Supplementary material to: Do ternary liquid mixtures exhibit negative main Fick diffusion coefficients?

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1 Partial molar volumes of a binary mixture

The molar volume of a binary liquid mixture at constant temperature and pressure is in general given by

$$v = x_1 v_1 + x_2 v_2, \tag{1}$$

On the other hand, the molar volume of a *volumetrically ideal* binary mixture is

$$v = \frac{M}{\rho} = \frac{x_1 M_1}{\rho} + \frac{x_2 M_2}{\rho} = x_1 v_1^0 + x_2 v_2^0, \tag{2}$$

where M and M_i are the molar mass of the mixture and its components.

In a *volumetrically non-ideal* mixture, the total volume is not the weighted sum of the pure component volumes v_i^0 and the partial molar volumes v_i depend on mixture composition such that they can be smaller or larger than v_i^0 due to volumetric contraction or dilatation.

Considering Eq. (1) under isothermal-isobaric conditions leads to

$$dv = x_1 dv_1 + v_1 dx_1 + x_2 dv_2 + v_2 dx_2. \tag{3}$$

The Gibbs-Duhem equation yields $x_1 dv_1 + x_2 dv_2 = 0$ so that

$$dv = v_1 dx_1 + v_2 dx_2. \tag{4}$$

From the closure $x_1 + x_2 = 1$, it follows that $dx_1 = -dx_2$. Substituting this into Eq. (4) yields $dv = v_1 dx_1 - v_2 dx_1$ and

$$\frac{dv}{dx_1} = v_1 - v_2 = v_1 - \frac{v - x_1 v_1}{x_2}, \tag{5}$$

considering Eq. (1). Finally,

$$v_1 = v + (1 - x_1)\frac{dv}{dx_1}. \tag{6}$$

Accordingly, the values of v_1 and v_2 obviously depend on mixture composition.

2 Examined compositions

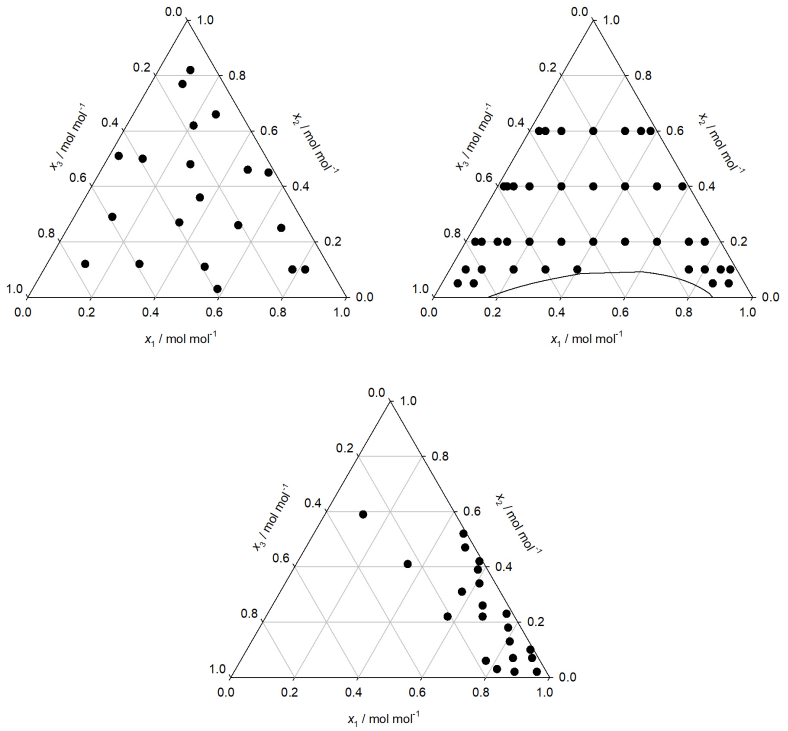

Figure 1: Compositions in terms of mole fractions at which their diffusion coefficients were measured : (a) THN – IBB – nC_{12}; (b) cyclohexane – toluene – methanol; (c) water – ethanol – TEG.

