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Vapor–Liquid Equilibria of Methanol + Hexane, Methanol + Heptane, Ethanol + Hexane, Ethanol + Heptane, and Ethanol + Octane at 298.15 K

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The vapor–liquid equilibria for the five alkanol + alkane binary systems methanol + hexane, methanol + heptane, ethanol + hexane, ethanol + heptane, and ethanol + octane were measured by a flow-type apparatus at 298.15 K. The values of the activity coefficient are greater than unity. The experimental results obtained were correlated by several equations for activity coefficients, and these correlations are compared.

Introduction

We have developed a flow-type apparatus to measure the vapor pressures of a solvent containing a salt (*1*), vapor–liquid equilibria of mixtures (*2*), and the salt effect on vapor–liquid equilibria in mixtures (*3, 4*). In this paper, vapor–liquid equilibria (VLE) are reported at 298.15 K for the five alkanol + alkane binary systems methanol + hexane, methanol + heptane, ethanol + hexane, ethanol + heptane, and ethanol + octane. The present results are compared with literature values. The present results have been correlated by several activity coefficient equations, and these correlations are compared.

Experimental Section

Table 1. Constants in the Antoine Equation[a] and Vapor Pressure at 298.15 K

	constants (*5–9*)			
component	A	B	C	$p°$/kPa
methanol	8.080 97	1582.271	239.726	16.938
ethanol	8.112 20	1592.864	226.184	7.865
hexane	6.910 58	1189.640	226.280	20.006
heptane	6.893 86	1264.370	216.640	6.114
octane	6.931 42	1358.800	209.855	1.865

[a] $\log(p°/\text{kPa}) = A - B/(t/°\text{C} + C)$.

Equipment and Procedures. A flow-type apparatus was used. A detailed description of the equipment and operating procedure is given elsewhere (*1–4*). An advantage of the present experimental method is considered to be the simplicity and ease of operation though the accuracy of data obtained by the method using gas chromatography is somewhat less than that by the static methods. In this work, we held three glass cells in a thermostat. One cell contained the binary mixture alkanol + alkane in which the mole fraction of the alkanol is given by x_1, one contained pure alkanol, and the third contained the pure alkane. The carrier gas (helium) was very slowly passed through each cell individually to establish equilibrium. Then, helium gas saturated with alkanol and alkane was introduced into a gas chromatograph. The amount of vapor of each sample was detected at the height of a peak on a recorder, a thermal-conductivity detector having been used. Gaskuropack 54 (0.18–0.25 mm porous polymer beads) supplied by GL Sciences Co. was used as a packing material, and the peaks of alkanol and alkane were separated. We measured the peak height of each pure substance supplied from the appropriate cell and those of both alkanol and alkane from the mixture cell at several temperatures close to 298.15 K. First, the peak heights of alkanol and alkane in the binary mixture at 298.15 K were each determined by interpolation using the almost linear relation between the peak height and temperature. Next, the corresponding temperature (t_1* or t_2*) that showed the same peak height was found for each pure alkanol and alkane by changing the temperature of the thermostat to about 266 K. The partial pressures p_1 of alkanol and p_2 of alkane in the binary mixture were calculated from the following equations:

$$p_1 = p_1°(t_1^*) \tag{1}$$

$$p_2 = p_2°(t_2^*) \tag{2}$$

where $p°$ denotes the saturated vapor pressures of each pure component, which can be obtained from a vapor pressure equation such as the Antoine equation given in Table 1 (*5–9*). The vapor-phase mole fraction was obtained from the following equation assuming that the vapor phase is ideal:

$$y_1 = p_1/(p_1 + p_2) \tag{3}$$

Materials. All chemicals used in this study were of guaranteed reagent grade, and their mass-fraction purities are reported by the supplier, Wako Pure Chemicals Co., to be higher than 0.997, 0.995, 0.960, 0.990, and 0.980 for methanol, ethanol, hexane, heptane, and octane, respectively. They were used as received because no impurities were detected with gas chromatography. No significant amount of water was detected in the alcohols.

