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BINARY MIXTURES OF CYCLOHEXANONE, 2-BUTANONE, 1,4-DIOXANE AND 1,2-DIMETHOXYETHANE
Thermodynamic properties

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Abstract

Densities and sound velocities of binary mixtures of cyclohexanone, 2-butanone, 1,4-dioxane and 1,2-dimethoxyethane were measured at 298.15 K and also the densities at 303.15 K. Excess volumes were determined from densities. Isentropic compressibilities were determined from densities and sound velocities, and excess thermal expansion factors were determined from excess volumes of two temperatures. Excess isothermal compressibilities and excess isochoric heat capacities were then estimated using excess isobaric heat capacities previously reported. Excess volumes and excess isentropic and isothermal compressibilities were negative except for cyclohexanone+1,4-dioxane system.

Keywords: binary mixtures, excess isentropic and isothermal compressibilities, excess isochoric heat capacity, excess volume and thermal expansion factor

Introduction

Excess thermodynamic properties of binary mixtures containing cyclohexanone or 2-butanone have been reported, focussing on the difference between linear and cyclic species [1–8]. In previous paper [9], excess enthalpies H^E and excess isobaric heat capacities C_p^E of six binary mixtures of cyclic ketone, cyclohexanone, linear ketone, 2-butanone, cyclic diether, 1,4-dioxane, and linear diether, 1,2-dimethoxyethane have been measured and discussed. Dipole-dipole interaction plays most important role in these mixtures, and the recombination of dipole-dipole interaction in the mixtures reduces H^E to be resulted less than 300 J mol^{-1}. The orientation of dipole moments is due to the molecular shape of components and non-random mixing is observed. In this paper, the densities ρ and sound velocities u of these combinatorial mixtures were measured at 298.15 K except the mixture [x cyclohexanone+(1–x) 1,4-dioxane] already reported [1]. The densities of six mixtures were measured at 303.15 K, too. Excess volumes V^E, excess isentropic compressibilities κ_S^E, excess

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thermal expansion factors α^E, excess isothermal compressibilities κ_T^E, and excess isochoric heat capacities C_V^E were estimated. These volumetric properties are discussed in terms of the molecular shapes, (cyclic or linear), and dipole moments.

Experimental

Cyclohexanone (Aldrich, >99.8%), 2-butanone (Wako Pure Chemical, dehydrated; water content<0.00005 mass fraction), 1,4-dioxane (Wako Pure Chemical, dehydrated, water content<0.00005 mass fraction), and 1,2-dimethoxyethane (Aldrich, dehydrated, water content<0.00005 mass fraction) were used without further purification. The purity of the materials were better than 0.9997 mole fraction except for cyclohexanone, the purity of which was better than 0.9990 mole fraction, by g.l.c. using a high sensitive column for polar liquids (Shimadzu, GC-8A, column; TSG-1 for polar liquids).

Densities ρ were measured by a vibrating tube densimeter (Anton Paar, DMA602). The temperature was controlled within ±0.001 K. The accuracy is ±0.00001 g cm^{-3} restricted by the accuracy of pycnometry of standard samples, and the reproducibility is ±0.000003 g cm^{-3}. The details of measurement are described elsewhere [10].

Sound velocities u were measured by a sing around method (Cho-Onpa Co, UVM-2). The cell was immersed in a water bath controlled at T=298.15±0.0003 K. The precision was better than 0.05 m s^{-1}. The details of measurement are described elsewhere [11].

The procedures estimating isentropic and isothermal compressibilities, and isochoric heat capacity from densities and sound velocities of mixtures are reported elsewhere [12]. Excess expansion factor is estimated from excess volumes at two temperatures by the procedure described in a previous paper [13].

Results and discussion

The values of the properties, κ_S, κ_T, and C_V obtained for the pure components are given in Table 1, together with isobaric heat capacities C_p and dipole moment μ. The values of V^E at 303.15 K for the mixtures are given in Table 2. The values of ρ and u at 298.15 K for the mixtures are given in Table 3, together with the derived excess properties, V^E, κ_S^E, κ_T^E, C_V^E and α^E. They are expressed by using the following Redlich– Kister equation (1) [16];

$$V^E \text{ or } \kappa_S^E \text{ or } \kappa_T^E \text{ or } C_V^E \text{ or } \alpha^E = x(1-x)\sum A_i(1-2x)^{i-1} \quad (1)$$

In Eq. (1), x is mole fraction of the first component, the parameters A_i are estimated by the least squares method. The parameters A_i are given in Table 4 with standard deviations σ.

