J. Chem. Eng. Data **1996,** *41,* 1219−1222

Vapor−Liquid Equilibria for Water + Diacetone Alcohol, Ethyl Methanoate + Water, and Ethyl Methanoate + Phenol

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The total pressure and vapor and liquid compositions have been measured for water + diacetone alcohol at 340.00 K and 370.00 K and for ethyl methanoate + phenol and ethyl methanoate + water at 300.00 K and 320.00 K. Measurements were made by either a recirculating still or a transpiration method depending on the total pressure of the mixture. The results were correlated using the Redlich−Kister equation, the Wilson equation, and the NRTL equation, with allowance for vapor nonideality.

Introduction

This work constitutes a contribution to Project 805, Experimental Data on Mixtures, of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. The aim of this project is to sponsor solubility, vapor−liquid equilibrium, and infinite dilution activity coefficient measurements of mixtures of industrial importance. There exist no reliable measurements of the vapor−liquid equilibria on the mixtures reported in this work.

Experimental Section

Materials. The diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) was pure grade (Lachema, Czechoslovakia). This compound is thermally unstable at higher temperatures; therefore, it was purified by distillation twice under vacuum, stored over molecular sieves 4A, and kept in a refrigerator. About 0.1 mass % of impurities was found by gas chromatography. Ethyl methanoate, 98% (Fluka, Switzerland), contains about 2 volume % ethyl alcohol, which was removed by rectification from P_2O_5. After this procedure, less than 0.1 mass % of impurities was found by gas chromatography. Phenol, analytical grade (Reactivul, Roumania), was used without further purification. The melting point was determined as (313.65 ± 0.1) K. Water was twice redistilled from $KMnO_4$ in quartz equipment.

Equipment and Procedure. The density was measured with a DMA 60+602 vibrating tube densimeter (Paar, Austria). The temperature was controlled to ±0.01 K. The accuracy of density determination was estimated to be better than 2×10^{-5} g·cm^{-3}. The refractive index was measured using an Abbe-type refractometer (Carl Zeiss, Germany) with ±0.0001 resolution. Vapor−liquid equilibria were measured by means of two different methods depending on the total pressure of mixture. The circulation method was used for water + diacetone alcohol, while the two other systems were measured using the saturation method. Both of the methods, along with the equipment and the procedure used, are described in detail in the previous paper by Linek *et al.* (1996).

Table 1. Refractive Index of the Mixtures at T = 298.15 K

x_A	n^D	$10^4\{x_A - x_A(\text{calc})\}$	$10^4\{n^D - n^D(\text{calc})\}$
	Water (A) + Diacetone Alcohol (B)[a]		
0.0	1.4219[b]	0	0
0.1006	1.4219		
0.2038	1.4219		
0.2744	1.4216		
0.3968	1.4206		
0.4587	1.4198		
0.5458	1.4178		
0.6596	1.4134[b]	−2	−0
0.7827	1.4033[b]	10	1
0.8416	1.3950[b]	−22	−1
0.8881	1.3850[b]	−13	−0
0.9150	1.3772[b]	5	0
0.9252	1.3735[b]	7	0
0.9352	1.3697[b]	11	0
0.9551	1.3607[b]	15	0
0.9802	1.3464[b]	9	0
1.0	1.3325[b]	0	0
mean		10	0
	Ethyl Methanoate (A) + Phenol (B)		
0.9687	1.3642		
0.9783	1.3622		
0.9931	1.3590		
0.9959	1.3583		
0.9991	1.3575		
1.0	1.3573		

[a] Note: for water + diacetone alcohol (calc) denotes the value calculated from eq 1 with A_1 = 0.636 920, A_2 = 1.227 12, and A_3 = −2.729 72. [b] Included in correlation.

Results

Diacetone Alcohol + Water. The components are miscible over the whole mole fraction range at ambient temperature. Both refractometric and densimetric analyses were used since the changes of refractive index with composition for the low water content mixtures are too small, while the density changes are small at the low diacetone alcohol concentration region. Moreover, the density−composition relationship shows a maximum at approximately 95 mole % water. The dependence of refractive index on composition at 298.15 K is given in Table 1.

