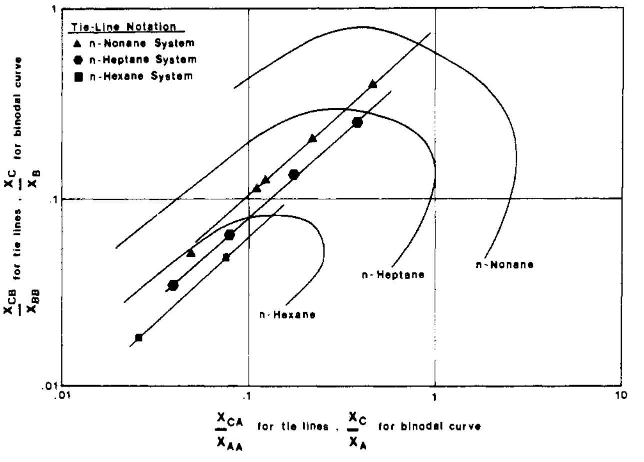

**Figure 2.** Hand (*3*) correlation for estimation of plait points.

| | |
|---|---|
| $X$ | weight fraction |
| $Z$ | constant in eq 2 |

*Subscripts*

| | |
|---|---|
| A | solvent liquid, methyl alcohol |
| B | extractant liquid, alkane |
| C | solute, trimethyl borate |
| AA | solvent in solvent rich layer |
| BB | extractant in extract layer |
| CA | solute in solvent rich layer |
| CB | solute in extract layer |

**Registry No.** Methanol, 67-56-1; trimethyl borate, 121-43-7; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-nonane, 111-84-2.

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# Density of Cyclodecane from 25 to 192 °C

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**The density of a purified sample of cyclodecane has been measured from 25 to 192 °C by densimetry. The results are well described by $d/(\mathrm{g\ cm^{-3}}) = 0.873\,40 - (0.784\,24 \times 10^{-3})(t/°\mathrm{C}) + (0.5005 \times 10^{-6})(t/°\mathrm{C})^2 - (0.2018 \times 10^{-8})(t/°\mathrm{C})^3$ with a standard deviation of $5 \times 10^{-5}$ g cm$^{-3}$.**

During an investigation of the physical properties of binary mixtures containing cyclodecane (*1*) we have measured the orthobaric density of cyclodecane at 17 temperatures from 25.69 to 191.80 °C. The starting material was obtained from the Chemical Samples Company; it was dried over anhydrous calcium chloride and then fractionated in a 1-m column packed with glass helices. The impurity level estimated by gas–liquid chromatography using a column packed with FFAP on Diatomite CLQ, and flame-ionization detection, and nitrogen carrier gas was 99.5 mol%. The refractive index was found to be 1.4714 in exact agreement with the value reported by Plattner and Hulstkamp (*2*).

The density measurements were carried out by using the actual hydrostatic density balance described by Hales and Gundry (*3*). The cell was calibrated with twice-distilled water by using the densities reported by Kell (*4*). The temperature was measured to ±3 mK using a platinum resistance thermometer and an Automatic Systems Laboratory Ltd ac resistance bridge that had been calibrated at the National Physical Laboratory, London. The results of the measurements are listed in column 2 of Table I; we estimate their precision to be about $\pm 7 \times 10^{-4}$ g cm$^{-3}$. They are well described by the expression

$$d/(\mathrm{g\ cm^{-3}}) = 0.873\,40 - (0.784\,24 \times 10^{-3})(t/°\mathrm{C}) + (0.5005 \times 10^{-6})(t/°\mathrm{C})^2 - (0.2018 \times 10^{-8})(t/°\mathrm{C})^3 \quad (1)$$

Table I. Densities ($d$) of Cyclodecane at Different Temperatures ($t$)

| | $d/(\mathrm{g\ cm^{-3}})$ | | |
|---|---|---|---|
| $t$/°C | exptl | eq 1 | lit.[a] |
| 25.691 | 0.853 62 | 0.853 55 | 0.854 21 |
| 29.691 | 0.850 49 | 0.850 51 | 0.851 18 |
| 38.098 | 0.844 05 | 0.844 14 | 0.844 89 |
| 45.952 | 0.838 22 | 0.838 23 | 0.839 13 |
| 54.075 | 0.832 14 | 0.832 14 | 0.833 29 |
| 62.584 | 0.825 80 | 0.825 80 | 0.827 32 |
| 71.239 | 0.819 35 | 0.819 34 | 0.821 40 |
| 80.222 | 0.812 66 | 0.812 67 | 0.815 44 |
| 89.239 | 0.806 00 | 0.805 97 | 0.809 65 |
| 99.034 | 0.798 71 | 0.798 68 | 0.803 59 |
| 108.800 | 0.791 43 | 0.791 40 | 0.797 80 |
| 120.056 | 0.782 92 | 0.782 97 | 0.791 46 |
| 131.000 | 0.774 70 | 0.774 72 | 0.785 64 |
| 142.289 | 0.766 13 | 0.766 13 | |
| 153.967 | 0.757 15 | 0.757 15 | |
| 166.250 | 0.747 60 | 0.747 58 | |
| 191.798 | 0.727 16 | 0.727 16 | |

