Total Vapor Pressure Measurements for Heptane + 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 vapor pressure measurements at 313.15 K are reported for binary systems of heptane 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 type apparatus and were fitted to the modified Margules equation using Barker's method. The four-parameter modified Margules equation represents the data to within an average absolute deviation of approximately 0.03 kPa.

Introduction

In a previous study (Barton et al., 1996), total pressure measurements for binary mixtures of methanol with seven pentanol isomers were reported. The purpose of that work was to obtain data that would be useful in studying the effect of isomer structure on cross-association between different alcohol molecules.

When applied to binary mixtures of alcohols, most association models require values for the self-association constants of each alcohol in addition to the cross-association constant. Rather than try to obtain all three association constants from a binary alcohol + alcohol isotherm, it is better to obtain the self-association constants from other data; specifically from binary data for each alcohol mixed with a nonpolar diluent. These self-association constants may then be specified apriori in the fit of the association model to the binary alcohol + alcohol mixture leaving only the value of the cross-association constant to be determined from that data.

The purpose of the present study was to obtain data that would allow the determination of the self-association constants for the pentanol isomers. To this end, vapor−liquid equilibrium data at 313.15 K are presented here for mixtures of heptane with each of seven isomers of pentanol.

Several sets of vapor−liquid equilibrium data have been reported previously for these systems. Isothermal results for heptane + 1-pentanol are available at 313.15 K (Zielkiewicz, 1994), 348.15 K (Trinh et al., 1972), 363.27 and 373.32 K (Treszczanowicz and Treszczanowicz, 1979), and at 348.15, 358.15, and 368.15 K (Machova et al., 1988). Other systems for which isothermal VLE have been published include heptane + 2-pentanol and heptane + 2-methyl-1-butanol (Wolfova et al., 1991), heptane + 3-methyl-1-butanol (Machova et al., 1988), and heptane + 3-pentanol (Wolfova et al., 1990), all at 348.15, 358.15, and 368.15 K. In addition, Wolfova et al.(1990) also reported data for heptane + 2-methyl-2-butanol at 328.15, 338.15, and 348.15 K.

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 a resolution 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 the liquid phase mole fraction is made as part of the data reduction procedure as described by Bhethanbotla 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 chromatographic analysis, as given by the manufacturer) 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 99.2 (heptane). A different lot of heptane (99.7% purity) was used for the heptane + 1-pentanol run. 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 where they are compared to the values reported by Butler et al. (1935), Thomas and Meatyard (1963), Ambrose and Sprake (1970), and Barton et al. (1996) and with the compilations of Ambrose and Walton (1989) and the Thermodynamic Research Center (1996). Generally, good agreement is found between the reported results and those of the present study. The six vapor pressures measured for the same lot of heptane agree to within ±0.025 kPa, which is at the limit of experimental uncertainty. The vapor pressure of heptane from the heptane + 1-pentanol run was slightly higher (0.09 kPa) than the average of the other six determinations.

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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 Heptane

	P_i^{sat}/kPa						
substance	this work	Barton	TRC	Ambrose and Walton	Butler *et al.*	Thomas and Meatyard	Ambrose and Sprake
heptane	12.309[a]						12.338
1-pentanol	0.891	0.887	0.834[b]	0.872		1.00	
2-pentanol	2.260	2.281	2.262		2.298	2.28	
3-pentanol	2.914	2.961	3.001			2.93	
2-methyl-1-butanol	1.395	1.388	1.317[b]			1.36	
2-methyl-2-butanol	5.662	5.737	5.236		5.758		
3-methyl-1-butanol	1.243	1.287	1.067[b]		1.260		
3-methyl-2-butanol	3.617	3.509	3.416			3.546	

[a] Average of seven runs. Standard deviation = .042 kPa [b] 313.15 K is outside the range of the TRC table.

