| | |
|---|---|
| $A_0$, $A_1$ | 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

$$K = \frac{x_A}{x_{MA}x_{MF}} \frac{\gamma_A}{\gamma_{MA}\gamma_{MF}} \qquad (1)$$

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

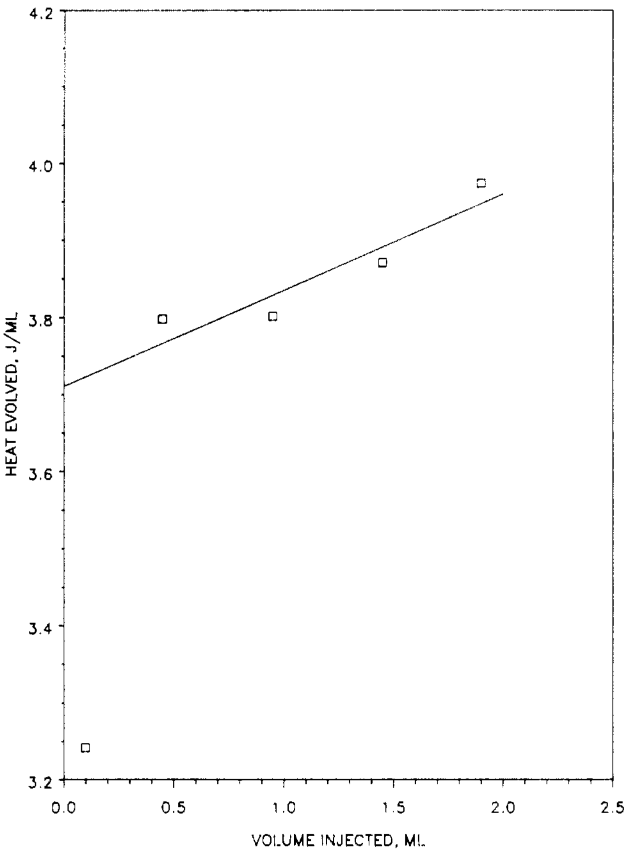

**Figure 1.** Heat evolved for a series of five injections of a maleic anhydride/*p*-dioxane mixture ($x_{MA}$ = 0.4995) into pure *p*-dioxane. The experimental enthalpy was obtained by extrapolating to zero volume injected.

heat evolved due to mixing (all experiments were exothermic) by means of the system heat capacity which had been determined previously by calibration. Isoperibol operation indicates a system which, except for a small heat leak correction due to the constant temperature of the surroundings, is adiabatic.

**Table I. Densities of Maleic Anhydride/*p*-Dioxane Mixtures at 318.15 K (*1*)**

| mole fraction maleic anhydride | density, g/cm$^3$ |
|---|---|
| 0 | 1.0039 |
| 0.1699 | 1.057 |
| 0.3306 | 1.106 |
| 0.6286 | 1.201 |
| 0.7683 | 1.247 |

**Table II. Experimental Heats ($\bar{H}_D$) and Deviation of Calculated Values for Injection of Pure *p*-Dioxane into Four 2-Methylfuran/*p*-Dioxane Mixtures at 318.15 K[a]**

| $x_{MF}$ | $\bar{H}_D$, J/mol | dev,[b] J/mol |
|---|---|---|
| 0.2583 | -49 | 4 |
| 0.5111 | -168 | -18 |
| 0.7544 | -417 | -1 |
| 1.0 | -739 | 0 |

[a] $x_{MF}$ is the mole fraction 2-methylfuran in the flask. $\bar{H}_D$ is joules per mole injected. [b] Deviation is value calculated with Gmehling model minus experimental value.

**Table III. Experimental Heats ($\bar{H}_{MF}$) and Deviation of Calculated Values for Injection of Pure 2-Methylfuran into Four 2-Methylfuran/*p*-Dioxane Mixtures at 318.15 K[a]**

| $x_{MF}$ | $\bar{H}_{MF}$, J/mol | dev,[b] J/mol |
|---|---|---|
| 0.7490 | -53 | 6 |
| 0.4998 | -206 | 18 |
| 0.2546 | -430 | 22 |
| 0.0 | -703 | 2 |

[a] $x_{MF}$ is mole fraction 2-methylfuran. $\bar{H}_{MF}$ is joules per mole injected. [b] Deviation is value calculated with Gmehling model minus experimental value.