3 Tabular data for examined mixtures

Table 1: Ternary mixture THN (1) – IBB (2) – nC_{12}(3): specific density ρ kg/m^3, the molar volume v cm^3/mol calculated by Eq. (18), their diffusion coefficients $D_{ij}^V/10^{-10}$ m^2/s measured at T=298.15 and normal pressure in the volume reference frame [1, 2] and transfered to the molar and mass reference frames.

					volume				mass				molar			
#	x_1	x_2	ρ	v	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	D_{11}^m	D_{12}^m	D_{21}^m	D_{22}^m	D_{11}^M	D_{12}^M	D_{21}^M	D_{22}^M
1	0.03	0.51	798.73	190.12	12.69	0.32	-4.88	8.70	12.74	0.35	-5.13	8.65	12.83	0.42	-5.02	8.56
2	0.10	0.77	845.14	165.22	11.36	0.12	-2.84	8.55	11.43	0.17	-3.18	8.48	11.55	0.28	-3.23	8.36
3	0.10	0.82	850.33	161.66	10.80	-0.13	-1.85	9.13	10.80	-0.11	-2.04	9.12	10.83	-0.09	-2.02	9.10
4	0.11	0.50	814.08	183.44	12.44	0.33	-5.17	8.15	12.55	0.39	-5.54	8.05	12.75	0.56	-5.54	7.85
5	0.12	0.12	777.82	209.20	11.33	-0.17	-3.80	9.03	11.37	-0.14	-3.95	8.98	11.47	-0.08	-3.97	8.88
6	0.12	0.29	793.37	197.31	11.48	0.13	-4.44	7.85	11.54	0.18	-4.68	7.79	11.68	0.29	-4.70	7.65
7	0.21	0.62	851.54	165.70	12.66	1.46	-6.48	5.63	13.06	1.68	-7.45	5.22	13.75	2.31	-7.93	4.54
8	0.26	0.66	867.68	158.22	10.86	0.98	-3.91	6.20	11.17	1.15	-4.66	5.89	11.69	1.65	-5.10	5.37
9	0.27	0.48	846.97	170.093	11.55	1.07	-5.52	5.77	11.86	1.24	-6.28	5.46	12.44	1.77	-6.71	4.88
10	0.29	0.12	810.73	193.63	10.46	0.04	-3.98	7.47	10.59	0.13	-4.30	7.34	10.89	0.36	-4.52	7.05
11	0.34	0.27	837.22	178.49	10.72	0.31	-5.19	6.61	10.95	0.46	-5.75	6.37	11.44	0.84	-6.10	5.88
12	0.36	0.36	853.14	170.29	10.09	0.40	-4.07	6.33	10.31	0.55	-4.61	6.10	10.77	0.94	-4.98	5.64
13	0.46	0.46	890.83	153.96	9.89	0.83	-4.26	5.30	10.27	1.07	-5.12	4.91	11.03	1.74	-5.78	4.16
14	0.50	0.11	854.57	175.07	8.12	-0.30	-2.61	6.64	8.27	-0.18	-2.95	6.49	8.62	0.06	-3.26	6.14
15	0.53	0.26	881.08	161.71	8.32	0.22	-3.46	5.23	8.59	0.41	-4.06	4.96	9.16	0.89	-4.56	4.39
16	0.53	0.45	906.18	148.21	8.81	1.00	-2.35	5.29	9.12	1.18	-3.00	4.98	9.70	1.75	-3.57	4.40
17	0.58	0.03	862.68	173.38	7.03	-0.03	-0.63	6.26	7.08	0.03	-0.73	6.22	7.18	0.15	-0.83	6.11
18	0.67	0.25	913.97	149.54	8.15	0.44	-2.91	5.04	8.47	0.66	-3.59	4.72	9.14	1.26	-4.22	4.05
19	0.78	0.10	920.69	150.08	6.99	-0.56	-2.02	6.00	7.20	-0.35	-2.47	5.78	7.69	0.02	-2.93	5.30
20	0.82	0.10	931.33	146.40	6.56	-0.76	-1.31	6.25	6.70	-0.58	-1.62	6.11	7.03	-0.32	-1.93	5.78

