0.783 | 1.0042 | 0.6769 |
| 0.00700 | 0.784 | 1.0042 | 0.6769 |
| 0.01388 | 1.246 | 1.0091 | 0.5176 |
| 0.02067 | 1.633 | 1.0143 | 0.4233 |
| 0.02737 | 2.001 | 1.0198 | 0.3610 |
| 0.03398 | 2.313 | 1.0254 | 0.3166 |
| 0.04694 | 2.942 | 1.0368 | 0.2576 |
| 0.05955 | 3.517 | 1.0484 | 0.2200 |
| Cyclohexane (1)–2-Butanol (2) | | | |
| 0.00579 | 0.751 | 1.0032 | 0.8038 |
| 0.00580 | 0.757 | 1.0032 | 0.8038 |
| 0.01145 | 1.212 | 1.0068 | 0.6736 |
| 0.01707 | 1.615 | 1.0108 | 0.5802 |
| 0.02264 | 1.970 | 1.0150 | 0.5104 |
| 0.03357 | 2.575 | 1.0238 | 0.4136 |
| 0.04427 | 3.149 | 1.0330 | 0.3499 |
| 0.05473 | 3.669 | 1.0424 | 0.3048 |
| Cyclohexane (1)–Isobutyl Alcohol (2) | | | |
| 0.00575 | 0.557 | 1.0036 | 0.6019 |
| 0.00579 | 0.565 | 1.0036 | 0.6019 |
| 0.01143 | 0.938 | 1.0078 | 0.4415 |
| 0.02260 | 1.516 | 1.0168 | 0.2999 |
| 0.03352 | 2.053 | 1.0261 | 0.2343 |
| 0.04420 | 2.532 | 1.0356 | 0.1959 |
| 0.05464 | 3.016 | 1.0450 | 0.1704 |
| 0.06486 | 3.450 | 1.0545 | 0.1522 |
| Cyclohexane (1)–*tert*-Butyl Alcohol (2) | | | |
| 0.00482 | 0.289 | 1.0036 | 0.9694 |
| 0.00954 | 0.551 | 1.0073 | 0.9446 |
| 0.00954 | 0.577 | 1.0073 | 0.9446 |
| 0.01417 | 0.873 | 1.0109 | 0.9241 |
| 0.02317 | 1.374 | 1.0180 | 0.8922 |
| 0.03182 | 1.880 | 1.0250 | 0.8686 |
| 0.04014 | 2.368 | 1.0319 | 0.8505 |
| 0.04817 | 2.831 | 1.0386 | 0.8362 |

The activity coefficients of the solute are calculated by using infinitely dilute alcohol as the reference state. From Gibbs–Duhem equation and eq 5

$$\ln \gamma_2 x_1 = -(1-\phi) - \int_0^z \frac{(1-\phi)}{z}\,dz \tag{11}$$

is obtained following a treatment analogous to that given by Prigogine and Defay (*6*).

By taking into consideration the form of eq 6, the integration of eq 11 can be done analytically. The following result is obtained:

$$\hat{\gamma}_2^{(n)} = \frac{\exp\left[-\dfrac{z^{(n)}}{A_0 + A_1 z^{(n)}}\right]}{x_1^{(n)}\left[1 + \dfrac{A_1 z^{(n)}}{A_0}\right]^{1/A_1}} \tag{12}$$

To present the activity coefficients on the basis of monomers as the stoichiometric species, the following transformation can be made

$$\hat{\gamma}_2 = n\hat{\gamma}_2^{(n)} x_2^{(n)}/x_2 \tag{13}$$

in which $n = 4$ for *tert*-butyl alcohol and $n = 2$ for the remaining alcohols considered in this study. The need for the factor $n$ arises from the fact that $\hat{\gamma}_2$ must be unity at infinite dilution.

The factors which convert one kind of activity coefficient in the other in eq 10 and 13 result from the respective mass balance:

$$x_1^{(n)}/x_1 = n x_2^{(n)}/x_2 = 1 + (n-1)x_2^{(n)} \tag{14}$$

Table II gives mole fractions, experimental freezing point lowerings, and activity coefficients calculated in the described manner.