Injections were made with a 2.5-mL Gilmont Micrometer syringe which could be read to ±0.0002 mL. The silvered flask and the Gilmont syringe were submerged in a temperature bath which was held to within 0.05 K of 318.15 K. In addition to approximately 100 mL of liquid, the silvered flask contained a heater (used in the calibration to determine the system heat capacity), a stirrer, and a temperature sensor. The bath temperature was measured with a mercury in glass thermometer with a calibration traceable to the National Bureau of Standards. The temperature in the flask varied during a run but typically remained within 0.05 K of the bath temperature. Temperature changes in the flask which occurred due to injections, heat leak, and resistance heating during the heat capacity calibrations were measured with the Tronac thermistor bridge and recorded on a strip chart recorder. Each of the 100 divisions on the recorder chart corresponded approximately to 0.0009 K. Injection volumes were typically 0.5 mL, except when the concentrations of the solutions in the flask and syringe were similar, and in this case 1 mL was injected. Figure 1 shows results for injections into pure dioxane in which an initial injection of 0.2 mL of a mixture containing 49.95 mol % maleic anhydride and 50.05 mol % dioxane was followed by three 0.5-mL injections and a 0.4-mL injection. The heat evolved per milliliter injected was determined for each injection, plotted as shown in Figure 1, and extrapolated to zero volume injected. The extrapolation was generally done by omitting the point for the first injection and extrapolating a least-squares line through the remaining points. Since the heat evolved per milliliter injected is a derivative quantity, the points are plotted in Figure 1 at "average" volumes injected rather than actual volumes injected (i.e., at 0.1, 0.45, 0.95, 1.45, and 1.9 mL rather than 0.2, 0.7, 1.2, 1.7, and 2.1 mL). Volumes injected were converted to masses by means of the densities given in Table I (*1*). The density used for methylfuran at 318.15 K was 0.8890 g/cm$^3$ (*1*). When 0.5 mL of liquid was injected, an equivalent volume of vapor was expelled along the stirrer shaft so as to maintain a constant pressure in the flask of 1 atm. For the assumption that this vapor is expelled before the vapor-phase composition equilibrates with the new liquid-phase composition, vaporization effects are relatively small. The largest error due to vaporization would occur in the methylfuran experiments and can be estimated approximately, by the equation below, to be about 2 J/mol.

$$\text{error due to vaporization} = \frac{V}{NRT}(P_{vpMF}\Delta H_{MF}^{v} - P_{vpD}\Delta H_{D}^{v}) \tag{2}$$

The subscripts MF and D refer to methylfuran and dioxane, $P_{vp}$ is vapor pressure, $\Delta H^v$ is the heat of vaporization, $N$ is the moles of liquid in the flask (about 1 mol), and $V$ is the vapor space in the flask (about 5 cm$^3$). For the data shown in Figure 1, the extrapolated value (to zero volume injected) is 3.716 J/ml, but could be taken to be higher or lower by about 0.08 J/ml, which corresponds to ±6.4 J/mol, or ±2%. The scatter in the data in Figure 1 was typical, with the scatter in other runs less in some cases and more in others. The maximum error for all runs was estimated to be the smaller of ±20 J/mol or ±10%.

Maleic anhydride (99%) and 2-methylfuran (99%) were obtained from the Aldrich Chemical Co.; *p*-dioxane (99%) was obtained from the Fisher Scientific Co. Maleic anhydride was further purified by vacuum sublimation and was stored in a moisture-free nitrogen environment; *p*-dioxane and 2-methylfuran were further purified by distillation. Stock solutions were prepared by weight and exposed only to nitrogen during their

**Table IV. Experimental Heats ($\bar{H}_D$) and Deviation of Calculated Values for Injection of Pure *p*-Dioxane into Five Maleic Anhydride/*p*-Dioxane Mixtures at 318.15 K**[a]

| $x_{MA}$ | $\bar{H}_D$, J/mol | dev,[b] J/mol |
|---|---|---|
| 0.1996 | -50 | 2 |
| 0.3509 | -320 | 0 |
| 0.4995 | -826 | 11 |
| 0.6534 | -1511 | -23 |
| 0.8009 | -2302 | 0 |

[a] $x_{MA}$ is mole fraction maleic anhydride, $\bar{H}_D$ is joules per mole injected. [b] Deviation is value calculated with Gmehling model minus experimental value.

