Supporting Information

Set-up and validation of a *PρT* measuring device. Volumetric behavior of the mixture 1,8-cineole+ethanol

José M. Lasarte, Luis Martín, Elisa Langa, José S. Urieta and Ana M. Mainar.*

Group of Applied Thermodynamics and Surfaces (GATHERS), Aragon Institute for Engineering Research (I3A), Facultad de Ciencias, Universidad de Zaragoza, Zaragoza 50009, Spain.

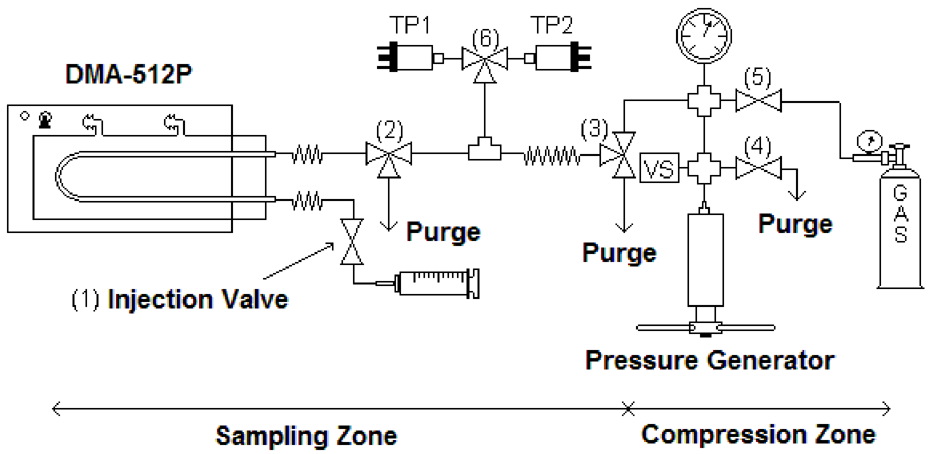
Corresponding Author Email: ammainar@unizar.es. Fax: +34 976 761 202. Phone +34 976 761 200

Number of Pages: 10

Number of Figures: 2

Number of Tables: 5

Figure S1. Experimental device: (1), (4) and (5) two-way valves; (2), (3) and (6) three-way valves; TP1 and TP2 transmitters up to 16 and 70 MPa; (VS) safety valve.



Description of the device

The measuring principle lays on the determination of the oscillation period of an U-shaped tube that contains the sample. The device consists of a densimeter (Anton Paar DMA-512 P) coupled with an evaluation unit (mPDS 2003v3) and a sampling-pressurizer system. The cell temperature is controlled by a circulating bath Julabo F34-HL. The temperature is measured by a calibrated Pt-100 probe located close to the measuring cell and connected to an ΑΣΛ F200 unit. The uncertainty in temperature is ±0.01 K. The pressurization of the samples is achieved with a pressure generator by nitrogen compression. The valves are selected to work with stainless steel tubes with an external diameter of 1/8". The small inner diameter of the high pressure tubes allows the sampling volume to be lower than 10 ml (5-8 ml). The pressure of the system was controlled by two pressure transmitters (STW-A09), with ±0.1 % full scale uncertainty of measurement, one operating up to 16 MPa, and the other, up to 70 MPa. In order to avoid risks, the sampling-pressurizer system includes a safety valve (VS) and all of its components (valves, tubes, and gauges) are oversized. To prevent accidents during the manual operation, the system also includes a second safety level, consisting of several screen-shields.

The apparatus is divided into two differentiated parts, the sample injection zone and the compression zone. The former contains the fluid whose density has to be determined and it is directly coupled with the densimeter. The pressure generated in the compression zone is controlled and read by the transmitters. The sample is pressurized by means of an inert gas, whose presence in the sampling zone is avoided by the existence of a long tube between valves 2 and 3. The compression zone is vertically placed, providing an easier manipulation.

Set-up and validation:

As it is known, density, ρ, is linearly related to the square of the measured oscillation period, Λ, by the following equation:

$$\Lambda^2(T,P) = K_1(T,P) + K_2(T,P)\cdot\rho(T,P) \tag{1}$$

where K_1 and K_2 are characteristic parameters of the apparatus. The evaluation of the equipment was accomplished by using two calibrating fluids, water (Milli-Q quality) and n-octane (purity, mole fraction >99.5 %). The liquids were degassed before use.

