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VAPOR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEMS ALLYL ALCOHOL-ETHYLBENZENE AND ALLYL ALCOHOL-*p*-XYLENE

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Introduction

With a view to utilizing alcohols as entraining agents for the separation of close-boiling hydrocarbons, isobaric vapor-liquid equilibrium data for the systems allyl alcohol-ethylbenzene and allyl alcohol-*p*-xylene were obtained at 760 ± 2 mmHg pressure. The system allyl alcohol-ethylbenzene, having a boiling range of 39.3°C , forms a constant-boiling mixture at 96.9°C , which is the normal boiling point of allyl alcohol. The vapor and liquid composition curves merge with each other at concentrations of allyl alcohol above 90 mole %. The system allyl alcohol-*p*-xylene, having a boiling range of 41.5°C , forms a constant-boiling mixture at 96.9°C and at concentrations above 93 mole %.

1. Experimental Procedure

Preliminary drying of allyl alcohol obtained from Riedel was done by refluxing for four hours with chemically pure potassium carbonate and was finally purified by distillation in a well-insulated glass column. The method of purification of ethylbenzene and *p*-xylene along with the details of the experimental set-up for obtaining vapor-liquid equilibrium data are described elsewhere²⁾. The physical properties of the pure compounds are listed in Table 1.

2. Results and Discussion

The activity coefficients were calculated using Eqs. (1) and (2):

$$\gamma_1 = \frac{\pi y_1}{P_1^0 x_1} \exp \left[\frac{(\pi - P_1^0)(B_{11} - V_1)}{RT} + \frac{\pi \delta_{12} y_2^2}{RT} \right] \quad (1)$$

$$\gamma_2 = \frac{\pi y_2}{P_2^0 x_2} \exp \left[\frac{(\pi - P_2^0)(B_{22} - V_2)}{RT} + \frac{\pi \delta_{12} y_1^2}{RT} \right] \quad (2)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (3)$$

Table 2 gives the vapor-liquid equilibrium data for these systems. The correlations used for the estimation of pure component properties of ethylbenzene and *p*-xylene have been described earlier²⁾. Based on the recommendations given elsewhere^{1,8)}, the vapor pressures, second virial coefficients and liquid molar volumes of allyl alcohol were estimated by the correlations of Thek-Stiel¹³⁾, O'Connell-Prausnitz¹¹⁾ and modified Goldhammer⁵⁾, respectively. The cross virial coefficients B_{12} were evaluated by employing the mixing rules described by O'Connell and Prausnitz¹¹⁾. The data for both these systems were found to be thermodynamically consistent by application of the tests of Herington⁶⁾, Norrish-Twigg¹⁰⁾ and Black³⁾. The function (D-J) in the Herington test for the systems allyl alcohol-ethylbenzene and allyl alcohol-*p*-xylene was found to be -12.92 and -11.91 , respectively. The activity coefficient-composition plot as shown in Figs. 1 and 2 for these systems indicate maxima-minima below compositions of about 10

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Table 1 Physical properties of materials

Material	Bp. [°C]	Refractive index at 30°C
allyl alcohol	96.9 96.9 (4)	1.4088 —
ethylbenzene	136.2 136.19 (15)	1.4908 1.4905 (14)
p-xylene	138.5 138.4 (7)	1.4908 1.4905 (14)

Table 2 Vapor-liquid equilibrium data

<i>t</i> [°C]	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂
System allyl alcohol (1)–ethylbenzene (2)				
96.9	0.965	0.966	0.998	3.133
96.9	0.935	0.936	1.000	3.177
96.9	0.871	0.888	1.019	2.799
96.9	0.886	0.894	1.007	2.995
97.2	0.796	0.844	1.050	2.440
97.7	0.712	0.811	1.109	2.058
98.2	0.647	0.794	1.172	1.796
99.1	0.546	0.772	1.310	1.498
100.0	0.454	0.753	1.489	1.310
100.8	0.409	0.753	1.611	1.182
102.6	0.323	0.723	1.843	1.090
104.1	0.263	0.688	2.049	1.074
106.8	0.185	0.656	2.538	0.981
109.3	0.150	0.618	2.726	0.968
111.8	0.123	0.586	2.907	0.940
114.5	0.100	0.496	2.796	1.025
System allyl alcohol (1)–p-xylene (2)				
96.9	0.967	0.968	0.996	3.253
96.9	0.942	0.942	0.997	3.358
96.9	0.870	0.891	1.022	2.814
97.2	0.800	0.855	1.060	2.414
97.8	0.716	0.828	1.122	1.974
98.4	0.651	0.818	1.194	1.671
99.3	0.552	0.790	1.316	1.455
100.2	0.472	0.773	1.461	1.292
101.5	0.398	0.766	1.647	1.119
103.3	0.316	0.742	1.888	1.023
105.6	0.245	0.714	2.174	0.959
108.8	0.182	0.666	2.461	0.934
111.3	0.138	0.648	2.907	0.865
113.8	0.114	0.602	3.045	0.882
116.0	0.098	0.556	3.054	0.906
120.5	0.067	0.413	2.889	1.016
121.0	0.066	0.416	2.916	0.998

mole % allyl alcohol. As shown in **Table 3**, the correlations of Wilson¹⁶⁾ and NRTL¹²⁾ fit the activity coefficient-composition data quite satisfactorily above 0.1 mole fraction of allyl alcohol. The constants in these correlations were evaluated by using the nonlinear least squares technique described by Nagahama *et al.*⁹⁾ minimizing $\ln(\gamma_1/\gamma_2)$ function. The value of the nonrandom constant, α_{12} , in the NRTL correlation was taken to be 0.47.

