Solid-Liquid-Vapor Equilibrium in the Methane–*n*-Eicosane and Ethane–*n*-Eicosane Binary Systems

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The solid-liquid-vapor three-phase equilibria in the methane–*n*-eicosane and ethane–*n*-eicosane systems were studied. A vapor-liquid isotherm at 40° C. was measured on the methane–*n*-eicosane system, and at 60° C. on the ethane–*n*-eicosane system. The experimental results were fitted with good accuracy to the Flory-Huggins solution model.

A KNOWLEDGE of multiphase equilibrium relations in hydrocarbon mixtures is of major importance in the design of separation processes.

A number of interesting studies of methane in liquid *n*-alkane binary systems have been reported (*1-3, 8, 11*). Rowlinson and coauthors (*18*) reported studies on binary systems consisting of ethane and some straight and branched paraffins above C_{23}. They reported partial miscibility in all these systems. Very recently, Kohn (*9*) reviewed and compared several simplified models of solution theory in predicting volumetric and phase data of methane in binary solutions of normal paraffinic solvents in the range of ethane through decane.

Each of the simpler binary solution theories features a pair of equations which relates the activity of each of the binary components in the system to the composition of the liquid phase. Three solution models are listed as the following equations in terms of component fugacity.

Raoult's Law.

$$\ln \frac{f_1}{f_1^\circ} = \ln x_1$$

Scatchard Regular Solution Theory.

$$\ln \frac{f_1}{f_1^\circ} = \ln x_1 + \bar{V}_1 \phi_2^2 \frac{A}{RT}$$

where ϕ = volume fraction of a component.

Flory-Huggins Regular Solution Model.

$$\ln \frac{f_1}{f_1^\circ} = \ln \phi + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) \phi_2 + \phi_2^2 \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2} \frac{\Delta U}{RT} \quad (1)$$

Raoult's law has been of considerable value as a characterization of solution ideality and invariably holds when the composition of a component in a solution approaches unit mole fraction. However, in general the law gives no information as to the directions of magnitude of deviations and this must be supplied either by experiment or by a realistic solution theory. It is generally known that certain binary systems display both positive and negative deviations from Raoult's law along the same isotherm. The Flory-Huggins model is the only one of the parameter equations which allows for this type of behavior. McCaffrey (*12*) has shown that the Flory-Huggins model forms a better criterion for evaluation of the fugacity of the systems ethane–*n*-octane and ethane *n*-eicosane than the Scatchard regular solution model.

To extend the work done by Kohn (*9*) to other systems and to apply simplified models for systems with methane and solvents higher than decane in the hydrocarbon series, a study of methane and eicosane was undertaken. The ethane–*n*-eicosane system was studied to test the Flory-Huggins model for solutes other than methane, as well as to define the solid-liquid-vapor three-phase region for this system.

EXPERIMENTAL

The apparatus described by Lee and Kohn (*10*) was used for the experimental determinations. The essential apparatus consists of a constant temperature bath in which the borosilicate glass equilibrium cell is mounted. A positive displacement pump is used to inject the pure gas component from a thermostated metal bomb to the equilibrium cell. The gas pressures inside the bomb and inside the equilibrium cell are measured by means of 16-inch dial Heise Bourdon tube pressure gages. The bath temperature is measured by a platinum resistance thermometer.

The methane and ethane gas used in this study were Matheson Co., pure grade material, listed as having 99% minimum purity. Both gases were further purified by adsorption in the case of methane and distillation and adsorption in the case of ethane. Vapor-liquid isotherms run on the purified gases give maximum differences between the dew point and the bubble point pressures less than 0.5 atm., with the center 90% distilling within 0.2 atm. This would indicate that the purified gases had purities in excess of 99.5 mole %. The eicosane (C_{20}) used in this study was a petroleum-derived Humphrey Wilkinson product labeled as having 99% minimum purity.

Vapor-liquid isotherms were determined at 40° C. for the methane–*n*-eicosane system and at 60° C. for the ethane–*n*-eicosane system. A weighed amount of C_{20} was charged into the cell, and a desired amount of solute gas was introduced into the cell. The mechanical stirrer facilitated mass transfer between the vapor phase and the liquid phase in the cell. At an apparent thermodynamic equilibrium state the necessary pressure, volume, and temperature readings were recorded (*15*).