In all the present mixtures, the dipole-dipole interactions play important role in the stability of the mixtures. The endothermic process due to disturbance of dipole-dipole interaction is canceled by the exothermic effect due to recombination of dipole-dipole interaction in the mixture [9]. These effects reflect to the other excess properties too.

Table 1 Physical properties of the pure components at 298.15 K

	Cyclohexanone	2-Butanone	1,4-Dioxane	1,2-Dimethoxyethane
ρ/g cm^{-3}	0.94215	0.79963	1.02792	0.86106
Literature value [15]	–	0.7997	1.02797	0.86370
κ_S/TPa^{-1}	535.57	880.23	537.97	854.11
κ_T/TPa^{-1}	695.0	1116.3	748.7	1085.8
C_V/J K^{-1} mol^{-1}	137.2	127.2	108.3	149.3
C_p/J K^{-1} mol^{-1}	177.79 [3]	161.27 [8]	150.75 [14]	189.98 [9]
Literature value [15]	179.3	158.91	150.65	193.3
μ/10^{-30} C m [15]	10.27	9.21	1.50	5.80

As shown in Fig. 1, excess volumes are negative at both temperatures except for the mixture [x cyclohexanone+(1–x)1,4-dioxane] which is slightly positive because of bulkiness of both globular molecules. In the case of the mixture of both linear molecules, 2-butanone and 1,2-dimethoxyethane, V^E are considerably negative due to molecular flexibility. The other mixtures of globular molecule and linear one are negative V^E. This suggests that linear molecules squeeze into the room formed by packing of globular molecules. The values of V^E of all systems are small, and also the values of α^E are small, as seen in Fig. 2, although the systems are polar-polar mixtures. The value of excess thermal expansion factor of less than 10^{-5} K^{-1} is almost comparable to error, in consideration with the precision of density measurement.

Excess isentropic and isothermal compressibilities show that the mixtures consist of globular and linear molecules are less compressible than the other mixtures, as

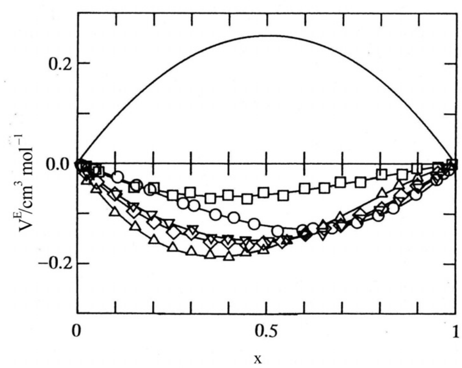

Fig. 1 Excess volumes of the mixtures, △ – x cyclohexanone+(1–x) 1,2-dimethoxyethane, ◇ – x cyclohexanone+(1–x), o – x 2-butanone, 2-butanone+(1–x) 1,4-dioxane, ▽ – x 2-butanone+(1–x) 1,2-dimethoxyethane, □ – x 1,4-dioxane+(1–x) 1,2-dimethoxyethane, —– x cyclohexanone+(1–x) 1,4-dioxane [1] at 298.15 K

Table 2 Excess volumes of the mixtures at 303.15 K

x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}
			x cyclohexanone+(1–*x*) 1,4-dioxane				
0.02468	0.024	0.29881	0.210	0.57920	0.250	0.89548	0.095
0.04954	0.047	0.33909	0.224	0.65451	0.236	0.95124	0.046
0.09474	0.086	0.38825	0.237	0.69586	0.211	0.97861	0.021
0.15119	0.131	0.43585	0.246	0.74546	0.191		
0.22125	0.174	0.49263	0.257	0.79933	0.161		
0.24279	0.185	0.52370	0.257	0.84485	0.131		
			x cyclohexanone+(1–*x*) 1,2-dimethoxyethane				
0.02747	–0.021	0.30430	–0.194	0.60158	–0.161	0.90871	–0.035
0.04999	–0.041	0.35160	–0.202	0.63054	–0.150	0.93059	–0.018
0.10119	–0.092	0.41293	–0.203	0.69661	–0.123	0.98571	–0.003
0.15255	–0.132	0.46029	–0.199	0.74435	–0.104		
0.20524	–0.159	0.51311	–0.190	0.78331	–0.085		
0.24951	–0.178	0.55348	–0.178	0.84850	–0.058		
			x cyclohexanone+(1–*x*) 2-butanone				
0.02774	–0.025	0.31148	–0.162	0.59249	–0.153	0.87663	–0.056
0.05228	–0.043	0.35907	–0.169	0.66048	–0.136	0.96043	–0.018
0.10242	–0.076	0.41543	–0.173	0.70257	–0.124	0.99075	–0.005
0.15471	–0.105	0.46045	–0.173	0.74376	–0.109		
0.20511	–0.128	0.51941	–0.168	0.80285	–0.085		