## Correlation of Activity Coefficients with Models

In order to appraise the interpretative ability of several simple models with regard to the activity coefficients calculated in the preceding section, a fit of them had to be made. The same objective function was used in all cases

$$\psi_\gamma = \sum_j^2 \sum_k^N \{1 - (\gamma_j/\hat{\gamma}_j)\}_k^2 \tag{15}$$

and standard deviations were determined according to

$$\sigma = 100\{\psi_1/(N-1)\}^{1/2} \tag{16}$$

$\gamma_j$ and $\hat{\gamma}_j$ are respectively calculated from the model and from the experimental data.

Two alternatives approaches were used to calculate $\gamma_j$: (a) As a function of the stoichiometric mole fraction on the basis of the monomeric alcohol species (standard deviation, $\sigma$); (b) As a function of the mole fraction calculated by assuming tetramers in *tert*-butyl alcohol and dimers in the remaining alcohols (standard deviation $\sigma^{(n)}$).

At first, the comparison of both alternatives was made for two classic models (van Laar and Wilson) and two kinds of ideal associated solution models.

Later on, two athermal associated solution models were used following only the second alternative, after realizing that it showed much better results than the first one.

The equations for calculating activity coefficients in each of the six models tried are the following:

***I. van Laar (7).***

$$\gamma_1 = \exp[A_{21}/\{1 + (A_{21}x_1/A_{12}x_2)\}^2] \tag{17}$$

$$\gamma_2 = \exp[A_{12}/\{1 + (A_{12}x_2/A_{21}x_1)\}^2 - A_{12}] \tag{18}$$

***II. Wilson (8).***

$$\gamma_1 = \tau_{21}\exp[x_2(\tau_{21}\Lambda_{21} - \tau_{12}\Lambda_{12})] \tag{19}$$

$$\gamma_2 = \tau_{12}\Lambda_{12}^* \exp[-x_1(\tau_{21}\Lambda_{21} - \tau_{12}\Lambda_{12}) - 1 + \Lambda_{21}^*] \tag{20}$$

in which

$$\Lambda_{ij} = (v_i/v_j)\exp[-(\lambda_{ij} - \lambda_{jj})/RT]; \quad \lambda_{ij} = \lambda_{ji} \tag{21}$$

$$\tau_{ij} = 1/(\Lambda_{ij}x_i + x_j); \quad i = 1, 2; j = 1, 2 \tag{22}$$

$\Lambda_{12}^*$ and $\Lambda_{21}^*$ are calculated for $T = T_0$.

***III. Ideal Associated Solution with Two Equilibrium Constants (9).***

$$\gamma_2 = x_m/x_2 \tag{23}$$

$$\gamma_1 = 1 + K_1\{x_m/(1 - K_2x_m)\}^2 \tag{24}$$

in which $x_m$ is the mole fraction of the presumptive real smallest species of the solute, determined iteratively from

$$x_2 = \frac{x_m[(1 - K_2x_m)^2 + K_1x_m(2 - K_2x_m)]}{[(1 - K_2x_m)^2 + K_1x_m]} \tag{25}$$

***IV. Ideal Associated with Equilibrium Constant Dependent on the Degree of Association (10).*** $\gamma_2$ is calculated with eq 23, but now $x_m$ is determined iteratively from

$$x_2 = \frac{\beta\Omega_m}{(1 - \Omega x_m)^{\beta+1}(1 + \beta\Omega) + (\beta + 1)\Omega x_m - 1} \tag{26}$$

in which

$$\Omega = 2K/(\beta + 1) \tag{27}$$

There are two limiting cases leading to special forms of eq 26. They are the following:

$$x_2 = \frac{2Kx_m}{2Kx_m + (1 - 2Kx_m)[2K + \ln(1 - 2Kx_m)]} \quad \text{when } \beta = 0 \tag{28}$$

$$x_2 = \frac{2Kx_m}{(2K + 1)\exp(-2Kx_m) + (1 - 2Kx_m)} \quad \text{when } \beta \rightarrow \infty \tag{29}$$

The activity coefficient of the solvent is given by

$$\gamma_1 = (1 - x_r)/x_1 \tag{30}$$

in which

$$x_r = \frac{(1 - x_m)^{-\beta} - 1}{\beta\Omega} \quad \text{when } 0 < \beta < \infty \tag{31}$$

$$x_r = -\frac{\ln(1 - 2Kx_m)}{2K} \quad \text{when } \beta = 0 \tag{32}$$

$$x_r = \frac{\exp(2Kx_m) - 1}{2K} \quad \text{when } \beta \rightarrow \infty \tag{33}$$

$K$ is the equilibrium constant for the transformation of the presumptive minor real species in its dimer.

