(14) Huang, T.C., Peng, M.Y., Hu, K.S., Soh, P.P.T., *J. Am. Chem. Soc.* **60**, 489 (1938).
(15) Husa, W.J., Rossi, D.A., *J. Am. Pharm. Assoc.* **31**, 270 (1942).
(16) Jeffrey, G.A., Mak, T.C.W., *Science* **149**, 178 (1965).
(17) Keenan, J.H., Keyes, F.G., "Thermodynamic Properties of Steam," Wiley, New York, 1936.
(18) Le Fèvre, R.J.W., Rayner, G.J., *J. Chem. Soc.* **1938**, p. 1921.
(19) Mosebach, R., *Z. Naturforsch.* **16B**, 614 (1961).
(20) Pummerer, R., Hofmann, J., *Ber.* **56B**, 1255 (1923); *CA* **17**, 3159 (1923).
(21) Squire, P.W., Caines, C.M., *Pharm. J.* **74**, 720, 784 (1905).
(22) Stranski, I.N., Klipping, G., Bogenschultz, A.F., Heinrich, H.J., Maennig, H., *Advan. Catalysis* **9**, 406 (1957).
(23) Utz, F., *Süddeut Apoth.-Ztg.* **59**, 832 (1919); *CA* **14**, 3345 (1920).
(24) Walker, J.F., "Formaldehyde," 3rd ed., Chap. 19, ACS Monograph 159, Reinhold, New York, 1964.
(25) Wells, A.F., "Structural Inorganic Chemistry," 3rd ed., p. 609, Clarendon Press, Oxford, 1962.
(26) Weissberger, A., Ed., "Techniques of Organic Chemistry," 3rd ed., Wiley, New York, 1959.
(27) White, E.T., Ph.D. thesis, University of London, 1964.

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Partial Miscibility Phenomena in the Ternary System Ethane–*n*-Nonadecane–*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*-nonadecane and *n*-eicosane in solution with ethane are presented at representative temperatures along the three phase (L_1-L_2-V) border curves. The lower critical solution temperature (LCST) points and the type-K singular points for the ternary mixtures represent nearly linear interpolations of the behavior of the ethane–*n*-nonadecane and ethane–*n*-eicosane binary systems. Both coexisting liquid phases were sampled at several temperatures and at over-all mole fractions of *n*-eicosane of approximately 0.25, 0.50, and 0.75 on an ethane-free basis. The analysis of these samples indicated that the distribution coefficients of the *n*-nonadecane and *n*-eicosane were independent of over-all composition but depended only on the temperature.

IN THE binary system study on partial miscibility of ethane with high molecular weight paraffinic hydrocarbons reported by Kohn (*3*), *n*-nonadecane was shown to be the lowest molecular weight normal paraffin hydrocarbon which is partially immiscible with ethane. The extension of the partial miscibility work to ternary systems seems necessary if further understanding of the immiscibility phenomenon is to be attained. This paper reports the immiscibility behavior of one ternary system in which the two high molecular weight paraffin hydrocarbons both form partially miscible liquid phases with ethane. Further work will report the immiscibility behavior of a ternary system in which only one of the high molecular weight components is partially immiscible with ethane.

EXPERIMENTAL

The apparatus, techniques, and experimental materials were identical to those reported previously (*1*–*5*). The constant molar ratio mixtures of *n*-nonadecane and *n*-eicosane were prepared from the pure components by weighing techniques. The mixtures were kept in closed bottles. Each sample bottle was heated prior to use so that the entire sample material was in the completely melted condition. The liquid sample was withdrawn from the sample bottle by means of a pipet having a hypodermic needle extension, which permitted the liquid to be introduced into the equilibrium cell through its long capillary neck. The mass added to the cell was determined by accurately weighing the cell on an analytical balance.

During the experimental runs, accurate amounts of pure ethane gas were added to the glass equilibrium cell from a high pressure bomb, through use of a positive displacement mercury pump. As the pressure rose in the thermostated cell and ethane dissolved into the liquid phase, a pressure was reached at which a trace of the second liquid (L_2) phase appeared on top of the original liquid (L_1) phase. At this point, the over-all mixture was essentially at the (L_1-L_2-V) phase border curve. The molar ratio of *n*-nonadecane to *n*-eicosane in the L_1 phase was thus identical to that originally charged to the equilibrium cell.