Table 2 Continued

x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}
0.25241	–0.145	0.56294	–0.159	0.85570	–0.064	–	–
			x 2-butanone+(1–x) 1,4-dioxane				
0.01627	–0.003	0.24279	–0.076	0.56192	–0.127	0.79842	–0.105
0.04513	–0.012	0.33606	–0.096	0.59793	–0.132	0.84842	–0.088
0.09187	–0.024	0.40099	–0.110	0.64726	–0.131	0.89861	–0.064
0.15700	–0.048	0.45089	–0.119	0.69991	–0.126	0.94957	–0.036
0.21683	–0.067	0.50175	–0.126	0.74895	–0.116	0.97647	–0.019
			x 2-butanone+(1–x) 1,2-dimethoxyethane				
0.01171	–0.012	0.30236	–0.136	0.59160	–0.152	0.89859	–0.054
0.07072	–0.048	0.37324	–0.147	0.64766	–0.142	0.94854	–0.030
0.09526	–0.059	0.39934	–0.145	0.69752	–0.130	0.97733	–0.011
0.15485	–0.090	0.44643	–0.148	0.75201	–0.113		
0.21512	–0.113	0.49134	–0.148	0.79473	–0.098		
0.25478	–0.124	0.54388	–0.151	0.84811	–0.078		
			x 1,4-dioxane+(1–x) 1,2-dimethoxyethane				
0.02393	–0.011	0.30458	–0.053	0.60463	–0.050	0.90609	–0.009
0.05262	–0.019	0.36375	–0.056	0.63729	–0.047	0.93846	–0.005
0.10408	–0.034	0.41327	–0.058	0.70109	–0.039	0.98930	–0.0004
0.15507	–0.045	0.46389	–0.058	0.73687	–0.032		
0.20685	–0.044	0.51354	–0.055	0.80871	–0.022		
0.25284	–0.049	0.55593	–0.052	0.85336	–0.018		

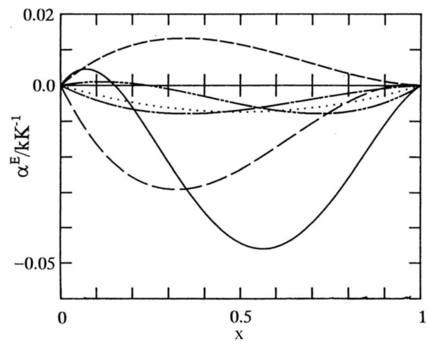

Fig. 2 Excess thermal expansion factors of the mixtures, – *x* cyclohexanone+(1–*x*) 1,2-dimethoxyethane, - - – *x* cyclohexanone+(1–*x*) 2-butanone, -·- – *x* 2-butanone+(1–*x*) 1,4-dioxane, -··- – *x* 2-butanone+(1–*x*) 1,2-dimethoxyethane, - - - – *x* 1,4-dioxane+(1–*x*) 1,2-dimethoxyethane, ··· – *x* cyclohexanone+(1–*x*) 1,4-dioxane

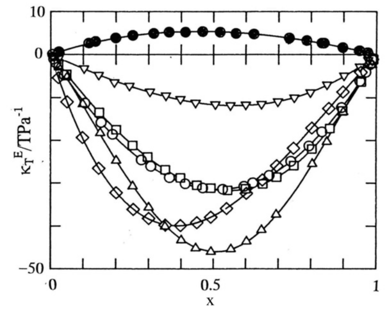

Fig. 3 Excess isothermal compressibilities of the mixtures, △ – *x* cyclohexanone+(1–*x*) 1,2-dimethoxyethane, ◇ – *x* cyclohexanone+(1–*x*) 2-butanone, o – *x* 2-butanone+(1–*x*) 1,4-dioxane, ▽ – *x* 2-butanone+(1–*x*) 1,2-dimethoxyethane, □ – *x* 1,4-dioxane+(1–*x*) 1,2-dimethoxyethane, ● – *x* cyclohexanone+(1–*x*) 1,4-dioxane [1] at 298.15 K