***V. Athermal Associated Solution with Two Equilibrium Constants.***

$$\gamma_1 = (r/x)\exp(y) \tag{34}$$

$$\gamma_2 = (r\phi_m/x_2)\exp(y/r) \tag{35}$$

in which

$$x = rx_1 + x_2 \tag{36}$$

$$y = 1 - r\{(x_1/x) + [1 - (K_1/K_2)]\phi_m - (K_1/K_2^2)\ln(1 - K_2\phi_m)\} \tag{37}$$

$$r = v_1/v_2 \tag{38}$$

**Table III. Parameters and Percentagewise Standard Deviations for Model I (van Laar)**

| solute | $A_{21}$ | $A_{12}$ | $\sigma$ | $A_{21}^{(n)}$ | $A_{12}^{(n)}$ | $\sigma^{(n)}$ |
|---|---|---|---|---|---|---|
| methanol | 2.97 | 0.119 | 4.04 | 3.01 | 0.061 | 4.16 |
| ethanol | 2.41 | 0.196 | 1.97 | 2.48 | 0.103 | 1.82 |
| 1-propanol | 2.23 | 0.164 | 1.53 | 2.28 | 0.086 | 1.29 |
| 2-propanol | 2.02 | 0.132 | 1.66 | 2.07 | 0.069 | 1.46 |
| 2-butanol | 1.96 | 0.193 | 1.07 | 2.02 | 0.101 | 0.52 |
| isobutyl alcohol | 2.17 | 0.096 | 3.32 | 2.22 | 0.050 | 3.32 |
| *tert*-butyl alcohol | 0.302 | 0.027 | 2.05 | 0.387 | 0.010 | 0.06 |

$\phi_m$ is the volume fraction of the presumptive minor species and is determined directly by

$$\phi_m = \frac{2x_2}{K_2x_2 + x + \{(K_2x_2 - x)^2 + 4K_1x_2x\}^{1/2}} \tag{39}$$

***VI. Athermal Associated Solution with Only One Equilibrium Constant, K, and Physical Interaction Contributions.*** (parameter $\chi$) (UMAS when $\beta = 0$) (*11*).

$$\gamma_1 = (r/x)\exp[\eta + \chi v_1\{1 - (rx_1/x)\}^2/RT] \tag{40}$$

$$\gamma_2 = (r\phi_m/x_2)\exp[(\eta/r) + (\chi v_1/r)\{(rx_1/x)^2 - 1\}/RT] \tag{41}$$

in which

$$\eta = 1 - r\{(x_1/x) + (\beta\phi_m/\alpha) + [(\beta - 1)(\alpha\ln\alpha)/K]\} \tag{42}$$

$$\alpha = 1 - K\phi_m \tag{43}$$

$$\phi_m = \frac{2x_2}{2Kx_2 + x + \{x(x + 4\beta Kx_2)\}^{1/2}} \tag{44}$$

Equations 42 and 44 give explicitly the dependence upon $\beta$, since other alternatives can be tried. The results of those alternatives are not reported in this paper, because they showed higher standard deviations. One alternative was $\beta = 1$ and adjustable $\chi$; the other fixed $\chi = 0$ and adjustable $\beta$.

In most cases, the computational procedure followed the Newton–Raphson method to localize the minimum of the objective function, $\psi_\gamma$. In some cases, it had to be replaced or complemented by a sort of trial and error procedure.

## Results and Discussion

Tables III–VIII give the respective optimum parameters and percentagewise standard deviations.

In the first four models, both alternatives (a) and (b) of calculating activity coefficients (stoichiometric and based on dimers or tetramers) are given. As the second alternative gave much better results, it was the only one tried for models V and VI.

Standard deviations were much lower when alternative (b) was used. Table IX allows to appreciate this conclusion: From its last column, it is easily visualized that ideal associated solution models III and IV give better results than van Laar and Wilson. However, the trend is just the reverse for *tert*-butyl alcohol in alternative (b), as it can be seen in Tables III and IV. Standard deviations were considerably lower for the van Laar and Wilson models, especially for the first one. The conclusion for *tert*-butyl alcohol is that, in this concentration region, there would be only tetramers and no other *n*-mers. The remaining alcohols would be in the form of dimer and higher *n*-mers.

