



Figure 5. Detail of isotherms near critical point of methane (methane-*n*-pentane system)

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Isobaric Binary Vapor-Liquid Equilibria in Cyclohexane-*tert*-Butyl Alcohol and 2,4-Dimethylpentane-*tert*-Butyl Alcohol Systems

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Measurements of binary vapor-liquid equilibria at 760 mm Hg pressure are reported for cyclohexane and 2,4-dimethylpentane separately with *tert*-butyl alcohol. The thermodynamic consistency of the experimental data under isobaric conditions is checked by Herington's area test, and the data are satisfactorily correlated by the two-parameter Wilson equation for both binary systems.

Cyclohexane and 2,4-dimethylpentane (2,4-DMP) are close boiling hydrocarbons forming a minimum boiling azeotrope (6) at 80.2°C. Their separation poses a problem and is facilitated by the use of polar solvents. Such situations are encountered in practical applications (74) during the purification of cyclohexane from commercial naphtha streams. Since most distillation processes are carried out at constant pressure rather than at constant temperature, temperature-composition (*t*-*x*-*y*) curves are more desirable for engineering calculations than pressure-composition curves, although from theoretical considerations the latter are preferred.

As part of our study of the vapor-liquid equilibrium (VLE) data of close boiling hydrocarbons in the presence of polar solvents, the VLE measurements of cyclohexane and 2,4-DMP have been studied with *tert*-butyl alcohol (TBA) at 760 mm Hg pressure. The generation of such binary equilibrium data on hydrocarbon-solvent systems helps in the development of correlations for testing the capability of predictive methods for multicomponent systems from binary data alone and also in better understanding the molecular processes in nonideal solutions. To the authors' knowledge, the VLE data

of these two binary systems have not been reported previously.

Experimental

Materials. Cyclohexane and 2,4-DMP (manufactured by Phillips Petroleum Co.) were of 99.0 mol % purity and were used as such without further purification. Tertiary butyl alcohol (obtained from M/S British Drug Houses, India) was dried over anhydrous calcium chloride and further purified by fractional distillation at a high reflux ratio in an Oldershaw column by collecting a heart cut and discarding the first 10% distillate and the last 15% residue. The important physical properties of the three components reported in Table I compare well with the literature values (7, 10).

Apparatus. The VLE data for the two binaries were studied in a modified Fowler-Norris (2) still with provision for vapor and liquid circulation. The reboiler, Cottrell pump, and equilibrium chamber were thoroughly lagged to avoid slugs of liquids rising up with vapors and for proper separation of vapor and liquid samples in the equilibrium chamber. The temperature in the equilibrium chamber was measured with the aid of mercury-in-glass thermometers within $\pm 0.05^\circ\text{C}$ after applying the following correction for the exposed stem (3):

$$t_c = t_o + 0.000158 \times l (t_o - t_m)$$

where t_c is the corrected temperature, t_o and t_m are the observed and mean temperatures of the exposed stem, respectively, and l is the length in $^\circ\text{C}$ of the exposed stem. The pressure in the system was maintained at 760 ± 0.5 mm Hg with the help of a suitable pressure-regulating device. To establish the equilibrium time, a number of trial runs on each system

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were carried out for the duration of 2, 3, and 4 hr. The results obtained in 3 and 4 hr were the same. The still was therefore operated for 4 hr, which is 1 hr more than required for establishment of equilibrium. About 2 ml each of the equilibrated samples was withdrawn in each case for the composition measurements.

Analyses. Binary cyclohexane-*tert*-butyl alcohol system. The compositions of equilibrated vapor and liquid phases were determined by refractive index measurements at 20°C, since there is a wide difference in the refractive indices of the two components constituting this binary system. For this purpose, a series of synthetic mixtures of the two components was made by exact weighing, and their index of refraction determined at 20°C to cover the whole range of composition. An Abbe-type refractometer with an accuracy of ± 0.0001 unit was used. The prism temperature was maintained within $\pm 0.1^\circ\text{C}$ by circulating a coolant from a constant temperature bath. The refractive index measurements were done immediately after withdrawing the equilibrated samples of both phases to eliminate any chance of change of composition.

The refractive index-composition data for the system are reported in Table II. The accuracy of the composition measurements is estimated to be within ± 0.003 mole fraction for both components.