The results were smoothed using the maximum likelihood method using the three-parameter equation,

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S0021-9568(96)00183-5 CCC: $12.00

Table 2. Density for Water (A) + Diacetone Alcohol (B) at T = 298.15 K[a]

x_A	ρ/g·cm^{-3}	$10^4\{x_A - x_B(\text{calc})\}$	$10^4\{\rho - \rho(\text{calc})\}$/g·cm^{-3}
0.0	0.9335[b]	0	0
0.1006	0.9372[b]	31	−4
0.2038	0.9427[b]	−9	1
0.2744	0.9464[b]	−12	1
0.3968	0.9536[b]	−9	1
0.4587	0.9577[b]	−4	0
0.5458	0.9639[b]	10	−1
0.6596	0.9734[b]	22	−1
0.7827	0.9854[b]	−16	1
0.8416	0.9917		
0.8881	0.9964		
0.9150	0.9986		
0.9253	0.9991		
0.9351	0.9995		
0.9551	0.9997		
0.9802	0.9984		
1.0	0.9971[b]	0	0
mean		14	0

[a] (calc) denotes the value calculated from eq 2 with $A_1 = -5.655\ 562$, $A_2 = -2.398\ 500$, and $A_3 = -0.990\ 238$. [b] Included in correlation.

$$n^D = x_A n_A^D + x_B n_B^D + x_A x_B (x_A A_1 + x_B A_2 - x_A x_B A_3) \quad (1)$$

assuming a standard deviation equal to $\sigma(x) = 0.001$ and $\sigma(n) = 0.0001$. For the correlation, only marked points in Table 1 were included. Equation 1 was used to calculate the composition from the measured refractive index of samples within the mole fraction of water range from 0.6 to 1.0. The dependence of density on composition at 298.15 K is given in Table 2.

The values were smoothed using the maximum likelihood procedure applied to the three-parameter equation,

$$\rho = (x_A M_A + x_B M_B)/[x_A M_A/\rho_A + x_B M_B/\rho_B + x_A x_B\{A_1 + A_2(x_B - x_A) + A_3(x_B - x_A)^2\}] \quad (2)$$

assuming standard deviation equal to $\sigma(x) = 0.001$ and $\sigma(\rho)/\rho = 0.0001\rho$. For the correlation, only marked points in Table 2 were included. Equation 2 was used to calculate composition from measured densities of samples within the mole fraction of water range from 0.0 to 0.6. Experimental vapor−liquid equilibrium data were measured using the circulation still at 340.00 K and 370.00 K and are summarized in Table 3. The only results on this system were those by Hack and Van Winkle (1954). However, the comparison is difficult since these were isobaric measurements. Nevertheless, the azeotropic behavior is in agreement: there is an azeotrope for the higher isotherm, while for the lower one, the azeotrope is vanishing (tangential).

Ethyl Methanoate + Phenol. The components are miscible over the whole mole fraction range at ambient temperature. The vapor phase composition was measured by refractive index. These samples contain from 0.96 to 1.0 mole fraction of ethyl methanoate; therefore, the calibration was carried out for these concentrations only. The results at 298.15 K are presented in Table 1, and for the purpose of evaluation, graphical representation was quite sufficient. The vapor−liquid equilibria were measured using the saturation method at two temperatures (300.00 K and 320.00 K), and the results are summarized in Table 3.

Ethyl Methanoate + Water. Limited miscibility takes place at ambient temperature; therefore, most samples from the middle of the concentration region were heterogeneous. An excessive amount of inert anhydrous solvent (butyl alcohol) was added in order to homogenize the two-phase condensed vapor samples. Following that, the content of water was determined using the Karl Fischer method. The composition of liquid samples was determined from the mass of the individual components. The vapor−liquid equilibria were measured at 300.00 K and 320.00 K. The results are summarized in Table 3.

