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Binary Total Pressure Measurements for Methanol with 1-Pentanol, 2-Pentanol, 3-Pentanol, 2-Methyl-1-butanol, 2-Methyl-2-butanol, 3-Methyl-1-butanol, and 3-Methyl-2-butanol at 313.15 K

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Total pressure measurements at 313.15 K are reported for binary systems of methanol with each of seven pentanol isomers: 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 2-methyl-2-butanol, 3-methyl-1-butanol, and 3-methyl-2-butanol. The results were obtained using a Van Ness apparatus and were fitted to the four-suffix Margules equation using Barker's method. The four-suffix Margules equation represents the data to within an average of approximately 0.02 kPa.

Introduction

It is generally accepted that alcohol molecules in solution form hydrogen-bonded complexes. Complexes in a mixture comprised of several alcohols may form by self-association (formation of a hydrogen bond between like alcohol molecules) or by cross-association (formation of a hydrogen bond between unlike alcohol molecules).

The thermodynamic data reported by Polak et al. (1970) for mixtures of methanol with each of the four butanol isomers indicate a pronounced effect of butanol isomer structure on the mixture thermodynamic properties. This may be attributed to different tendencies of the butanol isomers to self-associate and to cross-associate with methanol.

The eventual generalization of thermodynamic models which explicitly incorporate hydrogen bonding will require, among other things, the means to estimate self-association and cross-association constants for complexes containing isomeric alcohols. To provide additional information which will be useful in achieving this end, vapor−liquid equilibrium data at 313.15 K are presented here for mixtures of methanol with each of seven isomers of pentanol.

Only limited vapor−liquid equilibrium data have been reported previously for these systems. For methanol + 1-pentanol, Hill and Van Winkle (1952) and Wisniak and Tamir (1988) obtained isobaric data at 1.01 bars and Oracz (1986) obtained isothermal data at 313.15 K. Udovenko and Frid (1948) obtained isothermal data at 323.15, 333.15, and 343.15 K for methanol + 3-methyl-1-butanol.

Experimental Section

Apparatus and Procedure. The apparatus is essentially the same as described in detail by Bhethanabotla and Campbell (1991). It is of the Van Ness type (Gibbs and Van Ness, 1972) in which total pressure is measured as a function of overall composition in the equilibrium cell. Two modifications to the apparatus described by Bhethanabotla and Campbell have been made: The pressure gauge has been replaced with one of 0.001 kPa resolution as described by Pradhan et al. (1993), and the piston-injectors have been replaced with Ruska pumps (model 2200) having resolutions of 0.001 cm^3.

The overall composition in the equilibrium cell is changed by charging metered amounts of the pure components from their respective piston-injectors. The pressure in the cell is read after equilibration. The small correction (less than 0.001 in mole fraction) to convert the overall mole fraction in the equilibrium cell to liquid phase mole fraction is made as part of the data reduction procedure as described by Bhethanabotla and Campbell.

Experimental uncertainties are ±0.1% in pressure, ±0.02 K in temperature, and between ±0.0005 and ±0.001 in mole fraction, the smaller value applying at the extremes in composition.

Materials. All chemicals were obtained from Aldrich and had percent purities (by mass) of 99.7 (1-pentanol), 99.3 (2-pentanol), 99.7 (3-pentanol), 99.9 (2-methyl-1-butanol), 99.5 (2-methyl-2-butanol), 99.9 (3-methyl-1-butanol), 99.6 (3-methyl-2-butanol), and 99.98 (methanol). All chemicals were degassed by vacuum distillation and were used without additional purification. The pure component vapor pressures measured in this study are reported in Table 1 and are compared with results of Butler et al. (1935) and Thomas and Meatyard (1963) and with the compilations of Ambrose and Walton (1989) and the Thermodynamic Research Center (1996). Generally, the values reported here fall within the range of those obtained from the literature.

