Partial Miscibility Phenomena in the Ternary System Ethane–*n*-Hexadecane–*n*-Eicosane

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Pressure, composition, and molar volumes of the two liquid phases which coexist for constant molar ratio mixtures of *n*-hexadecane and *n*-eicosane with ethane are presented at representative temperatures along the phase (L_1-L_2-V) border curves. The lower critical solution temperature (LCST) and type *K* points are a linear function of the original mole fraction of *n*-hexadecane in *n*-eicosane. The three-phase behavior disappears when the mole fraction *n*-hexadecane in *n*-eicosane is 0.660 and the temperature and pressure are 40.15° C. and 54.45 atm., respectively. The coexisting liquid phases were sampled at several temperatures and over-all molar ratios of *n*-hexadecane to *n*-eicosane. These data were represented in terms of distribution coefficients.

THE lowest normal saturated hydrocarbon that is partially immiscible with ethane is *n*-nonadecane (*4*). Kim *et al.* (*2*) have extended the study to the ternary system of ethane, *n*-nonadecane, and *n*-eicosane at varying molar ratios of *n*-nonadecane to *n*-eicosane. In this system, both *n*-nonadecane and *n*-eicosane are partially immiscible with ethane when combined as binary mixtures. This study reports data on the ternary system of ethane, *n*-hexadecane, and *n*-eicosane. The binary system consisting of ethane and *n*-hexadecane is miscible in all proportions. By substituting *n*-hexadecane for *n*-nonadecane, further knowledge of the partial miscibility phenomena has been gained which will eventually lead to an understanding of the phenomenon and an assessment of its possibly commercial application. Detailed composition and molar volume data hve been obtained for the two liquid phases up to the *n*-hexadecane–*n*-eicosane composition where the partial immiscibility disappears. Samples of the two immiscible liquid phases have been analyzed chromatographically to assess the heavy hydrocarbon separational effect between the two liquid phases.

EXPERIMENTAL

The apparatus, experimental techniques, and chemicals were reported previously (*1–5, 7*). Binary mixtures of *n*-hexadecane and *n*-eicosane were prepared to known compositions by weighing on an analytical balance, stored in sealed bottles, and transferred to the equilibrium cell via a pipet, with a hypodermic tubing extension to clear the long thin neck of the cell.

Experimental runs to determine detailed composition and molar volume data were performed in a 10-ml. borosilicate glass cell. The material added to the cell was weighed on an analytical balance. Accurately known quantities of ethane were added to the cell from a high pressure reservoir via a positive displacement mercury pump. The pressure inside the equilibrium cell was taken on a Bourdon tube gage, which was frequently compared with an accurate dead weight gage. The pressures are believed to be correct to ±0.07 atm. Temperatures of the equilibrium phases were taken on a platinum resistance thermometer which was immersed in the bath liquid. The thermometer was calibrated using an NBS platinum resistance thermometer. The temperatures of the equilibrium cell are believed to be correct to ±0.02° C. Equilibrium of the phases within the cell was obtained by stirring the contents of the cell with a magnetically actuated steel ball, which was inside the cell. Equilibrium was assumed to have been attained when no change in pressure or liquid level could be observed after stirring of the cell contents for time periods up to 15 minutes.

By varying the amount of heavy hydrocarbon charged to the cell and the amount of ethane admitted, either the mass of the heavier (L_1) or the lighter (L_2) liquid phase could be maximized with only small amounts of the minor liquid phase and vapor phase present. Thus the composition and molar volume of points on each leg of the (L_1-L_2-V) phase border curves were determined by stoichiometric analysis.

The sampling technique and analysis were presented in detail by McCaffrey (*6*) and summarized by Kim *et al.* (*2*). The samples of the two liquid phases were withdrawn from a 90-ml. sight glass rocking bomb, through 0.02-inch hypodermic tubing. The ethane was allowed to flash to the atmosphere, while 15- to 20-ml. samples of liquid were being collected in small glass receptacles. A Beckman GC-2A gas-liquid chromatograph was used to analyze the samples. The chromatograph was calibrated with the samples used in the sampling and stoichiometric work. The ethane used (Matheson Co.) was purified as described by Ma and Kohn (*5*). The heavy hydrocarbons were the pure grade (Humprey-Wilkinson Corp.) and were stated to be 99 mole % minimum purity. They were used without further purification.