Results and Discussion

The experimental p_1, p_2, and y_1 are presented in Tables 2–6. The reliability of the present experimental procedures has already been ascertained in previous work (*1–4*). The accuracy of each measurement of partial pressure is considered to be within 2%. To examine the nonideality of the binary mixture, the activity coefficients were evalu-

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Table 2. Vapor–Liquid Equilibrium Data[a] for Methanol (1) + Hexane (2) at 298.15 K

x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2	x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2
0.067	14.50	19.79	0.423	12.78	1.06	0.500	16.70	19.64	0.460		
0.087	15.03	19.99	0.429	10.20	1.09	0.601	16.59	19.60	0.458		
0.100	15.43	19.80	0.438	9.11	1.10	0.700	16.60	19.70	0.457		
0.126	15.76	19.79	0.443	7.38	1.13	0.750	16.56	19.75	0.456		
0.144	16.01	19.77	0.447	6.56	1.15	0.780	16.55	19.73	0.456		
0.160	15.99	19.74	0.448	5.90	1.17	0.800	16.45	19.62	0.456	1.21	4.90
0.180	16.04	19.82	0.447	5.26	1.21	0.820	16.59	19.67	0.457	1.19	5.46
0.200	16.36	19.57	0.455	4.83	1.22	0.840	16.60	19.44	0.461	1.17	6.07
0.222	16.37	19.71	0.454			0.860	16.77	19.20	0.466	1.15	6.86
0.240	16.28	19.67	0.453			0.880	16.66	18.58	0.473	1.12	7.74
0.260	16.50	19.65	0.456			0.900	16.71	17.92	0.483	1.10	8.96
0.300	16.44	19.68	0.455			0.920	16.69	16.70	0.500	1.07	10.44
0.402	16.71	19.57	0.461			0.940	16.70	15.00	0.527	1.05	12.50

[a] Where x in the range 0.222–0.780 is an apparent value obtained by assuming a homogeneous liquid phase.

Table 3. Vapor–Liquid Equilibrium Data[a] for Methanol (1) + Heptane (2) at 298.15 K

x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2	x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2
0.040	13.41	6.09	0.688	19.79	1.04	0.450	16.29	5.96	0.732		
0.060	14.46	6.06	0.704	14.23	1.06	0.500	16.34	6.00	0.732		
0.070	14.93	6.08	0.711	12.59	1.07	0.600	16.21	5.94	0.732		
0.080	15.21	6.11	0.713	11.23	1.09	0.650	16.36	6.01	0.731		
0.100	15.44	6.03	0.719	9.12	1.10	0.700	16.24	5.95	0.732		
0.100	15.58	6.04	0.721	9.20	1.10	0.800	16.31	6.02	0.730		
0.120	15.75	5.99	0.724	7.75	1.11	0.860	16.26	6.03	0.729		
0.130	15.86	6.07	0.723	7.20	1.14	0.870	16.22	6.06	0.728		
0.150	16.02	6.03	0.727	6.31	1.16	0.880	16.32	6.06	0.729		
0.160	16.02	6.04	0.726			0.900	16.35	5.87	0.736	1.07	9.59
0.180	16.24	6.07	0.728			0.900	16.24	5.96	0.731	1.07	9.75
0.200	16.03	5.99	0.728			0.930	16.51	5.59	0.747	1.05	13.05
0.200	16.14	5.99	0.729			0.940	16.49	5.40	0.753	1.04	14.71
0.300	15.98	5.96	0.728			0.950	16.63	5.00	0.769	1.03	16.36
0.400	16.10	5.94	0.731			0.970	16.82	4.01	0.807	1.02	21.88

[a] Where x in the range 0.160–0.880 is an apparent value obtained by assuming a homogeneous liquid phase.