Table 2. Saturated Liquid Volumes V_i^L and Second Virial Coefficients for Single Components B_{ii} and Mixtures B_{ij} Used for Heptane (1) + Pentanol Isomer (2) Systems at 313.15 K

	B_{22}/ ($cm^3 mol^{-1}$)	B_{12}/ ($cm^3 mol^{-1}$)	V_2^L/ ($cm^3 mol^{-1}$)
1-pentanol(2)	−4473	−1686	110.1
2-pentanol(2)	−4037	−1535	111.2
3-pentanol(2)	−3761	−1507	109.8
2-methyl-1-butanol(2)	−4871	−1614	109.8
2-methyl-2-butanol(2)	−3207	−1388	111.5
3-methyl-1-butanol(2)	−5602	−1626	110.6
3-methyl-2-butanol(2)	−4462	−1454	110.2

[a] For heptane(1), B_{11}/($cm^3 mol^{-1}$) = −2563 and V_1^L/($cm^3 mol^{-1}$) = 150.3.

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

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

where γ_i is the activity coefficient of species i in the liquid phase and ϕ_i is the fugacity coefficient of species i in the vapor phase. The fugacity f_i^L of pure liquid i is obtained from

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

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-parameter form of the modified Margules equation (Abbott and Van Ness, 1975)

$$\frac{G^E}{RT} = x_1 x_2\left(A_{21}x_1 + A_{12}x_2 - \frac{\alpha_{12}\alpha_{21}x_1x_2}{\alpha_{12}x_1 + \alpha_{21}x_2}\right) \tag{3}$$

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 0.15 for all systems as recommended by Tsonopoulos. Saturated liquid volumes for the pentanols and heptane were obtained from the TRC Thermodynamic Tables (1996).

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 between calculated and experimental pressures are given for each system in Table 3. $P-x$ data are given for each system in Table 4. The data are represented by the G^E model generally to within an average of ±0.03 kPa with a maximum deviation of ±0.10 kPa.

Direct comparison between literature data and the data reported here can be made only for heptane + 1-pentanol. A comparison of the results of this work with those of Zielkiewicz (1994) is shown in Figure 1 where excellent agreement between the two sets of data is observed. To compare the two sets of data quantitatively, we have calculated pressures at the liquid compositions reported by Zielkiewicz using the parameters obtained from fits to our data set. Pure component vapor pressures reported by Zielkiewicz were used in these calculations. The pressures calculated in this manner agreed with the experimental pressures of Zielkiewicz to within an average deviation of 0.015 kPa (maximum deviation of 0.035 kPa).

Quantitative interpretation by an association model of the results presented here will be done later as part of a more comprehensive analysis. However, some qualitative aspects of the results will be discussed here. Using the logic applied by Polak et al. (1970) to methanol + butanol isomer systems, we expect that dispersive forces would be

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

heptane (1) with	A_{12}	A_{21}	α_{12}	α_{21}	ΔP_{avg}/kPa	ΔP_{max}/kPa
1-pentanol (2)	1.4928	3.1195	1.3670	10.2239	0.019	0.047
2-pentanol (2)	1.4234	2.8523	1.3002	10.0546	0.021	0.040
3-pentanol (2)	1.3614	2.6828	1.2029	9.7573	0.024	0.068
2-methyl-1-butanol (2)	1.5048	3.0365	1.3378	10.0708	0.025	0.097
2-methyl-2-butanol (2)	1.1628	2.5356	1.1564	10.0812	0.024	0.078
3-methyl-1-butanol (2)	1.5308	3.1218	1.3845	10.0546	0.008	0.017
3-methyl-2-butanol (2)	1.3769	2.5988	1.1723	5.9117	0.017	0.043