RESULTS

Table I presents smoothed temperature, pressure, composition, and molar volume data on the liquid phase for five molar ratios of *n*-hexadecane to *n*-eicosane. The average deviations of the experimental data on the phase border curves are: ±0.05 atm. for the pressure, ±0.008 for the mole fraction ethane, and ±1.49 ml. per gram mole for the molar volume.

Figure 1 presents the smoothed composition data for the five molar ratios of *n*-hexadecane to *n*-eicosane and includes the curve for the binary system of ethane and *n*-eicosane presented by Kim (*1*). The data in Figure 1 and Table I can be used to show that a linear relationship exists between the temperature range ($T_{\text{type } K} - T_{\text{LCST}}$) of immiscibility and the mole fraction of *n*-hexadecane on an ethane free basis. When the LCST temperature and type *K* temperatures were plotted *vs.* the ethane-free mole fraction *n*-hexadecane, nearly straight lines intersecting at 0.660 mole fraction *n*-hexadecane resulted. In other words, a partial miscibility region exists for *n*-hexadecane and *n*-eicosane with ethane when the mole fraction *n*-hexadecane

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in *n*-eicosane is less than 0.660. The temperature and pressure corresponding to this point are 40.15° C. and 54.45 atm., respectively.

The results of the liquid phase sampling work are presented in Table II. The difference in the molar ratios of *n*-hexadecane to *n*-eicosane shows the existence and extent of the separational effect. The results were correlated

Table I. Smoothed Values of Pressure, Composition, and Molar Volume of the Two Liquid Phases Coexisting along Three-Phase (L_1-L_2-V) Border Curves

		L_1 Phase		L_2 Phase	
Temp., °C.	Press., Atm.	Mole fraction ethane	Molar volume, ml./g. mole	Mole fraction ethane	Molar volume, ml./g. mole
		R = 0.1442			
34.76[a]	49.93	0.9720	94.8	0.9720	94.8
35.00	50.17	0.9595	93.3	0.9740	96.8
35.40	50.63	0.9528	93.1	0.9883	99.0
35.80	51.08	0.9483	93.2	0.9904	101.0
36.20	51.53	0.9444	93.4	0.9924	103.7
36.60	51.98	0.9408	93.2	0.9940	107.5
37.00	52.44	0.9382	92.6	0.9959	116.2
37.13[b]	52.55	0.9375	92.3	0.9975	130
		R = 0.2837			
35.75[a]	50.83	0.9735	94.8	0.9735	94.8
36.00	51.15	0.9604	93.3	0.9862	99.7
36.40	51.60	0.9542	93.2	0.9896	102.6
36.80	52.06	0.9495	93.4	0.9917	105.8
37.20	52.52	0.9457	93.6	0.9938	112.2
37.58[b]	52.95	0.9425	89.6	0.9975	135
		R = 0.5552			
36.99[a]	52.25	0.9760	94.9	0.9760	94.9
37.40	52.71	0.9595	93.4	0.9915	107.9
37.80	53.17	0.9540	92.7	0.9940	115.8
38.20	53.63	0.9507	89.0	0.9965	129.0
38.23[b]	53.65	0.9905	88.5	0.9975	135
		R = 1.0450			
38.50[a]	53.65	0.9780	95.0	0.9780	95.0
38.60	53.73	0.9727	93.8	0.9760	103.2
38.80	54.02	0.9670	93.0	0.9902	110.0
39.00	54.24	0.9637	90.5	0.9937	117.5
39.12[b]	54.37	0.9625	87.5	0.9970	135
		R = 1.4691			
39.40[a]	54.60	0.9795	95.0	0.9795	95.0
39.50	54.71	0.9745	93.0	0.9870	109.0
39.60	54.86	0.9720	91.5	0.9915	120.0
39.65[b]	54.90	0.9710	87.0	0.9965	135

[a] LCST point. [b] Type K singular point.

