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Thermochimica Acta 267 (1995) 323–332
thermochimica acta

Excess thermodynamic properties of mixtures of cyclohexanone and benzene at 298.15 and 308.15 K and the effect of excess expansion factor[1]

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Received 20 November 1994; accepted 24 January 1995

Abstract

Excess molar isobaric heat capacity, density and speed of sound of a cyclohexanone and benzene mixture were measured at 298.15 and 308.15 K. From densities, excess volumes were calculated at two temperatures and the excess expansion factor of the mixture was estimated. The excess expansion factor was negative and large, and affected the estimation of isothermal compressibility and isochoric heat capacity from density, speed of sound, isobaric heat capacity and expansion factor.

Keywords: Thermodynamic properties; Temperature dependence; Excess expansion factor; Cyclohexanone; Benzene

1. Introduction

As for normal non-polar mixtures, the excess expansion factor is small and less than 1% of the value of the whole expansion factor of the mixture, namely the whole expansion factor of mixture α is about $10^{-3}\,K^{-1}$ and the excess expansion factor α^E is about several $10^{-6}\ K^{-1}$. On the other hand, in many cases of polar mixtures, α^E is found to be more than several $10^{-5}\ K^{-1}$ and has reached the order of $10^{-4}\ K^{-1}$ in a few measurements of polar mixtures in our laboratory. In the case of the order of $10^{-6}\,K^{-1}$, α^E hardly affects the estimation of isothermal compressibility κ_T and isochoric heat capacity $C^E{}_{V,m}$ of the

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[1] Presented at the 30th Anniversary Conference of the Japan Society of Calorimetry and Thermal Analysis, Osaka, Japan, 31 October–2 November 1994.

SSDI 0040-6031 (95) 02489-1

mixture, even if it is neglected. On the contrary, in the case above 10^{-5} K^{-1}, α^E seriously affects the estimation, and if it is neglected and excess values of compressibility or isochoric heat capacity are small, then inversion of sign, positive or negative, occurs, for example in $C^E_{V,m}$ in this system. In this paper, we report the thermodynamic properties of the mixture $\{xC_6H_{10}O + (1-x)C_6H_6\}$ at 298.15 and 308.15 K, and the effects on isothermal compressibility and isochoric heat capacity.

2. Experimental

Benzene (Wako Pure Chemical, special grade) was fractionally distilled as usual by a column with Helipak [1]. The mole purity was better than 99.95% by GLC (stationary phase, silicon) and the Karl-Fischer method. Cyclohexanone (Wako Pure Chemical, special grade) was also distilled at reduced pressure of approximately 50 mmHg by a 1-m spinning band column. The mole purity was better than 99.92% by GLC (stationary phase, TSG1 supplied by Shimadzu Ltd.).

Excess isobaric heat capacities were measured by a home-made flow microcalorimeter for heat capacity. Densities were measured by a vibrational-tube densimeter (Anton Paar, DMA602), the speed of sound by a sing-around method (Cho-Onpa Co., UVM-2). The details of the measurements are given elsewhere [2–4]. The accuracy of the excess heat capacity was better than ±0.02 J K^{-1} mol^{-1}. The reproducibility of densimetry was ±0.000003 g cm^{-3} and its accuracy was ±0.00001 g cm^{-3} owing to the accuracy of pychnometry. The reproducibility of the speed of sound was ±0.03 m s^{-1} and its accuracy ±0.3 m s^{-1} by stability drift of our apparatus.

3. Results and discussion

The thermodynamic properties of materials used at 298.15 and 308.15 K are given in Table 1.

Table 1

Physical properties of the materials used at 298.15 and 308.15 K

Property	Cyclohexanone		Benzene	
T/K	298.15	308.15	298.15	308.15
$\rho/(g\ cm^{-3})$	0.94199	0.93317	0.87366	0.86306
Literature[a]	0.9452 (293.15)	0.93761 (303.15)	0.87360	
$u/(m\ s^{-1})$	1407.6	1365.9	1299.6	1252.9
κ_S/TPa^{-1}	535.8	574.4	677.7	738.0
κ_T/TPa^{-1}	695.0	738.2	967.8	1036.4
$C_{V,m}/(J\ K^{-1}\ mol^{-1})$	137.2	140.4	94.7	98.0
$C_{p,m}/(J\ K^{-1}\ mol^{-1})$	177.97	180.41	135.21	137.55
α/K^{-1}	0.000945		0.001228	
Literature[a]	0.000955		0.001213	

[a] From Ref. [1].