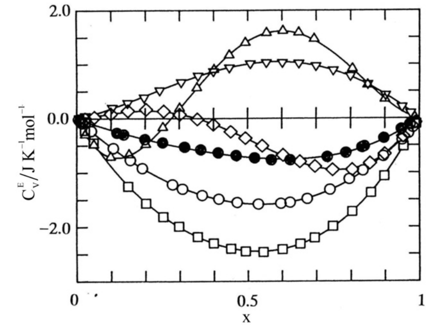

Fig. 4 Excess isochoric heat capacities of the mixtures, △ – *x* cyclohexanone+(1–*x*) 1,2-dimethoxyethane, ◇ – *x* cyclohexanone+(1–*x*) 2-butanone, o – *x* 2-butanone+(1–*x*) 1,4-dioxane, ▽ – *x* 2-butanone+(1–*x*) 1,2-dimethoxyethane, □ – *x* 1,4-dioxane+(1–*x*) 1,2-dimethoxyethane, ● – *x* cyclohexanone+(1–*x*) 1,4-dioxane [1] at 298.15

Table 3 Densities, sound velocities, excess volumes, excess isentropic and isothermal compressibilities, excess isochoric heat capacities and excess thermal expansion factor of the mixtures at 298.15 K

x	ρ/g cm^{-3}	u/m s^{-1}	V^E/cm^3 mol^{-1}	κ_S^E/TPa^{-1}	κ_T^E/TPa^{-1}	C_V^E/J K^{-1} mol^{-1}	α^E/kK^{-1}
			x cyclohexanone+(1–x) 1,2-dimethoxyethane				
0	0.860959	1166.63	–	–	–	–	–
0.02478	0.863252	1173.15	–0.035	–4.00	–3.0	–0.30	0.003
0.04975	0.865408	1179.15	–0.052	–6.80	–5.3	–0.49	0.004
0.09910	0.869781	1191.60	–0.098	–12.76	–11.5	–0.71	0.004
0.15277	0.874376	1204.92	–0.127	–17.91	–18.3	–0.68	–0.000
0.20188	0.878583	1217.11	–0.154	–21.92	–24.7	–0.48	–0.006
0.25188	0.882761	1229.36	–0.169	–24.98	–30.7	–0.17	–0.014
0.30124	0.886830	1241.32	–0.176	–27.21	–35.7	0.19	–0.022
0.35138	0.890961	1253.47	–0.183	–28.81	–40.1	0.56	–0.029
0.40136	0.895048	1265.52	–0.187	–29.76	–43.3	0.90	–0.036
0.44646	0.898644	1276.33	–0.178	–29.98	–45.2	1.17	–0.041
0.49255	0.902347	1287.27	–0.173	–29.68	–46.0	1.40	–0.044
0.55484	0.907249	1302.12	–0.154	–28.56	–45.4	1.58	–0.046
0.60269	0.911020	1313.44	–0.140	–27.11	–43.6	1.62	–0.045
0.64877	0.914626	1324.26	–0.124	–25.21	–40.9	1.59	–0.043
0.69427	0.918187	1335.02	–0.107	–23.05	–37.3	1.47	–0.039
0.80501	0.926780	1361.16	–0.059	–16.19	–25.5	0.91	–0.025
0.84967	0.930275	1372.21	–0.043	–13.29	–20.3	0.61	–0.018
0.89966	0.934219	1383.55	–0.028	–8.86	–13.3	0.35	–0.011
0.98663	0.941113	1404.64	–0.006	–1.35	–2.4	0.01	–0.001
1	0.942146	1407.77					