The following relations apply:

$$K_1(T,P) = \frac{\rho_1\cdot\Lambda^2_{\mathrm{H_2O}} - \rho_{\mathrm{H_2O}}\cdot\Lambda^2_{\mathrm{oct}}}{\rho_{\mathrm{oct}} - \rho_{\mathrm{H_2O}}} \tag{2}$$

$$K_2(T,P) = \frac{\Lambda^2_{\mathrm{oct}} - \Lambda^2_{\mathrm{H_2O}}}{\rho_{\mathrm{oct}} - \rho_{\mathrm{H_2O}}} \tag{3}$$

where $\Lambda_{\mathrm{H_2O}}$, Λ_{oct}, $\rho_{\mathrm{H_2O}}$, and ρ_{oct} are the oscillation periods and the densities of water and n-octane, respectively. In addition to the uncertainties provided by both temperature and pressure, the main contribution to the experimental uncertainty on density derived from that of the data of the two calibrating substances. Milli-Q water was chosen since its density is known with a high accuracy over large ranges of *P* and *T*. The n-octane calibration was chosen for the study of the 1,8-cineole+ethanol mixture due to its more appropriate density range. The validation of the device was done by measuring the densities of the *n*-hexane+1-hexanol mixtures at (278.15–313.15) K and (0.1–20) MPa.

Table S1. Density, ρ, versus temperature, pressure, and mole fraction for mixtures of 1-hexanol (1)+n-hexane (2).

	ρ / kg·m^{-3}									
	P / MPa					**P / MPa**				
	0.1	**5**	**10**	**15**	**20**	**0.1**	**5**	**10**	**15**	**20**
x_1	**T /K = 278.15**					**T /K = 298.15**				
0	670.8	675.9	680.5	683.5	688.7	654.2	659.5	664.7	669.2	673.2
0.1058	687.1	691.8	696.3	699.2	704.2	670.5	675.5	680.5	685.0	688.7
0.2097	703.3	708.0	712.2	715.2	719.9	687.0	691.8	696.7	700.9	704.7
0.3099	719.1	723.6	727.7	730.6	735.1	703.0	707.7	712.4	716.4	720.1
0.4149	735.7	740.0	744.0	746.8	751.1	720.1	724.6	729.0	732.9	736.4
0.4764	745.6	749.8	753.6	756.4	760.6	730.1	734.5	738.8	742.6	746.0
0.6110	767.1	771.0	774.6	777.4	781.3	752.1	756.2	760.2	763.8	767.1
0.7116	783.2	786.9	790.3	793.0	796.6	768.5	772.3	776.2	779.6	782.8
0.8055	798.1	801.6	804.9	807.5	811.0	783.7	787.3	791.0	794.2	797.3
0.9039	813.6	817.0	820.2	822.8	826.0	799.5	802.9	806.4	809.6	812.7
1	829.2	832.2	835.1	837.8	840.7	815.1	818.3	821.5	824.6	827.5
x_1	**T /K = 283.15**					**T /K = 303.15**				
0	667.5	671.8	676.2	680.7	684.4	649.8	655.5	660.2	664.9	669.3
0.1058	683.8	687.8	692.0	696.3	699.9	666.1	671.6	676.0	680.7	684.8
0.2097	699.9	703.9	708.0	712.2	715.7	682.8	688.0	692.4	696.9	700.9
0.3099	715.6	719.6	723.5	727.5	731.0	698.8	704.0	708.2	712.4	716.3
0.4149	732.4	736.2	740.0	743.8	747.1	715.9	720.8	724.8	728.8	732.7
0.4764	742.2	745.9	749.7	753.4	756.6	726.0	730.7	734.7	738.6	742.3
0.6110	763.9	767.3	770.8	774.3	777.5	748.1	752.4	756.2	759.9	763.5
0.7116	780.0	783.3	786.6	789.9	793.0	764.6	768.6	772.2	775.8	779.2
0.8055	794.9	798.0	801.2	804.3	807.5	779.9	783.7	787.1	790.5	793.9
0.9039	810.3	813.3	816.4	819.6	822.6	795.9	799.4	802.8	806.0	809.3
1	825.8	828.7	831.6	834.5	837.4	811.4	814.8	818.0	821.1	824.2
x_1	**T /K = 288.15**					**T /K = 308.15**				
0	664.0	668.5	672.9	677.6	681.3	645.1	651.1	656.3	661.2	666.0
0.1058	680.2	684.5	688.7	693.3	696.8	661.5	667.1	672.1	676.8	681.5
0.2097	696.3	700.6	704.7	709.1	712.6	678.3	683.7	688.4	693.1	697.6
0.3099	712.1	716.3	720.2	724.4	727.8	694.5	699.7	704.3	708.6	713.1
0.4149	728.8	732.9	736.6	740.6	743.9	711.7	716.7	721.0	725.2	729.3
0.4764	738.7	742.6	746.3	750.2	753.4	721.8	726.6	730.9	735.0	739.0
0.6110	760.4	764.0	767.5	771.2	774.3	744.1	748.5	752.6	756.4	760.2
0.7116	776.5	779.9	783.3	786.8	789.8	760.8	764.8	768.7	772.4	776.0
0.8055	791.4	794.6	797.9	801.2	804.2	776.3	780.0	783.7	787.1	790.6
0.9039	806.9	810.1	813.2	816.4	819.2	792.2	795.8	799.4	802.7	806.0
1	822.1	825.2	828.2	831.3	834.0	808.0	811.3	814.6	817.8	820.9
x_1	**T /K = 293.15**					**T /K = 313.15**				
0	658.8	663.7	668.8	672.8	677.4	641.3	647.3	652.8	657.4	662.5
0.1058	675.0	679.7	684.5	688.5	692.8	657.6	663.3	668.5	673.0	678.1
0.2097	691.4	696.1	700.7	704.4	708.7	674.2	679.7	684.8	689.2	694.1
0.3099	707.4	711.9	716.3	719.9	724.0	690.6	695.8	700.7	704.9	709.6
0.4149	724.3	728.5	732.8	736.3	740.1	707.9	712.9	717.5	721.5	725.9
0.4764	734.3	738.4	742.6	746.0	749.7	718.0	722.9	727.4	731.3	735.6