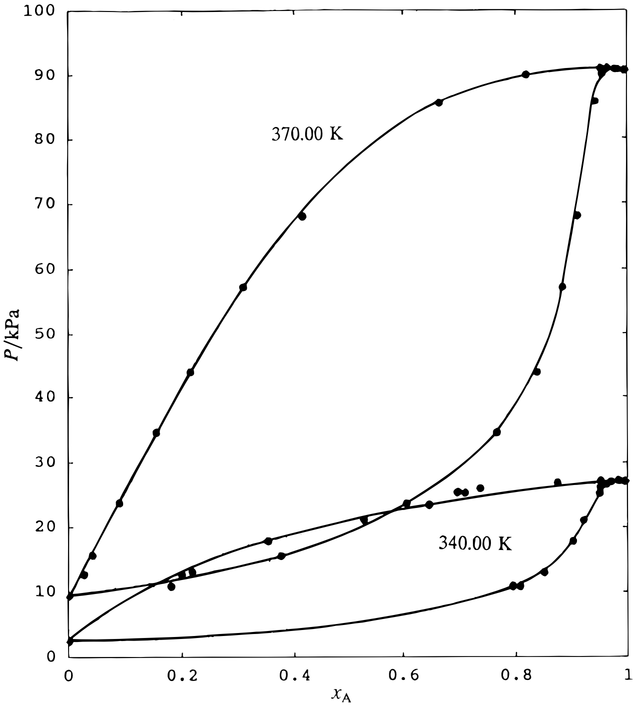

Figure 1. Liquid and vapor compositions for diacetone alcohol (A) + water (B) at 340 K and 370 K. Solid lines are calculated from the NRTL equation.

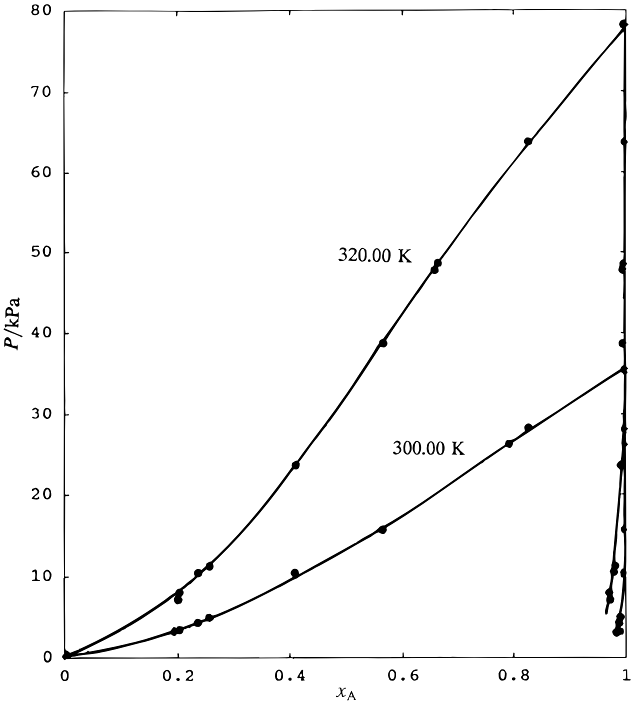

Figure 2. Liquid and vapor compositions for ethyl methanoate (A) + phenol (B) at 300 K and 320 K. Solid lines are calculated from the NRTL equation.

Azeotropic behavior in the system was determined by means of a small laboratory distillation column (30 cm long, 1.5 cm in diameter, filled with glass helices). The boiling point of the azeotrope was measured with an accuracy of ±0.05 K. The distilled-off heterogeneous samples of condensate were analyzed as described above. The pressure

Table 3. Vapor–Liquid Equilibrium for the Mixtures[a]