We have already reported excess enthalpy, $H^E{}_m$ for the mixture of benzene and cyclohexanone [5], and the system is exothermic and shows a minimum −285 J mol^{-1} at $x = 0.45$. Rao et al. [6] also reported $H^E{}_m$ and their values agreed with ours. Yang and Zhang [7] reported $H^E{}_m$ at 298.15 and 303.15 K, and their value at 298.15 K is slightly, say 5 J mol^{-1} at minimum, larger than ours. They reported that $H^E{}_m$ of the temperature 303.15 K is 40 J mol^{-1} larger than that of 298.15 K at minimum $x = 0.55$. This difference corresponds to $C^E{}_{p,m} = 8$ J K^{-1} mol^{-1} and is too large to compare with the amount of $H^E{}_m$. This $C^E{}_{p,m}$ value does not agree with our results described below.

The $C^E{}_{p,m}$ values obtained at 298.15 and 308.15 K are given in Table 2, and plotted in Fig. 1. In the figure, solid curves are calculated by the following equation:

$$F^E/(\text{unit}) = x(1-x)\Sigma A_i(1-2x)^{i-1} \tag{1}$$

where F^E is excess properties, the parameter A_i is determined by the least-squares method from the observed points. The parameters are given in Table 4 with standard deviations. $C^E{}_{p,m}$ of the higher temperature slightly shifted to positive from those of the lower temperature. They change sign from positive to negative with increase of x, at $x = 0.45$ for the temperature 298.15 K and $x = 0.65$ for 308.15 K, respectively. The positive effect

Table 2

Excess isobaric heat capacities of mixtures of cyclohexanone + benzene at 298.15 and 308.15 K

x	$C^E{}_{p,m}$	x	$C^E{}_{p,m}$
298.15 K			
0.02500	0.21	0.54997	−0.09
0.04999	0.36	0.59997	−0.10
0.09999	0.40	0.64997	−0.13
0.14998	0.41	0.69997	−0.15
0.19998	0.33	0.74998	−0.17
0.24998	0.28	0.79998	−0.16
0.29997	0.21	0.84998	−0.17
0.34997	0.16	0.89999	−0.14
0.39997	0.08	0.94999	−0.11
0.44997	0.01	0.97500	−0.04
0.49997	−0.05		
308.15 K			
0.02500	0.13	0.54997	0.09
0.04999	0.19	0.59997	0.05
0.09999	0.25	0.64997	−0.00
0.14998	0.38	0.69997	−0.02
0.19998	0.41	0.74998	−0.03
0.24998	0.38	0.79998	−0.02
0.29997	0.41	0.84998	−0.05
0.34997	0.32	0.89999	−0.05
0.39997	0.31	0.94999	−0.06
0.44997	0.19	0.97500	−0.04
0.49997	0.16		

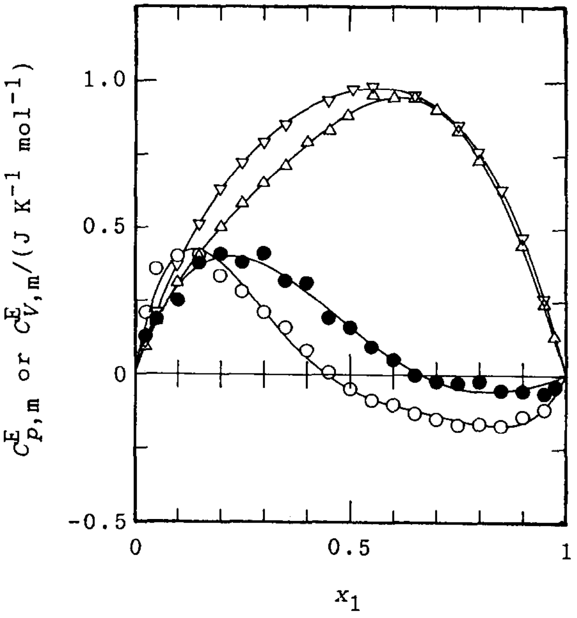

Fig. 1. Excess isobaric and isochoric heat capacities of the mixture $\{xC_6H_{10}O + (1 - x)C_6H_6\}$ at 298.15 and 308.15 K. ○, $C^E_{p,m}$ (298.15 K); ●, $C^E_{p,m}$ (308.15 K); △, $C^E_{V,m}$ (298.15 K); ▽, $C^E_{V,m}$ (308.15 K).

