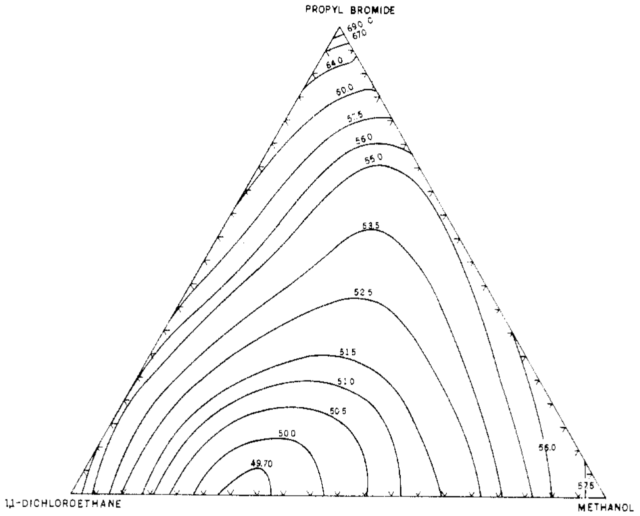

Figure 1. Isothermals for the ternary system at 760 mmHg.

Table VI. Parameters of T-x Correlation (eq 10, $N = 3$) for Methanol (1)-1,1-Dichloroethane (2)-Propyl Bromide (*3*) at 760 mmHg[a]

ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	mean D, %	rmsd
12	-46.33	5.278				
13	-51.377	3.803			2.03	0.154
23	-28.01	25.82				
12	-41.44	1.869	-35.44	6.058		
13	-46.88	16.42	-82.66	38.13	0.397	0.0238
23	-21.46	6.750	-25.67	-26.67		

[a] $t_1^0 = 64.68$ °C; $t_2^0 = 81.1$ °C; $t_3^0 = 70.55$ °C. $D = |(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})/T_{\mathrm{exptl}}|$; mean D, % $= (100/m)\sum D_i$.

been derived on the basis of the concept of "excess property" (*11*):

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + \ldots] \qquad (10)$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures as explained in ref *11*. The coefficients A_{ij}, B_{ij}, C_{ij} are multicomponent parameters which are determined directly from the multicomponent data. Figure 1 reports the isothermals obtained on the basis of the parameters A_{ij}, B_{ij} reported in Table VI by applying eq 10 for $N = 3$. These isothermals might be used for considering possible distillation paths in ternary systems as well as to conclude whether a ternary system exhibits azeotropic behavior.

As observed, whereas all binary systems have azeotropes, the ternary system does not exhibit a clear azeotropic behavior. It is possible that there is a ternary azeotrope very close in composition to that of the binary azeotrope between 1,1-dichloroethane and methanol. Table VI also contains the group of parameters A_{ij}, B_{ij}, C_{ij} for the T-x correlation (eq 10) which yield the smaller mean deviation between the calculated and observed values of T.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

A_{ij}, B_{ij}, etc.	multicomponent adjustable parameters in eq 8
B_{ii}, B_{ij}	virial coefficients, eq 2
N	number of components
P	total pressure, mmHg
P_i^0	vapor pressure of pure component i, mmHg
T	boiling temperature of a mixture, K
T_i^0	boiling temperature of pure component i, K
t	temperature, °C
x_i, y_i	mole fraction of component i in the liquid and vapor phases
α_i	coefficient, Antoine equation
β_i	coefficient, Antoine equation
γ_i	activity coefficient of component i
δ_i	coefficient, Antoine equation

Registry No. Methanol, 67-56-1; 1,1-dichloroethane, 75-34-3; propyl bromide, 106-94-5.

Literature Cited

(1) Boublikova, L.; Lu, B. C. Y. *J. Appl. Chem.* **1969**, *19*, 89.
(2) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(3) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill: New York, 1982.
(4) Tsonoupoulos, C. *AIChE J* **1974**, *33*, 263.
(5) McDermott, C.; Ellis, S. R. M. *Chem. Eng. Sci.* **1965**, *20*, 293.
(6) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1977**, *22*, 253.
(7) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.
(8) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1985**, *30*, 339.
(9) Tamir, A., Wisniak, J. *J. Chem. Eng. Data* **1986**, *31*, 383.
(10) Wisniak, J.; Tamir, A. *Chem. Eng. Sci.* **1975**, *30*, 335.
(11) Tamir, A. *Chem. Eng. Sci.* **1981**, *36*, 1453.
(12) TRC Tables. *Selected Values of Properties of Chemical Components*; Thermodynamics Research Center Data Project: College Station, TX, 1974.
(13) Perry, R. H. *Perry's Chemical Engineers' Handbook*, 6th ed.; McGraw-Hill: New York, 1984; p 3-58.