x_A	y_A	P/kPa	δx_A	δy_A	δP/kPa	δT/K	x_A	y_A	P/kPa	δx_A	δy_A	δP/kPa	δT/K
Water (A) + Diacetone Alcohol (B)													
T = 340.00 K													
0.0	0.0	2.33					0.8755	0.9635	26.75	0.0014	−0.0071	−0.01	0.08
0.1807	0.7948	10.77	0.0093	−0.0219	0.00	−0.03	0.9531	0.9730	27.10	0.0004	−0.0026	0.00	−0.00
0.1807	0.8070	10.77	0.0090	0.0100	0.00	−0.00	0.9840	0.9850	27.22	0.0001	−0.0002	0.00	−0.01
0.2190	0.8501	12.99	−0.0098	−0.0063	0.00	−0.05	0.9941	0.9941	27.22	−0.0004	0.0007	0.00	−0.02
0.3539	0.9032	17.98	−0.0226	−0.0081	0.01	−0.15	0.9967	0.9967	27.24	0.0000	0.0009	0.00	−0.04
0.5250	0.9221	21.02	0.0269	−0.0140	−0.02	0.20	0.9979	0.9979	27.23	0.0001	0.0008	0.00	−0.04
0.6970	0.9525	25.34	−0.0021	−0.0075	0.00	−0.05	0.9988	0.9988	27.21	0.0002	0.0006	0.00	−0.03
0.7099	0.9525	25.34	0.0033	−0.0081	−0.00	0.05	0.9990	0.9990	27.18	0.0000	0.0003	0.00	−0.01
0.7370	0.9550	26.02	−0.0056	−0.0084	0.01	−0.13	1.0	1.0	27.15				
T = 370.00 K													
0.0	0.0	9.35					0.6652	0.9408	85.61	0.0052	−0.0086	−0.03	0.07
0.0266	0.1994	12.65	0.0085	−0.0589	0.01	−0.44	0.8180	0.9550	89.88	−0.0008	−0.0027	0.03	−0.07
0.0404	0.3778	15.58	0.0042	−0.0363	0.01	−0.22	0.9550	0.9670	90.77	0.0000	−0.0005	0.01	−0.01
0.0860	0.6060	23.62	0.0003	−0.0282	0.01	−0.11	0.9820	0.9855	90.79	−0.0026	0.0030	−0.01	0.01
0.0860	0.6463	23.62	−0.0006	0.0093	−0.00	0.04	0.9936	9.9927	90.64	−0.0007	0.0004	−0.00	0.01
0.1524	0.7664	34.65	−0.0047	−0.0036	0.00	−0.02	0.9973	0.9967	90.52	−0.0004	0.0000	−0.00	0.01
0.2150	0.8375	43.87	−0.0054	0.0066	0.00	0.00	0.9987	0.9979	90.63	0.0006	0.0007	0.01	−0.03
0.3103	0.8838	57.12	−0.0096	−0.0005	0.01	−0.04	0.9993	0.9992	90.84	0.0014	0.0022	0.04	−0.08
0.4147	0.9107	68.00	−0.0016	−0.0031	0.00	−0.01	1.0	1.0	90.45				
Ethyl Methanoate (A) + Phenol (B)													
T = 300.00 K													
0.0	0.0	0.08					0.4093	0.9969	10.45	−0.0070	0.0003	0.02	−0.03
0.1931	0.9844	3.19	−0.0023	0.0025	0.00	−0.00	0.5633	0.9989	15.70	0.0077	0.0004	−0.05	0.05
0.2006	0.9882	3.36	−0.0012	0.0051	0.00	0.00	0.7921	0.9995	26.17	−0.0002	−0.0002	0.00	−0.00
0.2347	0.9894	4.25	0.0016	0.0019	−0.00	0.01	0.8258	0.9996	28.10	−0.0047	−0.0002	0.08	−0.05
0.2551	0.9907	4.80	0.0034	0.0013	−0.00	0.01	1.0	1.0	35.55				
T = 320.00 K													
0.0	0.0	0.32					0.5633	0.9973	38.78	0.0000	−0.0003	0.00	0.00
0.2006	0.9713	7.21	0.0076	0.0043	−0.01	0.02	0.6577	0.9975	47.86	0.0000	−0.0011	0.00	0.00
0.2006	0.9706	8.01	−0.0052	−0.0003	0.01	−0.01	0.6628	0.9982	48.51	−0.0012	−0.0004	0.03	−0.01
0.2347	0.9798	10.41	−0.0072	0.0006	0.01	−0.02	0.8258	0.9998	63.79	−0.0024	0.0003	0.11	−0.03
0.2551	0.9816	11.26	0.0008	0.0003	−0.00	0.00	1.0	1.0	78.22				
0.4093	0.9939	23.69	0.0047	0.0001	−0.03	0.02							
Ethyl Methanoate (A) + Water (B)													
T = 300.00 K													
0.0	0.0	3.53					0.0209	0.8909	31.83	0.0002	−0.0009	0.00	0.00
0.0034	0.4824	7.89	0.0006	−0.0675	0.02	−0.18	0.0230	0.9157	35.45	−0.0007	0.0125	−0.00	0.00
0.0075	0.7114	15.47	−0.0005	−0.0617	0.01	−0.08	0.0245[c]	0.9273[c]	36.59[c]	−0.0002	0.0209	−0.00	0.01
0.0110	0.7947	20.64	−0.0008	−0.0364	0.01	−0.04	1.0	1.0	35.48				
0.0143	0.8126	23.66	0.0003	−0.0405	−0.01	−0.04							
T = 320.00 K													
0.0	0.0	10.53					0.0200	0.8705	69.12	−0.0001	0.0198	−0.01	0.02
0.0048	0.6965	27.76	0.0002	0.0980	−0.06	0.20	0.0205	0.8759	69.53	0.0002	0.0243	−0.02	0.02
0.0082	0.7897	37.00	0.0000	0.0701	−0.05	0.10	0.0260[b]	0.8926[c]	81.02[c]	0.0007	0.0195	−0.01	0.01
0.0113	0.8271	47.04	−0.0003	0.0476	−0.03	0.05	1.0	1.0	78.20				
0.0147	0.8538	58.16	−0.0010	0.0318	−0.02	0.03							