dominant in benzene-rich solutions may be due to formation of a cyclohexanone–benzene pair by induced dipole–dipole interaction; on the other hand, the negative effect dominant in cyclohexanone-rich solution is due to breaking of the dipole–dipole interaction acting on cyclohexanone in the pure state. The maximum value of the temperature 298.15 K is 0.35 at $x = 0.25$, and the minimum value is –0.1 at $x = 0.85$. The temperature derivative of $C^E_{p,m}$, changes sign from negative to positive at $x = 0.2$.

The density ρ and speed of sound u obtained at 298.15 and 308.15 K for the mixture are given in Table 3, together with excess volumes V^E_m, excess isentropic and isothermal compressibilities κ^E_S and κ^E_T, and excess isochoric heat capacities $C^E_{V,m}$, calculated from ρ, u, $C_{p,m}$ and α by the procedures described elsewhere [3] except for the consideration of α^E in this time. V^E_m at 298.15 and 308.15 K are plotted in Fig. 2. Derived κ^E_T are plotted in Fig. 3, together with κ^E_S. The derivatives of κ^E_T and κ^E_S on temperature are negative. In this figure solid lines are smoothed curves calculated by Eq. (1).

V^E_m are almost parabolic and the value at 308.15 K (–0.26 cm^3 mol^{-1} minimum) is more negative than the value at 298.15 K (–0.22 cm^3 mol^{-1} minimum). V^E_m previously measured at 298.15 K agrees well with that at this time. The temperature derivative of V^E_m is negative. Interaction of dipole-induced dipole is larger than dipole–dipole interaction in pure liquid as is found from negative H^E_m and reduces the volume of the mixture. Rao et al. [6] have reported V^E_m at 298.15 K; their values are more negative by 0.06 cm^3 mol^{-1} minimum than ours. The reason for this discrepancy is not clear but may be due to different content of impurities.

Table 3

Densities, speeds of sound, excess volumes, excess isentropic and isothermal compressibilities, excess isochoric heat capacities of mixtures of cyclohexanone + benzene at 298.15 and 308.15 K

x	ρ/ g cm^{-3}	u/ m s^{-1}	V^E_m/ cm^3 mol^{-1}	κ^E_S/ TPa^{-1}	κ^E_T/ TPa^{-1}	$C^E_{V,m}$/ J K^{-1} mol^{-1}
298.15 K						
0	0.873661	1299.58				
0.02601	0.875968	1303.77	−0.025	−2.72	−3.6	0.09
0.05011	0.878203	1307.33	−0.060	−4.88	−6.7	0.18
0.10025	0.882570	1314.87	−0.109	−9.06	−13.0	0.31
0.15016	0.886742	1322.25	−0.146	−12.64	−18.6	0.40
0.20094	0.890843	1329.07	−0.176	−15.21	−23.1	0.50
0.25017	0.894687	1335.62	−0.198	−17.28	−26.9	0.58
0.29987	0.898471	1341.94	−0.215	−18.82	−29.8	0.65
0.35100	0.902174	1348.26	−0.220	−19.89	−31.9	0.71
0.40120	0.905733	1353.70	−0.223	−20.02	−32.8	0.79
0.45455	0.909430	1359.69	−0.223	−20.54	−33.7	0.83
0.49477	0.912102	1363.86	−0.215	−19.68	−32.8	0.88
0.55345	0.915926	1368.98	−0.202	−18.07	−30.9	0.95
0.60187	0.919093	1374.26	−0.197	−17.52	−29.9	0.94
0.64993	0.922090	1378.50	−0.183	−15.94	−27.6	0.94
0.70089	0.925196	1383.00	−0.164	−14.15	−24.8	0.90
0.75047	0.928122	1387.62	−0.141	−12.47	−21.9	0.83
0.79932	0.930994	1391.87	−0.122	−10.50	−18.6	0.73
0.89899	0.936599	1399.87	−0.068	−5.62	−10.3	0.44
0.95041	0.939383	1403.83	−0.036	−2.83	−5.4	0.24
0.97423	0.940642	1405.71	−0.019	−1.55	−2.9	0.13
1	0.941989	1407.56				
Previous measurement						
0.02340			−0.027			
0.09017			−0.096			
0.21917			−0.183			
0.27895			−0.207			
0.35032			−0.222			
0.39103			−0.226			
0.47942			−0.222			
0.51584			−0.219			
0.58475			−0.202			
0.64019			−0.187			
0.68444			−0.173			
0.74629			−0.145			
0.80800			−0.117			
0.86397			−0.087			
0.94486			−0.039			
308.15 K						
0	0.863083	1253.05				
0.02498	0.865425	1256.99	−0.038	−2.97	−4.5	0.11
0.05016	0.867758	1261.21	−0.066	−5.65	−8.7	0.21