0.6110	756.1	760	763.9	767.2	770.7	740.4	744.9	749.1	752.8	756.8
0.7116	772.4	776.1	779.7	782.8	786.2	757.0	761.2	765.2	768.8	772.6
0.8055	787.6	791.0	794.4	797.5	800.8	772.5	776.3	780.2	783.6	787.3
0.9039	803.2	806.5	809.8	812.8	816.0	788.6	792.1	795.8	799.1	802.6
1	818.7	821.9	824.9	827.9	830.7	804.2	807.6	811.0	814.3	817.6

Table S2. Isobaric thermal expansivity, α_P and isothermal compressibility, κ_T, as function of temperature, pressure and mole fraction for mixtures 1,8-cineole (1)+ethanol (2).

	α_p / kK^{-1}					κ_T / TPa^{-1}				
	P / MPa					*P* / MPa				
	0.1	**5**	**10**	**15**	**20**	**0.1**	**5**	**10**	**15**	**20**
x_1	*T* /K = 283.15									
0	1.082	1.039	1.009	0.976	0.955	1084	1020	963	912	866
0.0983	1.044	1.003	0.979	0.939	0.916	989	935	885	841	801
0.1991	1.017	0.978	0.949	0.920	0.897	910	863	820	781	745
0.2954	0.988	0.954	0.924	0.897	0.879	854	816	780	748	719
0.3901	0.976	0.939	0.913	0.888	0.870	826	789	755	724	696
0.4930	0.964	0.934	0.909	0.880	0.862	799	763	730	700	672
0.5980	0.954	0.925	0.903	0.875	0.857	787	750	716	685	657
0.6981	0.943	0.914	0.889	0.868	0.851	787	744	704	668	636
0.7967	0.941	0.912	0.887	0.859	0.842	751	717	686	658	632
0.8898	0.933	0.908	0.887	0.859	0.842	755	717	683	652	623
1	0.929	0.900	0.876	0.852	0.835	751	716	684	655	628
x_1	*T* /K = 298.15									
0	1.100	1.056	1.025	0.990	0.969	1194	1117	1048	988	935
0.0983	1.061	1.020	0.994	0.954	0.930	1043	983	928	879	836
0.1991	1.033	0.993	0.962	0.933	0.910	1003	946	894	848	806
0.2954	1.003	0.968	0.937	0.910	0.891	948	901	858	819	784
0.3901	0.991	0.952	0.926	0.899	0.881	916	872	830	793	759
0.4930	0.978	0.947	0.921	0.892	0.874	897	852	811	774	741
0.5980	0.967	0.938	0.915	0.886	0.868	877	831	790	752	718
0.6981	0.956	0.927	0.901	0.879	0.862	878	824	775	732	694
0.7967	0.954	0.925	0.899	0.871	0.853	847	805	766	731	699
0.8898	0.946	0.920	0.899	0.870	0.853	850	803	760	721	686
1	0.942	0.913	0.887	0.863	0.845	847	803	763	727	694
x_1	*T* /K = 313.15									
0	1.118	1.073	1.041	1.005	0.983	1338	1242	1158	1085	1021