Table 3 Continued

x	ρ/g cm^{-3}	u/m s^{-1}	V^E/cm^3 mol^{-1}	κ_S^E/TPa^{-1}	κ_T^E/TPa^{-1}	C_V^E/J K^{-1} mol^{-1}	α^E/kK^{-1}
			x cyclohexanone+(1–x) 2-butanone				
0	0.799630	1191.93					
0.02371	0.803700	1197.77	–0.020	–3.77	–5.4	–0.004	–0.005
0.05068	0.808241	1204.35	–0.037	–7.49	–11.0	0.02	–0.009
0.09916	0.816249	1215.89	–0.061	–13.31	–19.3	0.08	–0.016
0.14885	0.824428	1227.72	–0.095	–18.38	–26.5	0.14	–0.022
0.20235	0.832974	1240.21	–0.117	–22.69	–32.2	0.16	–0.026
0.25395	0.841080	1252.15	–0.137	–25.81	–36.1	0.13	–0.028
0.30077	0.848190	1262.73	–0.139	–27.75	–38.2	0.07	–0.029
0.35188	0.855972	1274.32	–0.157	–29.35	–39.8	–0.02	–0.029
0.39892	0.862891	1284.69	–0.157	–29.97	–39.9	–0.12	–0.028
0.44959	0.870286	1295.78	–0.163	–30.03	–39.2	–0.25	–0.026
0.49299	0.876454	1305.18	–0.158	–29.63	–37.9	–0.37	–0.024
0.54233	0.883387	1315.73	–0.155	–28.60	–35.9	–0.51	–0.021
0.60326	0.891716	1328.62	–0.141	–26.71	–32.4	–0.68	–0.017
0.65178	0.898247	1338.72	–0.129	–24.65	–29.2	–0.80	–0.014
0.69579	0.904128	1347.69	–0.123	–22.45	–25.9	–0.89	–0.011
0.74662	0.910711	1358.01	–0.102	–19.47	–21.8	–0.95	–0.008
0.80373	0.918081	1369.55	–0.089	–15.88	–17.1	–0.95	–0.004
0.85641	0.924643	1380.00	–0.062	–12.03	–12.5	–0.83	–0.002
0.89876	0.929869	1388.29	–0.043	–8.71	–8.7	–0.66	–0.001
0.95268	0.936443	1398.77	–0.019	–4.23	–4.1	–0.34	–0.000
1	0.942146	1407.77					

Table 3 Continued

x	ρ/g cm^{-3}	u/m s^{-1}	V^E/cm^3 mol^{-1}	κ_S^E/TPa^{-1}	κ_T^E/TPa^{-1}	C_V^E/J K^{-1} mol^{-1}	α^E/kK^{-1}
			x 2-butanone+(1–x) 1,4-dioxane				
0	1.027920	1344.74					
0.00853	1.025907	1343.31	–0.003	–0.86	–1.0	–0.05	–0.000
0.01631	1.024062	1342.00	–0.005	–1.64	–1.9	–0.09	–0.001
0.04222	1.017953	1337.68	–0.013	–4.16	–4.8	–0.23	–0.002
0.10636	1.002838	1327.17	–0.027	–9.99	–11.3	–0.55	–0.004
0.15577	0.991309	1319.27	–0.043	–14.06	–15.8	–0.77	–0.006
0.19056	0.983202	1313.72	–0.052	–16.69	–18.6	–0.92	–0.006
0.27935	0.962679	1299.84	–0.079	–22.37	–24.6	–1.22	–0.008
0.30782	0.956083	1295.38	–0.083	–23.86	–26.1	–1.30	–0.008
0.36505	0.942985	1286.59	–0.101	–26.40	–28.7	–1.42	–0.008
0.41370	0.931803	1279.12	–0.107	–28.01	–30.1	–1.49	–0.008
0.46761	0.919557	1270.88	–0.120	–29.11	–31.1	–1.55	–0.007
0.53002	0.905434	1261.42	–0.134	–29.72	–31.4	–1.58	–0.006
0.59559	0.890533	1251.65	–0.133	–29.25	–30.7	–1.57	–0.006
0.62328	0.884236	1247.50	–0.129	–28.78	–29.9	–1.55	–0.005
0.67317	0.872993	1240.06	–0.128	–27.28	–28.2	–1.48	–0.004
0.73869	0.858223	1230.29	–0.117	–24.40	–24.9	–1.31	–0.003
0.79480	0.845618	1222.01	–0.103	–20.85	–21.3	–1.12	–0.002
0.83511	0.836555	1216.04	–0.088	–17.86	–18.0	–0.96	–0.002

