

<i>P</i>	pressure, MPa
<i>T</i>	temperature, K
<i>x</i>	liquid mole fraction
<i>y</i>	vapor mole fraction
<i>v</i>	molar volume, cm ³ ·mol ⁻¹
<i>w</i>	acentric factor

Subscripts

<i>c</i>	critical property
<i>R</i>	reduced property
exptl	experimental property
calcd	calculated property
<i>P</i>	pressure
<i>y</i>	vapor mole fraction

Superscripts

<i>c</i>	parameter in equations A23 to A25
<i>R</i>	relative quantity

Greek Letters

δ	binary interaction parameter in Peng–Robinson equation of state
ϕ	fugacity coefficient
σ	standard deviation

Registry No. Methane, 74-82-8; dimethyl ether, 115-10-6; diethyl ether, 60-29-7.

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Vapor–Liquid Equilibrium Data for the Methane–Methylal Binary Mixture between 273 and 432 K up to the Critical Region

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Three static apparatuses were used to obtain vapor–liquid equilibrium data for the methane–methylal system at five different temperatures. Experimental data were represented by several models. The Soave equation used in combination with an excess Gibbs free energy equation for mixing rules was found the best. Similar calculations have been performed with the Soave, Peng–Robinson, and Mathias equations of state and with the Skjold–Jorgensen equation.

Introduction

Cubic equations of state have been extensively used for the prediction and correlation of high-pressure vapor–liquid equilibrium (1). Legret et al. (2) have shown that it is possible to correlate a large number of methane–hydrocarbon experimental binary data sets using the Soave (3) and Peng–Robinson (4) equations of state. Data related to methane with polar or slightly polar compounds are scarce. For this reason, we have measured vapor–liquid equilibria of the methane–methylal mixture. These data make possible the investigation of the ability of cubic equations of state with classical mixing rules to correlate the data. In the present work, more advanced equations recently proposed for very nonideal mixtures at high pressures

are tested: Mathias (5), Soave with nonclassical mixing rules (6), and Skjold–Jorgensen (7).

Experimental Section

Apparatus. The two first apparatuses A (8) and B (9) are based on a static method with sampling and analysis of both phases. The third apparatus (10) has a variable-volume cell which makes it possible to record pressure vs. volume data and then identify bubble pressures very accurately. Composition of the liquid phase is determined in the latter apparatus by a very accurate weighing of the components introduced separately inside the equilibrium cell. The third apparatus has been essentially used to test reliability of data obtained with the two other apparatuses.

Chemicals. Methane was supplied by Messer Griesheim with a certified minimum purity of 99.995% by volume. Methylal [CH₂(OCH₃)₂] was provided by Fluka with a GLC certified minimum purity of 99%. The chemicals were used without any further purification except for the careful degassing of methylal.

Results and Discussion

Experimental procedures used to carry out all the experimental work were described in previous papers for apparatus

Table I. Vapor-Liquid Equilibrium Data for the Methane (1)-Methylal (2) System Measured with Apparatus A^a