Received for review August 19, 1987. Accepted March 23, 1988.

Association Effects in the Methanol-1-Pentanol System

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

New vapor-liquid equilibria for the title system have been determined at 760 mmHg. The methanol-1-pentanol system shows strong positive deviations from ideal behavior, and thermodynamic consistency can only be explained on the basis of thermal effects and that methanol associates in the vapor phase. The boiling points were well correlated with the composition of the liquid phase.

The only literature reference to the title system is that of Hill and Van Winkle (*1*) who reported data on the vapor-liquid in different methanol-alcohol binary systems.

Inspection of the activity coefficients reported by Hill and Van Winkle indicates that they are not thermodynamically consistent and also that there are substantial numerical errors in the conversion of weight composition to molar composition. The *Dechema Data Series* (*2*) are also in error since they report the original data in molar terms, without correcting the mistakes.

0021-9568/88/1733-0432$01.50/0 © 1988 American Chemical Society

Table I. Physical Properties of Pure Components

compd	refractive index (25 °C)	normal bp, °C
methanol	1.3280[a]	64.68[a]
	1.3284[b]	64.70[b]
1-pentanol	1.4079[a]	137.00[a]
	1.4079[b]	137.8[b]

[a] This work. [b] Reference *11*.

Numerical recalculation of the equilibrium data and of the corresponding activity coefficients indicates that pentanol deviates positively from Raoult's law while methanol deviates negatively, a fact which is unacceptable from a thermodynamic point of view. The present work reports improved experimental data and possible explanations for the behavior of the activity coefficients.

It is well-known that the second virial coefficients of alcohols are in general more negative than the second virial coefficients of the corresponding alkanes. This arises because intermolecular interactions in the alkanes are augmented by dipole–dipole forces in the alcohols. The behavior of alcohols in the gas phase has been explained by the presence of dimeric and polymeric species, in addition to the monomer.

According to Lambert (*3*), when the maximum energy of dipole energy becomes larger that kT, where k is Boltzmann's constant, the possibility arises that a pair of molecules will form a dimer of fairly long life. This fact gives rise to a deviation from the gas laws which may expressed in the form $B = -RT/K$, where K is the association constant of the dimer. Lambert reports that methanol gives curved plots of log K against $1/T$, suggesting that association proceeds to degrees higher than the dimer. This hypothesis is substantiated by the results of Frurip et al. (*4*) who measured the thermal conductivity and molecular association of methanol and concluded that the main species present in that vapor are the monomer, dimer, and tetramer. This apparently occurs due to a favorably hydrogen-bonding arrangement in the cyclic tetrameric structure. Similar results have been reported by Kretschmer and Wiebe (*5*) for several alcohols.

Nothnagel et al. (*6*) applied the chemical theory of of vapor imperfections to derive empirical equations for dimerization constants of the pure components and the heteroassociation constant of the vapor mixture. The suggested equations are adaptable to polar as well as nonpolar mixtures, and they can be applied to any degree of association.

For mixtures of alcohols there is strong experimental evidence that suggests a large heat of mixing effect. Pollack et al. (*7*) measured the heats of mixing of methanol and the butanol isomers at 25 °C and found that the mixture with isobutyl alcohol was endothermic with a maximum excess energy of mixing of 157 J/mol. With *tert*-butyl alcohol the mixture was now exothermic with a maximum excess energy of mixing of 665 J/mol.

According to Pollack et al. (*7*), the observed differences in the excess properties must reflect differences in the shapes of the component molecules and the interaction between them. The Stockmayer potential functions reported by Cox (*8*) in his estimation of the second virial coefficients of the butanols point to the large intermolecular hydrogen bonding in their vapor phase.

Experimental Section

Purity of Materials**.** Analytical grade methanol (99.6+%) was supplied by Frutarom and 1-pentanol analytical grade (99%+) was purchased from Merck. The reagents were used without further purification after gas chromatographic analysis failed to show any significant impurities. Properties of the components appear in Table I.

Apparatus and Procedure**.** An all-glass modified Dvorak–Boublik recirculation still (*9*) was used in the equilibrium determinations. The experimental details have been described previously (*10*). All analyses were carried out by gas chromatography on a Packard-Becker 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with 20% OV-17 and was operated isothermally at 140 °C. Injector and detector temperatures were 230 and 220 °C, respectively. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried to convert the peak area ratio to composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C.