Table 3 Continued

x	ρ/g cm^{-3}	u/m s^{-1}	V^E/cm^3 mol^{-1}	κ_S^E/TPa^{-1}	κ_T^E/TPa^{-1}	C_V^E/J K^{-1} mol^{-1}	α^E/kK^{-1}
0.89507	0.823094	1207.25	–0.060	–12.25	–12.3	–0.70	–0.001
0.94965	0.810888	1199.27	–0.031	–6.40	–6.2	–0.40	–0.000
0.96796	0.806798	1196.63	–0.019	–4.08	–4.1	–0.28	–0.000
0.98139	0.803807	1194.63	–0.012	–2.46	–2.3	–0.17	–0.000
1	0.799660	1191.94					
			x 2-butanone+(1–x) 1,2-dimethoxyethane				
0	0.860959	1166.60					
0.00686	0.860635	1166.93	–0.005	–0.30	–0.3	0.01	0.000
0.02499	0.859779	1167.62	–0.018	–0.90	–0.9	0.05	0.000
0.10326	0.855921	1170.47	–0.060	–3.04	–3.3	0.20	0.001
0.14823	0.853665	1172.18	–0.085	–4.40	–4.8	0.29	0.001
0.19590	0.851155	1174.05	–0.101	–5.71	–6.5	0.39	0.001
0.24205	0.848712	1175.18	–0.118	–6.10	–7.3	0.52	–0.000
0.30467	0.845243	1177.05	–0.130	–6.82	–8.7	0.67	–0.001
0.35393	0.842537	1178.32	–0.148	–7.24	–9.6	0.79	–0.002
0.39919	0.839889	1179.64	–0.149	–7.55	–10.4	0.87	–0.003
0.44565	0.837148	1180.94	–0.152	–7.93	–11.2	0.94	–0.004
0.50726	0.833434	1182.37	–0.154	–7.74	–11.6	1.01	–0.005
0.55420	0.830519	1183.49	–0.150	–7.73	–11.8	1.03	–0.006
0.60084	0.827531	1184.54	–0.141	–7.31	–11.7	1.03	–0.007
0.64921	0.824471	1185.57	–0.141	–7.08	–11.5	1.02	–0.008
0.69946	0.821087	1186.65	–0.123	–6.38	–10.9	0.97	–0.008

Table 3 Continued

x	ρ/g cm^{-3}	u/m s^{-1}	V^E/cm^3 mol^{-1}	κ_S^E/TPa^{-1}	κ_T^E/TPa^{-1}	C_V^E/J K^{-1} mol^{-1}	α^E/kK^{-1}
0.74922	0.817709	1187.61	–0.108	–5.76	–10.0	0.89	–0.008
0.79943	0.814232	1188.56	–0.091	–4.77	–8.8	0.78	–0.007
0.84977	0.810686	1189.37	–0.073	–3.78	–7.0	0.63	–0.006
0.90167	0.806899	1190.27	–0.046	–2.42	–4.9	0.43	–0.005
0.95033	0.803345	1191.21	–0.027	–1.57	–2.8	0.21	–0.003
0.97537	0.801408	1191.51	–0.007	–0.49	–1.3	0.10	–0.001
1	0.799600	1191.95					
			x 1,4-dioxane+(1–*x*) 1,2-dimethoxyethane				
0	0.861264	1166.83					
0.02399	0.864603	1170.23	–0.006	–3.30	–2.3	–0.22	0.002
0.04864	0.868062	1173.73	–0.012	–6.57	–4.6	–0.45	0.004
0.05698	0.869264		–0.017				0.004
0.14969	0.882675	1188.37	–0.047	–18.04	–13.5	–1.25	0.009
0.20207	0.890315	1196.18	–0.048	–22.69	–17.5	–1.56	0.011
0.25201	0.897873	1203.93	–0.063	–26.80	–21.2	–1.81	0.013
0.29822	0.904813	1211.17	–0.057	–29.67	–23.9	–1.99	0.013
0.35176	0.913184	1219.78	–0.069	–32.53	–26.9	–2.18	0.013
0.39856	0.920485	1227.50	–0.062	–34.23	–28.8	–2.30	0.013
0.45026	0.928849	1236.30	–0.070	–35.63	–30.5	–2.40	0.012
0.49322	0.935748	1243.66	–0.057	–35.93	–31.2	–2.45	0.011