Table 3 (*continued*)

x	ρ/ g cm^{-3}	u/ m s^{-1}	V^E_m/ cm^3 mol^{-1}	κ^E_S/ TPa^{-1}	κ^E_T/ TPa^{-1}	$C^E_{V,m}$/ J K^{-1} mol^{-1}
0.09930	0.872147	1269.00	–0.117	–10.39	–15.9	0.37
0.15033	0.876642	1276.66	–0.170	–14.41	–22.2	0.51
0.20010	0.880893	1283.89	–0.198	–17.50	–27.0	0.63
0.25028	0.884857	1290.86	–0.224	–19.91	–30.8	0.72
1	0.933164	1365.93				
0	0.863035	1252.96				
0.29997	0.888596	1297.39	–0.241	–21.61	–33.6	0.79
0.35037	0.892381	1303.79	–0.251	–22.72	–35.5	0.85
0.45012	0.899595	1315.68	–0.258	–23.33	–36.8	0.93
0.50555	0.903404	1321.53	–0.250	–22.51	–36.0	0.97
0.55194	0.906509	1326.40	–0.240	–21.61	–34.8	0.98
1	0.933162	1365.92				
0	0.863081	1252.88				
0.64968	0.912822	1336.08	–0.208	–18.77	–30.7	0.95
0.74987	0.919018	1345.19	–0.166	–14.48	–24.2	0.85
0.79739	0.921820	1349.36	–0.139	–12.12	–20.4	0.76
0.85235	0.925005	1353.96	–0.106	–9.09	–15.5	0.63
0.90014	0.927706	1357.88	–0.075	–6.28	–10.9	0.47
0.94952	0.930437	1361.88	–0.040	–3.27	–5.7	0.26
1	0.933217	1365.85				

Table 4

The parameter of Eq. (1) for excess properties of the mixtures at 298.15 and 308.15 K

Property	A_1	A_2	A_3	A_4	s
298.15 K					
$C^E_{p,m}$/(J K^{-1} mol^{-1})	–0.20	1.50	2.45	3.74	0.03
V^E_m/(cm^3 mol^{-1})	–0.866	–0.287	–0.171		0.003
κ^E_S/TPa^{-1}	–78.16	–26.14	–4.82		0.23
α^E/K^{-1}	–0.000131	–0.000038	0.000031		–
κ^E_T/TPa^{-1}	–130.4	–25.4			0.4
$C^E_{V,m}$/(J K^{-1} mol^{-1})	3.56	–1.71	0.84	1.26	0.01
308.15 K					
$C^E_{p,m}$/(J K^{-1} mol^{-1})	0.64	2.36	1.22		0.02
V^E_m/(cm^3 mol^{-1})	–1.002	–0.318	–0.140		0.002
κ^E_S/TPa^{-1}	–90.73	–28.92	–3.72		0.06
α^E/K^{-1}	–0.000125	–0.000021	–0.000010		
κ^E_T/TPa^{-1}	–145.9	–35.6			0.3
$C^E_{V,m}$/(J K^{-1} mol^{-1})	3.85	–0.69	1.32		0.005