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

heptane (1)+ 1-pentanol (2)		heptane (1) + 2-pentanol (2)		heptane (1) + 3-pentanol (2)		heptane (1)+ 2-methyl- 1-butanol (2)	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	0.891	0.0000	2.260	0.0000	2.914	0.0000	1.395
0.0299	2.392	0.0294	3.612	0.0295	4.165	0.0219	2.521
0.0594	3.673	0.0593	4.760	0.0594	5.242	0.0444	3.540
0.1296	6.041	0.0992	6.026	0.0993	6.433	0.0992	5.560
0.1566	6.765	0.1490	7.278	0.1489	7.605	0.1491	6.949
0.1985	7.702	0.1984	8.257	0.1992	8.535	0.1992	8.021
0.2485	8.583	0.2487	9.042	0.2489	9.274	0.2492	8.855
0.3000	9.297	0.2990	9.670	0.2992	9.882	0.2989	9.503
0.3476	9.821	0.3491	10.186	0.3494	10.394	0.3493	10.027
0.3991	10.279	0.3992	10.616	0.3993	10.811	0.3992	10.446
0.4492	10.631	0.4493	10.976	0.4494	11.178	0.4109	10.555
0.4494	10.714	0.4494	10.980	0.4494	11.154	0.4496	10.904
0.4992	11.006	0.4993	11.290	0.4994	11.460	0.4996	11.092
0.5493	11.244	0.5494	11.550	0.5494	11.723	0.5497	11.339
0.5995	11.447	0.5991	11.787	0.5994	11.964	0.5996	11.655
0.6496	11.630	0.6493	11.984	0.6494	12.164	0.6499	11.746
0.6981	11.780	0.6993	12.167	0.6994	12.348	0.6997	11.918
0.7492	11.932	0.7456	12.311	0.7496	12.502	0.7495	12.070
0.7974	12.054	0.7998	12.470	0.8041	12.636	0.7998	12.203
0.8499	12.182	0.8500	12.572	0.8501	12.724	0.8496	12.324
0.9000	12.312	0.9006	12.636	0.8981	12.771	0.9001	12.424
0.9400	12.391	0.9370	12.656	0.9399	12.755	0.9401	12.455
0.9701	12.442	0.9697	12.603	0.9699	12.644	0.9703	12.468
1.0000	12.387	1.0000	12.290	1.0000	12.288	1.0000	12.310

heptane (1) + 2-methyl- 2-butanol (2)		heptane(1) + 3-methyl- 1-butanol(2)		heptane(1)+ 3-methyl- 2-butanol(2)	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	5.662	0.0000	1.243	0.0000	3.617
0.0292	6.619	0.0296	2.762	0.0296	4.853
0.0592	7.469	0.0592	4.050	0.0597	5.912
0.0995	8.434	0.0986	5.482	0.0994	7.059
0.1492	9.417	0.1489	6.927	0.1493	8.211
0.1994	10.228	0.1987	8.027	0.1991	9.119
0.2492	10.891	0.2488	8.887	0.2490	9.857
0.2993	11.446	0.2989	9.561	0.2994	10.464
0.3494	11.911	0.3490	10.093	0.3491	10.956
0.3995	12.299	0.3993	10.518	0.3994	11.376
0.4495	12.620	0.4488	10.862	0.4496	11.747
0.4498	12.648	0.4990	11.152	0.4996	12.055
0.4998	12.922	0.4992	11.144	0.4997	12.000
0.5496	13.142	0.5493	11.379	0.5496	12.242
0.5998	13.328	0.5992	11.586	0.5993	12.471
0.6494	13.476	0.6494	11.764	0.6496	12.687
0.6958	13.587	0.6992	11.936	0.6995	12.816
0.7498	13.678	0.7493	12.074	0.7497	12.968
0.8000	13.724	0.7991	12.199	0.7995	13.075
0.8493	13.716	0.8493	12.314	0.8999	13.150
0.9002	13.630	0.8992	12.418	0.9405	13.071
0.9371	13.474	0.9389	12.470	0.9707	12.839
0.9699	13.142	0.9690	12.478	1.0000	12.255
1.0000	12.331	1.0000	12.300		