<i>T</i> , K	<i>P</i> , MPa	<i>x</i> ₁	Δ <i>x</i> ₁	<i>y</i> ₁	Δ <i>y</i> ₁	<i>K</i> ₁	Δ <i>K</i> ₁	10 ⁻² <i>K</i> ₂	10 ⁻² Δ <i>K</i> ₂
273.6	1.00 ₃	0.028	0.001	0.978	0.002	34.9	1.3	2.26	0.2
273.6	2.02	0.057	0.002	0.9865	0.0008	17.3	0.6	1.43	0.06
273.6	4.00	0.114	0.004	0.9889	0.0008	8.67	0.3	1.25	0.07
273.6	5.95	0.173	0.005	0.9882	0.0009	5.71	0.2	1.43	0.08
273.6	8.04	0.225	0.006	0.9870	0.0008	4.39	0.1	1.68	0.08
273.6	9.87	0.274	0.007	0.986	0.002	3.60	0.1	1.93	0.02
273.6	12.71	0.352	0.009	0.972	0.002	2.76	0.08	4.32	0.03
273.6	15.08	0.411	0.010	0.958	0.004	2.33	0.07	7.13	0.06
273.6	17.53	0.471	0.009	0.948	0.003	2.01	0.04	9.83	0.05
273.6	20.15	0.547	0.009	0.925	0.003	1.69	0.03	16.56	0.07
313.4	1.03	0.023	0.002	0.857	0.006	37.3	3.5	14.6	0.6
313.4	2.01	0.050	0.002	0.930	0.006	18.6	0.9	7.37	0.6
313.4	3.99	0.101	0.004	0.953	0.004	9.44	0.4	5.23	0.5
313.4	6.05	0.154	0.005	0.958	0.003	6.22	0.2	4.96	0.4
313.4	8.03	0.205	0.007	0.958	0.003	4.67	0.2	5.28	0.4
313.4	10.05	0.262	0.008	0.959	0.002	3.66	0.1	5.56	0.3
313.4	12.47	0.315	0.008	0.951	0.003	3.02	0.09	7.15	0.5
313.4	13.22	0.342	0.009						
313.4	15.05	0.394	0.009	0.938	0.004	2.38	0.06	10.2	0.8
313.4	17.50	0.453	0.010	0.922	0.004	2.04	0.05	14.3	1.0
313.4	20.25	0.543	0.010	0.888	0.005	1.64	0.04	24.5	1.6
352.7	1.01 ₅	0.017	0.001	0.662	0.009	38.9	2.8	34.4	1.0
352.7	2.06 ₅	0.041	0.002	0.801	0.007	19.5	1.1	20.8	0.8
352.7	4.00	0.088	0.003	0.863	0.005	9.81	0.4	15.0	0.6
352.7	6.01	0.137	0.005	0.893	0.004	6.52	0.3	12.4	0.5
352.7	7.99 ₅	0.190	0.006	0.902	0.004	4.75	0.2	12.1	0.6
352.7	9.99	0.245	0.007	0.901	0.004	3.68	0.1	13.1	0.7
352.7	12.65	0.320	0.008	0.900	0.003	2.81	0.08	14.7	0.6
352.7	14.28	0.361	0.009	0.887	0.004	2.46	0.07	17.7	0.9
352.7	16.12	0.423	0.010	0.867	0.005	2.05	0.06	23.1	1.3

^a Δ*T* = ±0.2 K. Δ*P* = ±0.02 MPa.**Table II. Vapor-Liquid Equilibrium Data for the Methane (1)-Methylal (2) System Measured with Apparatus B^a**

<i>T</i> , K	<i>P</i> , MPa	<i>x</i> ₁	Δ <i>x</i> ₁	<i>y</i> ₁	Δ <i>y</i> ₁	<i>K</i> ₁	Δ <i>K</i> ₁	<i>K</i> ₂	Δ <i>K</i> ₂
393.6	2.44	0.037	0.002						
393.6	5.09	0.100	0.003	0.723	0.006	7.23	0.3	0.308	0.008
393.6	7.52	0.162	0.004	0.787	0.006	4.86	0.2	0.254	0.008
393.6	10.08	0.230	0.005	0.794	0.006	3.45	0.1	0.268	0.010
393.6	12.81	0.302	0.006	0.791	0.005	2.62	0.07	0.299	0.010
393.6	14.95	0.370	0.006	0.772	0.006	2.09	0.05	0.362	0.013
393.6	16.27	0.417	0.006	0.743	0.006	1.78	0.04	0.441	0.015
432.1	3.26	0.035	0.002	0.314	0.008	8.97	0.7	0.711	0.010
432.1	4.16	0.058	0.002	0.422	0.007	7.28	0.4	0.614	0.009
432.1	6.64	0.120	0.003	0.586	0.007	4.88	0.2	0.470	0.010
432.1	8.63	0.172	0.004	0.622	0.008	3.62	0.1	0.457	0.012
432.1	10.59	0.229	0.005	0.634	0.006	2.77	0.09	0.475	0.011
432.1	12.61	0.289	0.006	0.635	0.006	2.20	0.07	0.513	0.013
432.1	14.60	0.350	0.006	0.599	0.007	1.71	0.5	0.617	0.016

^a Δ*T* = ±0.5 K. Δ*P* = ±0.02 MPa.

A (8), apparatus B (9), and apparatus C (11).

Isothermal vapor-liquid equilibrium results are reported in Tables I and II and plotted in Figure 1. The partition coefficients are plotted in Figure 2 as a function of pressure.

