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Measurements of Density and Heat Capacity for Binary Mixtures {*x* Benzonitrile + (1 −*x*) (Octane or Nonane)}[†]

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Densities and isobaric heat capacities per unit volume have been measured for binary mixtures {x benzonitrile + $(1 - x)$ octane} and {x benzonitrile + $(1 - x)$ nonane} in the temperature ranges of (283.15 to 318.15) K and (283.15 to 313.15) K, respectively. Measurements covered the whole composition range at the ambient pressure. From these measured data, the excess molar volumes, excess isobaric thermal expansivities, and excess isobaric molar heat capacities were calculated and fitted with the Redlich−Kister equation. The excess molar volumes, excess isobaric thermal expansivities, and excess isobaric molar heat capacities of both systems were found to exhibit the S-shaped curves against the composition and the feature of the nonrandomness mixing. The dependences of these properties on the temperature and composition were analyzed and discussed in terms of the natures of the two pure components and the molecular interactions in the mixtures.

Introduction

Thermodynamic properties, such as heat capacity and density, are of high interest in the industrial processes as well as the progress of thermodynamic theories. Systematic studies of those properties of mixtures and their excess properties as functions of temperature and concentration can give insight into the molecular structure of mixtures, provide information on the interaction between components, and are essential for designing and testing theoretical models of mixtures.

Benzonitrile is a self-associated liquid with a large permanent electric dipole moment of $13.94 \cdot 10^{-30}$ C·m[1−3] and is of industrial interest, especially in pharmaceutical chemistry. Alkanes are typical molecular liquids, and the properties of the solutions with alkane being one of the components have been widely investigated. Benzonitrile and alkanes are so different in shape and size, as well as other chemical natures, but they may form binary solutions with upper critical solution points being not far from the ambient temperature, which are easily experimentally accessible. Therefore, the liquid−liquid phase equilibriums and their critical phenomena have been extensively investigated.[4−6] However, the systematic studies of the excess thermodynamic properties of the solutions of benzonitrile + alkanes both near and far from the critical points over a whole composition range are relatively scarce.[7,8]

In this work, we report the new measurements of the density and the isobaric heat capacity per volume at various temperatures and compositions for the binary mixtures {x benzonitrile + $(1 - x)$ octane} and {x benzonitrile + $(1 - x)$ nonane}, from which the excess molar volumes, excess isobaric thermal expansivities, and excess isobaric molar heat capacities are obtained. The results are discussed in terms of the natures of the two pure components and the interactions in the mixtures.

Experimental Section

Materials. Benzonitrile (C_6H_5CN, mass fraction purity > 0.99), octane (C_8H_{18}, mass fraction purity > 0.995), and nonane (C_9H_{20}, mass fraction purity > 0.99), were purchased from Alfa Aesar, Sigma-Aldrich, and Sinopharm Chemical Reagent Co., Ltd., respectively. These chemicals were used without further purifications other than stored over freshly activated molecular sieves of the type 0.4 nm. A series of binary mixtures of {x benzonitrile + $(1 - x)$ octane} and {x benzonitrile + $(1 - x)$ nonane} with various mole fractions x were prepared with a precision of about ± 0.0001 in x. Each sample was partially degassed in an ultrasonic bath just before the measurements.

Apparatus and Procedure. A vibrating-tube densimeter (Anton Paar model DMA-5000 M) with automatic viscosity correction was used to measure the densities of the pure components and the binary mixtures. The temperature in the cell was regulated to ± 0.001 K by a Peltier unit and measured by the built-in platinum resistance thermometers with an accuracy of ± 0.01 K and a repeatability of ± 0.001 K. The accuracy and the repeatability in the density measurements were stated by the manufacturer to be $(\pm 5 \cdot 10^{-6}$ and $\pm 1 \cdot 10^{-6})$ $g \cdot cm^{-3}$, respectively. However, the experimental uncertainty in the density was viscosity-dependent;[9] it was estimated to be about $\pm 2 \cdot 10^{-5}$ $g \cdot cm^{-3}$ for the systems we studied. The overall experimental repeatability was estimated to be less than $\pm 1 \cdot 10^{-5}$ $g \cdot cm^{-3}$. The densities of all samples were measured at a slow mode of automatically changing the temperature with a successive increment of 0.25 K. The measured results at the slow mode were compared with those measured at the static mode, and the differences were found to be within the instrumental uncertainty, which indicated that the slow mode ensured the thermal equilibrium.

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Table 1. Experimental Densities ρ for {x Benzonitrile + (1 − x) Octane} at Selected Temperatures T