Data Reduction

Data were reduced using Barker's method (Barker, 1953), in which the parameters in an expression for the excess Gibbs free energy of the liquid phase are obtained by minimizing the sum of the squares between the measured and calculated pressures. Calculated pressures are obtained from

$$P_{\text{calc}} = \frac{\gamma_1 x_1 f_1^{L}}{\phi_1^{v}} + \frac{\gamma_2 x_2 f_2^{L}}{\phi_2^{v}} \qquad (1)$$

where γ_i is the activity coefficient of species i in the liquid phase and ϕ_i^{v} is the fugacity coefficient of species i in the

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Table 1. Comparison of Pure Component Vapor Pressures P_i^{sat} at 313.15 K to Values Obtained from the Literature for Pentanol Isomers and Methanol

	P_i^{sat}/kPa				
substance	this work	TRC	Ambrose and Walton (1989)	Butler et al. (1935)	Thomas and Meatyard (1963)
methanol	35.398[a]	35.443	35.440		
1-pentanol	0.887	0.834[b]	0.872		1.00
2-pentanol	2.281	2.262		2.298	2.28
3-pentanol	2.961	3.001			2.93
2-methyl-1-butanol	1.388	1.317[b]			1.36
2-methyl-2-butanol	5.737	5.236		5.758	
3-methyl-1-butanol	1.287	1.067[b]		1.260	
3-methyl-2-butanol	3.509	3.416			3.546

[a] Average of seven runs. Standard deviation = 0.026 kPa. [b] 313.15 K is outside the range of the TRC table.

Table 2. Saturated Liquid Volumes V^L_i and Second Virial Coefficients for Single Components B_{ii} and Mixtures B_{ij} Used for Methanol (1) + Pentanol Isomer (2) Systems at 313.15 K[a]

	B_{22}/ $cm^3\ mol^{-1}$	B_{12}/ $cm^3\ mol^{-1}$	V_2^L/ $cm^3\ mol^{-1}$
1-pentanol (2)	−4540	−2853	110.2
2-pentanol (2)	−4037	−2561	111.3
3-pentanol (2)	−3761	−2472	109.8
2-methyl-1-butanol (2)	−4871	−2812	109.8
2-methyl-2-butanol (2)	−3207	−2298	111.6
3-methyl-1-butanol (2)	−5602	−3019	110.6
3-methyl-2-butanol (2)	−4462	−2720	110.2

[a] For methanol (1), $B_{11}/cm^3\ mol^{-1} = -1465$ and $V_1^L/cm^3\ mol^{-1} = 41.5$.

Table 3. Values of Parameters Appearing in Eq 3 and Resulting Average Deviations ΔP_{av} and Maximum Deviations ΔP_{max} for Methanol (1) + Pentanol Isomer (2) Systems at 313.15 K

methanol (1) with	A_{12}	A_{21}	C	ΔP_{av}/ kPa	ΔP_{max}/ kPa
1-pentanol (2)	0.1651	0.3717	0.2071	0.020	0.040
2-pentanol (2)	−0.0765	0.1356	0.2207	0.015	0.033
3-pentanol (2)	−0.1629	0.0789	0.2366	0.011	0.019
2-methyl-1-butanol (2)	0.1198	0.3310	0.2185	0.017	0.041
2-methyl-2-butanol (2)	−0.2337	−0.2096	0.5123	0.009	0.025
3-methyl-1-butanol (2)	0.1353	0.3234	0.1755	0.024	0.047
3-methyl-2-butanol (2)	−0.1242	0.0782	0.2201	0.023	0.049

vapor phase and where the fugacity f_i^L of pure liquid i is obtained from

$$f_i^L = \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^L}{RT}(P - P_i^{sat})\right] \qquad (2)$$

where ϕ_i^{sat} is the fugacity coefficient of pure species i at its vapor pressure. Liquid phase activity coefficients were modeled by the four-suffix Margules equation:

$$\frac{G^E}{RT} = x_1x_2(A_{21}x_1 + A_{12}x_2 - Cx_1x_2) \qquad (3)$$

and vapor phase fugacity coefficients were calculated using the two-term virial equation (explicit in pressure).

Values of second virial coefficients and saturated liquid volumes used in these calculations are given in Table 2. Second virial coefficients were calculated using the correlation of Tsonopoulos (1974). For the pure pentanol isomers, the substance specific parameter b which appears in the correlation was estimated from Figure 8 in Tsonopoulos's paper. In the calculation of second virial cross-coefficients, the binary interaction coefficient k_{12} was assumed to be zero for all systems. Saturated liquid volumes were obtained from the TRC Thermodynamic Tables (1996).