**Table V. Experimental Heats ($H$) and Deviation of Calculated Values for Injection of Three Different Maleic Anhydride/*p*-Dioxane Mixtures into Pure *p*-Dioxane at 318.15 K**[a]

| $x_{MA}$ | $H$, J/mol | dev,[b] J/mol |
|---|---|---|
| 0.3509 | 57 | 1 |
| 0.4995 | 298 | -2 |
| 0.6534 | 633 | -107 |

[a] $x_{MA}$ is mole fraction maleic anhydride in the injected mixture; $H$ is joules evolved per mole of mixture injected. [b] Deviation is value calculated with Gmehling model minus experimental value.

**Table VI. Pure-Component Parameters for Gmehling Equation**

| | $T^*$, K | $V^*$, L/mol | $\Delta S°/R$ | $-\Delta H°/R$, K | ref |
|---|---|---|---|---|---|
| *p*-dioxane | 430.8 | 0.0578 | -13.50 | 3702 | *5–9* |
| maleic anhydride | 465.0 | 0.0517 | -14.93 | 6845 | *10* |
| 2-methylfuran | 371.3 | 0.0585 | -13.03 | 3395 | *1, 11, 12* |

**Table VII. Binary Parameters for Gmehling Equation**

| | $k_{ij}$ | $\Delta S°_{ij}/R$ | $-\Delta H°_{ij}/R$, K |
|---|---|---|---|
| *p*-dioxane/maleic anhydride | −0.1119 | −12.37 | 4761 |
| *p*-dioxane/2-methylfuran | 0.0051 | −12.92 | 3670 |

preparation. These stock solutions were used to fill the syringe and flask, and at this time did come into contact with the atmosphere.

## Results

Experimental results for the 2-methylfuran/*p*-dioxane binary are shown in Tables II and III. Both of these components are liquids and are miscible over the entire composition range so injections of each pure component were made into mixtures with compositions shown in Tables II and III. The experimentally determined heats were equal to the partial molar enthalpies of the injected compound (where the reference state is the pure liquid at 318.15 K). Experimental heats for *p*-dioxane injections are given in Table II; those for 2-methylfuran injections are in Table III.

For the maleic anhydride/*p*-dioxane binary one set of experiments consisted of injection of *p*-dioxane into mixtures with the compositions shown in Table IV. These heats were equivalent to dioxane partial molar enthalpies and are listed in Table IV. At 318.15 K, maleic anhydride is a solid so its partial molar enthalpy could not be measured directly. Thus, solutions of maleic anhydride in *p*-dioxane with the three compositions shown in Table V were injected into pure *p*-dioxane. For this case, the heats evolved are equal to the enthalpies, $H$, of the injected mixture, and are related to partial molar enthalpies by

$$H = x_{MA}^{in}\bar{H}_{MA}^{in} + x_D^{in}\bar{H}_D^{in} \qquad (3)$$

where $x_i^{in}$ is the mole fraction of component i in the injected mixture, $\bar{H}_i^{in}$ is the partial molar enthalpy of component i at the concentration of the injected solution, and the subscripts MA and D refer to maleic anhydride and *p*-dioxane. The reference state for maleic anhydride is the infinitely dilute state. Values of $H$ for the injection of the three different mixtures are shown in Table V.