	$\rho/(\mathrm{g\cdot cm^{-3}})$							
x	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K
0	0.71076	0.70676	0.70274	0.69871	0.69466	0.69058	0.68649	0.68237
0.0220	0.71494	0.71093	0.70690	0.70286	0.69879	0.69471	0.69060	0.68647
0.0576	0.72195	0.71792	0.71387	0.70981	0.70572	0.70162	0.69749	0.69334
0.1020	0.73107	0.72701	0.72294	0.71885	0.71474	0.71061	0.70647	0.70229
0.1999	0.75243	0.74832	0.74420	0.74006	0.73590	0.73173	0.72754	0.72333
0.2998	0.77616	0.77201	0.76784	0.76366	0.75946	0.75525	0.75102	0.74678
0.4001	0.80202	0.79783	0.79363	0.78941	0.78518	0.78093	0.77667	0.77239
0.4637	0.81957	0.81535	0.81112	0.80689	0.80263	0.79837	0.79409	0.78979
0.4997	0.82990	0.82568	0.82144	0.81719	0.81293	0.80865	0.80435	0.80004
0.5004	0.83012	0.82590	0.82166	0.81741	0.81314	0.80886	0.80456	0.80025
0.6001	0.86070	0.85642	0.85214	0.84785	0.84355	0.83923	0.83490	0.83056
0.7001	0.89421	0.88988	0.88555	0.88122	0.87687	0.87251	0.86815	0.86378
0.7998	0.93065	0.92627	0.92190	0.91752	0.91313	0.90874	0.90434	0.89994
0.9001	0.97069	0.96628	0.96187	0.95746	0.95305	0.94863	0.94421	0.93978
0.9500	0.99186	0.98744	0.98301	0.97859	0.97417	0.96974	0.96531	0.96088
0.9801	1.00505	1.00062	0.99619	0.99177	0.98734	0.98291	0.97848	0.97405
1	1.01399	1.00955	1.00512	1.00069	0.99626	0.99183	0.98740	0.98296

Table 2. Experimental Densities ρ for {x Benzonitrile + (1 − x) Nonane)} at Selected Temperatures T

	$\rho/(\mathrm{g\cdot cm^{-3}})$						
x	T = 285.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
0	0.72454	0.72222	0.71835	0.71446	0.71055	0.70663	0.70270
0.0239	0.72845	0.72613	0.72224	0.71834	0.71442	0.71049	0.70654
0.0499	0.73281	0.73047	0.72657	0.72265	0.71872	0.71477	0.71081
0.0989	0.74140	0.73905	0.73511	0.73116	0.72720	0.72322	0.71923
0.1985	0.76034	0.75795	0.75395	0.74994	0.74593	0.74189	0.73784
0.2542	0.77177	0.76936	0.76534	0.76130	0.75725	0.75319	0.74911
0.2998	0.78158	0.77916	0.77511	0.77105	0.76697	0.76289	0.75879
0.4005	0.80492	0.80247	0.79837	0.79426	0.79014	0.78600	0.78185
0.4966	0.82964	0.82716	0.82301	0.81885	0.81468	0.81050	0.80631
0.5998	0.85912	0.85660	0.85240	0.84819	0.84396	0.83973	0.83548
0.6996	0.89101	0.88845	0.88418	0.87991	0.87563	0.87134	0.86705
0.7999	0.92693	0.92434	0.92000	0.91567	0.91133	0.90699	0.90264
0.9001	0.96724	0.96461	0.96022	0.95583	0.95144	0.94705	0.94265
0.9497	0.98896	0.98632	0.98191	0.97749	0.97308	0.96867	0.96425
0.9805	1.00305	1.00040	0.99597	0.99155	0.98713	0.98270	0.97827
1	1.01221	1.00955	1.00512	1.00069	0.99626	0.99183	0.98740

The isobaric heat capacity per unit volume (C_pV^{-1}) was measured using a Micro DSCIII scanning calorimeter from Setaram, which is based on the Tian-Calvet's principle and capable of obtaining the values of heat capacities over a wide range of temperatures from a small sample (about 1 cm^3). A special heat capacity vessel supplied by Setaram was used in the measurements, which avoided the presence of the vapor phase over the liquid; thus, no vapor phase correction was needed.[10] In determination of C_pV^{-1}, three steps of measurements of heat flow (HF) were carried out at each temperature. In each of the three measurements, the reference vessel was always filled with heptane, while the sample vessel was filled with heptane, butanol, and the liquid sample to be investigated separately. The heptane and butanol were used as calibration liquids, whose molar heat capacities C_p and densities ρ were taken from literature[11−13] and converted into the isobaric heat capacity per unit volume through $C_pV^{-1} = C_p\cdot\rho/M$ with M being the molar mass of the sample. The isobaric heat capacity per unit volume of the sample $(C_pV^{-1})_s$ was calculated by:

$$(C_pV^{-1})_s = (C_pV^{-1})_0 + [(C_pV^{-1})_r - (C_pV^{-1})_0][(HF_s - HF_0)/(HF_r - HF_0)] \quad (1)$$

where $(C_pV^{-1})_0$ and $(C_pV^{-1})_r$ are the isobaric heat capacities per unit volume of heptane and butanol, and HF$_0$, HF$_r$, and HF$_s$ are the heat flows of heptane, butanol, and the liquid sample, respectively. The measurements were performed in the scan down model at a scanning rate of 0.15 K·min^{-1} at the ambient pressure and in the temperature ranges of (283.15 to 318.15) K and (283.15 to 313.15) K for the mixtures {x benzonitrile + (1 − x) octane} and {x benzonitrile + (1 − x) nonane}, respectively. The repeatability in measurements of C_pV^{-1} was estimated to be ± 5·10^{-4} J·K^{-1}·cm^{-3}, which was in consistent with that reported in the literature.[14] However the overall uncertainty including that reported for the two reference samples in the literature[11−13] was estimated to be about ± 2·10^{-3} J·K^{-1}·cm^{-3}, much higher than ± 5·10^{-4} J·K^{-1}·cm^{-3}.