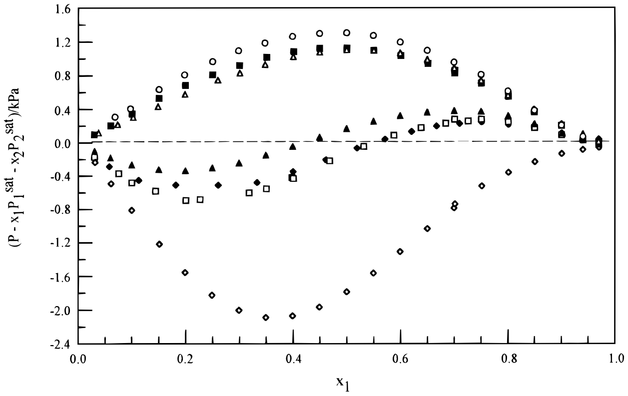

Figure 1. Deviation from Raoult's law versus liquid phase mole fraction x_1 of methanol for methanol (1) + isomeric pentanol (2) systems at 313.15 K: (○) 1-pentanol; (■) 3-methyl-1-butanol; (△) 2-methyl-1-butanol; (▲) 2-pentanol; (♦) 3-methyl-2-butanol; (□) 3-pentanol; (◇) 2-methyl-2-butanol.

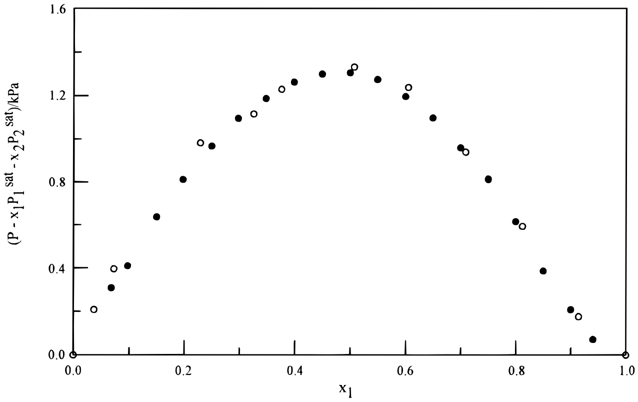

Figure 2. Deviation from Raoult's law versus liquid phase mole fraction x_1 of methanol for methanol (1) + 1-pentanol (2) at 313.15 K: (●) this work; (○) Oracz, 1986.

Results

The results of the data reduction procedure are a set of corrected liquid phase mole fractions for each pressure and values for the parameters appearing in the G^E model. Parameter values and resulting average and maximum deviations in pressure are given for each system in Table 3. The data are represented by the G^E model generally to within an average of ±0.02 kPa with a maximum deviation of ±0.05 kPa.

The results presented here will not be interpreted in terms of an association model because the self-association constants for the pentanol isomers (which must be known a priori) are not yet available. However, some qualitative aspects of the results will be discussed.

$P-x$ data at 313.15 K for the seven systems examined here are given in Table 4. The measured pressures are

Table 4. Total Pressure P as a Function of Liquid Phase Mole Fraction x_1 for Methanol (1) + Pentanol Isomer (2) at 313.15 K