[a] δ = experimental − calculated (NRTL). [b] Extrapolated. [c] Heteroazeotrope.

in the measuring system was maintained automatically by means of manostat and measured indirectly by determination of the boiling point of water in an ebulliometer connected in parallel.

Data Reduction

In the data reduction, a maximum likelihood procedure was used as described in the previous paper (Linek et al., 1996). A symmetrical objective function was evaluated using standard deviations estimated as $\sigma(x) = \sigma(y) = 0.001$, $\sigma(P) = 0.001\ P$, and $\sigma(T) = 0.02$ K for phase compositions, pressure, and temperature, respectively. The real gas phase behavior was taken into account and was described using the virial equation of state. The virial coefficients B were calculated using the Hayden and O'Connell (1975) method, and the molar volumes V were calculated using a generalized Watson relation (Hougen and Watson, 1947). The values for pure components and mixtures are summarized in Table 4. The necessary vapor pressures were evaluated from the Antoine equation parameters given in Table 5. The activity coefficients γ_x were fitted both to classical and to nonclassical equations expressed as follows:

Table 4. Calculated Virial Coefficients B and Molar Volumes V of the Pure Compounds and Mixtures

system	X/cm^3·mol^{-1}	T/K			
		300.00	320.00	340.00	370.00
water	B	−1936.4	−1215.4	−818.7	−501.3
	V	18.1	18.5	18.7	19.3
ethyl methanoate	B	−1246.2	−1053.1		
	V	80.9	83.1		
phenol	B	−3571.4	−2798.5		
	V	87.9	89.4		
diacetone alcohol	B			−2181.5	−1687.6
	V			130.1	134.5
water + diacetone alcohol	B_{AB}			−400.5	−322.0
ethyl methanoate + water	B_{AB}	−1688.5	−1388.5		
ethyl methanoate + phenol	B_{AB}	−449.5	−376.1		

(i) the Redlich–Kister equation

$$\ln \gamma_{x,A} = x_B^{\ 2}\ \{A_1 + A_2(4x_A - 1) + A_3(x_A - x_B)(6x_A - 1)\} \tag{3}$$

where A_1, A_2, and A_3 are adjustable parameters;

