pure n-heptane, while the critical pressure relationship below this composition was made the same to that produced from the critical values reported by Kay (*2*). In this comparison, the agreement appears to be close despite the fact that completely different procedures were used to establish these critical values. The recent direct measurements of Ekiner and Thodos (*1*) of the critical temperatures and critical pressures of the ethane–n-heptane system yielded relationships that were in closer agreement to those resulting in this study. These slight differences between this study, the work of Kay (*2*), and that of Ekiner and Thodos (*1*) are not serious but point to the experimental difficulty encountered in establishing values in the vicinity of the critical point.

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Vapor-Liquid Equilibria at 760 Mm. of Mercury for the System Vinyl Acetate–2,4-Dimethyl Pentane

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Vapor-liquid equilibrium data at 760 mm. of mercury pressure are reported for the system vinyl acetate–2,4-dimethyl pentane. An azeotrope is formed at 67.2° C. at a composition of 60.6 mole % vinyl acetate.

THE behavior of monomeric materials in hydrocarbon solvents with regard to separability is of interest to the polymer industry. Since it appears that vinyl acetate forms azeotropes with some of the normal paraffins containing seven carbon atoms or less, the vapor-liquid equilibrium of the branched chain compound, 2,4-dimethyl pentane–vinyl acetate system was investigated at 760 mm. of mercury pressure.

An azeotrope at 67.2° C. at the composition 60.6 mole % vinyl acetate was found. The data were correlated by the van Laar equation and were thermodynamically consistent based on the Redlich and Kister (*7*) consistency test.

The values of the van Laar constants, Carlson and Colburn modification (*1*), were: $A_{12} = 0.490$, $B_{12} = 0.495$ (subscript 1 refers to vinyl acetate).

MATERIALS

The vinyl acetate used in this investigation was obtained from Union Carbide Chemicals Co., and it was purified by fractionation in a packed column. The 2,4-dimethyl pentane obtained from the Phillips Petroleum Co. as 99% minimum purity material was not further purified.

Table I compares the experimental properties of the materials determined in this investigation with those reported in the literature.

EXPERIMENTAL PROCEDURE

A modified (*6*) Colburn equilibrium still (*4*) of the vapor-recirculation type was used to determine the vapor-

Table I. Physical Properties of Materials

	Vinyl Acetate		2,4-Dimethyl Pentane	
	Exptl.	Lit.	Exptl.	Lit.
760 Mm. boiling point, ° C.	72.5	72.5(*5*)	80.5	80.5(*2*)
Density, d 20/4	0.934	0.9343(*5*)	0.6676(25/4)	0.6683(*2*)
Ref. index, n_D 25°	1.3955	1.3956(*5*)	1.37886	1.37882(*2*)

Antoine constants for 2,4-DMP (*2*): $A = 6.8262$, $B = 1192.041$, $C = 221.634$; $\log p = A - [B/(C+t)]$ where p = mm. Hg, t = ° C.

Experimental Vapor Pressure–Temperature Relations for Vinyl Acetate

Temp., ° C.	Vapor Press., Mm. Hg	Temp., ° C.	Vapor Press., Mm. Hg
67	633.1	76	866.7
69	679.9	78	927.4
70	704.3	80	991.5
72	755.4	82	1059.2
74	809.5		

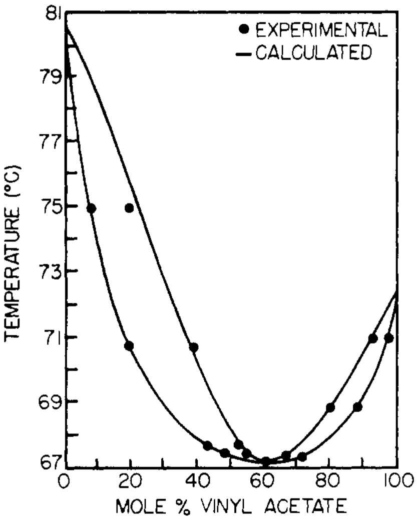

Figure 1. Boiling point diagram for vinyl acetate–2,4-dimethyl pentane system

liquid equilibrium data. Constant pressure was maintained by use of a manostat and measured with a mercury manometer, and the temperatures were measured with an iron-constantan thermocouple in conjunction with a Leeds and Northrup potentiometer.