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The procedure for the three-phase regions was essentially the same as for the two phases, except that the temperature of the bath was varied for the formation of the three phases under a particular value for the solute gas pressure in the cell. The solid-liquid-vapor state was located by a number of readings taken by first reducing the temperature and observing the pressure and temperature at which the solid phase began to crystallize out; then the temperature was increased to determine the point at which the solid crystals start melting. This procedure was repeated until the doubt of the true three-phase temperature was generally within 0.1° C.

RESULTS AND DISCUSSION

The smoothed experimental values of composition and molar volume of the liquid phase of the vapor-liquid isotherm at 40° C. for the methane–*n*-eicosane system are presented in Table I. The vapor phase is pure methane at all pressures. The temperature of the isotherm was controlled to within 0.25° C. The standard deviations of 35 experimental points from the smoothed data in Table I is 0.44 atm., 0.0016 mole fraction, and 0.33 ml. per gram mole. Similar smoothed pressure-composition data on the ethane–*n*-eicosane system are presented in Table I at a vapor-liquid isotherm temperature of 60° C. In this system the vapor phase is pure ethane at all pressures. The isothermal temperature was controlled to 0.05° C. The standard deviation of 34 experimental points from the smoothed data in Table I is 0.54 atm., 0.002 mole fraction, and 1.2 ml. per gram mole.

The three-phase vapor-liquid-solid smoothed values of pressure, composition, and molar volume for the methane–*n*-eicosane system are shown in Table II. It is assumed that in the three-phase equilibrium, the vapor phase is pure methane and the solid phase is pure *n*-eicosane. The vapor phase is assumed to be pure methane because of the extremely low volatility of *n*-eicosane at the temperature involved. The solid phase is assumed to be pure *n*-eicosane because of effect of high lattice strain energy on solid solutions. Elementary semitheoretical methods indicate that when the difference in the molar volumes of the two components in a solid solution is greater than about 20%, the solid lattice strain energy is so great that phase separation occurs. As the difference in molar volumes of the components becomes greater, the solubility becomes vanishingly small (*5*). The difference in molecular volumes of methane and *n*-eicosane is so great that it is unlikely that a solid solution can form in this system. The standard deviation of 14 experimental points from the smoothed data in Table II is 0.12° C., 1.91 atm., 0.0019 mole fraction, 0.42 ml. per gram mole.

Table I. Smoothed Values of Composition and Molar Volume of the Liquid Phase for C_1-C_{20} System at 40° C. and C_2-C_{20} System at 60° C.

Pressure, Atm.	Mole Fraction in Liquid Phase	Molar Volume, Ml./G. Mole
	C_1-C_{20} Methane	
1[a]	0.000	365.0
5	0.0179	359.6
10	0.0510	348.6
15	0.0785	339.9
20	0.1032	332.6
25	0.1268	324.5
30	0.1490	317.5
35	0.1701	310.7
40	0.1910	304.2
45	0.2108	298.8
50	0.2300	291.8
55	0.2489	285.8
60	0.2677	279.9
	C_2-C_{20} Ethane	
1[b]	0.000	364.0
5	0.1200	332.3
10	0.2338	299.0
15	0.3225	272.9
20	0.3975	250.8
25	0.4635	231.5
30	0.5230	213.7
35	0.5750	198.1
40	0.6220	184.3
45	0.6637	172.0
50	0.7020	160.8
55	0.7360	150.7
60	0.7700	140.8

[a] Air saturated *n*-eicosane at 40°. [b] Air saturated *n*-eicosane at 60°.

Table II. Smoothed Values of Pressure, Composition, and Molar Volume of the Liquid Phase for Solid-Liquid-Vapor Three-Phase Lines of C_1-C_{20} and C_2-C_{20} Systems

Temp., ° C.	Pressure, Atm.	Mole Fraction	Molar Volume, Ml./G. Mole
	C_1-C_{20} Methane		
36.0	6.75	0.0348	353.22
35.8	8.85	0.0465	349.50
35.6	11.62	0.0620	344.50
35.40	14.60	0.0775	339.40
35.2	18.40	0.0961	333.45
35.0	22.30	0.1145	327.50
34.80	27.10	0.1360	320.62
34.6	32.51	0.1592	313.15
34.4	38.70	0.1860	304.50
34.20	45.43	0.2142	295.40
34.0	52.82	0.2450	285.65
	C_2-C_{20} Ethane		
2	24.00		
4	25.53		
6	27.04		
8	28.44		
10	29.48		
12	30.12		
14	30.30	0.905	99.6
16	30.38	0.853	112.4
18	29.78	0.814	123.7
20	28.62	0.755	141.3
22	26.89	0.707	155.5
24	24.41	0.644	174.6
26	21.39	0.567	196.9
28	18.02	0.487	220.6
30	14.35	0.400	246.7
32	10.41	0.308	273.5
34	6.15	0.203	304.9
26.4[a]	1.00	0.000	364.9

[a] Air-saturated freezing point of *n*-eicosane.