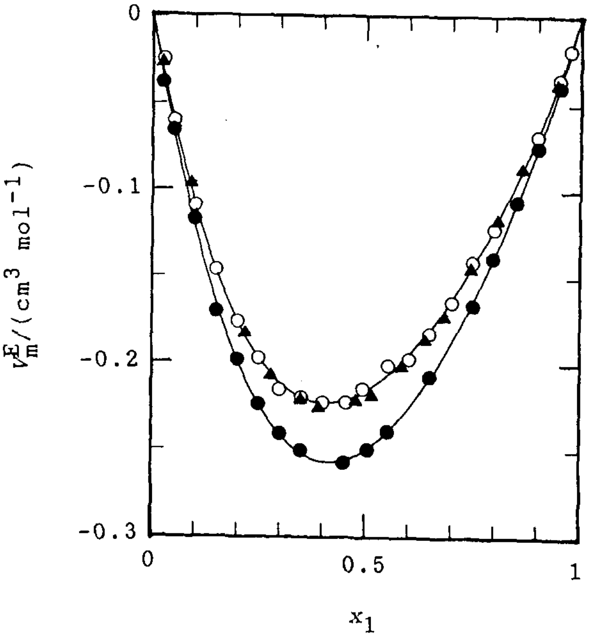

Fig. 2. Excess volume of the mixture $\{xC_6H_{10}O + (1-x)C_6H_6\}$ at 298.15 and 308.15 K. ○, V^E_m (298.15 K); ▲, previous ones (298.15 K); ●, V^E_m (308.15 K).

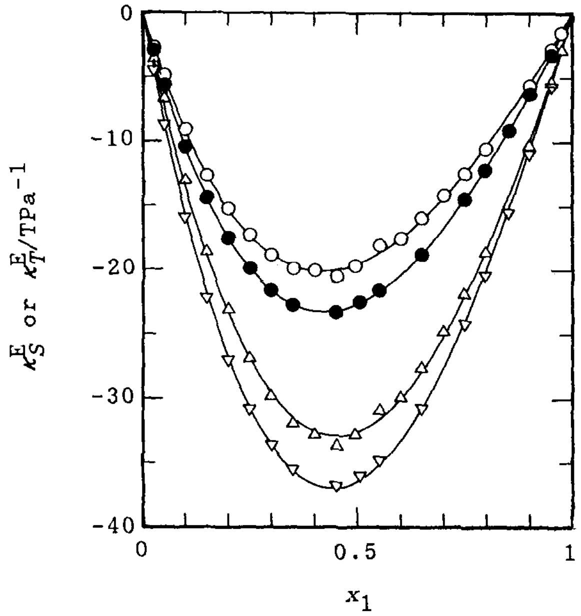

Fig. 3. Excess isentropic and isothermal compressibilities of the mixture $\{xC_6H_{10}O + (1-x)C_6H_6\}$ at 298.15 and 308.15 K. ○, κ^E_S (298.15 K); ●, κ^E_S (308.15 K); △, κ^E_T (298.15 K); ▽, κ^E_T (308.15 K).

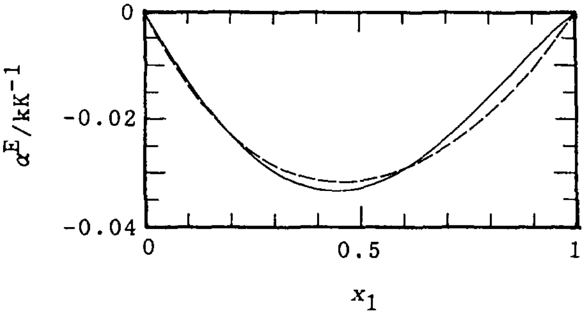

Fig. 4. Excess expansion factor of the mixture $\{xC_6H_{10}O + (1-x)C_6H_6\}$. Solid line, 298.15 K; broken line, 308.15 K.

From V^E_m obtained at two temperatures, 298.15 and 308.15 K, the excess expansion factor α^E is calculated by the following equation:

$$\alpha^E = \frac{(dV^E/dT)_p - V^E\alpha^{id}}{V^{id} + V^E} \tag{2}$$

$(dV^E/dT)_p$ is the temperature derivative of V^E_m or the difference between V^E_m at two temperatures, V^{id} and α^{id} are the ideal values of the volume and expansion factor of the mixture, respectively. Estimated α^E is negative and is minimum -3.3×10^{-5} K^{-1} at ap-