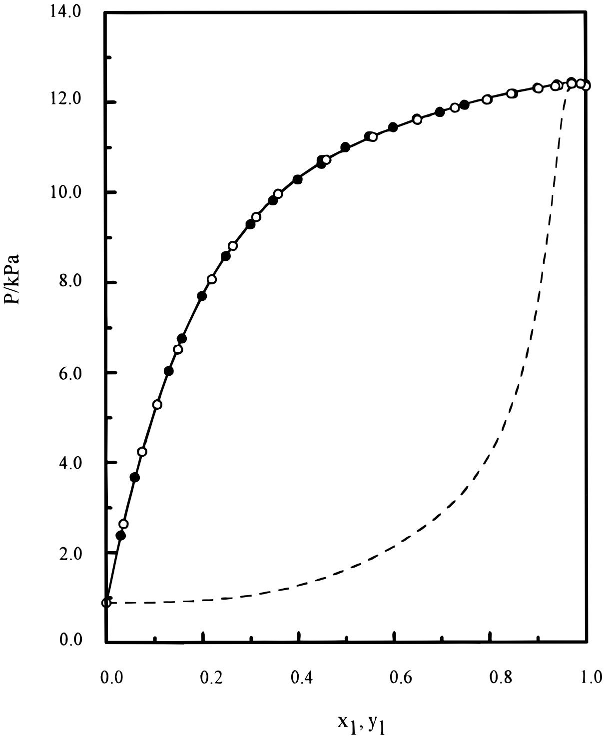

Figure 1. Pressure P versus liquid phase mole fraction x_1 and vapor phase mole fraction y_1 for heptane (1) + 1-pentanol (2) at 313.15 K: (●) experimental $P-x_1$ result, this study; (○) experimental $P-x_1$ result, Zielkiewicz, 1994; solid line is fitted $P-x_1$ result; dashed line is predicted $P-y_1$ result.

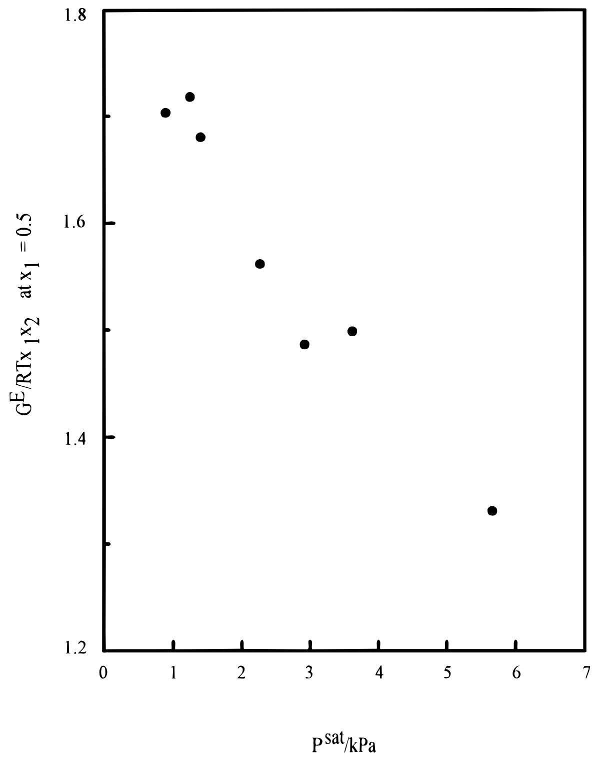

Figure 2. G^E/RTx_1x_2 at equimolar composition versus vapor pressure P^{sat} of the pentanol isomer for heptane (1) + pentanol isomer (2) systems at 313.15 K.

similar for all seven systems examined here. Consequently, the differences in the excess Gibbs free energy functions for these systems are likely caused primarily by the amount of self-association that occurs between the molecules of the isomeric pentanols.

At a given mole fraction, an increase in the number of hydrogen bonds would lead to an increase in solution nonideality. Hence, heptane + pentanol isomer systems for which the isomer has a stronger tendency to self-associate should have larger values of G^E. Also, pentanol isomers showing the greatest tendency to self-associate would be expected to have the lowest pure component vapor pressures. It is expected then that there would be an inverse correlation between G^E (at a given mole fraction) and pentanol isomer vapor pressure. In Figure 2, the function G^E/RTx_1x_2 (evaluated at $x_1 = 0.5$) is plotted for each of the seven systems examined here versus vapor pressure (at 313.15 K) of the corresponding pentanol isomer. As expected, there is an inverse correlation between the two quantities.

Furthermore, the three points in Figure 2 with the highest values of G^E correspond to the primary isomers (1-pentanol, 2-methyl-1-butanol, and 3-methyl-1-butanol), while the three points in the middle group correspond to the secondary isomers (2-pentanol, 3-pentanol, and 3-methyl-2-butanol). The point with the lowest G^E corresponds to 2-methyl-2-butanol, the only tertiary alcohol examined here. Thus, self-association of pentanol isomers increases in the direction of tertiary to primary. Previously, the same pattern was found for cross-association between butanol isomers and methanol (Polak et al., 1970) and between pentanol isomers and methanol (Barton et al., 1996).

Literature Cited

Abbott, M. M.; Van Ness, H. C. Vapor-Liquid Equilibrium: Part III. Data Reduction with Precise Expressions for G^E. *AIChE J.* **1975**, *21*, 62−71.