It is convenient to compare standard deviations of alternative (b) for the six and the seven solutes in all models. Table X summarizes the results.

Athermal associated solution models V and VI show better results than the former four models in both columns. However, a careful examination of Table VIII indicates that there is a sort of compensation effect in model VI, arising from the physical

**Table IV. Parameters[a] and Percentagewise Standard Deviations for Model II (Wilson)**

| solute | $\lambda_{12}-\lambda_{22}$ | $\lambda_{12}-\lambda_{11}$ | $\sigma$ | $(\lambda_{12}-\lambda_{22})^{(n)}$ | $(\lambda_{12}-\lambda_{11})^{(n)}$ | $\sigma^{(n)}$ |
|---|---|---|---|---|---|---|
| methanol | 2693 | -510 | 1.03 | 3075 | -700 | 0.94 |
| ethanol | 1921 | -184 | 1.03 | 2304 | -380 | 0.54 |
| 1-propanol | 1796 | -180 | 1.01 | 2178 | -373 | 0.51 |
| 2-propanol | 1802 | -308 | 1.17 | 2180 | -497 | 0.82 |
| 2-butanol | 1449 | -41 | 0.95 | 1832 | -238 | 0.25 |
| isobutyl alcohol | 1958 | -303 | 2.05 | 2336 | -486 | 1.99 |
| *tert*-butyl alcohol | 551 | 27 | 2.04 | 1252 | -311 | 0.14 |

[a] $\lambda_{ij}-\lambda_{jj}$ is given in cal/mol.

**Table V. Parameters and Percentagewise Standard Deviations for Model III (Two-Constant Ideal Associated Solution)**

| solute | $K_1$ | $K_2$ | $\sigma$ | $K_1^{(n)}$ | $K_2^{(n)}$ | $\sigma^{(n)}$ |
|---|---|---|---|---|---|---|
| methanol | 87.2 | 177 | 0.62 | 176 | 354 | 0.33 |
| ethanol | 30.0 | 58.5 | 1.03 | 59.4 | 118 | 0.37 |
| 1-propanol | 32.1 | 53.5 | 0.92 | 64.9 | 107 | 0.09 |
| 2-propanol | 35.8 | 44.5 | 1.02 | 72.3 | 89.2 | 0.49 |
| 2-butanol | 20.2 | 32.6 | 0.96 | 41.0 | 65.2 | 0.11 |
| isobutyl alcohol | 68.8 | 62.4 | 1.60 | 138.5 | 125 | 1.34 |
| *tert*-butyl alcohol | 2.70 | 0.0 | 2.20 | 12.7 | 0.0 | 0.74 |

**Table VI. Parameters and Percentagewise Standard Deviations with Model IV (Ideal Associated Solution with Gradually Varying Equilibrium Constant)**

| solute | $K$ | $\beta$ | $\sigma$ | $K^{(n)}$ | $\beta^{(n)}$ | $\sigma^{(n)}$ |
|---|---|---|---|---|---|---|
| methanol | 116 | 0.177 | 0.89 | 232 | 0.179 | 0.70 |
| ethanol | 35.2 | 0.000 | 1.12 | 70.7 | 0.000 | 0.57 |
| 1-propanol | 35.4 | 0.091 | 1.01 | 71.5 | 0.105 | 0.44 |
| 2-propanol | 37.1 | 0.482 | 1.11 | 74.8 | 0.499 | 0.65 |
| 2-butanol | 21.3 | 0.014 | 0.96 | 43.2 | 0.035 | 0.20 |
| isobutyl alcohol | 68.3 | 1.397 | 1.52 | 137 | 1.408 | 1.24 |
| *tert*-butyl alcohol | 2.5 | $\infty$ | 2.30 | 11.6 | $\infty$ | 1.06 |