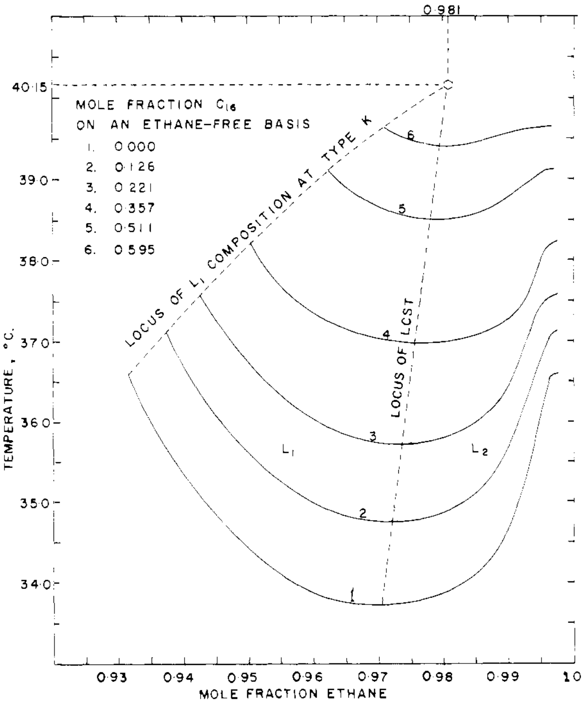

Figure 1. Smoothed phase border curves in the L_1-L_2-V region

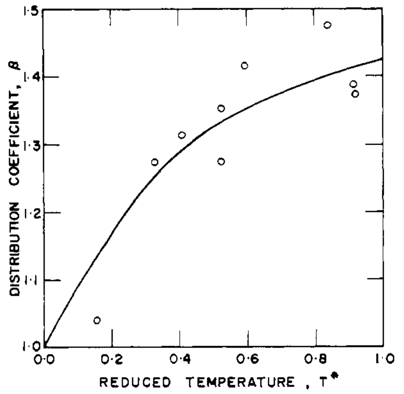

Figure 2. Distribution coefficient vs. reduced temperature for C_2-C_{16}-C_{20}

Table II. Separational Effect in Ethane–*n*-Hexadecane–*n*-Eicosane System

			Molar Ratio *n*-Hexadecane to *n*-Eicosane		Distribution Coefficient		
Temp., °C.	Press., Atm.	Mole Fraction Hexadecane Charged to Cell	Liquid 1, R_1	Liquid 2, R_2	β_{exp}	β_{smooth}	Reduced Temp., T^*
36.00	51.20	0.127	0.138	0.187	1.355	1.344	0.524
36.00	51.24	0.127	0.149	0.190	1.275	1.344	0.524
36.75	51.98	0.127	0.133	0.195	1.467	1.413	0.840
36.94	52.38	0.127	0.144	0.200	1.389	1.425	0.920
37.17	52.04	[a]	0.494	0.513	1.040	1.140	0.160
37.50	52.70	0.357	0.510	0.647	1.317	1.304	0.411
37.69	52.59	[a]	0.424	0.602	1.421	1.363	0.596
38.60	53.96	0.511	0.729	0.928	1.274	1.263	0.329
39.00	54.36	0.511	0.778	1.063	1.366	1.426	0.924

[a] LCST and type K temperatures determined experimentally to assess reduced temperature, T^*. Mole fraction hexadecane charged to cell not known at start of run.