Error calculations were performed in the following way. For apparatuses A and B, we have

$$z_i = \frac{1}{1 + \sum_{j \neq i} A_j R_{ij}} \quad z_i = x_i \text{ or } y_i \quad (1)$$

and then

$$\Delta z_i = z_i^2 \sum_{j \neq i} (R_{ij} \Delta A_j + A_j \Delta R_{ij}) \quad (2)$$

with

$$\frac{\Delta R_{ij}}{R_{ij}} = \frac{\Delta R_i}{R_i} + \frac{\Delta R_j}{R_j} \quad (3)$$

Δ*A_j* values are estimated from the dispersion of *A_j* and *A_i*

values obtained by analyses of five samples at least. Δ*R_i* and Δ*R_j* are the mean quadratic deviations resulting from the calibration of the chromatograph detector.

For the apparatus C errors on liquid mole fractions are given by

$$\Delta x_1 = x_1 \left[\Delta m_1 / m_1 + \frac{\Delta m(1/M_1 + 1/M_2)}{m_1/M_1 + m_2/M_2} \right] \quad (4)$$

where Δ*m*₁ = Δ*m*₂ = Δ*m* = 2 × 10⁻³ g.

The accuracies in temperatures and pressures resulting from careful calibrations are given at the bottom of each table.

The following data were obtained with apparatus C. A loading of the cell was performed with a resulting total composition of *z*₁ = 0.0660 ± 0.0003. At two temperatures 353.1 ± 0.1 and 393.1 ± 0.1 K, the respective bubble pressures and saturated liquid molar volumes were measured: 2.99 ± 0.01 and 3.53 ± 0.01 MPa, and 95.4₅ ± 0.5 and 104.3 ± 0.6 cm³·mol⁻¹.

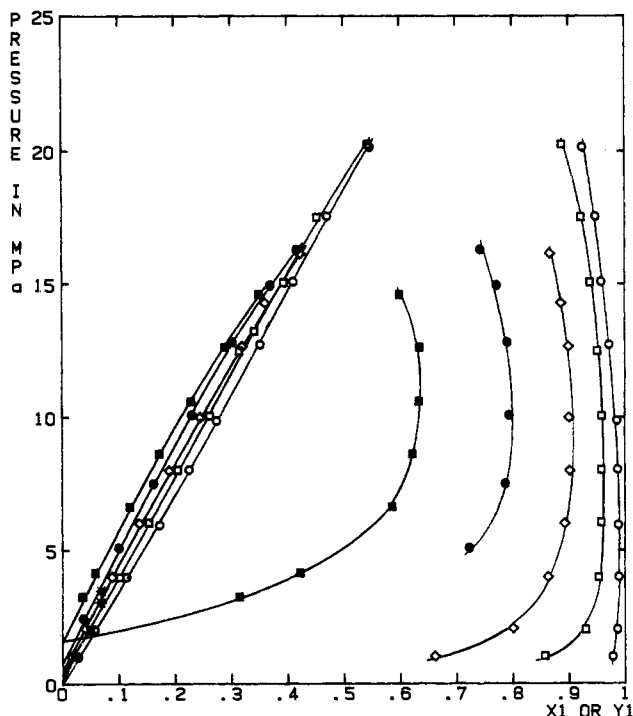


Figure 1. Pressure as a function of methane mole fraction in the system methane-methylal at 273.6 K (O); 313.4 K (□); 352.7 K (◇); 393.6 K (●); 432.1 K (■). *, data obtained with apparatus C.