**Table VII. Parameters and Percentagewise Standard Deviations with Model V (Athermal Associated Solution with Two Equilibrium Constants)**

| solute | $K_1^{(n)}$ | $K_2^{(n)}$ | $\sigma^{(n)}$ |
|---|---|---|---|
| methanol | 642 | 546 | 0.67 |
| ethanol | 122 | 137 | 0.03 |
| 1-propanol | 100 | 102 | 0.17 |
| 2-propanol | 106 | 85.7 | 0.60 |
| 2-butanol | 49.4 | 54.6 | 0.08 |
| isobutyl alcohol | 165 | 103 | 1.24 |
| *tert*-butyl alcohol | 10.6 | 0.82 | 0.03 |

**Table VIII. Parameters and Percentagewise Standard Deviations with Model VI (Athermal Associated Solution with Physical Interaction Contributions: $\beta = 0$)**

| solute | $K^{(n)}$ | $\chi^{(n)}$[a] | $\sigma^{(n)}$ |
|---|---|---|---|
| methanol | 578 | -31.5 | 0.19 |
| ethanol | 128 | 11.8 | 0.44 |
| 1-propanol | 101 | 0.62 | 0.20 |
| 2-propanol | 101 | -18.2 | 0.09 |
| 2-butanol | 49.8 | 6.5 | 0.12 |
| isobutyl alcohol | 140 | -25.2 | 0.79 |
| *tert*-butyl alcohol | 14.6 | -13.8 | 0.12 |

[a] $\chi^{(n)}$ is given in cal/mol.

**Table IX. Average Standard Deviations**

| model | (a) monomers | (b) dimers and tetramers |
|---|---|---|
| I | 2.23 | 1.80 |
| II | 1.33 | 0.74 |
| III | 1.19 | 0.50 |
| IV | 1.27 | 0.69 |

interaction parameter, $\chi$, since it shows to rational trend from one alcohol to the other.

Models III and V are the best ones for all alcohols, except for *tert*-butyl alcohol. Both of them consider two equilibrium chemical constants and no physical interaction contributions, but model V is athermal associated and model III is ideal associated. There is appreciable improvement in passing from the ideal associated model to the athermal associated solution model, even for *tert*-butyl alcohol. However, the magnitudes of the constants show that there would be practically tetramers and few octamers, with a low equilibrium constant (0.82) for all other *n*-mers, showing that they would be practically nonexistent.

**Table X. Average Standard Deviations for Alternative (b)**

| model | 6 alcohols[a] | 7 alcohols |
|---|---|---|
| I | 2.10 | 1.80 |
| II | 0.84 | 0.74 |
| III | 0.46 | 0.50 |
| IV | 0.63 | 0.69 |
| V | 0.46 | 0.40 |
| VI | 0.30 | 0.28 |

[a] *tert*-Butyl alcohol excluded.

**Table XI. Comparison of $K_2$ from Model V with $K_A$ Values Calculated by Nath and Bender (*12*)**

| | $K_A$ | $K_2^{(n)}$ |
|---|---|---|
| methanol | 924 | 546 |
| ethanol | 453 | 137 |
| 1-propanol | 290 | 102 |
| 2-propanol | 148 | 86 |
| 2-butanol | 96 | 55 |
| isobutyl alcohol | 134 | 103 |

When the magnitudes of the equilibrium constants for the formation of the higher *n*-mers are compared with those calculated from pure alcohol properties (*12*), there are important differences. Table XI shows them.

In the low concentration region herein examined, equilibrium constants are much lower than those calculated from pure alcohol properties. Maybe this is a clear indication for a composition dependence which ought to be introduced in athermal associated solution models in order to improve their fit to experimental data in the whole concentration range. It is well-known that the low concentration region is the most difficult to fit for most properties.

## Final Conclusions

When the solvent is cyclohexane and the solute is a light alcohol of very low concentration

(a) *tert*-butyl alcohol would be only in the form of tetramers; Wilson and especially van Laar models give almost perfect fits.

(b) The remaining alcohols herein studied would be as *n*-mers, with $n \geq 2$; the two-equilibrium-constant athermal associated solution model produces excellent fits.

(c) Association equilibrium constants are lower in magnitude in this concentration range than those calculated from pure alcohol properties. This conclusion should be taken into account in any effort to improve associated solution models to cover the whole composition range in a better way.