empirically in the manner used by Kim *et al.* (*2*). A distribution coefficient (β) and reduced temperature (T^*) were defined as follows:

$$\beta = R_2/R_1 \tag{1}$$

and

$$T^* = (T - T_{\text{LCST}})/(T_{\text{type } K} - T_{\text{LCST}}) \tag{2}$$

The resulting distribution coefficients and reduced temperatures are tabulated in Table II. Both the experimental distribution coefficients and smoothed distribution coefficients are presented in Table II. The smoothed distribution coefficients were determined from a modified version of a least squares computer program. A regular minimizing type of least squares program produces a polynomial fit of the data with the minimal standard deviation from the experimental data regardless of the possibility or impossibility of maxima or minima in the experimental variables. The modified version of the least squares program, which was used here, was biased by the authors' feeling that the largest value of β should be at the type K temperatures. The resulting smooth data presented in Table II and shown in Figure 2 fit the data with a standard deviation of ±0.054. Figure 2 appears to indicate that the distribution coefficient is not a function of the overall heavy hydrocarbon composition in the cell. If the data presented here on the separational effect on *n*-hexadecane and *n*-eicosane are compared with those of Kim *et al.* (*2*) on *n*-nonadecane and *n*-eicosane, evidently the separational effect is appreciably greater in the *n*-hexadecane–*n*-eicosane system. Thus the separational effect increases with an increase in the carbon number difference between the two heavy hydrocarbons.

NOMENCLATURE

L_1 = liquid phase less rich in ethane
L_2 = liquid phase more rich in ethane
LCST = lower critical solution temperature (the L_1 phase is critical with the L_2 phase in the presence of a vapor phase)
R = molar ratio of *n*-hexadecane to *n*-eicosane
R_1 = molar ratio of *n*-hexadecane to *n*-eicosane in the L_1 phase
R_2 = molar ratio of *n*-hexadecane to *n*-eicosane in the L_2 phase
T = temperature in ° C.
T^* = reduced temperature defined in Equation 2
T_{LCST} = temperature of LCST critical phenomenon for the *n*-hexadecane–*n*-eicosane composition charged to the cell
$T_{\text{type } K}$ = temperature of type K critical phenomenon for the *n*-hexadecane–*n*-eicosane composition charged to the cell
Type$K$ = type K singular point (the L_2 phase is critical with the vapor in the presence of the L_1 phase)
V = vapor phase
X = mole fraction *n*-hexadecane on ethane-free basis
β = distribution coefficient defined in Equation 1

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Thermodynamic Properties of Molten Mixtures of $CdCl_2$ and $PbCl_2$

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The enthalpies of mixtures in the system $CdCl_2$–$PbCl_2$ were determined over the temperature range 400° to 950° K. relative to 300° K. Measurements were made by drop calorimetry on compositions corresponding to mole fractions of $PbCl_2$ of 0.8808, 0.7749, 0.6468, 0.4277, and 0.2008 in addition to the pure components. Heat capacities averaged 20.4 and 19.7 cal. per mole –° K. for solid $PbCl_2$ and $CdCl_2$, respectively, and 26.6 cal. per mole –° K. for each in the liquid state. Enthalpies of fusion were 7.59 ±0.2 kcal. per mole for $CdCl_2$ at 841° K. and 4.2 ± 0.1 kcal. per mole for $PbCl_2$ at 774° K. Entropies were calculated from the enthalpy data for the components and mixtures. The experimental data and derived quantities indicate the system is ideal within an estimated experimental accuracy of ±1.5%.

THE PURPOSE of this work was to determine the enthalpies and entropies for mixtures in the binary system $PbCl_2$–$CdCl_2$ over a substantial temperature range.

The enthalpies were determined experimentally by drop calorimetry. The entropies were derived from the enthalpy measurements of the mixtures; permissible in this system since its phase diagram (*9*) shows no solid solutions or intermediate compounds.

Enthalpies of mixing may be obtained by taking the difference between the enthalpy of a mixture measured directly and the enthalpy of the pure components at the same temperature. This technique is not as well suited for precise determinations of the enthalpies of mixing as is the differential calorimeter method pioneered by Kleppa (*7*), but it does have the significant advantage of yielding information over the complete temperature range in addi-

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