0.0983	1.078	1.034	1.009	0.967	0.942	1241	1157	1082	1016	959
0.1991	1.049	1.007	0.976	0.946	0.922	1141	1068	1002	945	894
0.2954	1.018	0.982	0.950	0.922	0.903	1060	1002	949	902	859
0.3901	1.006	0.966	0.939	0.912	0.893	1025	969	919	873	832
0.4930	0.992	0.961	0.934	0.904	0.885	991	937	888	844	804
0.5980	0.982	0.951	0.928	0.898	0.880	970	915	865	820	780
0.6981	0.970	0.940	0.913	0.891	0.873	968	902	844	794	749
0.7967	0.968	0.938	0.912	0.882	0.864	937	886	839	797	759
0.8898	0.960	0.933	0.911	0.882	0.864	931	874	823	778	738
1	0.955	0.925	0.900	0.874	0.856	929	877	829	787	749

Table S3. Excess molar volume, V_m^E, as function of temperature, pressure and mole fraction for mixtures 1,8-cineole (1)+ethanol (2).

	$V_m^E \cdot 10^{-6}$/ $m^3 \cdot mol^{-1}$				
	***P* / MPa**				
	0.1	**5**	**10**	**15**	**20**
x_1	***T* /K = 283.15**				
0.0983	-0.26	-0.25	-0.25	-0.24	-0.23
0.1991	-0.43	-0.42	-0.40	-0.40	-0.38
0.2954	-0.56	-0.53	-0.51	-0.51	-0.49
0.3901	-0.63	-0.60	-0.59	-0.58	-0.57
0.4930	-0.66	-0.64	-0.62	-0.61	-0.59
0.5980	-0.64	-0.62	-0.61	-0.59	-0.58
0.6981	-0.54	-0.54	-0.52	-0.52	-0.50
0.7967	-0.42	-0.40	-0.39	-0.38	-0.36
0.8898	-0.25	-0.26	-0.25	-0.23	-0.22
x_1	***T* /K = 298.15**				
0.0983	-0.24	-0.21	-0.21	-0.20	-0.19
0.1991	-0.43	-0.41	-0.40	-0.39	-0.38
0.2954	-0.59	-0.55	-0.54	-0.52	-0.51
0.3901	-0.66	-0.63	-0.60	-0.59	-0.57
0.4930	-0.68	-0.66	-0.63	-0.63	-0.60
0.5980	-0.65	-0.64	-0.61	-0.59	-0.57
0.6981	-0.57	-0.56	-0.54	-0.52	-0.49
0.7967	-0.45	-0.43	-0.40	-0.37	-0.36
0.8898	-0.28	-0.27	-0.24	-0.24	-0.21
x_1	***T* /K = 313.15**				
0.0983	-0.27	-0.27	-0.26	-0.26	-0.26
0.1991	-0.45	-0.44	-0.43	-0.42	-0.40
0.2954	-0.60	-0.58	-0.56	-0.55	-0.53
0.3901	-0.67	-0.65	-0.64	-0.62	-0.61
0.4930	-0.70	-0.67	-0.65	-0.64	-0.62
0.5980	-0.67	-0.65	-0.62	-0.61	-0.59
0.6981	-0.59	-0.57	-0.55	-0.53	-0.51
0.7967	-0.43	-0.41	-0.40	-0.40	-0.38
0.8898	-0.27	-0.26	-0.23	-0.22	-0.22

Table S4. Calculated density, ρ, of the mixture 1,8-cineole (1)+ethanol (2) using Peng-Robinson and Sako-Wu-Prausnitz equations of state.