In a similar manner during experimental runs in which smaller amounts of the heavy hydrocarbon liquids were charged to the cell, the composition and molar volume of the L_2 phase were determined under conditions at which only trace amounts of L_1 phase were present. The sampling technique and method of analysis were presented in detail by McCaffrey (5). Experimental sampling was accomplished by using a 90-ml. Jerguson gage cell fitted with two sampling ports. The lower sampling port was at the bottom of the equilibrium cell and the second was above the L_1-L_2 interface and below the L_2-V interface when the three phases were present in the cell. The sampling ports were connected via hypodermic tubing to 1/16-inch needle valves. When these valves were opened very slowly, samples of the liquid phases passed to a small glass receptacle. The ethane was allowed to flash to the atmosphere while the *n*-nonadecane and *n*-eicosane were collected as a liquid phase. Samples of approximately 15 to 20 µl. were taken. The samples were analyzed on a Beckman GC-2A gas-liquid chromatograph. The column packing was 20% by weight silicone-gum rubber on a firebrick substrate, and the chromatograph was operated at a constant temperature of 250° C.

RESULTS

Table I presents smoothed composition, pressure, and molar volume data on the liquid phases for three molar ratios of *n*-nonadecane and *n*-eicosane. The raw experimental data on the liquid phases were reproducible to ±0.0005 mole fraction, ±0.02° C., and ±0.05 atm. The molar volumes of the L_2 liquid phase were reproducible to ±0.2 ml. per gram mole while those of the L_1 liquid phase were reproducible to ±0.06 ml. per gram mole.

Figure 1 shows the smoothed composition data for the three constant molar ratios of *n*-nonadecane to *n*-eicosane and includes the curves for the two pure components in binary solution with ethane. Figure 1 and Table I show that the partial miscibility temperature range is reduced in an almost linear fashion by addition of *n*-nonadecane to *n*-eicosane.

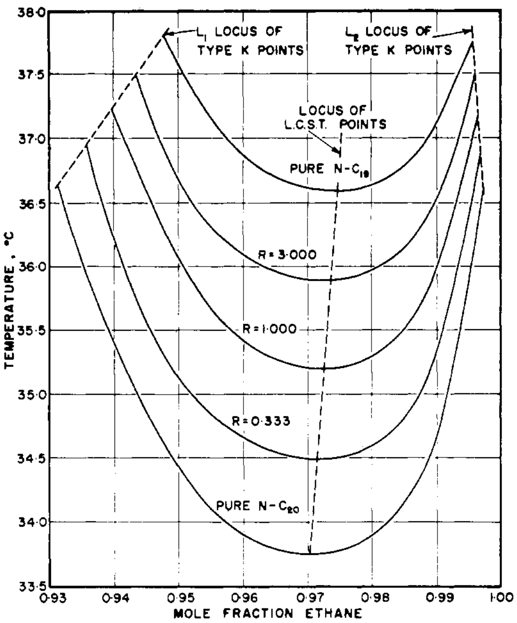

Figure 1. Smoothed phase border curves in the (L_1-L_2-V) region

The results of the sampling work are presented in Table II. The temperature, pressure, mole fraction of *n*-nonadecane in *n*-eicosane charged to the cell, and molar ratio of *n*-nonadecane to *n*-eicosane in each liquid phase were observed experimentally. The difference of the molar ratios of the heavy hydrocarbons in the two liquid phases shows the existence of a small separational effect. A distribution coefficient (β), which is a measure of this effect, was defined as follows:

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

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

		L_1 Phase		L_2 Phase	
Temp., ° C.	Press., Atm.	Comp. mole fract. ethane	Mol. vol., ml./g. mole	Comp. mole fract. ethane	Mol. vol., ml./g. mole
		$R = 0.333$			
34.49[a]	49.590	0.9718	93.90	0.9718	93.90
34.80	49.942	0.9554	93.38	0.9849	97.07
35.20	50.400	0.9489	94.17	0.9892	99.30
35.60	50.858	0.9448	94.69	0.9917	101.53
36.00	51.313	0.9413	94.80	0.9938	104.30
36.40	51.772	0.9385	94.56	0.9954	108.43
36.80	52.230	0.9363	93.78	0.9970	115.23
37.02[b]	52.479	0.9354	92.88	0.9977	125.60
		$R = 1.000$			
35.19[a]	50.318	0.9722	95.10	0.9722	95.10
35.40	50.554	0.9604	94.23	0.9834	97.80
35.80	51.013	0.9532	94.32	0.9888	100.23
36.00	51.241	0.9507	94.41	0.9902	101.62
36.40	51.701	0.9468	94.43	0.9923	104.84
36.80	52.158	0.9431	94.12	0.9944	109.50
37.26[b]	52.688	0.9396	92.50	0.9968	123.60
		$R = 3.00$			
35.89[a]	51.063	0.9735	95.70	0.9735	95.70
36.20	51.418	0.9570	94.18	0.9864	99.23
36.40	51.645	0.9534	94.10	0.9891	100.52
36.80	52.107	0.9489	93.81	0.9922	103.60
37.20	52.563	0.9456	92.97	0.9946	108.70
37.47[b]	52.880	0.9435	92.07	0.9960	119.00

[a] L.C.S.T. point. [b] Type-K singular point.