## Glossary

| | |
|---|---|
| $a_1$ | activity of the solvent |
| $A$, $B$ | constants (see eq 3) |

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| | |
|---|---|
| $A_0$, $A_1$ | constants (see eq 6) |
| $A_{12}$, $A_{21}$ | van Laar parameters |
| $c_p$ | heat capacity |
| $K$, $K_A$, $K_1$, $K_2$ | chemical equilibrium constants |
| $n$ | number of monomeric units |
| $N$ | number of experimental data points |
| $r$ | molar volumetric ratio, $v_1/v_2$ |
| $R$ | gas constant |
| $S$ | extent of supercooling |
| $T$ | absolute temperature |
| $T_0$ | melting point of the solvent |
| $T_s$ | lowest temperature of supercooled solution |
| $v_1$, $v_2$ | molar volumes of solvent and solute |
| $x$ | see eq 38 |
| $x_1$, $x_2$ | mole fractions of solvent and solute |
| $x_m$ | mole fraction of minor real species |
| $x_r$ | see eq 31 |
| $y$ | see eq 37 |
| $z$ | mole fraction ratio $x_2/x_1$ |
| $\alpha$ | see eq 43 |
| $\beta$ | parameter in ideal associated solution model |
| $\gamma_1$, $\gamma_2$ | activity coefficients of solvent and solute |
| $\Delta$ | difference |
| $\eta$ | see eq 42 |
| $\theta$ | freezing point depression calculated from a model |
| $\hat{\theta}$ | corrected experimental freezing point depression |
| $\theta_m$ | measured experimental freezing point depression |
| $\lambda_{ij}$, $\Lambda_{ij}$ | Wilson equation parameters |
| $\lambda_1$ | heat of fusion of solvent |
| $\sigma$ | standard deviation |
| $\tau_{ij}$ | Wilson equation parameters |
| $\phi$ | osmotic coefficient |
| $\phi_m$ | volume fraction of minor real species |
| $\chi$ | Scatchard–Hildebrand-type parameter |
| $\psi_\theta$, $\psi_\gamma$ | objective functions |
| $\Omega$ | see eq 27 |

**Registry No.** Cyclohexane, 110-82-7; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 2-butanol, 78-92-2; isobutyl alcohol, 78-83-1; *tert*-butyl alcohol, 75-65-0.

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# Calorimetric Measurements at 318.15 K for the Maleic Anhydride/Dioxane and 2-Methylfuran/Dioxane Binaries and Their Correlation with a Modified Gmehling Equation of State

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**Partial molar enthalpies for the binary systems 2-methylfuran/*p*-dioxane and maleic anhydride/*p*-dioxane were measured via titration, isoperibol calorimetry at 318.15 K. The behavior of both binaries was correlated within experimental uncertainty with a three-parameter version of the Gmehling equation of state. Two-parameter models could successfully correlate the 2-methylfuran/*p*-dioxane binary but not the maleic anhydride/*p*-dioxane binary.**

## Introduction

Maleic anhydride and 2-methylfuran undergo a reversible Diels–Alder reaction and in the solvent *p*-dioxane, large concentrations of these reacting species can be obtained. The equilibrium constant for this reaction is related to concentration by

$$K = \frac{x_A}{x_{MA}x_{MF}} \frac{\gamma_A}{\gamma_{MA}\gamma_{MF}} \tag{1}$$

where $x$ and $\gamma$ are the mole fraction and activity coefficient, the subscripts MA and MF represent the two reactants, maleic anhydride and 2-methylfuran, and A represents their Diels–Alder adduct. There are any number of models which can normally be used for activity coefficient correlation, but in reacting systems, extremely large deviations from ideality can occur which render many of the existing models unacceptable. In particular, previous work (*1*, *2*) with the methylfuran/maleic anhydride/dioxane system as well as difference spectroscopy suggested the presence of various complexes, presumably involving the solvent, *p*-dioxane. In order to characterize this behavior as well as to address the general topic of highly nonideal solution behavior in reacting systems, we undertook to measure and correlate heat of mixing data for the *p*-dioxane/methylfuran and *p*-dioxane/maleic anhydride binaries.

## Experimental Section

Data were taken with a Tronac Model 550 calorimeter which was operated in the isoperibol mode. The procedure (*1*, *2*, *3*) consisted of measuring the change in temperature of the contents of a 100-mL silvered flask which resulted from the injection of a known amount of material at a known concentration. This temperature change was then converted to an amount of

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