Table 3 Continued

x	ρ/g cm^{-3}	u/m s^{-1}	V^E/cm^3 mol^{-1}	κ_S^E/TPa^{-1}	κ_T^E/TPa^{-1}	C_V^E/J K^{-1} mol^{-1}	α^E/kK^{-1}
0.54524	0.944469	1252.91	–0.063	–35.93	–31.7	–2.46	0.010
0.60131	0.953866	1263.12	–0.049	–34.84	–31.3	–2.41	0.009
0.65344	0.962920	1272.86	–0.048	–33.11	–30.2	–2.31	0.007
0.69457	0.970090	1280.69	–0.037	–31.05	–28.6	–2.20	0.006
0.74847	0.979835	1291.25	–0.037	–27.73	–25.9	–1.99	0.005
0.80394	0.989911	1302.45	–0.021	–23.31	–22.0	–1.72	0.003
0.85925	1.000376	1313.97	–0.021	–18.04	–17.2	–1.37	0.002
0.89787	1.007691	1322.16	–0.009	–13.68	–13.1	–1.06	0.001
0.95440	1.018812	1334.56	–0.007	–6.58	–6.4	–0.52	0.000
0.99146	1.026191	1342.82	–0.001	–1.29	–1.2	–0.10	0.000
1	1.027909	1344.77					

Table 4 Parameters and standard deviations of Eq. (1) of express functions of mixtures

	A1	A2	A3	A4	σ
	x cyclohexanone+(1–*x*) 1,4-dioxane				
$V^{E}_{303.15K}$/cm^{3}mol^{-1}	1.013	–	–	–	0.003
α^{E}/K^{-1}	–3.0E–05	–	–	–	–
κ^{E}_{T}/TPa^{-1}	21.6	4.3	–	–	0.1
C^{E}_{V}/JK^{-1}mol^{-1}	–2.87	1.15	–0.65	–	0.02
	x cyclohexanone+(1–*x*) 1,2-dimethoxyethane				
$V^{E}_{303.15K}$/cm^{3}mol^{-1}	–0.768	–0.408	0.113	–	0.003
V^{E}/cm^3 mol^{-1}	–0.675	–0.461	–	–	0.003
α^{E}/K^{-1}	–1.77E–04	1.03E–04	2.16E–04	–	–
κ^{E}_{S}/TPa^{-1}	–118.3	–26.51	–4.7	–	0.14
κ^{E}_{T}/TPa^{-1}	–184.0	9.0	70.8	–	0.3
C^{E}_{V}/(J K^{-1} mol^{-1})	5.74	–7.43	–12.09	–	0.01
	x cyclohexanone+(1–*x*) 2-butanone				
$V^{E}_{303.15K}$/cm^3 mol^{-1}	–0.674	–0.206	–	–	0.001
V^{E}/cm^3 mol^{-1}	–0.629	–0.156	–	–	0.003
α^{E}/K^{-1}	–9.4E–05	–1.10E–04	–	–	–
κ^{E}_{S}/TPa^{-1}	–117.98	–33.39	–7.39	–	0.06
κ^{E}_{T}/TPa^{-1}	–150.7	–75.9	–9.6	–	0.08
C^{E}_{V}/J K^{-1}mol^{-1}	–1.56	6.05	–2.53	–1.35	0.02
	x 2-butanone+(1–*x*) 1,4-dioxane				
$V^{E}_{303.15K}$/cm^3 mol^{-1}	–0.507	0.227	–	–	0.002
V^{E}/cm^3 mol^{-1}	–0.495	0.237	–	–	0.003
α^{E}/K^{-1}	–2.7E–05	–2.3E–05	–	–	–
κ^{E}_{S}/TPa^{-1}	–118.30	16.50	–	–	0.04
κ^{E}_{T}/TPa^{-1}	–125.5	7.7	–	–	0.06
C^{E}_{V}/J K^{-1}mol^{-1}	–6.31	0.90	–0.52	–	0.02
	x 2-butanone+(1–*x*) 1,2-dimethoxyethane				
$V^{E}_{303.15K}$/cm^3 mol^{-1}	–0.621	–0.044	–	–	0.004
V^{E}/cm^3 mol^{-1}	–0.611	–0.063	–	–	0.003
α^{E}/K^{-1}	–2.1E–05	4.1E–05	–	–	–
κ^{E}_{S}/TPa^{-1}	–31.52	–3.21	–	–	0.16
κ^{E}_{T}/TPa^{-1}	–46.5	12.7	–	–	0.1
C^{E}_{V}/JK^{-1}mol^{-1}	4.01	–1.82	–0.87	–	0.01