Table 2: Ternary mixture cyclohexane (1)+ toluene (2)+ methanol (3): specific density ρ kg/m^3, the molar volume v cm^3/mol calculated by Eq. (21), their diffusion coefficients $D_{ij}^V/10^{-10}$ m^2/s measured at T=298.15 and normal pressure in the volume reference frame [3, 4, 5] and transferred to the molar and mass reference frames.

					volume				mass				molar			
#N	x_1	x_2	ρ	v	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	D_{11}^m	D_{12}^m	D_{21}^m	D_{22}^m	D_{11}^M	D_{12}^M	D_{21}^M	D_{22}^M
1	0.02	0.40	832.58	68.57	1.89	-0.13	-1.34	0.91	1.89	-0.12	-1.37	0.90	1.90	-0.11	-1.48	0.89
2	0.03	0.20	813.98	56.08	1.85	-0.07	-0.99	1.25	1.85	-0.07	-1.05	1.25	1.83	-0.07	-1.08	1.27
3	0.03	0.20	813.98	56.08	1.93	-0.05	-1.02	1.24	1.93	-0.04	-1.07	1.24	1.91	-0.06	-1.09	1.26
4	0.03	0.40	832.57	69.27	1.98	-0.16	-1.35	0.94	1.98	-0.15	-1.39	0.94	2.01	-0.13	-1.47	0.91
5	0.03	0.60	844.93	82.49	1.82	-0.22	-1.20	0.94	1.83	-0.21	-1.21	0.94	1.91	-0.14	-1.36	0.86
6	0.05	0.05	790.68	47.61	1.65	-0.10	-0.38	1.80	1.65	-0.09	-0.41	1.80	1.63	-0.09	-0.39	1.83
7	0.05	0.05	790.74	47.61	1.72	-0.03	-0.36	1.85	1.72	-0.03	-0.39	1.85	1.70	-0.02	-0.38	1.88
8	0.05	0.10	798.65	50.90	1.67	-0.13	-0.61	1.61	1.67	-0.12	-0.65	1.61	1.64	-0.12	-0.65	1.64
9	0.05	0.20	811.68	57.49	1.39	-0.33	-0.56	1.42	1.40	-0.31	-0.59	1.41	1.43	-0.27	-0.68	1.38
10	0.05	0.20	811.68	57.49	1.38	-0.37	-0.54	1.45	1.38	-0.35	-0.57	1.44	1.43	-0.30	-0.67	1.40
11	0.05	0.40	830.24	70.68	1.81	-0.18	-1.33	0.93	1.82	-0.17	-1.36	0.92	1.81	-0.16	-1.48	0.93
12	0.05	0.40	830.27	70.68	1.80	-0.19	-1.29	0.94	1.81	-0.18	-1.33	0.93	1.81	-0.17	-1.44	0.93
13	0.05	0.60	842.72	83.90	2.03	-0.03	-1.52	0.78	2.04	-0.02	-1.54	0.77	1.98	-0.06	-1.67	0.84
14	0.10	0.05	787.29	51.13	1.21	-0.41	-0.30	1.92	1.22	-0.39	-0.33	1.91	1.19	-0.34	-0.33	1.94
15	0.10	0.10	794.92	54.42	1.23	-0.41	-0.51	1.65	1.24	-0.39	-0.54	1.64	1.21	-0.35	-0.57	1.67
16	0.10	0.20	807.61	61.01	1.35	-0.40	-0.76	1.34	1.36	-0.38	-0.80	1.33	1.34	-0.36	-0.86	1.35
17	0.10	0.20	807.61	61.01	1.40	-0.39	-0.81	1.33	1.41	-0.37	-0.85	1.31	1.38	-0.35	-0.90	1.34
18	0.10	0.40	826.10	74.20	1.39	-0.63	-0.80	1.30	1.40	-0.60	-0.83	1.28	1.54	-0.47	-1.00	1.14
19	0.10	0.60	838.66	87.41	1.87	-0.09	-1.31	0.86	1.89	-0.08	-1.33	0.84	1.80	-0.13	-1.42	0.93
20	0.13	0.20	805.82	63.11	1.12	-0.57	-0.64	1.46	1.14	-0.54	-0.68	1.44	1.14	-0.47	-0.79	1.44
21	0.13	0.20	805.82	63.11	1.17	-0.61	-0.61	1.50	1.19	-0.58	-0.65	1.48	1.21	-0.51	-0.75	1.46
22	0.20	0.10	789.28	61.41	0.71	-0.83	-0.38	1.72	0.73	-0.81	-0.41	1.71	0.70	-0.67	-0.46	1.73
23	0.20	0.10	789.28	61.41	0.74	-0.80	-0.43	1.69	0.76	-0.78	-0.46	1.67	0.72	-0.65	-0.50	1.71
24	0.20	0.20	801.24	68.00	0.71	-0.90	-0.34	1.62	0.72	-0.87	-0.36	1.60	0.80	-0.70	-0.54	1.52
25	0.20	0.20	801.24	68.00	0.81	-0.81	-0.45	1.56	0.83	-0.78	-0.48	1.54	0.86	-0.64	-0.63	1.51
26	0.20	0.40	819.15	81.18	1.04	-0.66	-0.77	1.24	1.07	-0.64	-0.80	1.22	1.11	-0.51	-1.01	1.17
27	0.20	0.40	819.15	81.18	1.20	-0.48	-0.97	1.04	1.23	-0.46	-1.01	1.02	1.17	-0.41	-1.14	1.08
28	0.20	0.60	831.84	94.40	1.98	0.17	-1.39	0.66	2.01	0.19	-1.41	0.64	1.68	-0.05	-1.30	0.96