## Correlation of Results

The data in Tables II and III for the *p*-dioxane/2-methylfuran binary were successfully correlated with a number of two-parameter models (such as the Wilson equation) but attempts to fit the data in Tables IV and V for the *p*-dioxane/maleic anhydride binary to various two-parameter models were unsuccessful. However, the data were successfully correlated with a three-parameter version of the equation of state model presented by Gmehling et al. (*4*). In this model an equation of state is coupled with a chemical theory whereby pure components can form dimers, and in mixtures, cross dimers can be formed. The equation of state is

$$z = z(\text{repulsive}) + z(\text{attractive}) \qquad (4)$$

where

$$z(\text{repulsive}) = 1 + \langle c\rangle\left[\frac{4\xi - 2\xi^2}{(1-\xi)^3}\right] \qquad (5)$$

$$z(\text{attractive}) = \sum_{n=1}^{2}\sum_{m=1}^{5}\frac{mA_{nm}\langle cT^*\rangle\langle T^*\rangle^{(n)}\langle v^*\rangle^m}{T^n v^m} \qquad (6)$$

and

$$\xi = \frac{\pi 2^{1/2}\langle v^*\rangle}{6v} \qquad (7)$$

Brackets, ⟨ ⟩, indicate a mixture property: mixing rules and values of the constants, $A_{nm}$, are given in Gmehling et al. (*4*). Dimerization equilibrium constants are calculated by

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (8)$$

$c$ is set equal to unity, so there are four parameters for each pure component, $T^*$, $v^*$, $\Delta H°$, and $\Delta S°$. Values of these four parameters were determined for each of the three compounds as part of this study from pure-component vapor pressures and liquids volumes. Parameters and references to data are listed in Table VI. The three binary parameters, $\Delta H°_{ij}$, $\Delta S°_{ij}$, and $k_{ij}$ are listed in Table VII. $\Delta H°_{ij}$ and $\Delta S°_{ij}$ are the parameters which characterize the extent of cross dimer formation, and the binary interaction parameter, $k_{ij}$, adjusts the i–j interaction energy. In Gmehling's original two-parameter formulation, $\Delta H°_{ij}$ was taken as the average of the pure-component $\Delta H°$ values, but this formulation did not allow the results to be fit within experimental accuracy. To our knowledge, this model has not previously been used to describe heat of mixing data.

Results for the *p*-dioxane/methylfuran binary calculated with the parameters in Tables VI and VII are shown in Figure 2, and deviations between the calculated and experimental values are tabulated in Tables II and III. The mean absolute deviation of these eight points is 8.9 J/mol, which is consistent with the earlier error discussion.

Results for the *p*-dioxane/maleic anhydride binary are shown in Figures 3 and 4. Figure 3 shows the partial molar enthalpy of *p*-dioxane; the points on this plot are data from Table IV. Figure 4 shows the mixture enthalpy as a function of composition; the points on this plot are the data in Table V. When the Gibbs–Duhem equation was used to generate information equivalent to that in Table V from the data in Table IV, it was apparent that the last point in Table V was not thermodynamically consistent with the other seven data points. Only the seven thermodynamically consistent points were used to determine the parameters in Table VII, although the eighth point

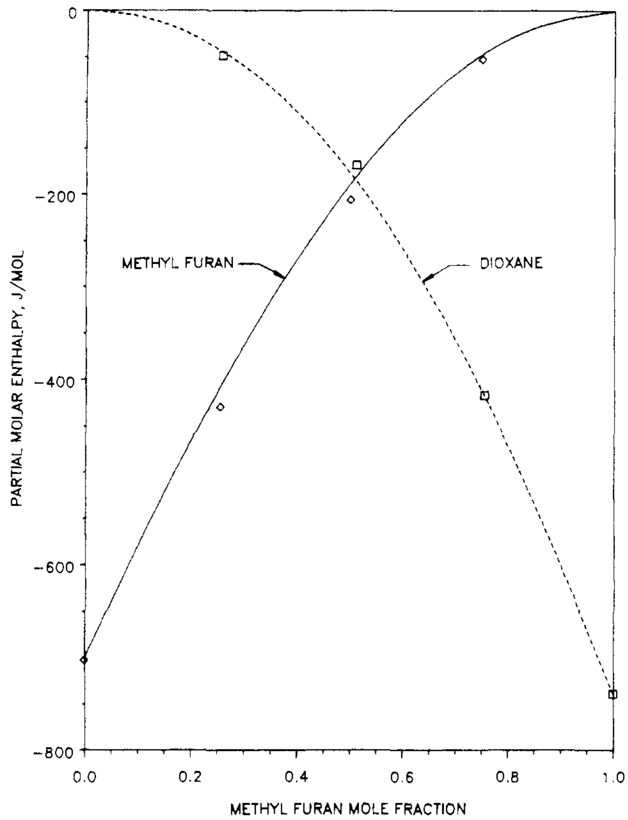

**Figure 2.** Experimental and calculated partial molar enthalpies for 2-methylfuran (—) and *p*-dioxane (– –) at 318.15 K. Calculated values are from the Gmehling equation, □ are data from Table II, and ◇ are data from Table III.