Results and Discussion

The densities at various mole fractions and temperatures in the temperature ranges of (283.15 to 318.15) K and (283.15 to 313.15) K with an interval of 0.25 K for the binary mixtures {x benzonitrile + (1 − x) octane} and {x benzonitrile + (1 − x) nonane}, respectively, were measured. Only a part of the results is listed in Tables 1 and 2. However all of the measured densities ρ at various temperatures T for each of compositions in one phase region were fitted to a polynomial equation:

$$\rho = \sum_{i=1}^{n} A_i(T/K - 283.15)^{i-1} \quad (2)$$

by the least-squares method. In eq 2, A_i is the temperature polynomial coefficient; n is the number of the polynomial coefficients which was determined by using an F-test. The values of A_i are listed in Table 3 along with the corresponding standard deviation σ:

Table 3. Temperature Polynomial Coefficients A_i in Equation 2 for Experimental Densities and the Standard Deviations σ of Fitting

x	$A_1 \cdot 10^3$	$A_2 \cdot 10^4$	$A_3 \cdot 10^7$	$\sigma \cdot 10^3$	x	$A_1 \cdot 10^3$	$A_2 \cdot 10^4$	$A_3 \cdot 10^7$	$\sigma \cdot 10^3$
	{x Benzonitrile + (1 − x) Octane}					{x Benzonitrile + (1 − x) Nonane}			
0^a	710.755	−7.971	−3.956	0.0020	0^b	726.084	−7.709	−2.886	0.0021
0.0220^a	714.941	−7.995	−3.946	0.0024	0.0239^b	730.002	−7.733	−2.943	0.0023
0.0576^a	721.948	−8.036	−3.906	0.0023	0.0499^b	734.362	−7.764	−2.928	0.0023
0.1020^a	731.065	−8.088	−3.766	0.0024	0.0989^b	742.966	−7.828	−2.808	0.0019
0.1999^a	752.423	−8.190	−3.488	0.0026	0.1985^b	761.928	−7.950	−2.570	0.0015
0.2998^a	776.160	−8.286	−3.101	0.0028	0.2542^b	773.377	−8.014	−2.483	0.0016
0.4001^a	802.015	−8.356	−3.109	0.0038	0.2998^b	783.196	−8.063	−2.426	0.0016
0.4637^a	819.566	−8.416	−2.601	0.0037	0.4005^c	806.557	−8.161	−2.504	0.0023
0.4997^a	829.902	−8.427	−2.997	0.0014	0.4966^c	831.295	−8.260	−2.328	0.0009
0.5004^a	830.121	−8.430	−2.957	0.0028	0.5998^c	860.797	−8.375	−2.068	0.0009
0.6001^a	860.696	−8.529	−2.314	0.0020	0.6996^b	892.711	−8.512	−1.423	0.0014
0.7001^a	894.209	−8.638	−1.601	0.0019	0.7999^b	928.662	−8.649	−0.843	0.0013
0.7998^a	930.645	−8.738	−0.979	0.0028	0.9001^b	968.993	−8.767	−0.476	0.0020
0.9001^a	970.688	−8.811	−0.536	0.0022	0.9497^b	990.726	−8.818	−0.227	0.0015
0.9500^a	991.858	−8.842	−0.248	0.0023	0.9805^b	1004.819	−8.841	−0.244	0.0021
0.9801^a	1005.050	−8.852	−0.170	0.0022	1^a	1013.983	−8.858	−0.096	0.0033
1^a	1013.983	−8.858	−0.096	0.0033					

[a] In the temperature range (283.15 to 318.15) K. [b] In the temperature range (283.15 to 313.15) K. [c] In the temperature range (284.65 to 313.15) K.

Table 4. Experimental Isobaric Molar Heat Capacities C_p for {x Benzonitrile + (1 − x) Octane} at Selected Temperatures T

	$C_p/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$							
x	T = 283.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K
0	248.20	250.10	252.06	254.08	256.16	258.28	260.45	262.66
0.0219	246.32	248.19	250.11	252.10	254.14	256.24	258.38	260.56
0.0576	243.69	245.52	247.38	249.32	251.30	253.34	255.43	257.56
0.1021	240.66	242.38	244.17	246.00	247.92	249.87	251.88	253.94
0.1999	234.51	235.90	237.41	239.04	240.74	242.50	244.34	246.23
0.2998	229.04	229.53	230.52	231.82	233.28	234.82	236.47	238.12
0.4002	224.38	222.59	223.06	224.03	225.26	226.66	228.12	229.73
0.4637	219.83	217.33	217.69	218.58	219.78	221.13	222.51	
0.5001	215.93	213.90	214.32	215.28	216.50	217.77	219.26	220.74
0.6001	203.15	203.61	204.57	205.76	207.09	208.41	209.85	211.38
0.7003	192.17	193.38	194.65	195.97	197.33	198.73	200.16	201.61
0.7999	182.68	183.92	185.20	186.53	187.88	189.25	190.63	192.02
0.9000	173.26	174.47	175.71	176.98	178.27	179.58	180.92	182.23
0.9500	168.41	169.62	170.83	172.09	173.36	174.65	175.96	177.25
0.9801	165.44	166.62	167.83	169.07	170.34	171.61	172.89	174.17
1	163.43	164.61	165.82	167.06	168.32	169.59	170.87	172.15

$$\sigma = \left(\frac{\sum (\rho_{\mathrm{exp}} - \rho_{\mathrm{cal}})}{N - n} \right)^{1/2} \tag{3}$$

where N is the number of experimental data points; the subscripts "exp" and "cal" denote experimental values and calculated ones, respectively.