Ambrose, D.; Sprake, C. H. S. Thermodynamic Properties of Organic Oxygen Compounds XXV. Vapor Pressures and Normal Boiling Temperatures of Aliphatic Alcohols. *J. Chem. Thermodyn.* **1970**, *2*, 631−645.

Ambrose, D.; Walton, J. Vapor Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols. *Pure Appl. Chem.* **1989**, *61*, 1395−1403.

Barker, J. A. Determination of Activity Coefficients from Total Pressure Measurements. *Austr. J. Chem.* **1953**, *6*, 207−210.

Barton, D. P.; Bhethanabotla, V. R.; Campbell, S. W. 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. *J. Chem. Eng. Data* **1996**, *41*, 1138−1140.

Bhethanabotla, V. R.; Campbell, S. W. P-x Measurements for Ethanol-n-Heptane-Isobutanol at 303.15 K. *Fluid Phase Equilib.* **1991**, *62*, 239−258.

Butler, J. A. V.; Ramchandani, C. N.; Thomson, D. W. The Solubility of Non-electrolytes. Part I. The Free Energy of Hydration of Some Aliphatic Alcohols. *J. Chem. Soc. (London)* **1935**, 280−285.

Gibbs, R. E; Van Ness, H. C. Vapor-Liquid Equilibrium from Total Pressure Measurements. A New Apparatus. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410−413.

Machova, I.; Linek, J.; Wichterle, I. Vapor-Liquid Equilibria in the Heptane-1-Pentanol and Heptane-3-Methyl-1-Butanol System at 75, 85 and 95 °C. *Fluid Phase Equilib.* **1988**, *41*, 257−267.

Polak, J.; Murakami, S; Lam, V. T.; Pflug, H. D.; Benson, G. C. Molar Excess Enthalpies, Volumes, and Gibbs Free Energies of Methanol-Isomeric Butanol Systems at 25 °C. *Can. J. Chem.* **1970**, *48*, 2457−2465.

Pradhan, A. G.; Bhethanabotla, V. R.; Campbell, S. W. Vapor-Liquid Equilibrium Data for Ethanol-n-Heptane-1-Propanol and Ethanol-n-Heptane-2-Propanol and Their Interpretation by a Simple Association Model. *Fluid Phase Equilib.* **1993**, *84*, 183−206.

Thomas, L. H.; Meatyard, R. Viscosity and Molecular Association. Part IV. Association of Monohydric Alcohols and some Hindered Phenols. *J. Chem. Soc. (London)* **1963**, 1986−1995.

Treszczanowicz, T; Treszczanowicz, A. J. Vapor-Liquid Equilibriums of Nonelectrolyte Mixtures. Part III. Vapor-Liquid Phase Equilibriums of Binary Systems Formed by 1-Pentanol and Alkanes. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1979**, *27,* 689−695.

Trinh, B. T.; Ramalho, R. R.; Kallguine, S. Application of Wilson's Equation to Determination of Vapor-Liquid Equilibrium Data and Heats of Mixing for Nonideal Solutions. *Can J. Chem Eng.* **1972**, *50*, 771−776.

TRC Data Bases for Chemistry and Engineering, TRC Thermodynamic Tables-Non-Hydrocarbons; Thermodynamics Research Center of the Texas Engineering Experiment Station: Texas A&M University System, 1996; 1965, k-5031; 1965, k-5010; 1966, d-5031; 1991, d-1460.

Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J.* **1974**, *20*, 263−272.

Wolfova, J.; Linek, J.; Wichterle, I. Vapor-Liquid Equilibria in the Heptane-3-Pentanol and Heptane-2-Methyl-2-Butanol Systems at Constant Temperature. *Fluid Phase Equilib.* **1990**, *54*, 69−79.

Wolfova, J.; Linek, J.; Wichterle, I. Vapor-Liquid Equilibria in the Heptane-2-Pentanol and Heptane-2-Methyl-1-Butanol System at 75, 85 and 95 °C. *Fluid Phase Equilib.* **1991**, *64*, 281−289.

Zielkiewicz, J. (Vapor+Liquid) Equilibria in (Heptane + Propan-2-ol or Butan-2-ol or 2-Methylpropan-1-ol or 2-Methylpropan-2-ol or Pentan-1-ol) at the Temperature of 313.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 919−923.

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