methanol (1) + 1-pentanol (2)		methanol (1) + 2-pentanol (2)		methanol (1) + 3-pentanol (2)		methanol (1) + 2-methyl-1-butanol (2)		methanol (1) + 2-methyl-2-butanol (2)		methanol (1) + 3-methyl-1-butanol (2)		methanol (1) + 3-methyl-2-butanol (2)	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	0.887	0.0000	2.281	0.0000	2.961	0.0000	1.388	0.0000	5.737	0.0000	1.287	0.0000	3.509
0.0681	3.544	0.0298	3.164	0.0299	3.761	0.0375	2.782	0.0307	6.413	0.0297	2.397	0.0575	5.056
0.0970	4.641	0.0595	4.072	0.0750	5.025	0.0731	4.090	0.0607	7.047	0.0598	3.533	0.1123	6.637
0.1502	6.703	0.0997	5.317	0.0996	5.716	0.1021	5.162	0.0997	7.883	0.1002	5.054	0.1812	8.778
0.1973	8.502	0.1495	6.913	0.1437	7.046	0.1482	6.859	0.1508	8.994	0.1500	6.939	0.2600	11.286
0.2495	10.458	0.1991	8.542	0.1999	8.761	0.1984	8.709	0.1989	10.082	0.1993	8.773	0.3325	13.630
0.2975	12.242	0.2490	10.226	0.2265	9.634	0.2593	10.947	0.2486	11.288	0.2495	10.611	0.3995	15.896
0.3470	14.040	0.2985	11.924	0.3174	12.666	0.3002	12.420	0.2987	12.596	0.2995	12.428	0.4605	17.983
0.3983	15.885	0.3486	13.680	0.3500	13.774	0.3477	14.136	0.3493	14.011	0.3503	14.259	0.5184	19.970
0.4486	17.657	0.3987	15.445	0.3976	15.456	0.3996	15.988	0.3987	15.495	0.4004	16.037	0.5708	21.745
0.4992	19.408	0.4486	17.207	0.4002	15.527	0.4493	17.731	0.4489	17.087	0.4491	17.735	0.6204	23.417
0.5487	21.084	0.4990	18.982	0.4680	17.941	0.4993	19.458	0.4995	18.769	0.4997	19.466	0.6666	24.957
0.5993	22.751	0.5490	20.726	0.5309	20.157	0.5494	21.157	0.5491	20.462	0.5496	21.142	0.7098	26.363
0.6490	24.366	0.5992	22.457	0.5873	22.122	0.5990	22.810	0.5993	22.208	0.6004	22.813	0.7501	27.668
0.6993	25.962	0.6493	24.159	0.6380	23.861	0.6491	24.433	0.6494	23.967	0.6505	24.429	0.7507	27.687
0.7496	27.548	0.6995	25.838	0.6839	25.405	0.6995	26.047	0.6996	25.706	0.7006	26.026	0.8006	29.247
0.7495	27.548	0.7496	27.488	0.7006	25.993	0.6994	26.045	0.7012	25.802	0.7007	26.061	0.8504	30.793
0.7995	29.074	0.7998	29.102	0.7257	26.788	0.7495	27.598	0.7511	27.496	0.7506	27.611	0.9003	32.321
0.8494	30.565	0.7996	29.088	0.7504	27.611	0.7997	29.126	0.8008	29.134	0.8005	29.158	0.9402	33.537
0.8999	32.129	0.8497	30.656	0.8003	29.199	0.8493	30.640	0.8507	30.741	0.8494	30.639	0.9702	34.473
0.9399	33.372	0.9011	32.247	0.8502	30.752	0.9001	32.195	0.9004	32.312	0.9002	32.212	1.0000	35.384
1.0000	35.373	0.9399	33.464	0.9000	32.281	0.9402	33.437	0.9402	33.540	0.9400	33.399		
		0.9701	34.431	0.9401	33.521	0.9694	34.339	0.9704	34.464	0.9700	34.367		
		1.0000	35.412	0.9701	34.468	1.0000	35.364	1.0000	35.400	1.0000	35.413		
				1.0000	35.437								

plotted in Figure 1 as deviations from Raoult's law as a function of methanol mole fraction. It is interesting to note that all three primary alcohols show strictly positive deviations from Raoult's law and that the single tertiary alcohol (2-methyl-2-butanol) shows strictly negative deviations. The three secondary alcohols (3-methyl-2-butanol, 2-pentanol, and 3-pentanol) each show negative deviations for low methanol mole fractions and positive deviations for high methanol mole fractions. The general pattern in which the excess Gibbs free energies of these mixtures decrease in the direction from primary pentanol to tertiary pentanol is the same as was found for methanol−butanol systems by Polak et al. (1970).

Direct comparison between literature data and the data reported here can be made only for methanol + 1-pentanol. A comparison of the results of this work with those of Oracz (1986) is shown in Figure 2. The agreement between the two sets of data is excellent, and the model fitted to the results of this work predicts pressures that agree with those reported by Oracz to within an average deviation of 0.03 kPa (maximum deviation of 0.09 kPa).

Udovenko and Frid (1948) obtained isothermal vapor−liquid equilibrium data for methanol + 3-methyl-1-butanol at 323.15, 333.15, and 343.15 K and reported that the activity coefficients were independent of temperature. Consequently, the parameter values at 313.15 K given in Table 3 for this system were used to calculate pressures at 323.15 K. The resulting average deviation between calculated pressures and those reported at 323.15 K by Udovenko and Frid was 1.61 kPa, indicating a large discrepancy between their results and those of this study.

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