[a] Reference 5.

with a standard deviation of $5 \times 10^{-5}$ g cm$^{-3}$. Values calculated from this expression are listed in column 3 of Table I. The only other results we have been able to find in the literature that extend over a reasonable range of temperature are those of Meyer and Hotz (*5*) and the fourth column contains values at our temperatures calculated from their fitting equation. The agreement is reasonably good at the lower end of the common temperature range but becomes increasingly poor at the upper end of the range. At 20 °C our extrapolated value of 0.8579 compares reasonably well with that quoted by Plattner and

Hulstkamp (*2*), 0.8585, and that by Tarova-Pollack, 0.8581 (*6*).

## Glossary

$d$ density, g cm$^{-3}$
$t$ temperature, °C

**Registry No.** Cyclodecane, 293-96-9.

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# Excess Enthalpy and Liquid–Liquid Equilibrium Surfaces for the Cyclohexane–2-Propanol–Water System from 293.15 to 323.15 K

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**Excess enthalpy data and liquid–liquid equilibrium (LLE) coexistence curves have been measured for ternary mixtures containing cyclohexane, 2-propanol, and water. Binary heats of mixing for cyclohexane–2-propanol and 2-propanol–water mixtures were measured at 293.15, 298.15, 303.15, and 323.15 K over the entire composition range with a Tronac flow calorimeter. Ternary, single-phase heats of mixing were measured at 293.15, 298.15, 303.15, and 308.15 K. Ternary liquid–liquid coexistence curves were measured at 298.15, 303.15, and 308.15 K by using the titration technique; tie lines were obtained from Karl Fischer water analyses of coexisting phases in conjunction with the measured coexistence curves. These results have been used to evaluate the explicit temperature dependence of liquid mixture models currently used to correlate LLE data against the Gibbs–Helmholtz identity which relates excess enthalpy and excess free energy. Existing models were found to be inadequate to predict phase behavior from excess enthalpy data using this identity. A recently proposed enthalpy-based method, previously used for binary systems, can be used to obtain reasonable binodal curves from heats of mixing although predicted tie lines are unreliable.**

## Introduction

Because of the importance of liquid–liquid equilibria (LLE) data to development of chemical and physical processes such as liquid–liquid extraction and tertiary oil recovery, efforts have been made to correlate LLE data using the same excess free energy ($g^E$) models that have proved effective in correlating vapor–liquid equilibrium (VLE) data (*1*, *2*). On the other hand, if the temperature dependence of existing $g^E$ models is correct, then predictions of LLE data (as opposed to correlation of the experimental data) from excess enthalpy data, $h^E$, should be possible based on the Gibbs–Helmholtz equation

$$h^E = [\partial(g^E/T)/\partial(1/T)]_{P,x} \qquad (1)$$

In theory, $g^E$ models could be differentiated to obtain the corresponding $h^E$ function in terms of the adjustable parameters of the models. These parameters could then be used in the original $g^E$ function to predict LLE. The agreement of such predictions with experimental data constitutes a stringent test of the model's assumed temperature dependence. The use of such a technique for prediction of binary LLE can be found elsewhere (*3*) and is tested here for ternary LLE. Generally, $h^E$ and LLE data have been correlated separately by using these models (*1*, *2*, *4*, *5*), but limited simultaneous fitting of LLE and $h^E$ data has been done (*6*).

We report here experimental excess enthalpy data and LLE coexistence curves for the cyclohexane–2-propanol–water system over a small temperature range. These data have been used to test the explicit temperature dependence of liquid mixture models currently used for LLE correlation and that of an enthalpy-based local-composition model (EBLCM) recently proposed by Rowley and Battler (*3*) for prediction of binary LLE from $h^E$ data. That method has been extended to ternary systems in this work.

## Experimental Section

Heats of mixing were measured with a commercial, Tronac Model 450/550, isothermal calorimeter with a flow insert of design similar to that of Christensen et al. (*7*). As the calorimeter has been adequately described elsewhere, only modifications made in this laboratory will be detailed here. Two ISCO high-precision, positive-displacement, syringe-type pumps were used to establish constant flow rates through the flow mixing cell. The pumps' stepper motors were driven at constant but variable flow rates by a North Star Horizon microcomputer and a frequency-to-voltage converter built by Alan Pennock, a laboratory technician. The pumps (of variable flow rate from 0.008 to 200 mL/h) were calibrated over the range 0.10–1.30 mL/min by using replicate flow runs of distilled water. Pump calibrations were linear and indicated a reliability of better than 0.2% of the set flow rate over the entire calibrated range; the maximum observed deviation in replicate calibration runs was 0.4% at one of the slower flow rates. The pumps were thoroughly cleaned whenever a change in components was made and thoroughly rinsed and purged several times with the new fluid whenever a new component or mixture was introduced into the pump cylinders. Additionally, measured densities of the fluid before and after pumping were compared as a contamination check.

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