The molar volume V_m was calculated using the relation:

$$V_m = (xM_1 + (1 - x)M_2)/\rho \tag{4}$$

where x is the mole fraction of the benzonitrile; the subscripts "1" and "2" denote benzonitrile and alkane, respectively; ρ is the density of the solution with a particular mole fraction x. The isobaric thermal expansivity α_p, defined by $(1/V_m)(\partial V_m/\partial T)_p$, may be expressed by:[15]

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{5}$$

The values of α_p may be calculated through eqs 2 and 5. Another approach to calculate the isobaric thermal expansivity is numeric differentiation of the experimental density with respect to temperature.[14] No significant differences between the above two methods were observed for the systems under study.

The isobaric heat capacity per unit volume C_pV^{-1} measured at various mole fractions and temperatures was converted to the isobaric molar heat capacity C_p using the following equation:

$$C_p = C_pV^{-1}(xM_1 + (1 - x)M_2)/\rho \tag{6}$$

where the density at a particular mole fraction was obtained by interpolation from the measured densities at various mole fractions for the same binary system. Tables 4 and 5 list the values of the isobaric molar heat capacities at the selected temperatures for the octane system and the nonane system, respectively. The dependence of the isobaric molar heat capacity on temperature is expressed by the form of eq 2, with ρ and A_i being replaced by $C_p/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$ and C_i. The values of C_i determined by the least-squares method along with the standard deviations σ of the fits defined by the form of eq 3 are collected in Table 6.

The experimental densities ρ, the isobaric molar heat capacities C_p, and the isobaric thermal expansivities α_p of the pure components determined in this work at the selected temperatures are listed and compared with the corresponding literature values[1,2,11,14,16−18] in Table 7. The agreements between our data and the literature values are satisfactory.

The excess molar properties were calculated using the following expression:

$$Y^{\mathrm{E}} = Y - Y^{\mathrm{id}} \tag{7}$$

where Y^{E} stands for $V_m^{\mathrm{E}}/(\mathrm{cm^3 \cdot mol^{-1}})$, $\alpha_p^{\mathrm{E}}/\mathrm{K^{-1}}$, or $C_p^{\mathrm{E}}/(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$ and Y^{id} is the corresponding ideal values calculated by:[19]

$$V_m^{\mathrm{id}} = xV_{m,1}^* + (1 - x)V_{m,2}^* \tag{8}$$

$$C_p^{\mathrm{id}} = xC_{p,1}^* + (1 - x)C_{p,2}^* \tag{9}$$

$$\alpha_p^{\mathrm{id}} = \phi\alpha_{p,1}^* + (1 - \phi)\alpha_{p,2}^* \tag{10}$$

Table 5. Experimental Isobaric Molar Heat Capacities C_p for {x Benzonitrile + (1 − x) Nonane} at Selected Temperatures T

	C_p/(J·mol^{-1}·K^{-1})						
x	T = 285.15 K	T = 288.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
0	278.38	279.60	281.72	283.86	286.11	288.40	290.76
0.0239	275.60	276.80	278.87	280.98	283.18	285.48	287.76
0.0499	272.83	274.01	276.02	278.11	280.26	282.50	284.75
0.0989	267.94	269.06	270.98	272.97	275.01	277.16	279.34
0.1984	258.53	259.47	261.13	262.87	264.72	266.66	268.65
0.2543	253.53	254.27	255.70	257.26	258.97	260.77	262.65
0.3000	249.70	250.12	251.28	252.66	254.22	255.89	257.63
0.4004	242.40	241.04	241.24	242.16	243.44	244.94	246.59
0.4968	234.22	230.79	230.43	231.16	232.33	233.66	235.16
0.6000	217.32	216.76	217.29	218.27	219.53	220.89	222.37
0.6996	202.24	202.88	204.10	205.37	206.74	208.21	209.67
0.8000	189.20	189.97	191.28	192.63	194.00	195.39	196.84
0.9000	176.74	177.48	178.75	180.02	181.35	182.67	184.01
0.9498	170.45	171.18	172.40	173.65	174.93	176.22	177.48
0.9805	166.46	167.19	168.41	169.64	170.89	172.18	173.44
1	163.90	164.63	165.82	167.06	168.32	169.59	170.87