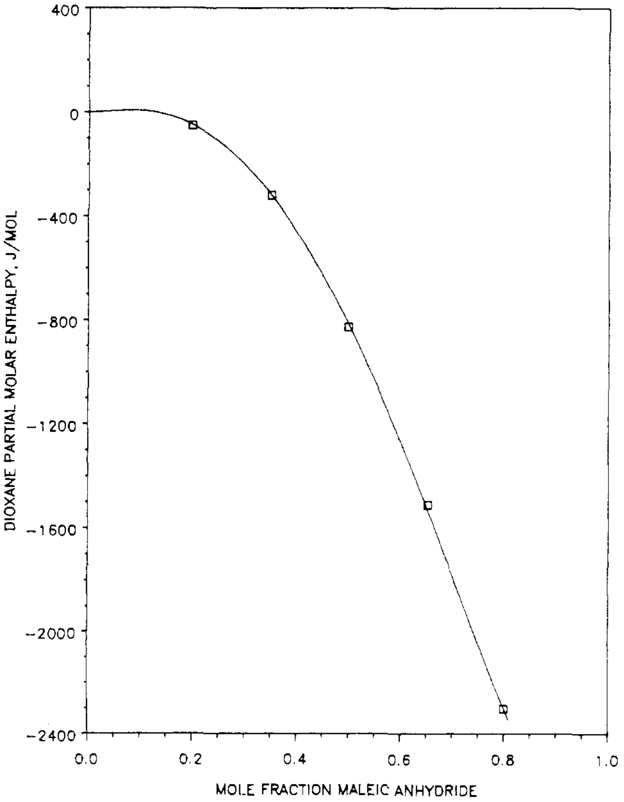

**Figure 3.** Experimental and calculated partial molar enthalpies of *p*-dioxane in the *p*-dioxane/maleic anhydride binary at 318.15 K. The curve is calculated with the Gmehling equation and the points are the experimental data in Table IV.

is shown in Figure 4 for comparison. Deviations for all eight points are listed in Tables IV and V, and it can be seen that except for the bad data point all deviations are within experimental uncertainty. The mean absolute deviation of these seven points from the correlation is 5.6 J/mol. The lowest mean absolute deviation which could be obtained for the various two-parameter correlations which were examined was 54 J/mol, well above experimental uncertainty. Figure 4 shows that although rather large heat effects would be obtained at higher maleic anhydride concentrations, the equation of state model predicts a negative enthalpy at maleic anhydride mole fractions less than about 0.28. Although the reliability of this prediction cannot be evaluated by any of the data in Tables IV and V, the negative values are consistent with the experimentally observed positive slope of Figure 1. In fact, all three of the experiments indicated by the data points in Figure 4 demonstrated similar slopes (positive). Three-parameter models (*13*) other than the Gmehling model were not evaluated.