Table 4. Vapor–Liquid Equilibrium Data for Ethanol (1) + Hexane (2) at 298.15 K

x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2	x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2
0.040	4.77	19.72	0.195	15.15	1.03	0.600	6.88	18.45	0.272	1.46	2.31
0.060	5.21	19.71	0.209	11.03	1.05	0.700	6.99	17.75	0.283	1.27	2.96
0.080	5.54	19.68	0.220	8.81	1.07	0.800	7.15	16.17	0.307	1.14	4.04
0.100	5.70	19.53	0.226	7.25	1.08	0.860	7.33	14.11	0.342	1.08	5.04
0.130	6.04	19.62	0.235	5.91	1.13	0.900	7.43	12.26	0.377	1.05	6.13
0.200	6.29	19.22	0.246	4.00	1.20	0.920	7.48	10.67	0.412	1.03	6.67
0.301	6.51	19.10	0.254	2.75	1.37	0.940	7.57	9.23	0.451	1.02	7.69
0.400	6.62	18.92	0.259	2.11	1.58	0.960	7.69	7.19	0.517	1.02	8.99
0.501	6.78	18.82	0.265	1.72	1.89						

Table 5. Vapor–Liquid Equilibrium Data for Ethanol (1) + Heptane (2) at 298.15 K

x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2	x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2
0.060	5.28	6.02	0.467	11.19	1.05	0.650	6.68	5.57	0.545	1.31	2.60
0.100	5.73	6.00	0.488	7.28	1.09	0.700	6.72	5.50	0.550	1.22	3.00
0.120	5.88	5.98	0.496	6.23	1.11	0.740	6.81	5.46	0.555	1.17	3.43
0.160	6.03	5.86	0.507	4.79	1.14	0.780	6.88	5.35	0.563	1.12	3.98
0.200	6.25	5.92	0.514	3.98	1.21	0.800	6.86	5.17	0.570	1.09	4.23
0.240	6.47	5.80	0.527	3.43	1.25	0.840	6.94	4.87	0.588	1.05	4.97
0.300	6.44	5.95	0.520	2.73	1.39	0.880	7.09	4.40	0.617	1.02	6.00
0.400	6.46	5.69	0.532	2.05	1.55	0.900	7.17	4.17	0.632	1.01	6.83
0.500	6.56	5.68	0.536	1.67	1.86	0.940	7.46	3.14	0.704	1.01	8.56
0.600	6.66	5.62	0.543	1.41	2.30						

ated by

$$\gamma_1 = y_1 p / x_1 p_1^\circ \tag{4}$$

$$\gamma_2 = (1 - y_1)p/(1 - x_1)p_2^\circ \tag{5}$$

where $p = p_1 + p_2$, and are given in Tables 2–6. Methanol (1) + hexane (2) and methanol (1) + heptane (2) show phase separation in the liquid phase as shown in Table 7 (*10*, *11*). Therefore, the x_1 value shown in Tables 2 and 3 outside the mutual solubility limit is an apparent value obtained by assuming a homogeneous liquid phase. In the range where two liquid phases coexist, the partial pressures and vapor phase mole fraction become constant. It is found from Table 2 that methanol (1) + hexane (2) shows constant partial pressures (p_1 = 16.5 kPa and p_2 = 19.7 kPa) and constant vapor phase mole fraction (y_1 = 0.456) at 298.15 K, where these values are obtained as arithmetic averaged values of data points outside the mutual solubility limit. Similarly, Table 3 shows that the constant p_1, p_2, and y_1 of methanol (1) + heptane (2) are 16.2 kPa, 6.00 kPa, and 0.730, respectively. The present five alkanol + alkane binary systems indicate a large positive deviation from Raoult's law; namely, the activity coefficients are much larger than unity as shown in Tables 2–6.