Table 6. Temperature Polynomial Coefficients C_i in Equation 2 for Experimental Isobaric Molar Heat Capacities and the Standard Deviations σ of Fitting

x	C_1	C_2	$C_3 \cdot 10^3$	$C_4 \cdot 10^4$	$C_5 \cdot 10^5$	$C_6 \cdot 10^6$	$C_7 \cdot 10^7$	σ
{x Benzonitrile + (1 − x) Octane}								
0[a]	248.185	0.378	1.02					0.004
0.0219[a]	246.308	0.371	1.06					0.004
0.0576[a]	243.690	0.359	1.09					0.006
0.1021[a]	240.656	0.340	1.15					0.005
0.1999[a]	234.460	0.281	1.60					0.016
0.2998[a]	228.907	0.089	8.34	−0.96				0.031
0.4002[a]	224.090	−0.633	84.81	−41.58	10.16	−0.96		0.056
0.4637[b]	219.502	−1.033	169.30	−125.9	51.64	−10.75	0.884	0.039
0.5001[a]	215.504	−0.679	92.11	−46.88	11.80	−1.14		0.058
0.6001[a]	203.005	0.099	6.69	−0.79				0.034
0.7003[a]	192.150	0.243	0.81					0.009
0.7999[a]	182.661	0.250	0.51					0.009
0.9000[a]	173.248	0.243	0.43					0.007
0.9500[a]	168.410	0.240	0.43					0.006
0.9801[a]	165.415	0.239	0.33					0.008
1[a]	163.407	0.239	0.32					0.008
{x Benzonitrile + (1 − x) Nonane}								
0[b]	277.568	0.401	1.28					0.011
0.0239[b]	274.809	0.393	1.32					0.015
0.0499[b]	272.053	0.383	1.37					0.012
0.0989[b]	267.207	0.363	1.38					0.012
0.1984[b]	257.898	0.307	1.72					0.016
0.2543[b]	253.018	0.244	2.64					0.033
0.3000[b]	249.495	0.095	9.38	−1.16				0.035
0.4004[c]	244.253	−1.246	159.8	−86.80	23.39	−2.435		0.048
0.4968[c]	240.861	−4.628	781.9	−661.5	301.6	−69.85	6.439	0.125
0.6000[c]	217.871	−0.420	50.28	−16.78	2.12			0.040
0.6996[b]	201.820	0.215	1.60					0.021
0.8000[b]	188.700	0.253	0.60					0.014
0.9000[b]	176.250	0.246	0.45					0.013
0.9498[b]	169.966	0.241	0.35					0.014
0.9805[b]	165.991	0.237	0.39					0.012
1[a]	163.407	0.239	0.32					0.008

[a] In the temperature range (283.15 to 318.15) K. [b] In the temperature range (283.15 to 313.15) K. [c] In the temperature range (284.65 to 313.15) K.

$$\phi = xV^{*}_{\mathrm{m},1}/V^{\mathrm{id}}_{\mathrm{m}} \tag{11}$$

where ϕ is the volume fraction of the benzonitrile and the asterisk (*) denotes the pure components. The uncertainties in the determinations of $V^{\mathrm{E}}_{\mathrm{m}}$, α^{E}_{p}, and C^{E}_{p} are related to the repeatabilities in the measurements of ρ, C_p, and the uncertainty in the determination of the mole fraction of the solution. They were estimated to be ± 0.004 cm^3·mol^{-1}, ± 2·10^{-6} K^{-1}, and ± 0.08 J·mol^{-1}·K^{-1}, respectively.

The performance of the densimeter and the calorimeter for determinations of the excess molar volume and the excess molar heat capacity was tested with the binary mixtures {benzene + cyclohexane}. The standard deviations between our results and the most reliable values selected from the literatures[20,21] were 0.004 cm^3·mol^{-1} for $V^{\mathrm{E}}_{\mathrm{m}}$ and 0.03 J·mol^{-1}·K^{-1} for C^{E}_{p}, respectively, which is compatible with the experimental uncertainties.

The above three excess properties at various x were fitted to the Redlich−Kister equation:[22]

$$Y^{\mathrm{E}} = x(1 - x)\sum_{\mathrm{i}=1}^{n} B_{\mathrm{i}}(1 - 2x)^{\mathrm{i}-1} \tag{12}$$

by the least-squares method for the selected temperatures to obtain the coefficients B_{i} at various temperatures, which along with the corresponding standard deviations σ are listed in Table

Table 7. Comparison of Densities ρ, Isobaric Thermal Expansivities α_p, and Isobaric Molar Heat Capacities C_p of the Pure Components at Selected Temperatures Obtained in This Work with Those Reported in the Literature

