Vapor-Liquid Equilibria in Mixtures of *n*-Alcohols and Their Esters

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Sweeney and Rose (*1*) have recently reported a successful prediction of vapor-liquid equilibria in binaries of acetates and alcohols using a theory of liquid mixtures developed by Barker (*2*, *3*). In this treatment the liquid is assumed to have a quasicrystalline structure in which there is short-range order and long-range disorder. The molecules are assumed to occupy well-defined sites on a regular lattice and the interactions of the molecules with their neighbors are considered. The interaction energies are assumed to depend upon the nature of the molecular surfaces which are adjacent to each other and if suitable values are assigned to these energy terms, it is possible to calculate the excess chemical potential of the mixture and the activity coefficients. Sweeney and Rose showed that for the homologous set of binary mixtures of normal alcohols and their acetates

$$(C_nH_{2n+1}OH \text{ and } C_nH_{2n+1}COOCH_3)$$

a single set of interaction energies, obtained by fitting to data for one member of the set, can be used to predict vapor-liquid equilibria for the others.

In this way Sweeney and Rose showed that the same interaction energies satisfactorily correlated C_1, C_2, C_4, and C_6 data. The purpose of this note is to show that two of the missing members of the series can also be successfully correlated with the same interaction energies.

PROPANOL-PROPYL ACETATE

Measurements of vapor-liquid equilibrium in *n*-propanol–*n*-propyl acetate were reported independently in 1959 by Smirnova (*4*) and Pick et al. (*5*). The two sets of data are in close agreement over the full concentration range. With the same values for interaction energies as were used by Sweeney and Rose, the vapor-liquid equilibrium data for this system at 760 mm. Hg were calculated. The resulting *y*-*x* plot is shown in Figure 1 with the experimental data of Smirnova. The method has predicted the equilibrium well except near the azeotrope, where differences of about 0.02 mole fraction between predicted and measured values are noted. As with other members of the set, the predicted azeotrope (0.56 mole fraction alcohol, 94.9°C.) differs from that observed (about 0.62 mole fraction alcohol, 94.7°C.).

AMYL ALCOHOL-AMYL ACETATE

Some measurements on the system amyl alcohol-amyl acetate have been reported by Croil (*6*). This work was done with Eastman Kodak *n*-amyl alcohol (Practical) No. P-568 and Eastman Kodak *n*-amyl acetate No. 2360. The boiling points of these reagents, which were not purified prior to the equilibrium determinations, were 134 to 137° and 147 to 149°C., respectively. Equilibrium data were obtained on a Cottrell-Choppin still, an improved type of Othmer still, with samples analyzed by refractive indexes. The resulting data are not very precise, and additional work with purer reagents is clearly required. However it is interesting to find that the alcohol-rich portion of the *y*-*x* curve, considered to be the most reliable by the author, fits the predicted relation very well, as is shown in Figure 2. The data are given in Table 1.

METHANOL-ETHYL ACETATE

Sweeney and Rose also applied their treatment to one alcohol-ester binary outside the homologous set, *n*-hexanol–methyl/caproate and found that the equilibrium could not be predicted with as good accuracy as for systems within the series. Considerably better agreement between the theoretical treatment and experimental data is shown by the system methanol-ethyl acetate, which is also outside the series. Equilibrium data reported by Nagata

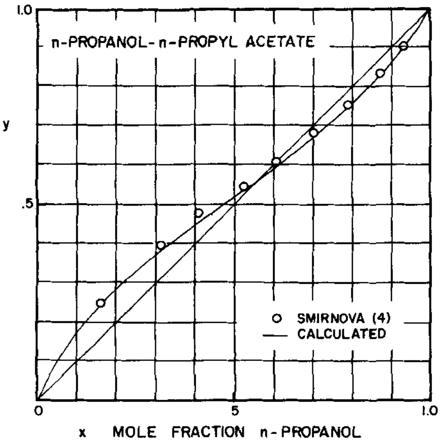

Fig. 1. Vapor-liquid equilibrium of *n*-propanol –*n*-propyl acetate at 760 mm. Hg.

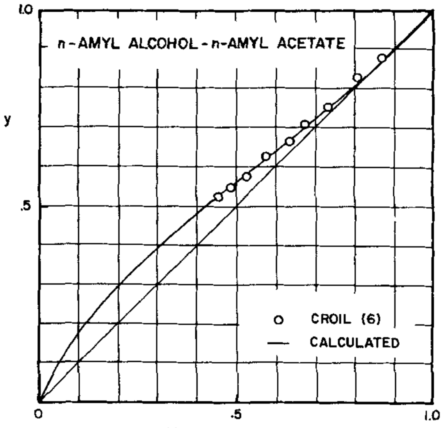

Fig. 2. Vapor-liquid equilibrium of *n*-amyl alcohol–*n*-amyl acetate at 755.8 mm. Hg.