Table 6. Vapor–Liquid Equilibrium Data for Ethanol (1) + Octane (2) at 298.15 K

x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2	x_1	p_1/kPa	p_2/kPa	y_1	γ_1	γ_2
0.060	5.05	1.86	0.731	10.71	1.06	0.660	6.95	1.73	0.801	1.34	2.72
0.101	5.66	1.86	0.752	7.13	1.11	0.720	6.90	1.75	0.798	1.22	3.35
0.140	6.05	1.85	0.766	5.50	1.15	0.760	7.01	1.65	0.809	1.17	3.69
0.190	6.27	1.84	0.773	4.20	1.22	0.800	6.97	1.69	0.805	1.11	4.53
0.220	6.46	1.84	0.778	3.73	1.27	0.820	7.08	1.62	0.814	1.10	4.82
0.241	6.60	1.86	0.780	3.48	1.31	0.860	7.03	1.58	0.817	1.04	6.05
0.280	6.65	1.84	0.784	3.02	1.37	0.880	7.15	1.51	0.825	1.03	6.77
0.400	6.74	1.80	0.789	2.14	1.61	0.900	7.19	1.41	0.836	1.02	7.54
0.500	6.78	1.74	0.796	1.72	1.87	0.920	7.24	1.38	0.840	1.00	9.23
0.560	6.79	1.79	0.792	1.54	2.18	0.960	7.56	0.93	0.890	1.00	12.47
0.620	6.88	1.76	0.796	1.41	2.49						

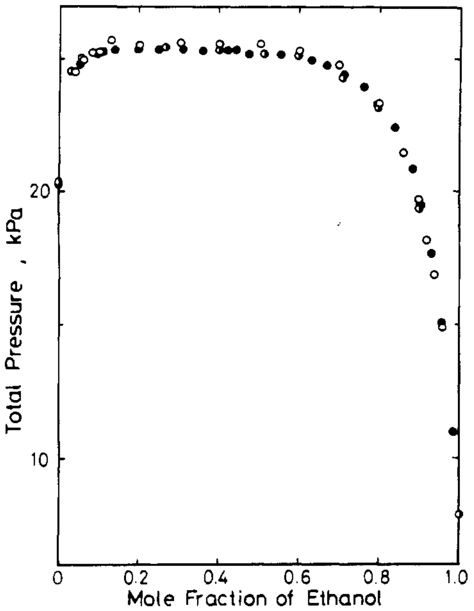

Figure 1. Total pressure of ethanol (1) + hexane (2) at 298.15 K: (○) this work, (◑) Smith and Robinson (*14*), (●) Hwang and Robinson (*12*).

Table 7. Mutual Solubility Data for Methanol (1) + Hexane (2) and Methanol (1) + Heptane (2) at 298.15 K

mixture	x_1 upper phase	x_1 lower phase	ref
methanol (1) + hexane (2)	0.2100	0.7980	10
methanol (1) + heptane (2)	0.1530	0.8995	11

Among the five binary systems, vapor–liquid equilibria of methanol (1) + hexane (2), methanol (1) + heptane (2), and ethanol (1) + hexane (2) have been reported at the same temperature. The $p-x$ relation of methanol (1) + hexane (2) was reported by Hwang and Robinson (*12*). Yasuda et al. (*13*) measured the $x-y$ relation for methanol (1) + heptane (2). The $p-x$ relation of ethanol (1) + hexane (2) was determined by Smith and Robinson (*14*) and Hwang and Robinson (*12*). The present results were compared with these literature values, and good agreement between them was shown. A typical illustration is shown in Figure 1. The $p-x$ relations of ethanol (1) + heptane (2) at 303.15 and 313.15 K were reported by Van Ness and Abbott (*15*) and Janaszewski et al. (*16*), respectively. The $p-x$ relation of ethanol (1) + octane (2) at 313.15 K was measured by Janaszewski et al. (*16*). Among these higher temperature $p-x$ relations, the results of Van Ness and Abbott are relatively close in temperature and the $p-x$ relation coincides with the present data in tendency.

Several activity coefficient equations, such as the Wilson equation (*17*), the NRTL equation (*18*), and the improved Wilson equation (*19*, *20*), were adopted to correlate the present vapor–liquid equilibrium data. An improved Wilson equation has been found to give better correlation performance for phase equilibria. The improved Wilson equation is given as

$$\ln \gamma_i = C[1 - \ln(\textstyle\sum_j x_j\Lambda_{ij}) - \sum_k\{x_k\Lambda_{ki}/\sum_j x_j\Lambda_{kj}\} + \sum_k\{(1-\beta)x_k(x_i\lambda_{ki}\Lambda_{ki} - \sum_m x_m{}^2\lambda_{km}\Lambda_{km})/\sum_j\Lambda_{kj}x_j\}] \quad (6)$$