The procedure followed was the same as that reported previously (*6*) and is the standard procedure in this laboratory for vapor-liquid equilibria determinations.

The compositions of the vapor and liquid equilibrium samples were determined by refractive index measurements at 25° C. using a Bausch and Lomb precision refractometer with a sodium D light source and the mixture composition-refractive index calibration curve determined in the laboratory. Because there was a minimum in this curve at about 0.2 mole fraction vinyl acetate, a density-composition curve was utilized to check the compositions of the equilibrium samples from experimental density data.

DISCUSSION

Table II lists the pertinent experimental and calculated data for the binary system vinyl acetate-2,4-dimethyl pentane at 760 mm. of mercury pressure. Figure 1 is the temperature-composition diagram, and Figure 2 shows the activity coefficient-liquid composition curves for the system.

The activity coefficients were calculated by means of Equation 1

$$\gamma = \frac{yP_T}{xP} \tag{1}$$

The data correlated very well with the Carlson and Colburn (*1*) modified van Laar binary Equations 2 and 3.

$$\log \gamma_1^* = \frac{Ax_2^2}{\left[\frac{A}{B}x_1 + x_2\right]^2} \tag{2}$$

$$\log \gamma_2^* = \frac{Bx_1^2}{\left[x_1 + \frac{B}{A}x_2\right]^2} \tag{3}$$

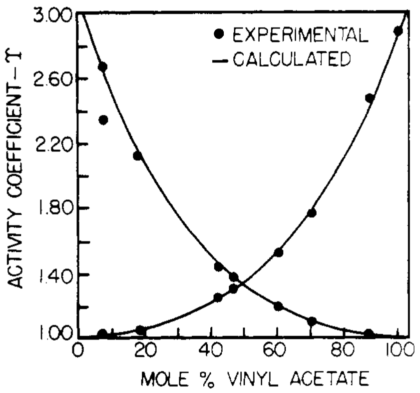

Figure 2. Activity coefficient *vs.* composition for vinyl acetate–2,4-dimethyl pentane system

Table II. Temperature Composition and Activity Coefficient Data

Temp., °C.	Experimental				Calculated	
	x_1	y_1	γ_1	γ_2	γ_1^*	γ_2^*
80.5	0.00	0.00	. . .	1.0	3.09	. . .
75.0	0.073	0.187	2.32	1.03	2.65	1.01
70.8	0.188	0.381	2.13	1.03	2.12	1.04
67.7	0.421	0.513	1.41	1.26	1.47	1.22
67.4	0.470	0.541	1.37	1.31	1.38	1.29
67.2	0.606	0.606	1.19	1.52	1.19	1.51
67.37	0.709	0.662	1.11	1.76	1.10	1.77
68.9	0.879	0.792	1.01	2.47	1.02	2.40
71.0	0.965	0.922	1.00	2.99	1.00	2.82
72.2	1.00	1.00	1.00	. . .	1.00	3.12

Subscript 1 refers to vinyl acetate.

The Redlich and Kister thermodynamic consistency test (*7*) modified by Herington (*3*) for isobaric data showed the data to be thermodynamically consistent with the positive and negative areas on a log γ_1/γ_2 *vs.* x plot agreeing within 1.0%.

The estimated possible error in terms of mole fraction of the vinyl acetate in the vapor is ± 0.005.

NOMENCLATURE

A, B = van Laar constants (Carlson & Colburn modification)
γ = experimental activity coefficient
γ^* = calculated activity coefficient
x, y = composition of liquid and vapor, mole fraction, respectively
P = vapor pressure, mm. Hg
P_T = total pressure, mm. Hg

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