Table 3: DCMIX2 in different systems (continued).

					volume				mass				molar			
#	x_1	x_2	ρ	v	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	D_{11}^m	D_{12}^m	D_{21}^m	D_{22}^m	D_{11}^M	D_{12}^M	D_{21}^M	D_{22}^M
29	0.30	0.10	785.43	68.35	0.37	-1.13	0.25	1.83	0.36	-1.11	0.27	1.84	0.55	-0.91	0.05	1.65
30	0.30	0.20	796.66	74.93	0.71	-0.86	-0.50	1.45	0.73	-0.84	-0.53	1.43	0.69	-0.69	-0.61	1.46
31	0.30	0.40	813.89	88.11	1.02	-0.72	-0.55	1.39	1.04	-0.70	-0.58	1.36	1.09	-0.57	-0.74	1.31
32	0.30	0.60	826.42	101.32	1.55	-0.07	-0.41	1.42	1.56	-0.07	-0.42	1.41	1.46	-0.06	-0.51	1.51
33	0.35	0.60	824.14	104.76	2.03	0.19	-0.31	1.55	2.04	0.20	-0.31	1.54	1.89	0.05	-0.17	1.69
34	0.35	0.60	824.14	104.76	2.03	0.18	-0.31	1.55	2.03	0.19	-0.31	1.54	1.88	0.05	-0.18	1.69
35	0.38	0.60	823.10	106.82	2.06	-0.06	0.34	2.35	2.05	-0.07	0.35	2.36	2.19	0.00	0.32	2.22
36	0.38	0.60	823.10	106.82	2.07	-0.06	0.34	2.36	2.06	-0.07	0.35	2.37	2.20	0.00	0.32	2.23
37	0.38	0.60	823.08	106.82	1.91	-0.21	0.54	2.59	1.90	-0.23	0.55	2.60	2.14	-0.03	0.38	2.36
38	0.40	0.10	782.93	75.23	0.19	-1.34	-0.12	1.85	0.20	-1.33	-0.13	1.84	0.24	-1.02	-0.24	1.79
39	0.40	0.20	793.40	81.81	0.42	-1.13	-0.21	1.67	0.43	-1.12	-0.23	1.66	0.51	-0.85	-0.40	1.58
40	0.40	0.40	809.86	94.99	0.90	-0.85	-0.29	1.61	0.92	-0.84	-0.31	1.59	1.04	-0.64	-0.52	1.47
41	0.40	0.40	809.84	94.99	0.76	-0.98	-0.13	1.73	0.77	-0.98	-0.14	1.72	0.99	-0.69	-0.42	1.50
42	0.50	0.20	790.90	88.63	0.21	-1.33	0.09	1.85	0.21	-1.35	0.09	1.85	0.43	-0.97	-0.19	1.64
43	0.50	0.20	790.90	88.63	0.29	-1.30	0.04	1.83	0.30	-1.31	0.04	1.83	0.49	-0.97	-0.21	1.64