	T	ρ / $\mathrm{g \cdot cm^{-3}}$		$\alpha_p \cdot 10^3$ / $\mathrm{K^{-1}}$		C_p / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	K	this work	literature	this work	literature	this work	literature
octane	283.15	0.71076	0.7107[13]	1.122		248.20	248.45[11]
	288.15	0.70676	0.7067[13]	1.133	1.142[17]	250.10	250.43[11]
	293.15	0.70274	0.70267[16] 0.7027[13]	1.146	1.451[17]	252.06	252.47[11]
	298.15	0.69871	0.69862[16] 0.6986[13]	1.158	1.164[16] 1.148[17]	254.08	254.15[16] 254.56[11] 254.51[14]
	303.15	0.69466	0.6946[13]	1.170	1.160[17]	256.16	256.68[11]
	308.15	0.69058	0.6905[13]	1.183	1.185[17]	258.28	258.83[11]
	313.15	0.68649	0.6864[13]	1.196		260.45	261.02[11]
	318.15	0.68237	0.6823[13]	1.209		262.66	263.25[11]
nonane	283.15	0.72609	0.7255[13]	1.062		277.57	277.93[11]
	288.15	0.72222	0.7216[13]	1.071	1.074[18]	279.60	280.03[11]
	293.15	0.71835	0.71772[16] 0.7178[13]	1.081	1.082[18]	281.72	282.21[11]
	298.15	0.71446	0.71375[16] 0.7139[13]	1.091	1.092[18]	283.86	284.55[16] 284.43[11]
	303.15	0.71055	0.7100[13]	1.101	1.102[18]	286.11	286.68[11]
	308.15	0.70663	0.7061[13]	1.111	1.112[18]	288.40	288.95[11]
	313.15	0.70270		1.122		290.76	291.21[11]
benzonitrile	283.15	1.01399		0.874		163.43	163.35[2]
	288.15	1.00955	1.00948[16]	0.878		164.61	
	293.15	1.00512		0.882		165.82	
	298.15	1.00069	1.0006[16]	0.886		167.06	166.52[2] 166.90[1]
	303.15	0.99626	0.99628[16]	0.890		168.32	
	308.15	0.99183		0.894		169.59	
	313.15	0.98740		0.898		170.87	
	318.15	0.98296		0.902		172.15	

8. The number of parameters listed in Table 8 was determined by using an F-test. The dependences of the excess quantities on the mole fraction of the benzonitrile at the selected temperatures are shown in Figures 1 to 3 with the lines being the values calculated by eq 12, which evidence the good agreements between the calculated and the experimental values.

As shown in Figure 1, the excess molar volumes for both mixtures show positive deviations from the ideality in the alkane-rich region and negative deviations at the higher mole fractions of the benzonitrile. In other words, the clear S-shaped composition dependences can be observed. Two contrary effects result in the observed S-shaped excess molar volumes for the systems under investigation. First, the positive contribution to $V_{\mathrm{m}}^{\mathrm{E}}$ mainly results from the destructions of the dispersive interactions, dipolar order, and orientational order of the pure liquids when the two components are mixed with each other; the system with one component being the longer alkyl chain has larger values of $V_{\mathrm{m}}^{\mathrm{E}}$, because the longer alkyl chain has higher orientational order. Secondly, the negative contribution mainly results from the geometrical fitting of one component into the gaps between the molecules of the other component (the packing effect). The latter predominates in a large concentration range, except for the small alkane-rich region, where the packing effect is not sufficient to overcome the positive contributions to $V_{\mathrm{m}}^{\mathrm{E}}$. The temperature dependences of $V_{\mathrm{m}}^{\mathrm{E}}$ for both systems show that in the alkane-rich region, the higher the temperature, the more positive $V_{\mathrm{m}}^{\mathrm{E}}$; whereas in the benzonitrile-rich region, the dependence is inversed. It indicates that both positive and negative contributions to the excess molar volumes are enhanced by an increase of temperature. As shown in Figure 1, the excess molar volumes at various temperatures are crossing each other within narrow concentration intervals in the vicinity of the mole fractions $x = 0.2$ and $x = 0.5$ for the octane system and the nonane system, respectively. It seems that the stable, almost temperature-independent structures are formed at the corresponding compositions.

The excess isobaric thermal expansivity, α_p^{E}, is plotted against composition at 298.15 K for both systems in Figure 2, where the values only at a unique temperature are shown because the variation of this property with temperature is insignificant as compared with its uncertainty in the measurements. As can be seen, the values of α_p^{E} also show the S-shaped composition dependences and change their signs from positive to negative at the compositions around $x = 0.2$ and $x = 0.5$, for the octane system and the nonane system, respectively, which are consistent with the results of $V_{\mathrm{m}}^{\mathrm{E}}$.

In principle, when a system is close enough to its critical point, the anomaly originated from the long-range concentration fluctuation may be observed. However, for the volume properties, no such anomalies could be detected as the temperatures approach to the critical values around (283 and 284) K for the octane system[4,5] and the nonane system,[6] respectively. It may be attributed to the fact that the critical fluctuations affect slightly the first-order excess magnitudes, but strongly some second-order ones, such as excess isobaric molar heat capacity.[23,24]

Figure 3 shows the plots of the excess isobaric molar heat capacity versus the mole fraction x of benzonitrile for each of the two studied systems. In the alkane-rich region, the values of C_p^{E} are negative and change to positive ones as the mole fractions of the benzonitrile exceed 0.03 and 0.05 for the octane system and the nonane system, respectively. The small negative C_p^{E} found in the alkane-rich region may be attributed to the destructions of the orientational order of the alkane molecules. This negative deviation of C_p^{E} for the nonane system is more significant than that for the octane system because of its higher orientation orders being destructed. The considerably large value of C_p^{E} located in the

Table 8. Parameters B_i in Equation 12 and the Standard Deviation σ of Fitting for Excess Molar Volumes V_m^E, Excess Thermal Expansibilities α_p^E, and Excess Molar Heat Capacities C_p^E