Binary 2,4-DMP-*tert*-butyl alcohol system. In this case, the compositions of the equilibrated samples were determined by density measurements because the difference in the refractive indices of the two components is very small, whereas the difference in their density values is appreciable. A series of synthetic mixtures was prepared by weighing exactly appropriate amounts of the two components to cover the entire range. The densities of these mixtures were determined at $20^\circ \pm 0.1^\circ\text{C}$ with a 1-ml capacity bicapillary pycnometer previously calibrated with the double distilled pure water. The

Table I. Physical Properties of Chemicals Used

Component	Density at 20°C		Refractive index at 20°C		Normal bp, °C
	Exptl	Lit	Exptl	Lit	
Cyclohexane	0.7784	0.7785	1.4262	1.42623	80.7
2,4-Dimethyl-pentane	0.6726	0.6727	1.3814	1.38145	80.5
<i>tert</i> -Butyl alcohol	0.7855	0.7856	1.3837	1.38380	82.2

Table II. Composition-Refractive Index/Density Data for Two Binary Systems

Cyclohexane(1)-TBA(2) system		2,4-DMP(1)-TBA(2) system	
x_1	Refractive index at 20°C	x_1	Density at 20°C
0.000	1.3837	0.000	0.7855
0.044	1.3880	0.050	0.7765
0.111	1.3908	0.071	0.7729
0.167	1.3930	0.154	0.7590
0.256	1.3970	0.210	0.7499
0.365	1.4000	0.249	0.7435
0.466	1.4032	0.312	0.7350
0.572	1.4080	0.425	0.7200
0.672	1.4108	0.512	0.7100
0.754	1.4160	0.624	0.6995
0.840	1.4184	0.734	0.6901
0.885	1.4213	0.854	0.6815
0.953	1.4237	0.935	0.6760
1.000	1.4262	1.000	0.6726

pycnometer containing the sample was kept in a constant temperature bath ($\pm 0.1^\circ\text{C}$) for about 30 min to enable the sample to attain the desired temperature. The data on density-composition measurements for the 2,4-DMP-TBA system are also given in Table II. The reproducibility in density determinations was of the order of $\pm 0.003 \text{ g/cm}^3$; therefore, the accuracy in composition measurements is estimated to be ± 0.0030 mole fraction for each component.

Results and Discussion

The liquid-phase activity coefficients were calculated using the following rigorous equation (16):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^s} + \frac{(B_{ii} - v_i^L)(P - P_i^s)}{RT} + \frac{P \delta_{ii}(1 - y_i)^2}{RT} \quad (1)$$

where $\delta_{ij} = 2 B_{ij} - B_{ii} - B_{jj}$ and the pure component second virial coefficients and cross coefficients B_{ij} ($i \neq j$) are functions of temperature only for a given binary system.

This equation takes into account the corrections for real gas behavior, nonideal solution effects in the vapor phase, and deviations of vapor pressures from liquid-phase fugacities. However, it assumes that the vapor-phase of the mixture as well as the pure component vapor are adequately described by the volume-explicit virial equation of state truncated after the second term and also that pure component liquid volumes are incompressible over the pressure range under consideration (8).

The second virial coefficients of the nonpolar components, viz., cyclohexane and 2,4-DMP, were calculated with the empirical correlation of Pitzer and Curl (7) based on a three-parameter theory of corresponding states as given by Equation 2:

$$\frac{P_{ci} B_{ii}}{RT_{ci}} = f_{B(T_R)}^{(0)} + \omega_i f_{B(T_R)}^{(1)} \quad (2)$$

where $f_{B(T_R)}^{(0)}$ and $f_{B(T_R)}^{(1)}$ are empirically determined functions.

For the polar component TBA, the recent empirical correlation of Tsouopoulos (15) given in Equation 3 was used:

$$\frac{P_{ci} B_{ii}}{RT_{ci}} = f_{(T_R)}^{(0)} + \omega_i f_{(T_R)}^{(1)} + \frac{a}{T_R^6} - \frac{b}{T_R^8} \quad (3)$$

The cross coefficient B_{ij} in the mixing term, δ_{ij} , was calculated using suitable mixing rules recommended by Prausnitz et al. (9).

The critical temperatures and pressures required for the calculation of second virial coefficients of the two hydrocarbon components and the polar solvent were taken from published values (1, 17). The acentric factor, ω_i , for the two hydrocarbons and the TBA as reported in the literature (13, 15) was utilized for calculation of second virial coefficients. The liquid molar volumes for hydrocarbons were obtained by fitting three values into the quadratic equation (9), and for the *tert*-butyl alcohol, it was estimated by the correlation of Yen and Woods (20). The pure component vapor pressures were calculated by use of the Antoine equation in the form:

$$\log_{10} P = A - \frac{B}{C + t}$$

and by utilizing various constants reported by Dreisbach (1) for cyclohexane and 2,4-DMP and by Hala et al. (4) for TBA. The critical volumes required for calculation of the second virial cross coefficient of the three components are reported by Reid and Sherwood (12).