	ρ / kg·m^{-3}									
	Peng–Robinson					**Sako–Wu–Prausnitz**				
	***P* / MPa**					***P* / MPa**				
	0.1	**5**	**10**	**15**	**20**	**0.1**	**5**	**10**	**15**	**20**
x_1	***T* /K = 283.15**					***T* /K = 283.15**				
0	748.7	750.5	752.2	753.9	755.4	801.6	804.7	807.7	810.5	813.3
0.0983	795.5	797.7	799.8	801.7	803.6	805.5	809.5	813.3	817.0	820.5
0.1991	833.1	835.6	838.0	840.2	842.4	814.1	818.7	823.2	827.5	831.6
0.2954	862.4	865.1	867.7	870.2	872.5	825.1	830.3	835.2	835.2	844.2
0.3901	886.6	889.5	892.3	895.0	897.4	837.7	843.1	848.3	853.2	857.7
0.4930	909.1	912.2	915.2	917.9	920.5	852.5	858.1	863.4	868.3	872.9
0.5980	928.9	932.2	935.2	938.1	940.7	868.3	873.9	879.1	884.0	888.5
0.6981	945.5	948.8	951.7	954.8	957.6	883.5	889.0	894.1	898.8	903.3
0.7967	960.0	963.4	966.5	969.5	972.2	898.5	903.7	908.6	913.2	917.4
0.8898	972.4	975.8	978.9	981.9	984.7	912.5	917.4	922.1	926.4	930.4
1	985.5	988.9	992.1	995.1	997.9	928.7	933.2	937.6	941.5	945.2
x_1	***T* /K = 298.15**					***T* /K = 298.15**				
0	737.6	739.8	741.8	743.8	745.7	782.8	786.3	789.7	793.0	796.2
0.0983	784.2	786.7	789.2	791.6	793.8	786.7	791.3	795.7	799.8	803.8
0.1991	821.7	824.7	838.0	830.1	832.6	795.8	801.2	806.3	811.1	815.7
0.2954	851.2	854.4	857.4	860.3	863.0	807.6	813.5	819.1	824.3	829.3
0.3901	875.6	879.0	882.3	885.3	888.2	821.1	827.3	833.2	838.6	843.7
0.4930	898.5	902.0	905.4	908.6	911.6	837.1	843.4	849.4	854.9	860.0
0.5980	918.6	922.4	925.9	929.1	932.2	854.1	860.3	866.2	871.6	876.7
0.6981	935.6	939.3	942.9	946.2	949.3	870.4	876.5	882.3	887.5	892.4
0.7967	950.4	954.3	957.9	961.2	964.3	886.5	892.4	897.8	902.9	907.5
0.8898	963.1	966.9	970.6	973.9	977.0	901.5	907.1	912.2	917.0	921.4
1	976.6	980.5	984.1	987.5	990.6	918.9	924.0	928.8	933.2	937.2
x_1	***T* /K = 313.15**					***T* /K = 313.15**				
0	725.6	728.2	730.6	733.0	735.2	762.9	766.9	770.9	774.7	778.3
0.0983	771.9	774.9	777.9	780.6	783.2	766.8	772.1	766.7	781.9	786.4
0.1991	809.5	813.0	816.3	819.4	822.3	776.5	782.7	788.5	794.0	799.2
0.2954	839.1	842.9	846.4	849.8	852.9	789.2	795.9	802.3	808.2	813.7
0.3901	863.9	867.9	871.6	875.1	878.4	803.7	810.8	817.4	823.5	829.2
0.4930	887.1	891.2	895.2	898.8	902.2	820.9	828.0	834.7	840.9	846.6
0.5980	907.7	912.0	916.0	919.7	923.2	839.1	846.2	852.8	858.8	864.4
0.6981	925.0	929.4	933.4	937.2	940.7	856.7	863.6	869.9	875.8	881.2
0.7967	940.2	944.6	948.8	952.6	956.1	874.0	880.5	886.6	892.2	897.3
0.8898	953.3	957.7	961.8	965.6	969.1	890.1	896.2	902.0	907.2	912.1
1	967.2	971.6	975.7	979.5	983.0	908.7	914.4	919.6	924.5	928.9

Table S5. Calculated density. ρ. of the mixture 1.8-cineole (1) + ethanol (2) using SAFT and PC-SAFT equations of state.