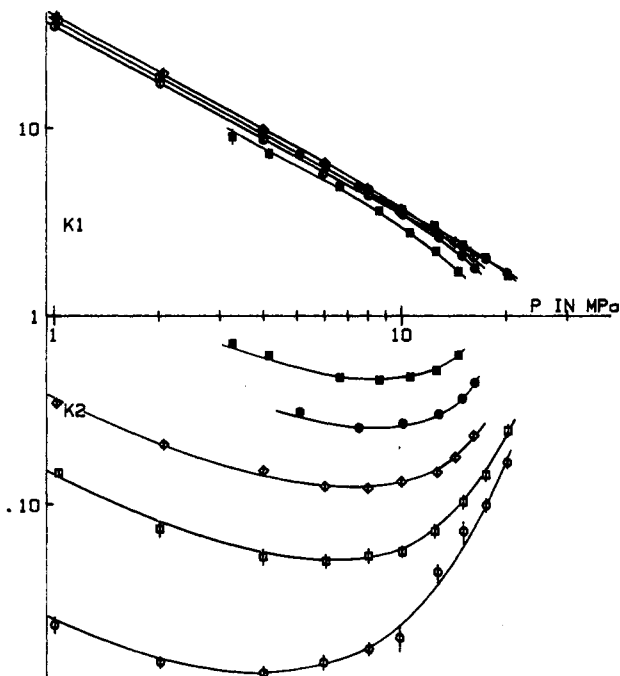


Figure 2. Partition coefficients as a function of pressure for the methane-methylal system at 273.6 K (O); 313.4 K (□); 352.7 K (◇); 393.6 K (●); 432.1 K (■).

The bubble values obtained with apparatus C are in good agreement with data obtained with apparatus A at 352.7 K and apparatus B at 393.6 K (deviations are less than 0.003 in liquid mole fraction). This study demonstrates the ability of the three different apparatuses to give reliable data. The consistency of the results should be emphasized.

Representation of Experimental Data. Three cubic equations of state with classical mixing rules, Soave's (3), Peng and Robinson's (4), and Mathias' (5), were used to represent the data at the five temperatures. The Soave and Peng-Robinson equations of state have one adjustable binary parameter. The

Table III. Critical Parameters and Acentric Factors

component	crit press., MPa	crit temp., K	acentric factor
methane ^a	4.60	190.6	0.008
methylal ^b	3.95	480.6	0.286

^a From ref 12. ^b From ref 13.

Table IV. Vapor-Liquid Equilibrium Data Representation

eq of state	parameters used	σ_x	σ_y
Soave (3)	$k_{12} = 0$	0.127	0.029
	$k_{12} = 0.106$	0.048	0.023
Peng-Robinson (4)	$\delta_{12} = 0$	0.139	0.04
	$\delta_{12} = 0.113$	0.047	0.029
Mathias (5)	null parameters	0.103	0.025
	$k_{a12}^0 = 0.07; k_{b12}^0 = -0.0225$	0.038	0.024
	$k_{a12}^0 = -0.065; k_{b12}^0 = -0.048$	0.033	0.021
	$k_{a12}^1 = 0.453; k_{b12}^1 = 0.074$		
Soave + nonclass.	null parameters	0.158	0.032
mixing rules (6)	$A_{12}^0 = 0.857; A_{12}^0 = 0.227$	0.022	0.012
	Skjold-Jorgensen (7)	$k_{ij}^* = 0.946; k_{ij}^j = -0.204$	0.027
	$\alpha_{ij} = -1.31$		

Mathias equation has either two or four adjustable parameters.

Soave's cubic equation of state combined with special mixing rules, as proposed by Huron and Vidal (6), was used as a very attractive method to improve data representation. In this equation, the excess Gibbs free energy is expressed in the Redlich-Kister form, implying two adjustable parameters. Also, the noncubic equation of state from Skjold-Jorgensen (7) with density-dependent local composition mixing rules was tested here with three adjustable parameters.

Binary interaction parameters were adjusted by minimizing the following objective function:

$$Q = \sum_{j=1}^n (x_{j,\text{exptl}} - x_{j,\text{calcd}})^2 + \sum_{j=1}^n (y_{j,\text{exptl}} - y_{j,\text{calcd}})^2 \quad (5)$$

In the above, vapor and liquid compositions were chosen as independent variables.

Critical parameters and acentric factors are given in Table III.

All the results of the modeling are reported in Table IV. Standard relative deviations given in this table were calculated through

$$\sigma_{z_i} = 100 \left[\frac{\sum_{i=1}^n (z_{i,\text{exptl}} - z_{i,\text{calcd}})^2}{n-1} \right]^{1/2} \quad (6)$$

If used in a predictive way (i.e., without binary adjustable parameters), all the equations give poor results (deviations of about 0.15 on x and 0.03 on y). One adjustable parameter in the Soave and Peng-Robinson equations of state allows to cut down the deviations on x to 0.05, but it has almost no effect on y .