Table II. The Separational Effect in the Ethane–*n*-Nonadecane–*n*-Eicosane System

Temp., ° C.	Pressure, Atm.	Mole Fraction *n*-Nonadecane Charged to Cell	Molar Ratio of *n*-Nonadecane to *n*-Eicosane Liquid 1 R_1	 Liquid 2 R_2	Distribution Coefficient, β	Reduced Temperature, T^*
35.10	50.19	0.2718	0.454	0.492	1.094	0.241
35.10	50.16	0.2718	0.455	0.486	1.068	0.241
35.40	50.72	0.2718	0.350	0.378	1.080	0.360
35.40	50.71	0.2718	0.343	0.380	1.108	0.360
35.60	50.75	0.5082	0.979	1.058	1.081	0.198
36.10	51.30	0.2718	0.458	0.507	1.106	0.636
36.10	51.32	0.2718	0.463	0.509	1.097	0.636
36.20	51.25	0.7481	3.063	3.226	1.053	0.196
36.20	51.46	0.5082	0.988	1.089	1.102	0.488
36.40	51.86	0.2718	0.388	0.412	1.219	0.755
36.40	51.83	0.2718	0.343	0.389	1.134	0.755
36.80	51.97	0.7481	3.112	3.390	1.089	0.575
36.80	52.10	0.5082	1.006	1.130	1.123	0.777
37.20	52.38	0.7481	3.102	3.512	1.132	0.827

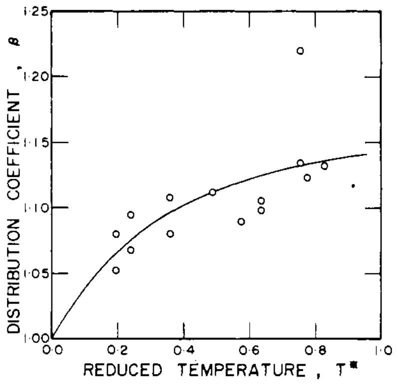

Figure 2. Distribution coefficient vs. reduced temperature for C_2-C_{19}-C_{20}

The distribution coefficient was correlated empirically as a function of a reduced temperature defined as follows:

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

The critical temperatures (T_{LCST} and $T_{\text{type }K}$) used were those of a binary mixture whose composition is the same as that of the over-all ethane-free composition in the cell. The values of the distribution coefficient (β) and the reduced temperature (T^*) are also presented in Table II. The distribution coefficient is plotted against the reduced temperature in Figure 2, and a smooth curve has been drawn through the data. Figure 2 shows that the distribution coefficient is not a function of the over-all heavy hydrocarbon composition in the cell. The average deviation of the experimental distribution coefficients from the smooth curve is ±0.019.

NOMENCLATURE

L_1 = liquid phase less rich in ethane
L_2 = liquid phase richer in ethane
LCST = lower critical solution temperature (L_1 is in critical identity with L_2 in the presence of vapor phase)
R = molar ratio of *n*-nonadecane to *n*-eicosane
R_1 = molar ratio of *n*-nonadecane to *n*-eicosane in the L_1 phase
R_2 = molar ratio of *n*-nonadecane 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*-nonadecane-*n*-eicosane composition charged to the cell
$T_{\text{type }K}$ = temperature of type K critical phenomena for the *n*-nonadecane–*n*-eicosane composition charged to the cell
Type K = singular point (L_2 is in critical identity with V in the presence of L_1 phase)
V = vapor phase
β = distribution coefficient defined in Equation 1

LITERATURE CITED

(1) Kim, Y.J., M.S. thesis, University of Notre Dame, Notre Dame, Ind., 1964.
(2) Kohn, J.P., *A.I.Ch.E. J.* 7, 514–18 (1961).
(3) Kohn, J.P., Kim, Y.J., Pan, Y.C., J. CHEM. ENG. DATA **11**, 333 (1966).
(4) Ma, Y.H., Kohn, J.P., *Ibid.*, 7, 3 (1964).
(5) McCaffrey, D.S., Jr., Ph.D. thesis, University of Notre Dame, Notre Dame, Ind., 1967.

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