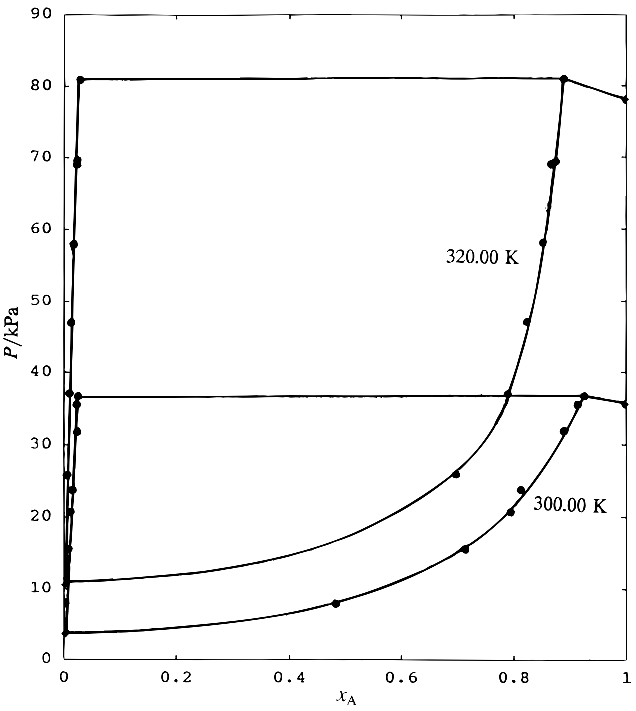

Figure 3. Liquid and vapor compositions for ethyl methanoate (A) + water (B) at 300 K and 320 K. Solid lines are calculated from the NRTL equation.

Table 5. Constants for the Antoine Vapor Pressure Equation, log(p/kPa) = $A - B/(T/\mathrm{K} + C)$, Applicable to the Temperature Ranges Studied

compound	A	B	C	ref
water	7.091 71	1668.21	−45.15	Dreisbach (1955)
ethyl methanoate	6.440 16	1298.224	−34.477	Farkova (1994)
phenol	6.993 09	2011.4	−51.15	Dreisbach (1959)
diacetone alcohol	7.627 32	2400.556	−9.36	Boublik (1973)

(ii) the Wilson equation

$$\ln \gamma_{x,A} = \ln(x_A + x_B\Lambda_{AB}) + x_B\Lambda_{AB}/(x_A + x_B\Lambda_{AB}) - x_B\Lambda_{BA}/(x_B + x_A\Lambda_{BA}) \quad (4)$$

where $\Lambda_{AB} = (V_B/V_A)\exp[-A_{AB}/RT]$ and $\Lambda_{BA} = (V_A/V_B)\exp[-A_{BA}/RT]$, where V_A and V_B are the molar volumes and A_{AB} and A_{BA} are adjustable parameters;

(iii) the NRTL equation

$$\ln \gamma_{x,A} = x_B^2\{\tau_{BA}[G_{BA}/(x_A + x_BG_{BA})]^2 + \tau_{AB}G_{AB}/(x_B + x_AG_{AB})^2\} \quad (5)$$

where $\tau_{AB} = A_{AB}/RT$, $\tau_{BA} = A_{BA}/RT$, $G_{AB} = \exp[-\alpha\tau_{AB}]$, and $G_{BA} = \exp[-\alpha\tau_{BA}]$ and A_{AB}, A_{BA}, and α are adjustable parameters determined by the maximum likelihood procedure. The expressions for the activity coefficient $\gamma_{x,B}$ can easily be obtained by interchanging subscripts A and B in eqs 3 through 5.

The results of the correlation are summarized in Table 6. The deviations in compositions, pressure, and temperature corresponding to the correlation using the NRTL equation are presented in Table 3 along with the direct experimental results. The experimental p, x, y values are illustrated in Figures 1−3.

For all mixtures, the distribution of the measurements about the various correlation results confirms that there are no significant or biased errors.