Table 4 Continued

	A1	A2	A3	A4	σ
	x 1,4-dioxane+(1–*x*) 1,2-dimethoxyethane				
$V^{E}_{303.15K}$/cm^3 mol^{-1}	–0.222	–0.112	–	–	0.003
V^{E}/cm^3 mol^{-1}	–0.244	–0.134	–		0.004
α^{E}/K^{-1}	4.6E–05	4.2E–05	–	–	–
κ_S^E/TPa^{-1}	–144.11	5.54	–1.72	–	0.06
κ_T^E/TPa^{-1}	–125.6	25.6	3.7	–	0.06
C_V^E/(J K^{-1} mol^{-1})	–9.77	1.05	–1.39	–	0.01

seen in Fig. 3 for κ_T^E. Because the free volumes of these mixtures are reduced by the flexible component molecules. The mixture of cyclohexanone+1,4–dioxane shows slightly positive κ_S^E and κ_T^E [1], consisted to its positive excess volume. On the other hand, the mixture of 2-butanone+1,2-dimethoxyethane shows slightly negative κ_S^E and κ_T^E, suggesting that linear molecules are better packed than bulky globular molecules. These two mixtures are randomly mixed. On the other hand, the other four mixtures show considerably negative κ_S^E and κ_T^E. The linear molecules squeezed in the room formed by globular molecules may not be so free to move.

As Fig. 4 shows, excess isochoric heat capacities of all systems are enhanced their features of C_p^E, negative values for C_p^E give more negative C_V^E, positive C_p^E values show more positive C_V^E. The curve of C_V^E of [*x* cyclohexanone+(1–*x*)2-butanone] shows an emphasized W-shaped because linear 2-butanone is not able to squeeze sufficiently between cyclohexanone molecules but expels globular cyclohexanone to form cluster. However, the curve of C_V^E of [*x* 1,4-dioxane+(1–*x*)1,2-dimethoxyethane lose W-shaped feature of C_p^E. The curve of C_V^E of [*x* cyclohexanone+(1–*x*), 2-dimethoxyethane] also seems to be W-shaped and to emphasize a concentration fluctuation slightly observed in C_p^E [9].

It is concluded that the behaviours of excess properties estimated at present are consistent with the results in the previous paper [9].

References

1 K. Tamura and A. Osaki, Thermochim. Acta, 352/353 (2000) 11.
2 K. Nishikawa, K. Tamura and S. Murakami, J. Chem. Thermodyn., 30 (1998) 229.
3 K. Nishikawa, K. Ohomuro, K. Tamura and S. Murakami, Thermochim. Acta, 267 (1995) 323.
4 K. Tamura, S. Murakami and R. Fujishiro, J. Chem. Thermodyn., 15 (1981) 47.
5 K. Ohomuro, K. Tamura and S. Murakami, J. Chem. Thermodyn., 29 (1997) 287.
6 K. Ohomuro, K. Tamura and S. Murakami, J. Chem. Thermodyn., 19 (1987) 163.
7 K. Ohomuro, K. Tamura and S. Murakami, J. Chem. Thermodyn., 19 (1987) 171.
8 K. Tamura, J. Chem. Thermodyn., 33 (2001) 1345.
9 S. Baluja, T. Matsuo and K. Tamura, J. Chem. Thermodyn., 33 (2001) 1545.

10 S. Miyanaga, K. Tamura and S. Murakami, J. Chem. Thermodyn., 24 (1992) 1077.
11 T. Takigawa and K. Tamura, J. Chem. Thermodyn., 32 (2000) 1045.
12 K. Tamura, K. Ohomuro and S. Murakami, J. Chem. Thermodyn., 15 (1983) 859.
13 K. Tamura, A. Osaki, S. Murakami, B. Laurent and J.-P. E. Grolier, Fluid Phase Equilibria, 173 (2000) 285.
14 T. Takigawa, H. Ogawa, M. Nakamura, K. Tamura and S. Murakami, Fluid Phase Equilib., 110 (1995) 267.
15 J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents, 4th Ed., Wiley, New York, 1986.
16 O. Redlich and A. T. Kister, Ind. Eng. Chem., 40 (1948) 345