44	0.50	0.40	806.78	101.81	1.28	-0.40	-0.29	1.51	1.29	-0.39	-0.30	1.50	1.27	-0.32	-0.35	1.52
45	0.58	0.40	805.07	107.22	2.17	-0.19	0.00	2.12	2.17	-0.18	0.00	2.12	2.28	-0.32	0.06	2.01
46	0.60	0.20	789.70	95.39	0.72	-0.86	-0.26	1.49	0.73	-0.86	-0.27	1.48	0.71	-0.72	-0.30	1.50
47	0.60	0.20	789.70	95.39	0.81	-0.87	-0.34	1.50	0.84	-0.85	-0.37	1.47	0.77	-0.77	-0.35	1.54
48	0.70	0.20	788.87	102.10	0.93	-0.68	-0.14	1.56	0.94	-0.68	-0.15	1.55	0.94	-0.57	-0.18	1.55
49	0.70	0.20	788.87	102.10	0.79	-0.76	-0.05	1.60	0.80	-0.77	-0.05	1.60	0.86	-0.60	-0.14	1.54
50	0.75	0.10	780.33	98.86	0.43	-1.10	-0.01	1.71	0.43	-1.12	-0.02	1.71	0.48	-0.84	-0.10	1.66
51	0.75	0.20	788.66	105.43	1.40	0.01	-0.25	1.29	1.42	0.02	-0.26	1.27	1.26	0.05	-0.15	1.44
52	0.75	0.20	788.66	105.43	1.13	-0.29	-0.02	1.51	1.14	-0.30	-0.02	1.51	1.15	-0.17	-0.06	1.49
53	0.80	0.10	780.46	102.18	0.51	-0.97	0.13	1.75	0.50	-1.00	0.14	1.76	0.63	-0.69	-0.01	1.63
54	0.85	0.05	776.42	102.20	0.48	-1.06	0.11	1.74	0.47	-1.08	0.12	1.75	0.57	-0.86	0.01	1.65
55	0.85	0.10	780.72	105.48	0.46	-0.85	0.46	1.91	0.42	-0.91	0.49	1.94	0.75	-0.39	0.14	1.62
56	0.88	0.10	780.88	107.46	0.65	-0.51	0.52	1.87	0.60	-0.57	0.56	1.91	0.94	0.06	0.18	1.57
57	0.90	0.05	777.04	105.49	0.51	-0.96	0.35	1.90	0.48	-1.01	0.37	1.93	0.74	-0.65	0.11	1.68

Table 4: Ternary mixture water (1)–ethanol (2)–triethylene glycol (3): specific density ρ kg/m^3, the molar volumes v cm^3/mol calculated by Eq. (22), their diffusion coefficients $D_{ij}^V/10^{-10}$ m^2/s measured at T=298.15 and normal pressure in the volume refernce frame [6] and transfered to the molar and mass reference frames.