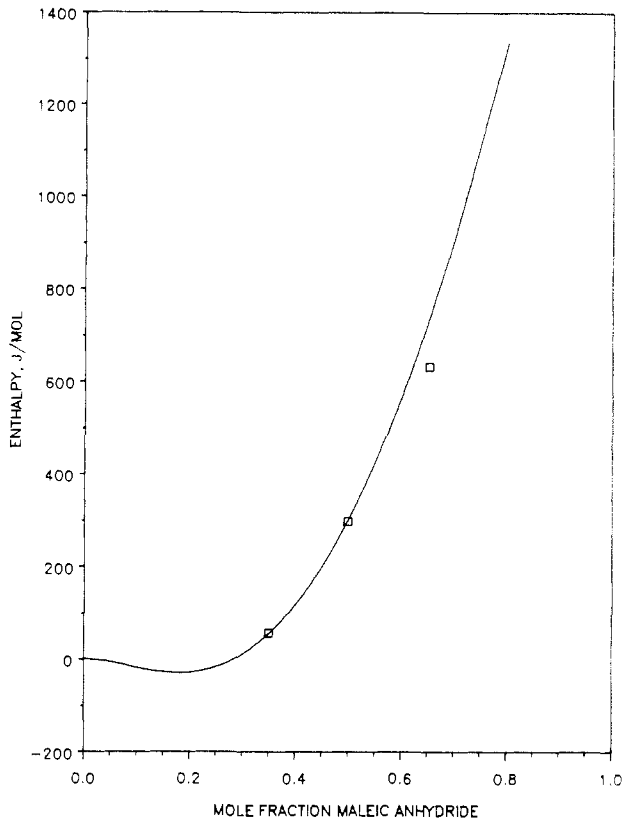

**Figure 4.** Experimental and calculated enthalpies of *p*-dioxane/maleic anhydride mixtures at 318.15 K. The curve is calculated with the Gmehling equation and the points are the experimental values in Table V.

## Summary

Calorimetric data at 318.15 K have been presented for the systems 2-methylfuran/*p*-dioxane and maleic anhydride/*p*-dioxane. Although the behavior of the first system could be described by a variety of two-parameter models three parameters were required to describe the behavior of the second binary. Thus both systems were fit to a three-parameter version of the Gmehling et al. (*4*) model. The immediate objective for this work was to develop the ability to calculate excess enthalpies and free energies for multicomponent mixtures containing the compounds which were studied. The Gmehling model can perform these calculations. It would be nice if model predictions could be compared to vapor–liquid equilibrium data as well as the enthalpy data which have been presented herein, but unfortunately, VLE data are not available. In fact, data on the solution behavior for any binaries which contain maleic anhydride are quite sparse and maleic anhydride properties cannot be predicted with UNIFAC. Thus, just the collection of data on these systems of polar molecules with their rather unusual molecular interactions, and the illustration of one method to successfully model this behavior, may ultimately be of more significance than the future application which we have in mind. That particular application is to successfully calculate the thermodynamic behavior of the reversible, liquid-phase reaction which occurs between maleic anhydride and 2-methylfuran in concentrated solutions and in the solvent, *p*-dioxane.

## Glossary

| | |
|---|---|
| $A_{nm}$ | constants in Gmehling equation, see eq 6 |
| $c$ | parameter in Gmehling equation, = 1 |
| $H$ | mixture enthalpy, J/mol |
| $\bar{H}_i$ | partial molar enthalpy of component i, J/mol |
| $\Delta H_i^v$ | enthalpy of vaporization of component i, J/mol |
| $\Delta H^\circ$ | parameter in Gmehling equation |
| $k_{ij}$ | binary interaction parameter in Gmehling equation |
| $K$ | reaction equilibrium constant |
| $N$ | moles of liquid |
| $P_{vpi}$ | vapor pressure of component i, bar |
| $R$ | gas constant |
| $\Delta S^\circ$ | parameter in Gmehling equation |
| $T$ | temperature, K |
| $T^*$ | pure-component parameter in Gmehling equation, K |
| $V$ | volume of vapor, $cm^3$ |
| $v^*$ | pure-component parameter in Gmehling equation, L/mol |
| $v$ | molar volume, L/mol |
| $x_i$ | mole fraction of component i |
| $z$ | compressibility factor |

*Subscripts*

| | |
|---|---|
| A | Diels-Alder adduct of 2-methylfuran and maleic anhydride |
| D | *p*-dioxane |
| MA | maleic anhydride |
| MF | 2-methylfuran |

*Superscripts*

| | |
|---|---|
| in | property of the injected solution |

*Greek Letters*

| | |
|---|---|
| $\gamma$ | activity coefficient |
| $\xi$ | reduced density, see eq 7 |
| $\pi$ | 3.14159 |

**Registry No.** *p*-Dioxane, 123-91-1; 2-methylfuran, 534-22-5; maleic anhydride, 108-31-6.

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