	T/K	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	σ
				{x Benzonitrile + (1 − x) Octane}						
$V_m^E/(cm^3 \cdot mol^{-1})$	283.15	−1.094	1.13	−0.53	0.68	0.71				0.0028
	288.15	−1.128	1.17	−0.44	0.67	0.64				0.0028
	293.15	−1.159	1.20	−0.38	0.66	0.60				0.0026
	298.15	−1.192	1.22	−0.34	0.67	0.59				0.0028
	303.15	−1.223	1.25	0.30	0.67	0.57				0.0028
	308.15	−1.258	1.28	−0.25	0.68	0.53				0.0027
	313.15	−1.296	1.31	−0.21	0.68	0.53				0.0030
	318.15	−1.335	1.34	−0.20	0.69	0.55				0.0029
$\alpha_p^E \cdot 10^3/K^{-1}$	283.15	−0.035	0.033	0.051						0.0009
	288.15	−0.036	0.034	0.048						0.0007
	293.15	−0.038	0.038	0.043						0.0006
	298.15	−0.039	0.040	0.040						0.0004
	303.15	−0.041	0.042	0.036						0.0003
	308.15	−0.043	0.045	0.031						0.0003
	313.15	−0.045	0.048	0.027						0.0004
	318.15	−0.047	0.051	0.024						0.0005
$C_p^E/(J \cdot mol^{-1} \cdot K^{-1})$	288.15	26.15	23.0	−54	−89	93	123	−63	−69	0.034
	293.15	21.7	13.7	−35	−36	58	15	−42		0.043
	298.15	18.8	9.1	−17	−19	7				0.063
	303.15	17.0	7.0	−13	−16	4				0.050
	308.15	15.4	5.8	−9.5	−14.8					0.046
	313.15	14.2	4.6	−8.3	−13.2					0.042
	318.15	13.4	3.4	−8.0	−11.4					0.051
				{x Benzonitrile + (1 − x) Nonane}						
$V_m^E/(cm^3 \cdot mol^{-1})$	285.15	−0.631	1.11	−0.11	0.67					0.0035
	288.15	−0.633	1.14	−0.09	0.66					0.0034
	293.15	−0.635	1.17	−0.06	0.64					0.0033
	298.15	−0.635	1.21	−0.04	0.63					0.0032
	303.15	−0.635	1.24	−0.02	0.61					0.0032
	308.15	−0.636	1.28	0.00	0.60					0.0033
	313.15	−0.636	1.32	0.02	0.60					0.0034
$\alpha_p^E \cdot 10^3/K^{-1}$	285.15	0.003	0.027	0.035						0.0008
	288.15	0.003	0.027	0.032						0.0008
	293.15	0.003	0.029	0.028						0.0007
	298.15	0.003	0.030	0.024						0.0005
	303.15	0.003	0.032	0.021						0.0004
	308.15	0.004	0.034	0.017						0.0003
	313.15	0.004	0.035	0.012						0.0003
$C_p^E/(J \cdot mol^{-1} \cdot K^{-1})$	288.15	32.5	14	−99	−40	186	17	−122		0.116
	293.15	25.0	9.0	−52	−24	85	4	−56		0.033
	298.15	20.9	6.3	−26	−17	14				0.068
	303.15	18.7	4.9	−20	−16	9				0.055
	308.15	17.0	3.7	−16.0	−13.6	6				0.040
	313.15	15.7	2.7	−11.6	−12					0.056

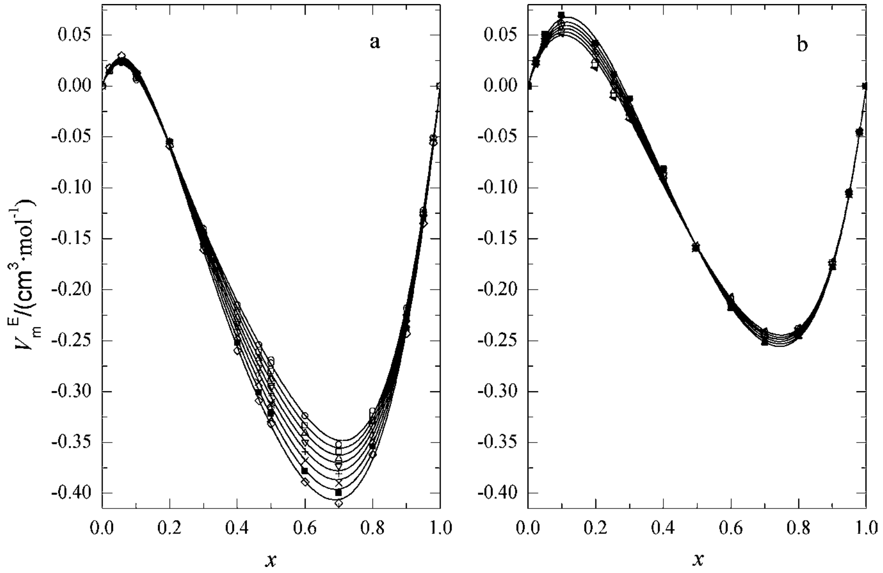

Figure 1. Excess molar volumes for (a) {x benzonitrile + (1 − x) octane} and (b) {x benzonitrile + (1 − x) nonane} at ○, 283.15 K; left-pointing triangle, 285.15 K; □, 288.15 K; △, 293.15 K; ▽, 298.15 K; +, 303.15 K; ×, 308.15 K; ■, 313.15 K; and ◇, 318.15 K. —, calculated values from eq 12 with the values of parameters listed in Table 8.