TABLE 1. EQUILIBRIUM DATA FOR THE SYSTEM AMYL ALCOHOL-AMYL ACETATE

Mole fraction alcohol in Liquid	Vapor	Temperature, °C.
0.456	0.521	140.55
0.489	0.547	140.00
0.530	0.577	139.50
0.577	0.626	138.85
0.639	0.664	138.20
0.674	0.710	137.75
0.738	0.756	137.35
0.804	0.828	136.85
0.870	0.878	136.45
1.000	1.000	136.00

Pressure: 755.8 mm. Hg.

(7) for this binary are presented in Figure 3, along with the equilibrium predicted by Barker's theoretical model using the same values for interaction energies as in the other systems. The fit of the theoretical curve is even better than for the most closely related systems within the series, that is, methanol-methyl acetate and ethanol-ethyl acetate. The Sweeney and Rose method thus has further verification within the homologous series, and for binary systems of alcohols and esters outside the series but with the esters of the same type.

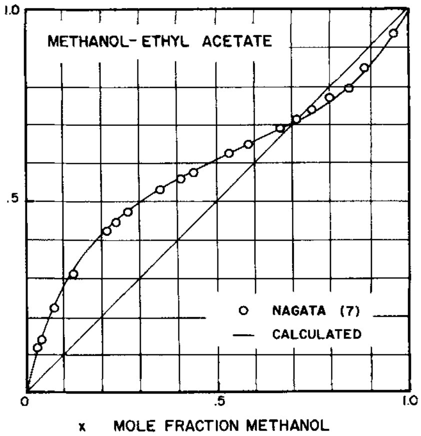

Fig. 3. Vapor-liquid equilibrium of methanol-ethyl acetate at 760 mm. Hg.

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Diffusion Coefficients for Organic Vapors in Polyvinyl Acetate

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For the diffusion of vapors into polymers, the Fick diffusion coefficient (*1*) varies with concentration. This has been attributed to swelling of the polymer and dilution effects of the condensed vapors. In particular the diffusion of organic vapors in polyvinyl acetate has been studied by Kokes and Long (*2*). Kokes and Long found experimentally that

$$\bar{D}_{ij}(C_i) = \bar{D}_0 e^{\beta C_i} \qquad (1)$$

where

$$D_{ij}(C_i) = \frac{d[C_i \bar{D}_{ij}(C_i)]}{dC_i} \qquad (2)$$

Because the diffusion coefficient $D_{ij}(C_i)$ changes rapidly with concentration in these systems, recent comments (*3*) have been made that a diffusion coefficient based on an activity gradient might not vary with concentration. This paper discusses the evaluation of diffusion coefficients based on an activity gradient for benzene, acetone, and propylamine in polyvinyl acetate.

The flux of organic vapor (*i*) through a polymer with mass fraction as a driving force for diffusion can be written as

$$n_i = \rho_i v - \rho D_{ij}(\omega_i) \nabla \omega_i \qquad (3)$$

If activity is considered the driving force for diffusion

$$n_i = \rho_i v - \rho D_{ij}(a_i) \nabla a_i \qquad (4)$$

Consideration of Equations (3) and (4) yields

$$D_{ij}(a_i) \nabla a_i = D_{ij}(\omega_i) \nabla \omega_i \qquad (5)$$

If we consider the fact that activity is a function of state, then

$$a_i = f(T, P, \omega_1, \omega_2, \ldots, \omega_{n-1}) \qquad (6)$$

Therefore

$$\nabla a_i = \left(\frac{\partial a_i}{\partial T}\right)_{P,\omega_i} \nabla T + \left(\frac{\partial a_i}{\partial P}\right)_{T,\omega_i} \nabla P + \sum_{k=1}^{k=n-1} \left(\frac{\partial a_i}{\partial \omega_k}\right)_{T,P,\omega_j} \nabla \omega_k \qquad (7)$$

For a binary system at constant temperature and pressure, Equation (7) reduces to

$$\nabla a_i = \left(\frac{\partial a_i}{\partial \omega_i}\right) \nabla \omega_i \qquad (8)$$