Results

The temperature–concentration measurements are reported in Table II and Figure 1. The activity coefficients were calculated from the following equations:

$$\ln \gamma_1 = \ln (Py_1/P_1^0x_1) + (B_{11} - v_1^L)(P - P_1^0)/RT + P(1 - y_1)^2\delta_{12}/RT \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

Table II. Experimental Vapor–Liquid Equilibrium Data for Methanol (1)–1-Pentanol (2) at 760 mmHg

			equation 1		Nothnagel (*5*)		Lambert (*2*)	
temp, °C	x_1	y_1	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
130.78	0.015	0.180	1.5993	1.0434	7.0789	1.1489	6.5356	1.1313
126.48	0.035	0.285	1.2068	1.0717	4.1909	1.2562	3.9373	1.2297
123.27	0.050	0.360	1.1575	1.0874	3.5107	1.3160	3.3424	1.3028
119.48	0.070	0.465	1.1781	1.0605	3.1312	1.3963	2.9846	1.3537
114.45	0.090	0.565	1.2732	1.0569	2.9878	1.4954	2.8621	1.4412
112.73	0.105	0.580	1.1741	1.1058	2.6753	1.5840	2.5646	1.5249
110.08	0.130	0.625	1.0996	1.1222	2.3716	1.6644	2.2779	1.5976
107.59	0.140	0.660	1.1565	1.1323	2.3804	1.7278	2.2898	1.6543
104.04	0.180	0.710	1.0713	1.1639	2.0670	1.8520	1.9926	1.7667
98.15	0.225	0.765	1.0921	1.2669	1.9251	2.1208	1.8617	2.0131
92.85	0.285	0.805	1.0746	1.4251	1.7280	2.4832	1.6763	2.3471
86.43	0.390	0.860	1.0356	1.5347	1.4896	2.9346	1.4517	2.7572
79.92	0.500	0.915	1.0613	1.5931	1.3735	3.2215	1.3504	2.9124
74.60	0.610	0.942	1.0812	1.8027	1.2788	3.6584	1.2607	3.3994
73.70	0.670	0.950	1.0207	1.9203	1.1936	3.9340	1.1780	3.6516
72.35	0.675	0.953	1.0742	1.9607	1.2188	4.0401	1.2049	3.7468
70.42	0.775	0.967	1.0082	2.1926	1.1168	4.5983	1.1069	4.2556
68.41	0.835	0.978	1.0174	2.2110	1.0894	4.7066	1.0829	4.3474
66.10	0.940	0.993	0.9996	2.3374	1.0271	5.0784	1.0248	4.6794

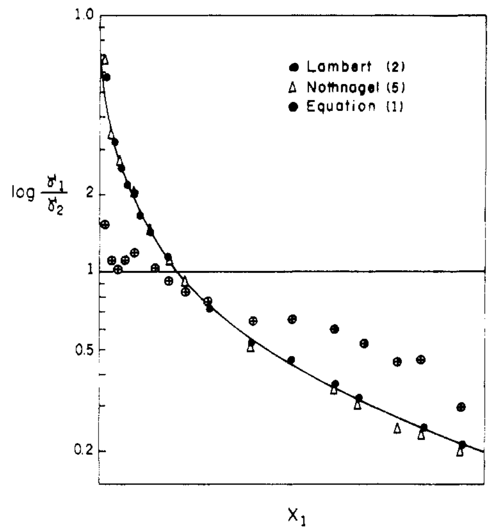

Figure 1. Boiling point diagram.

Table III. Antoine Constants (*11*)

	α_1	β_1	δ_1
methanol	7.897 50	1474.08	229.13
1-pentanol	7.177 58	1314.56	168.11

Vapor pressures of the pure components, P_i^0, were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i/(t + \delta_i) \quad (3)$$

constants of which appear in Table III (*11*). The molar virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (*12*, *13*) using the molar parameters suggested by the author. The activity coefficients reported in Table I are inconsistent by the area test (based on an application of the Gibbs–Duhem criteria assuming isothermal conditions) and by Herington's (*14*) criteria that take into account the thermal effects present in nonisothermal systems.

A reasonable possibility for the observed deviations is to assume that methanol associates in the vapor phase, so that the system actually behaves like a multicomponent one. Association constants were estimated by the methods of Lambert (*3*) and Nothnagel et al. (*6*) and activity coefficients were recalculated by using the model for binary solutions developed by Tamir and Wisniak (*15*) for associating mixtures, based on material balance of the monomeric and dimeric species present in the vapor. Not enough information was available to correct for higher polymers or heteroassociation. It was found that the Lambert method, although better, produced activity coefficients which were barely thermodynamically consistent when tested with the Herington criteria; these are also reported in Table I and show that both components deviate positively from Raoult's law.