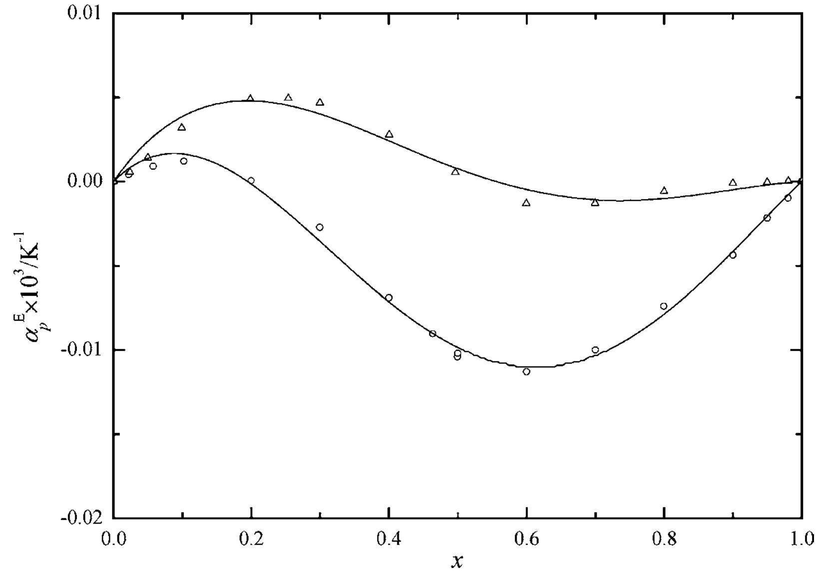

Figure 2. Excess isobaric thermal expensivities α_p^E at 298.15 K for ○, {x benzonitrile + $(1 - x)$ octane} and △, {x benzonitrile + $(1 - x)$ nonane}. —, calculated values from eq 12 with the values of parameters listed in Table 8.

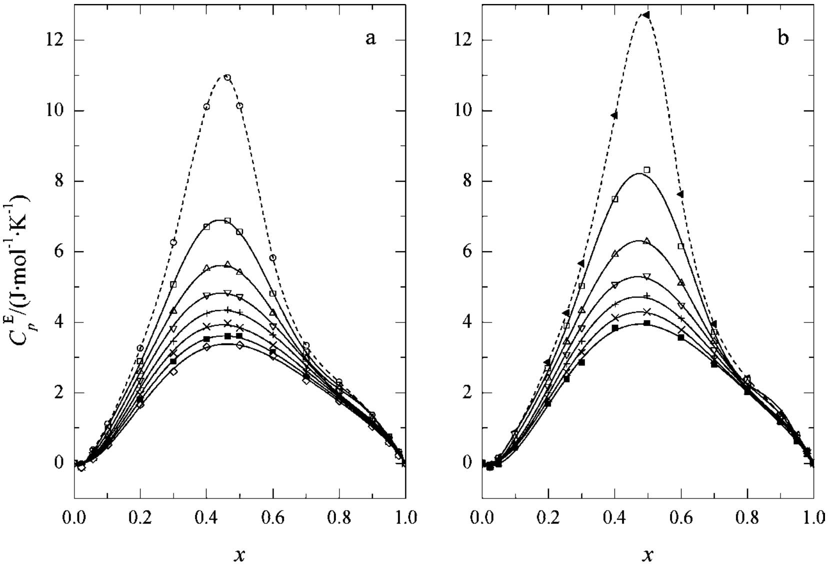

Figure 3. Excess isobaric molar heat capacities for (a) {x benzonitrile + $(1 - x)$ octane} and (b) {x benzonitrile + $(1 - x)$ nonane} at ○, 283.15 K; left-pointing triangle, 285.15 K; □, 288.15 K; △, 293.15 K; ▽, 298.15 K; +, 303.15 K; ×, 308.15 K; ■, 313.15 K; and ◇, 318.15 K. —, calculated values from eq 12 with the values of parameters listed in Table 8; ---, guide for the eyes.

central mole fraction region for each of the studied systems is originated from the nonrandomness[25,26] in the mixtures, which creates the additional structure orders during the mixing process. The positive C_p^E in the benzonitrile-rich region may be attributed to the disassociation of the dimers of the benzonitrile,[2,3] which suppresses the negative contributions from the destructions of the dipolar order of the benzonitrile molecules. The most rapid increases of C_p^E with decreases of the temperature for the octane system and the nonane system were detected at the mole fractions of benzotitrile of 0.462 and 0.494, respectively, which are consistent with the critical compositions of 0.464 and 0.497 reported previously.[4,6] At those compositions, the analytic polynomial eq 2 is incapable of fitting the temperature dependences of C_p even using up to seven polynomial coefficients as shown in Table 6. It was also found that fitting eq 12 with the measured C_p^E at the lower temperatures close to the critical points yielded large errors even using up to seven polynomial coefficients as shown in Table 8 and completely failed at (283.15 and 285.15) K for the octane system and the nonane system, respectively, illustrated by the data points linked with the dashed lines in Figure 3. It shows that the critical fluctuation in the vicinity of the critical points strongly affects the excess isobaric molar heat capacity and yields a critical anomaly.

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