Considering the equations with two or more parameters, shown in Table IV, it seems that Soave with nonclassical mixing rules is the best. The use of four instead of two parameters in the Mathias equation has no significant effect on the quality of the correlation. The equation from Skjold-Jorgensen which is noncubic in volume, and for this reason more difficult to handle, does not give better results than that of Mathias. It should be noted that the Soave equation of state with nonclassical mixing rules performs better with only two parameters than the Skjold-Jorgensen's one with three and the Mathias equation with four.

Glossary

A_i	chromatographic peak area for component i
A_{ij}	ratio of chromatographic peak areas, A_j/A_i
A_{ij}^0, A_{ij}^1	binary interaction parameters in Soave's equation of state with nonclassical mixing rules

k_{ij}	binary interaction parameter in Soave's equation of state
$k_{ajj}^0, k_{ajj}^1, k_{bjj}^0, k_{bjj}^1$	binary interaction parameters in Mathias' equation of state
k_{ij}^*, k_{ij}^f	binary interaction parameters in Skjold-Jorgensen equation of state
K	$=y/x$
n	number of experimental data
Q	objective function
R_i	response coefficient to component i
R_{ij}	ratio of chromatographic response coefficients, R_i/R_j
P	pressure, MPa
T	temperature, K
x	liquid mole fraction
y	vapor mole fraction
z	total composition

Subscripts

exptl	experimental property
calcd	calculated property
i, j	components i and j

Greek Letters

α_{ij}	binary interaction parameter in Skjold-Jorgensen equation of state
δ_{ij}	binary interaction parameter in Peng-Robinson equation of state
σ	standard deviation

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Thermodynamic Acid Dissociation Constant of the Protonated Form of Tris(hydroxymethyl)aminomethane in Water + 50 Mass % 2-Methoxyethanol Solvent from 278.15 to 318.15 K

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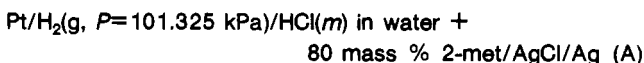
Electromotive force methods and cells without liquid junction have been utilized to determine the acidic dissociation constant of protonated tris(hydroxymethyl)aminomethane (Tris) [2-amino-2-(hydroxymethyl)-1,3-propanediol] in water + 50 mass % 2-methoxyethanol at nine temperatures from 278.15 to 318.15 K. The change of the dissociation constant with temperature has been used to calculate the changes of enthalpy and entropy when the dissociation takes place in the standard state. Comparisons with earlier measurements in water + 0 mass % 2-methoxyethanol and in water + 80 mass % 2-methoxyethanol are presented. The thermodynamic quantities for the transfer from water to water + 50 mass % 2-methoxyethanol are derived. The dissociation process is isoelectric, and the solvent dielectric constant is relatively high ($\epsilon = 51.5$ at 298.15 K); consequently, electrostatic charging effects are expected to be minimal, and the change in dissociation constant depends primarily on solute-solvent interactions. Equations showing the acidic dissociation constant as a function of temperature and solvent composition are presented.

Introduction

Tris(hydroxymethyl)aminomethane (Tris) is widely used in biochemical research for the preparation of buffers because of its low toxicity and pK near 8, which make it useful for pH

control in the clinical range (1), biological systems (2), and seawater (3, 4). Accurate measurements of the protonated Tris dissociation constant over a wide temperature range are desirable. The solvent effect on the acidic dissociation of TrisH^+ has been studied in aqueous mixtures of several organic constituents such as methanol (5, 6), methanol-propylene glycol mixtures (7), 2-propanol (8), and *N*-methylacetamide (9), to mention some.

In 1938, Ruehle (10) recommended the use of 2-methoxyethanol (2-met) as an excellent solvent for potentiometric titrations. Later the apparent dissociation constants of a considerable number of weak acid systems were determined in the solvent mixture water + 80 mass % 2-methoxyethanol (11). This solvent medium was chosen to permit adequate solubility of a wide variety of organic compounds without encountering the appreciable ion association that occurs at very low dielectric constants. In 1970, Thun, Staples, and Bates (12) reported a determination of the standard emf (E°) of the cell without liquid junction



where m is molality, over the temperature range 283.15–325.15 K. Using these E° values, Shanbhag, Vega, and Bates (13) determined the dissociation constants of acetic acid and TrisH^+ in the 80 mass % mixtures at the same range of temperature. The water + 80 mass % 2-methoxyethanol can be relatively volatile, especially for those experiments re-