	ρ / kg·m^{-3}									
	SAFT					PC-SAFT				
	P / MPa					*P* / MPa				
	0.1	5	10	15	20	0.1	5	10	15	20
x_1	*T* /K = 283.15					*T* /K = 283.15				
0	832.0	836.8	841.5	846.0	850.4	792.9	796.9	800.8	804.6	808.3
0.0983	867.4	872.5	877.5	882.3	887.0	828.8	833.0	837.1	841.1	844.9
0.1991	892.8	898.2	903.5	908.5	913.4	854.5	858.9	863.2	867.4	871.4
0.2954	910.6	910.6	921.7	927.0	932.1	872.7	877.3	881.8	886.1	890.3
0.3901	924.0	929.9	935.6	941.0	946.3	886.6	891.3	896.0	900.4	904.8
0.4930	935.4	941.5	947.3	953.0	958.4	898.5	903.4	908.2	912.9	917.4
0.5980	944.6	950.9	956.9	962.7	968.3	908.4	913.4	918.4	923.2	927.8
0.6981	951.8	958.2	964.4	970.3	976.0	916.2	921.4	926.5	931.4	936.1
0.7967	957.7	964.2	970.5	976.6	982.4	922.8	928.1	933.3	938.3	943.1
0.8898	962.6	969.2	975.6	981.7	987.6	928.3	933.7	939.0	938.3	949.0
1	968.1	974.8	981.3	987.5	993.4	934.5	940.0	945.4	950.5	955.5
x_1	*T* /K = 298.15					*T* /K = 298.15				
0	815.8	821.0	826.0	830.9	835.5	780.3	784.6	788.9	792.9	796.8
0.0983	850.5	856.0	861.4	866.6	871.5	816.1	820.6	825.0	829.2	833.3
0.1991	875.3	881.2	886.8	892.3	897.5	841.6	846.3	850.9	855.3	859.6
0.2954	892.7	898.8	904.7	910.4	915.8	859.6	864.5	869.3	873.9	878.3
0.3901	905.8	912.1	918.2	924.1	929.7	873.3	878.4	883.3	888.1	892.6
0.4930	916.9	923.4	929.8	935.8	941.6	885.2	890.4	895.5	900.4	905.8
0.5980	925.9	932.6	939.2	945.4	951.3	894.9	900.3	905.5	910.6	915.4
0.6981	932.9	939.8	946.5	952.8	958.9	902.6	908.1	913.5	918.7	923.6
0.7967	938.7	945.8	952.6	959.1	965.2	909.2	914.8	920.3	925.5	930.6
0.8898	943.5	950.7	957.6	964.2	970.5	914.7	920.7	926.0	931.3	936.5
1	949.3	956.5	963.5	970.2	976.5	921.1	926.9	932.5	938.0	943.2
x_1	*T* /K = 313.15					*T* /K = 313.15				
0	799.4	805.0	810.5	815.7	820.7	767.4	772.1	776.6	781.0	785.2
0.0983	833.4	839.4	845.2	850.7	856.0	803.1	807.9	812.6	817.2	821.5
0.1991	857.7	864.0	870.1	876.0	881.6	828.5	833.6	838.5	843.2	847.7
0.2954	874.6	881.3	887.7	893.7	899.6	846.4	851.6	856.7	861.6	866.3
0.3901	887.4	894.3	900.9	907.2	913.2	860.0	865.4	870.7	875.7	880.5
0.4930	898.3	905.4	912.2	918.7	924.9	871.7	877.3	882.7	887.9	892.9
0.5980	907.1	914.4	921.4	928.1	934.5	881.4	887.1	892.7	898.0	903.2
0.6981	913.9	921.4	928.6	935.5	942.0	889.1	895.0	900.7	906.1	911.3
0.7967	919.7	927.3	934.7	941.7	948.3	895.7	901.7	907.5	913.0	918.3
0.8898	924.6	932.3	939.8	946.8	953.5	901.3	907.3	913.2	918.8	924.2
1	930.6	938.4	945.9	953.1	959.8	908.0	914.1	920.0	925.7	931.1

Figure S2. Molecule of 1.8-cineole.