where

$$\Lambda_{ij} = \exp[-\{(1-\beta)x_j + \beta\}\lambda_{ij}] \quad (7)$$

$$\lambda_{ij} = R_{ij}/RT \quad (8)$$

where R_{ij} is the interaction energy parameter between components i and j, R is the gas constant, T is the absolute temperature, and β is an adjustable parameter. The parameter C is given as 1.3 (*19*) or 1.5 (*20*). The improved Wilson equation given by eq 6 seems flexible to correlate phase equilibria because it can be reduced to the original Wilson equation (*17*) or the modified Wilson equation of Nagatani (*21*) by letting β be unity or zero. We attempted to correlate the present vapor–liquid equilibrium data using several activity coefficient equations based on the relation $y_i = x_i\gamma_i p_i^\circ/p$.

The parameters contained in the activity coefficient equation were determined to minimize the following objective function:

$$F_{\mathrm{ob}} = (100/N)\sum^{N}|y_1^{\mathrm{calcd}} - y_1^{\mathrm{exptl}}|/y_1^{\mathrm{exptl}} \quad (9)$$

where N denotes the number of data points. First, the well-known Wilson equation (original form) and NRTL equation were adopted. The binary parameters determined and their correlation performances are shown in Table 8. Then, an improved Wilson equation was applied by adjusting the

Table 8. Correlation of Vapor–Liquid Equilibria for Alkanol (1) + Alkane (2) Using the Original Wilson Equation and NRTL Equation

	original Wilson eq ($C = 1, \beta = 1$)			NRTL eq			
mixture	R_{12}	R_{21}	dev[a]	α	τ_{12}	τ_{21}	dev[a]
methanol (1) + hexane (2)	8058	6426	0.9	0.437	2.35	2.48	0.9
methanol (1) + heptane (2)	7705	7640	0.7	0.445	2.86	2.79	0.7
ethanol (1) + hexane (2)	6708	3659	1.1	0.483	1.73	2.47	2.0
ethanol (1) + heptane (2)	6916	4041	1.9	0.458	1.73	2.31	2.4
ethanol (1) + octane (2)	6191	4747	1.6	0.465	1.96	2.26	1.7

[a] dev (%) = $(100/N)\sum^N[|y_1^{\mathrm{calcd}} - y_1^{\mathrm{exptl}}|/y_1^{\mathrm{exptl}}]$, where N is the number of data points.

Table 9. Correlation of Vapor–Liquid Equilibria for Alkanol (1) + Alkane (2) Using the Improved Wilson Equation

	$C = 1.3$				$C = 1.5$				C = adjustable				
mixture	β	R_{12}	R_{21}	dev[a]	β	R_{12}	R_{21}	dev[a]	C	β	R_{12}	R_{21}	dev[a]
methanol (1) + hexane (2)	0.389	5617	4960	0.6	0.137	5401	4923	0.7	1.34	0.103	7087	6003	0.5
methanol (1) + heptane (2)	0.225	6287	6375	0.8	0.108	5555	5681	1.0	1.19	0.045	13700	8013	0.6
ethanol (1) + hexane (2)	0.098	6862	4344	0.7	0.082	5385	3694	1.1	1.34	0.087	6501	4227	0.6
ethanol (1) + heptane (2)	0.012	8036	5020	1.3	0.008	5852	4287	1.8	1.16	0.087	12060	4889	0.7
ethanol (1) + octane (2)	0.020	7513	5592	1.4	0.054	5310	4562	1.6	1.12	0.106	20870	4729	0.7

[a] dev (%) = $(100/N)\sum^{N}[|y_1^{\mathrm{calcd}} - y_1^{\mathrm{exptl}}|/y_1^{\mathrm{exptl}}]$, where N is the number of data points.

parameters C and β. The parameters fitted to VLE and the correlation performances are given in Table 9. As shown in Table 8, the correlation performances of the Wilson and NRTL equations for ethanol binary systems are slightly less than those for methanol binary systems. On the other hand, an improved Wilson equation can give good correlations also for ethanol binary systems, as shown in Table 9, by adjusting both parameters C and β.

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