The VLE data for the system cyclohexane(1)-TBA(2) are reported in Table III along with the experimental activity coef-

efficient values. Table IV gives data for the 2,4-DMP(1)-TBA(2) system. Both of the hydrocarbon-alcohol systems form a minimum boiling azeotrope, and azeotropic data are in agreement with the data reported by Horsley (6).

The experimental data were tested for thermodynamic consistency under isobaric conditions by using Herington's area test method (5). The parameters D and J for the two systems are:

System	D	J
Cyclohexane-TBA	1.28	4.62
2,4-DMP-TBA	2.74	4.71

where

$$D = \frac{\text{Area above } x\text{-axis} - \text{area below } x\text{-axis}}{\text{Area above } x\text{-axis} + \text{area below } x\text{-axis}} = \frac{\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1}{\int_0^1 \left| \ln \frac{\gamma_1}{\gamma_2} \right| dx_1} \text{ and } J = 150|\theta|/T_{\min}$$

Since $D < J$ for both systems, Herington's area tests indicate that the experimental data for both systems are thermodynamically consistent.

In the present investigation, the experimental data were correlated with the two-constant Wilson equation (18) given below which gave a slightly better fit of the experimental data compared to other correlating equations, viz., Redlich-Kister (11) and Wohl-Margules (19):

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (4a)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (4b)$$

where

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(-\frac{\lambda_{12} - \lambda_{22}}{RT}\right)$$

The advantage of the Wilson equation is that it has built-in temperature dependence in the quantities $(\lambda_{ij} - \lambda_{ii})$ and $(\lambda_{ij} - \lambda_{jj})$ which are independent of temperature over a modest temperature interval. The constants in these equations were obtained by a least-squares fit of the experimental activity coefficients using a nonlinear multiple regression technique in an IBM 360 computer.

The constants of the correlating equations used in this investigation are:

System	Λ_{12}	Λ_{21}
Cyclohexane-TBA	0.7177	0.6826
2,4-DMP-TBA	0.7552	0.5246

Based on the values of calculated activity coefficients, the average absolute deviation between experimental and calculated values of y given by the correlation:

$$\overline{\Delta y_i} = \frac{\sum_j^N |\Delta y_i|}{n}$$

where $y_i = y_{\text{exptl}} - y_{\text{calcd}}$ is 0.012 mole

where $y_i = y_{\text{exptl}} - y_{\text{calcd}}$ is 0.012 mole fraction for the system cyclohexane-TBA and 0.016 mole fraction for the 2,4-

DMP-TBA system. The maximum percent deviation calculated as:

$$\text{Max \% dev in } y = \frac{y_{\text{exptl}} - y_{\text{calcd}}}{y_{\text{exptl}}} \times 100$$

is about 5.5% for cyclohexane-TBA and 6.0% for 2,4-DMP-TBA. This deviation is not large considering the experimental inaccuracies involved and the limitations of the correlating equation.

Conclusions

The isobaric VLE data for two new systems (hydrocarbon-alcohol) have been generated. The data will be useful for the design of distillation columns and for testing the accuracy of predictive methods.

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Table III. Vapor-Liquid Equilibrium Data for Cyclohexane(1)-TBA(2) System at 760 mm Hg

Liquid molar compn, x_1	Vapor molar compn, y_1	Activity coefficients		Equil temp, °C
		γ_1	γ_2	
0.048	0.105	1.740	1.038	81.2
0.121	0.190	1.648	1.048	79.6
0.164	0.247	1.643	1.087	78.3
0.185	0.274	1.640	1.124	77.7
0.258	0.350	1.579	1.153	76.0
0.296	0.394	1.550	1.171	75.2
0.340	0.436	1.500	1.244	74.5
0.384	0.479	1.481	1.263	73.8
0.511	0.570	1.418	1.446	72.1
0.630	0.630	1.334	1.595	71.3
0.665	0.639	1.280	1.707	71.4
0.710	0.678	1.244	1.726	72.0
0.765	0.711	1.186	1.826	72.6
0.892	0.846	1.102	1.920	75.7
0.919	0.881	1.082	1.908	76.8
0.932	0.900	1.076	1.886	77.3
0.960	0.937	1.050	1.906	78.5
0.965	0.944	1.037	1.889	79.0