The activity coefficients calculated with the help of the Lambert correlation were well correlated by the following Redlich–Kister (*16*) equation

$$\log \gamma_1/\gamma_2 = 0.510(x_2 - x_1) - 0.872(6x_1x_2 - 1) + 0.279(x_2 - x_1)(1 - 8x_1x_2) + 1.065(x_2 - x_1)^2(2x_1x_2 - 1) \quad (4)$$

with a coefficient of determination of 0.966 (Figure 2).

Boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (*17*):

$$T = x_1T_1 + x_2T_2 + x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \quad (5)$$

An optimization technique yielded the following values for the constants: $C_0 = -81.971$, $C_1 = 39.651$, $C_2 = -48.468$, and $C_3 = 65.410$, with an rmsd of 0.75.

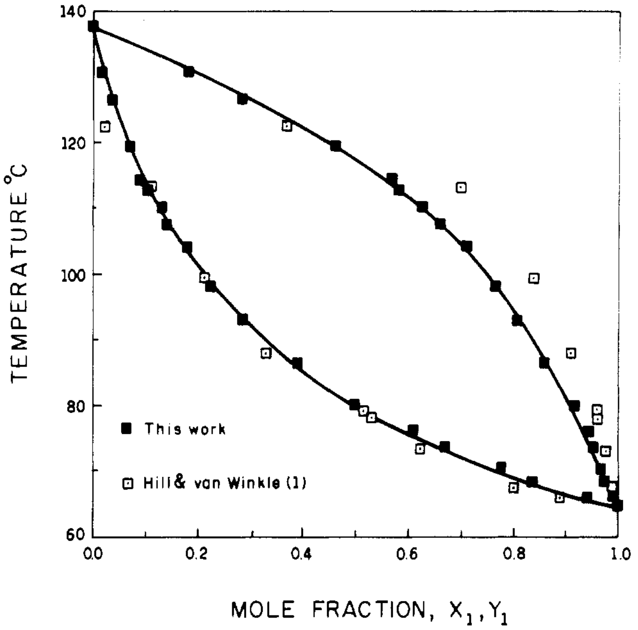

Figure 2. Activity coefficients.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical calculations.

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficient
n	number of experimental points
P	overall pressure, mmHg
P_i^0	vapor pressure of pure component, mmHg
R	gas constant
rmsd	root mean square deviation $(\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n)^{1/2}$
t, T	temperature, °C, K
v_i^L	molar volume of pure liquid i, mL/mol
x_i, y_i	molar fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

calcd	calculated
exptl	experimental
i, j	component i, j

Literature Cited

(1) Hill, W. D.; Van Winkle, M. *Ind. Eng. Chem.* **1952**, *44*, 205.
(2) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; *DECHEMA Chemistry Data Series*; Vol. 2, Part 2a; DECHEMA, 1977ff.
(3) Lambert, J. D. *Discuss. Faraday Soc.* **1953**, *15*, 226.
(4) Frurip, D. J.; Curtiss, L. A.; Blander, M. *Int. J. Thermophys.* **1981**, *2*, 115.
(5) Kretschmer, C. B.; Wiebe, R. *J. Am. Chem. Soc.* **1954**, *76*, 2579.
(6) Nothnagel, K. H.; Abrams, D. S.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1973**, *12*, 25.
(7) Pollack, J.; Murakami, S.; Lam, V. T.; Pflug, H. D.; Benson, G. C. *Can. J. Chem.* **1970**, *48*, 2475.
(8) Cox, J. D. *Trans. Faraday Soc.* **1961**, *57*, 1674.
(9) Boublikova, L.; Lu, B. C. Y. *J. Appl. Chem.* **1969**, *19*, 89.
(10) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(11) TRC Tables, *Selected Values of Properties of Chemical Compounds*; Thermodynamic Research Center Data Project: College Station, TX, 1974.
(12) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(13) Tsonopoulos, C. *AIChE J.* **1975**, *21*, 827.
(14) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(15) Tamir, A.; Wisniak, J. *Chem. Eng. Sci.* **1975**, *30*, 335.
(16) Redlich. O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.
(17) Wisniak, J.; Tamir, A. *Chem. Eng. Sci.* **1976**, *31*, 631.

Received August 19, 1987. Revised manuscript received April 12, 1988. Accepted July 7, 1988.