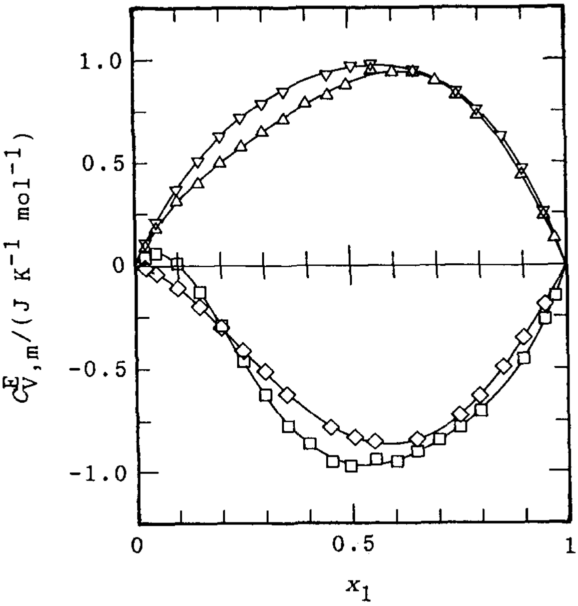

Fig. 5. Comparison with excess isochoric heat capacities for $\alpha^E = 0$. △, $C^E_{V,m}$ (298.15 K); ▽, $C^E_{V,m}$ (308.15 K); □, $C^E_{V,m}$ (298.15 K, $\alpha^E = 0$); ◇, $C^E_{V,m}$ (308.15 K, $\alpha^E = 0$).

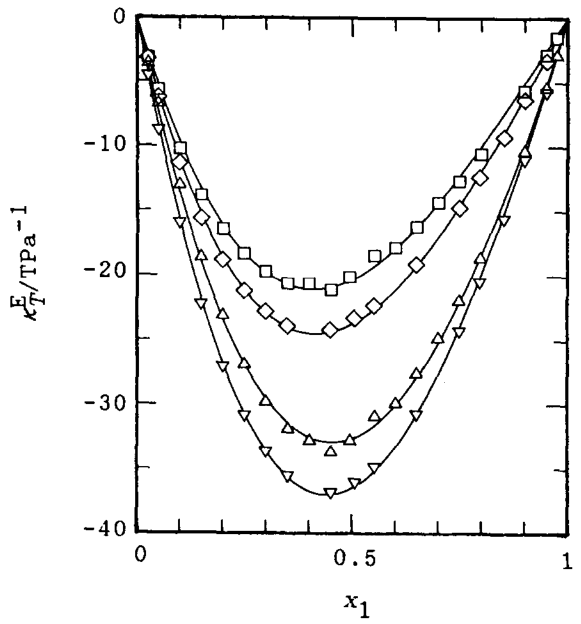

Fig. 6. Comparison with excess isothermal compressibility for $\alpha^E = 0$. △, κ^E_T (298.15 K); ▽, κ^E_T (308.15 K); □, κ^E_T (298.15 K, $\alpha^E = 0$); ◇, κ^E_T (308.15 K, $\alpha^E = 0$).

proximately $x = 0.45$ for 298.15 K, as shown in Fig. 4. This is about 3% of α for the mixture, and it gives 6% error to an additional term to κ_S for estimation of κ_T, if α^E is neglected. Finally it gives 1.5% error to the final value of κ_T in this case. Therefore κ^E_T considering α^E is more negative by about 15 TPa^{-1} than that assuming $\alpha^E = 0$ as seen in Fig. 6. This deviation is large compared with the whole excess values. For $C_{V,m}$ the situation is the same. A few % of error like this makes the sign of $C^E_{V,m}$ change to the opposite sign in the case of small $C^E_{p,m}$, such as in this system. In Fig. 5, we find $C^E_{V,m}$ considering α^E is positive and neglecting α^E is the same amount but opposite sign. As is seen in Fig. 1, $C^E_{V,m}$ is larger than $C^E_{p,m}$. Neglecting α^E makes the conclusion about the structure of liquid mixtures [8] misleading. In this case, with $C^E_{V,m}$ larger than $C^E_{p,m}$, neglecting α^E, however, gives the opposite conclusion.

α is considered to be the cross fluctuation of volume and enthalpy [10]. Positive α^E suggests that a stronger molecular interaction, like a hydrogen bond, in pure liquid is broken by mixing [9]. On the other hand, negative α^E is due to the formation of new molecular interaction in the mixture. Negative α^E means that fluctuation of the volume causing interaction energy in the mixture is less than in random mixing liquids. The interaction between benzene and ketone is stable but not so strong, and is consistent with negative H^E_m and V^E_m.

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