Conclusions

Vapor-liquid equilibrium data for allyl alcohol–ethylbenzene and allyl alcohol–p-xylene systems were obtained at 760 mmHg pressure. Both these systems formed constant-boiling mixtures at 96.9°C and at all concentrations of allyl alcohol above about 90 mole %. The data are thermodynamically consistent. The ac-

Fig. 1 Activity coefficient-composition diagram for allyl alcohol–ethylbenzene system **Fig. 2 Activity coefficient-composition diagram for allyl alcohol–p-xylene system****Table 3 Data fit in Wilson and NRTL correlations**

System	Wilson		NRTL	
	constants*	RMS deviation in <i>y</i> ₁	constants*	RMS deviation in <i>y</i> ₁
Allyl alcohol (1)–ethylbenzene (2)	$A_{12}=0.3261$ $A_{21}=0.4923$	0.015	$\tau_{12}=0.7223$ $\tau_{21}=1.0722$	0.015
Allyl alcohol (1)–p-xylene (2)	$A_{12}=0.3391$ $A_{21}=0.4514$		$\tau_{12}=0.8017$ $\tau_{21}=0.0462$	

* constants obtained by minimizing $\ln(\gamma_1/\gamma_2)$ function

tivity coefficient-composition plots give maxima-minima formation in the dilute allyl alcohol concentration region. The correlations of Wilson and NRTL fit the data well.

Nomenclature

<i>B</i>	= second virial coefficient	[cm ³ /mole]
<i>B</i> ₁₂	= cross virial coefficient	[cm ³ /mole]
<i>P</i> ^o	= vapor pressure of pure component	[mmHg]
<i>R</i>	= gas constant	[cal/mol·°K]
<i>T</i>	= absolute temperature	[°K]
<i>t</i>	= temperature	[°C]
<i>V</i>	= molar volume of pure component in liquid phase	[cm ³ /mole]
<i>x</i>	= mole fraction in liquid phase	[—]
<i>y</i>	= mole fraction in vapor phase	[—]

π	= total pressure of the system	[mmHg]
γ	= activity coefficient	[—]
δ_{12}	= interaction parameter as defined by Eq. (3)	[cm ³ /mole]
A_{12}, A_{21}	= constants in Wilson equation	[—]
τ_{12}, τ_{21}	= constants in NRTL equation	[—]
<Subscripts>		
1	= more volatile component	
2	= less volatile component	

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APPLICATION OF THE PERTURBATION THEORY TO VAPOR-LIQUID EQUILIBRIA OF SYSTEMS CONTAINING A POLAR SUBSTANCE

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In a previous paper⁴⁾, it was shown that the perturbation theory of Barker-Henderson in conjunction with the conformal solution theory proposed by Mansoori and Leland³⁾ is applicable to the correlation of vapor-liquid equilibria of systems containing ammonia. In the present study, the perturbation theory has been further applied to systems containing a polar substance other than ammonia. The vapor-liquid equilibria of the binary system consisting of a nonpolar substance and a polar substance (acetone, ethyl ether, methyl ethyl ketone or methyl acetate) were calculated by the same procedure as reported previously.

The pair-potential energy-function used is the Lennard-Jones (12-6) type, described in the previous paper:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where ϵ and σ are temperature-dependent potential parameters and are defined as follows:

$$\epsilon = \epsilon^\circ \mathcal{F}^2 \quad (2)$$

$$\sigma = \sigma^\circ \mathcal{F}^{-1/6} \quad (3)$$

$$\mathcal{F} = 1 + 7Q^4/20kT\epsilon^\circ(\sigma^\circ)^{10} + 3Q^2\alpha/4\epsilon^\circ(\sigma^\circ)^8 : \quad (4)$$

for nonpolar substance

$$\mathcal{F} = 1 + \mu^4/12kT\epsilon^\circ(\sigma^\circ)^6 + \mu^2\alpha/2\epsilon^\circ(\sigma^\circ)^6 : \quad (5)$$

for polar substance

where α , μ and Q are polarizability, dipole moment, and quadrupole moment, respectively. These parameters were determined by using vapor pressure data and saturated P - V - T relation for pure substances^{1,7)}. The values of these parameters for nonpolar substances are given in Table 1, where α is arbitrarily assumed to be zero. Figure 1 shows the vapor pressures and saturated volumes for methane calculated with two different sets of parameters. The pair-potential energy function containing the quadrupole moment seems to improve the calculated results. As shown in Fig. 2, the following linear relations were obtained between the reduced potential parameters and the acentric factor:

$$\epsilon^\circ/kT_c = 0.734 - 0.396\omega \quad (6)$$

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