								volume				mass				molar			
#	x_1	x_2	ρ	v_1	v_2	v_3	v	D_{11}^V	D_{12}^V	D_{21}^V	D_{22}^V	D_{11}^m	D_{12}^m	D_{21}^m	D_{22}^m	D_{11}^M	D_{12}^M	D_{21}^M	D_{22}^M
1	0.12	0.59	978.30	15.22	58.17	132.36	74.53	3.18	0.04	-0.48	2.79	3.17	0.01	-1.43	2.81	3.28	0.11	-0.65	2.69
2	0.35	0.41	1003.19	16.51	57.52	132.44	61.15	3.44	0.21	0.06	2.05	3.45	0.02	0.18	2.04	3.74	0.62	-0.80	1.75
3	0.47	0.52	866.59	16.68	57.73	131.12	39.17	6.37	0.62	-0.35	3.62	6.27	-0.03	-1.05	3.71	8.25	2.24	-3.97	1.74
4	0.50	0.47	895.80	16.88	57.73	131.26	39.42	6.41	4.07	-0.99	1.91	6.10	0.93	-2.94	2.21	11.85	6.90	-8.42	-3.53
5	0.57	0.22	1033.38	17.38	56.43	132.21	50.08	2.94	0.94	0.06	1.72	2.94	0.26	0.18	1.72	3.34	1.15	-0.52	1.32
6	0.57	0.31	975.82	17.31	56.83	131.77	43.30	5.02	4.41	-0.63	1.29	4.82	1.23	-1.69	1.49	8.46	5.55	-4.96	-2.16
7	0.57	0.42	885.42	17.14	57.22	131.13	35.11	5.56	2.74	-0.46	2.95	5.37	0.61	-1.30	3.14	9.00	4.36	-5.07	-0.49
8	0.58	0.39	900.05	17.22	57.10	131.25	36.19	6.10	2.43	-0.66	3.07	5.85	0.48	-1.89	3.32	9.53	4.28	-5.54	-0.36
9	0.61	0.34	930.46	17.36	56.86	131.35	36.49	5.33	1.45	-0.37	3.16	5.19	0.26	-1.00	3.30	7.26	2.61	-3.24	1.23
10	0.66	0.26	974.20	17.56	56.42	131.45	36.77	4.76	1.55	-0.04	3.03	4.71	0.35	-0.09	3.05	5.87	2.03	-1.58	1.93
11	0.68	0.22	995.89	17.63	56.20	131.51	37.50	3.80	0.91	-0.18	2.36	3.74	0.17	-0.46	2.43	4.64	1.44	-1.45	1.52
12	0.75	0.23	937.27	17.72	56.04	130.97	28.80	3.99	-0.70	0.04	3.65	4.02	-0.31	0.13	3.62	3.82	-0.20	0.00	3.82
13	0.77	0.06	1067.19	17.81	55.16	131.60	39.40	3.19	0.64	-0.23	1.90	3.12	0.11	-0.58	1.97	3.67	1.04	-0.96	1.42
14	0.78	0.18	968.39	17.81	55.73	132.00	29.16	4.20	0.34	-0.31	3.15	4.06	-0.03	-0.80	3.29	5.18	1.14	-1.84	2.17
15	0.81	0.13	1000.95	17.87	55.40	131.02	29.54	4.11	-0.26	-0.29	3.35	3.98	-0.21	-0.72	3.47	4.80	0.65	-1.43	2.65
16	0.82	0.03	1076.84	17.88	54.85	131.36	36.01	3.24	0.14	-0.20	2.13	3.17	-0.08	-0.49	2.20	3.62	0.76	-0.78	1.75
17	0.85	0.07	1034.91	17.92	54.97	130.98	29.56	4.04	-0.64	-0.13	3.43	3.99	-0.36	-0.32	3.49	4.35	0.30	-0.68	3.12
18	0.88	0.02	1059.48	17.95	54.60	130.95	29.98	4.14	-0.81	-0.22	3.10	4.05	-0.50	-0.52	3.19	4.65	0.61	-1.01	2.59
19	0.89	0.10	965.69	17.95	54.97	130.53	22.78	6.05	-0.97	-0.11	5.90	5.99	-0.41	-0.27	5.96	6.28	-0.03	-0.59	5.67
20	0.91	0.07	987.37	17.97	54.75	130.51	22.79	5.84	-1.90	-0.83	4.69	5.32	-0.95	-2.02	5.21	8.40	1.63	-4.86	2.13
21	0.95	0.02	1019.48	17.99	54.34	130.40	22.09	5.99	-3.98	-0.02	5.01	5.99	-1.95	-0.05	5.02	6.04	-0.17	-0.25	4.96

4 Acknowledgements

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