Table IV. Vapor-Liquid Equilibrium Data for 2,4-DMP(1)-TBA(2) System at 760 mm Hg

Liquid molar compn, x_1	Vapor molar compn, y_1	Activity coefficients		Equil temp, °C
		γ_1	γ_2	
0.053	0.100	2.020	1.051	79.4
0.158	0.257	1.837	1.137	76.6
0.177	0.280	1.821	1.161	75.8
0.196	0.303	1.806	1.169	75.4
0.220	0.332	1.781	1.172	75.0
0.281	0.383	1.673	1.227	73.6
0.326	0.432	1.635	1.240	72.9
0.368	0.462	1.558	1.270	72.6
0.409	0.514	1.501	1.289	71.9
0.499	0.562	1.435	1.398	71.4
0.601	0.621	1.342	1.509	71.2
0.702	0.665	1.252	1.750	71.3
0.804	0.720	1.121	1.861	73.0
0.864	0.781	1.068	2.128	74.8
0.932	0.882	1.041	2.239	77.2
0.987	0.976	1.014	2.382	79.8

Nomenclature

$\Lambda_{12}, \Lambda_{21}$ = Wilson parameters
 B_{ii} = pure component second virial coefficient, cm^3/mol
 B_{ij} = second virial cross coefficient, cm^3/mol
 D = Herington's parameter
 $f^{(0)}, f^{(1)}$ = dimensionless terms in Equation 3 of Tsonopoulos
 J = Herington's parameter
 P = total pressure, atm
 P_i^s = saturated vapor pressure of pure component i , atm
 P_{ci} = critical pressure of i , atm
 R = gas constant, $\text{cm}^3\text{-atm}/\text{deg-mol}$
 T = temperature, K
 T_{ci} = critical temperature of i , K
 T_R = reduced temperature
 V_i^L = liquid molar volume of i , cm^3/mol
 x_i = liquid molar composition
 y_i = vapor molar composition

Greek Letters

γ_i = liquid-phase activity coefficient of component i
 θ = range of boiling points of systems, $^\circ\text{C}$
 $\lambda_{12} - \lambda_{11}$ = energy parameters of Wilson equation, cal/mol
 $\lambda_{12} - \lambda_{22}$ = energy parameters of Wilson equation, cal/mol
 ω_i = acentric factor of component i

Subscripts

1, 2 = 1: cyclohexane in first system and 2,4-DMP in second system; 2: TBA in both cases

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High-Temperature Solubilities of Calcium Sulfate Hemihydrate and Anhydrite in Natural Seawater Concentrates

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Solubilities of the high-temperature calcium sulfate modifications, hemihydrate and anhydrite, are measured in natural seawater at temperatures up to 165°C. Scaling thresholds or concentration-temperature limits are determined over a temperature range of 91–162°C. A new graphical method of scaling threshold evaluation is described. Experimental data presented here are compared with literature values. Scaling thresholds calculated from the extended Debye-Hückel theory are in good agreement with the experimental results. A complete scaling threshold diagram for hemihydrate and anhydrite is also developed. Scaling threshold evaluation is important in the operation of desalting equipment, boilers, and cooling towers.

Understanding the solution chemistry of high-temperature calcium sulfate modifications is vitally important to the design and operation of saline water evaporators. Both hemihydrate and anhydrite scale may deposit by concentrating natural wa-

ters at temperatures above the ambient boiling point. The resultant scale composition cannot be predicted solely from solubility considerations but also depends on rates of transformation of metastable hemihydrate to anhydrite, the stable phase. The goal of modern distillation technology is directed toward increasing brine concentrations and/or operating temperatures so that lower product water costs can be achieved.

Nature has apparently contrived a system which opposes either of these tendencies because of potential scaling. First, solutions are brought closer to saturation as concentration increases. Second, the solubilities of both hemihydrate and anhydrite fall off rapidly with increasing temperature. Third, the rate of conversion of hemihydrate to anhydrite is accelerated at higher temperatures and brine concentrations. The third phenomenon severely limits evaporator residence time since anhydrite is so insoluble that practical evaporation cannot be achieved under conditions where this scale form is expected.

A most effective tool for prediction of scaling conditions is the scaling threshold diagram described by Glater and Fung (5) and Glater (3) and commonly referred to in the literature as a solubility diagram. Scaling thresholds represent a match of temperature and brine concentration corresponding to

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