Table 6. Parameters of Correlation Equations and Mean Deviations from the Wilson, NRTL, and Redlich−Kister Equations[a]

T/K	A_1	A_2	A_3	δx	δy	δP/kPa	δT/K
Water (A) + Diacetone Alcohol (B)							
Wilson Equation[b]							
340.00	4815.72	3905.07		0.0055	0.0067	0.01	0.06
370.00	5253.14	6076.50		0.0061	0.0107	0.02	0.10
NRTL Equation[b]							
340.00	554.548	1353.97	−3.5183	0.0057	0.0061	0.00	0.06
370.00	−154.218	2286.79	−1.7512	0.0029	0.0103	0.01	0.07
Redlich−Kister Equation							
340.00	1.1110	0.5230	0.5810	0.0079	0.0052	0.01	0.12
370.00	1.1640	0.7971	0.3248	0.0042	0.0103	0.04	0.14
Ethyl Methanoate (A) + Phenol (B)							
Wilson Equation[b]							
300.00	−882.612	−1655.25		0.0048	0.0022	0.03	0.03
320.00	1899.77	−3541.17		0.0034	0.0008	0.02	0.01
NRTL Equation[b]							
300.00	−1192.32	−850.13	3.0786	0.0035	0.0015	0.02	0.02
320.00	−2054.25	−3.9901	1.0772	0.0032	0.0008	0.02	0.01
Redlich−Kister Equation							
300.00	−1.1991	0.1571	−0.3569	0.0032	0.0018	0.02	0.02
320.00	−1.0425	0.3779	−0.0786	0.0030	0.0010	0.02	0.01
Ethyl Methanoate (A) + Water (B)							
NRTL Equation[b]							
300.00	7007.59	3617.50	0.0629	0.0005	0.0343	0.01	0.05
320.00	1847.72	5227.58	−1.4102	0.0004	0.0445	0.03	0.06
Redlich−Kister Equation							
300.00	4.3486	0.4335	−0.1477	0.0005	0.0344	0.01	0.05
320.00	3.0840	−0.7517	0.0036	0.0003	0.0445	0.03	0.06

[a] Note: Parameters of the Wilson equation are not given for ethyl methanoate (A) + water (B) since the equation is not suitable for immiscible systems. [b] A_1 (=A_{AB}) and A_2 (=A_{BA}) are expressed in J·mol^{-1}, $A_3 = \alpha$.

Acknowledgment

The authors wish to thank Mrs. S. Bernatova and Mrs. J. Wolfova for valuable assistance during experimental work.

Literature Cited

Aim, K. Measurement of vapor-liquid equilibrium in systems with components of very different volatility by the total pressure static method. *Fluid Phase Equilib.* **1978**, *2*, 119−142.

Boublik, T.; Fried, V.; Hala, E. *Vapour Pressures of Pure Substances*; Elsevier: Amsterdam, 1973.

Dreisbach, R. R. *Physical Properties of Chemical Compounds;* Advances in Chemistry Series No. 15; American Chemical Society: Washington, DC, 1955.

Dreisbach, R. R. *Physical Properties of Chemical Compounds II*; Advances in Chemistry Series No. 22; American Chemical Society: Washington, DC, 1959.

Farkova, J.; Wichterle, I.; Farkova, J.; Wichterle, I. Vapor pressures of some ethyl and propyl esters of fatty acids. *Fluid Phase Equilib.* **1994,** *90*, 143−148.

Hack, C. W.; Van Winkle, M. Vapor-liquid equilibria of the diacetone alcohol − water system at subatmospheric pressures. *Ind. Eng. Chem.* **1954**, *46*, 2392−2395.

Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem., Process Des. Dev..* **1975**, *14*, 209−216.

Hougen, O. A.; Watson K. M. *Chemical Process Principles, Part II*; J. Wiley: New York, 1947.

Linek, J.; Wichterle, I.; Marsh, K. N. Vapor-liquid equilibria for *N*-methyl-2-pyrrolidone + benzene, + toluene, + heptane, and + methylcyclohexane. *J. Chem. Eng. Data* **1996**, *41*, 1212−1218.

Received for review May 28, 1996. Accepted July 13, 1996.® Financial support for this work was provided by the Design Institute of Physical Property Data (DIPPR) of the American Institute of Chemical Engineers and the National Science Foundation through DIPPR Project 805/NSF(C)/89 and Project 805/(B)/89 and by the Grant Agency of the Czech Republic (Grant No. 104/96/0571).

JE960183Y

® Abstract published in *Advance ACS Abstracts,* November 1, 1996.