The pressure-composition-molar volume results in the three-phase vapor-liquid-solid line for the ethane–*n*-eicosane system are presented in Table II. In this three-phase equilibrium it is assumed that the vapor phase is pure ethane and the solid phase is pure *n*-eicosane. The reasons for this assumption are those given above for the methane–*n*-eicosane system. The standard deviation of 25 experimental points from the smoothed data in Table II is 0.17° C., 0.25 atm., 0.0051 mole fraction, and 1.10 ml. per gram mole. The composition and molar volumes for this system were not measured in the temperature range between 2° and 13° C. In this temperature region the slope of the three-phase line is positive and the composition of the liquid phase increases from about 0.91 mole fraction ethane at 13° C. to essentially pure ethane at 2° C. To measure accurate composition values in this range it is necessary to use laborious trial and error techniques which involve charging the cell with very small amounts of *n*-eicosane. This was not done.

The characteristic energy parameters (ΔU) in the Flory-Huggins solution model were computed at selected total pressures over the entire pressure range using the smoothed vapor-liquid isotherms of both binary systems. The computations were done as suggested by Kohn (*9*). The standard state for the solute component in the liquid state was taken as the hypothetical incompressible liquid under the temperature and pressure of the system and which obeyed the following vapor pressure equation.

$$\log Pr = A \frac{(1 - Tr)}{Tr} \tag{2}$$

where A was computed from the normal boiling point of pure solute gases (methane and ethane).

The standard state fugacity of the liquid solute components was computed from the equation

$$(f_2^\circ)|_{P,T} = P_2^\circ(f/P)|_{P_2^\circ,T} \exp\left[\overline{V}_2(P - P_2^\circ)/RT\right] \tag{3}$$

where $\overline{V}_2$ is the actual experimental partial molar volume at infinite dilution of the dissolved solute gas in the liquid.

Since the gas phases were in each system the pure solute gas at any conditions investigated, the fugacity coefficients for the pure gases were used to compute the fugacities of the dissolved methane and ethane, respectively. The fugacity coefficients for both methane and ethane were taken from Canjar and Manning (*4*).

The above procedure differed only slightly from that of Puri (*15*), who used a different constant in Equation 2 and used fugacity values from Matthews and Hurd (*13*) and the generalized values of Hougen (*6, 7*).

The average value of the interchange energy for the methane-*n*-eicosane system at 40° C. was found to be 2280 ± 90 cal. per gram mole and for the ethane-*n*-eicosane system at 60° C. was 1290 ± 108 cal. per gram mole.

The interchange energies are generally regarded as temperature-insensitive and may be regarded as constant over moderate temperature ranges, as found by Rodrigues *et al.* (*16*) in observations on the ethane-*n*-octane binary system.

The activity coefficients for the solvent components were then calculated from the Flory-Huggins model for the experimental compositions along the three-phase line and compared with those computed from the simple Van't Hoff isochore which is given as Equation 4.

$$\ln(\gamma_1 x_1) = \frac{\Delta H_f}{RT} \frac{(T - T_o)}{T_o} \tag{4}$$

The results of this comparison were excellent, as the calculated and computed activity coefficients were in agreement within 2% up to 30-atm. pressure in the methane-*n*-eicosane system and within 2% up to a composition of 0.400 mole fraction ethane in the ethane-*n*-eicosane system. The latent heats of fusion (ΔH_f) as reported by Perry (*14*) and Rossini (*17*) differed by 14.3%. For the system ethane-*n*-eicosane the model checks better with experimental results for heat of fusion as reported by Perry, while for the methane-*n*-neicosane system the results are slightly better represented with the Rossini value.

NOMENCLATURE

f = fugacity of component, atm.
P = total pressure on system, atm.
P° = vapor pressure of pure component, atm.
P_r = reduced pressure of component, P/P_c
R = universal gas constant
T = temperature of system, ° K.
T_r = reduced temperature of pure component
T_o = triple point temperature of pure component, ° K.
$\overline{V}$ = liquid partial molar volume, ml. per gram mole
γ = activity coefficient of component
ΔH_f = latent heat of fusion of pure solvent
ΔU = energy parameter in regular solution equation, cal./gram mole
ϕ = volume fraction of component
x_i = mole fraction of component

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