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EXCESS ENTHALPIES AND EXCESS HEAT CAPACITIES OF THE BINARY MIXTURES OF ACETONITRILE, DIMETHYLFORMAMIDE, AND BENZENE AT 298.15 K

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Excess enthalpies and excess isobaric heat capacities of binary mixtures consisting of acetonitrile, dimethylformamide and benzene were measured at 298.15 K. Excess enthalpy of acetonitrile + benzene is positive and that of acetonitrile + dimethylformamide is negative. That of dimethylformamide + benzene is positive and nearly equals to zero as shown in the previous report [1]. Excess heat capacities of acetonitrile + benzene and benzene + dimethylformamide change sign from negative to positive with increase of benzene. That of acetonitrile + dimethylformamide is not simple. It is slightly positive near both ends of mole fraction and not so large negative in the middle of mole fraction. The curve tends to flatten in that region.

Keywords: excess enthalpies, excess heat capacities, binary mixtures

Introduction

We are interested in thermodynamic properties of the mixtures containing components with the structures such as association, hydrogen-bonding, cluster and so on in the pure liquid. We recently reported the thermodynamic properties of the binary mixtures consisting of benzene, 2, 2, 2-trifluoroethan-1-ol and dimethylsulfoxide [2, 3]. The thermodynamic properties of the mixtures are not simply explained and the correlations between the properties are also complicated because of the effects of the molecular cluster and hydrogen-bonding. In this paper, excess enthalpies and heat capacities of binary mixtures of acetonitrile (AN), dimethylformamide (DMF) and benzene are reported. AN and DMF are

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dipolar liquids and have been reported that simple shape molecules AN orient antiparallel to each other [4] but wide-spread molecules DMF orient at random [5]. They are expected to form a new intermolecular correlation [1] and to produce a fluctuation of concentration by mixing with benzene.

Experimental

Benzene (special grade of Wako Pure Chemical) was fractionally distilled. Dimethylformamide (special grade of Wako Pure Chemical) was also fractionally distilled at reduced pressure by a spinning band distillation column (constructed by the central workshop of Osaka City University). Acetonitrile (guaranteed reagent of Tokyo Kasei) was used without further purification. The purities were estimated to be more than 99.9 mole% from g.l.c (Shimadzu, GC-3BT, column: silicon for benzene, and TSG1 for AN and DMF). The densities of AN, benzene and DMF were 0.77670, 0.87373 and 0.94400 $g \cdot cm^{-3}$, respectively, by means of a vibrational densimeter (Antron– Paar, DMA602). Excess enthalpy was measured by a revised LKB flow microcalorimeter (LKB–107001) and the details were reported in the previous paper [6]. The errors of measurements were less than ±0.2 per cent. Excess heat capacity was measured by using flow microcalorimeter which has been made in our laboratory [7]. The errors of measurements were less than 0.01 per cent of $C^{E}_{p,m} / C_{p,m}$. The $C_{p,m}$ of AN, benzene and DMF were 90.03, 135.91 and 147.22 $J \cdot K^{-1} mol^{-1}$, respectively.

Results and discussion

The values of excess enthalpies H^{E}_{m} observed in the mixtures of xAN + (1–x) benzene and xAN + (1–x)DMF are given in Table 1 and those of excess heat capacities $C^{E}_{p,m}$ obtained in the mixtures of xAN + (1– x)benzene, $x$benzene + (1–x) DMF and xAN + (1–x) DMF are given in Table 2.

The observed values are fitted to the Redlich-Kister equation by means of least squares method.

$$\frac{F^{E}}{(\mathrm{unit})} = x(1-x)\sum A_{i}(1-2x)^{i-1} \qquad (1)$$

The fitting parameters A_i are given in Table 3 with the estimated error s. The observed points and the curves calculated by the Eq. (1) are plotted in Figs 1 and 2 for excess enthalpies and for excess heat capacities, respectively.

Table 1 The values of excess enthalpies at 298.15 K, observed and calculated by Eq. (1)

x	H^E_m / J·mol^{-1}		x	H^E_m / J·mol^{-1}	
	observed	calculated		observed	calculated
xCH$_3$CN + (1 – x)C$_6$H$_6$					
0.05000	74.7	72.8	0.55000	460.4	460.2
0.10000	134.0	135.5	0.60000	462.8	463.0
0.15000	191.7	191.2	0.65000	455.3	455.6
0.20000	241.0	241.7	0.70000	436.9	436.9
0.25000	288.1	288.0	0.75000	405.8	405.5
0.30000	330.0	330.2	0.80000	360.5	360.2
0.35000	368.9	368.1	0.85000	299.4	299.4
0.40000	401.3	401.1	0.90000	221.1	220.9
0.45000	428.1	428.1	0.95000	121.6	122.3
0.50000	447.6	448.1			
xCH$_3$CN + (1 – x)(CH$_3$)$_2$NCHO					
0.05000	–40.0	–39.7	0.55000	–199.3	–198.9
0.10000	–75.3	–75.0	0.60000	–192.1	–191.9
0.15000	–106.3	–106.0	0.65000	–180.7	–180.9
0.20000	–133.2	–132.5	0.70000	–165.8	–166.0
0.25000	–155.2	–154.8	0.75000	–147.3	–147.3
0.30000	–169.6	–172.7	0.80000	–124.8	–124.9
0.35000	–186.8	–186.3	0.85000	–98.8	–98.9
0.40000	–196.1	–195.7	0.90000	–69.3	–69.3
0.45000	–201.1	–200.9	0.95000	–36.5	–36.3
0.50000	–202.2	–201.9			

The xCH$_3$CN + (1–x)C$_6$H$_6$ *system*

H^E_m of this mixture has been reported by Absood *et al.* [8] and Di Cave *et al.* [9]. Their results are in good agreement with ours as seen in Fig. 1. The H^E_m are positive and maximum value is approximately 450 J·mol^{-1}, which value is not so large as expected from the breaking of the dipolar interaction of AN. The excess partial molar enthalpy of AN at infinite dilution is smaller than that of benzene. It suggests that the antiparallel dipolar pair of AN molecules is left unbroken even in the dilute mixture. The analysis of H^E_m by postulating the mixing of AN–dimer and benzene gives a perfect parabolic curve, as shown in Fig. 3. The AN–dimer which cancels dipole moment by antiparallel molecular orientation behaves in the benzene mixture as if it were a non-polar molecule. The maximum value is 450 J·mol^{-1}, however, it is not sufficiently large in consideration of the immis-

Table 2 The values of excess heat capacities at 298.15 K, observed and calculated by Eq. (1)

x	$C^{E}_{p,m}$ / J·K^{-1}·mol^{-1}		x	$C^{E}_{p,m}$ / J·K^{-1}·mol^{-1}	
	observed	calculated		observed	calculated
	xCH$_3$CN + (1 – x)C$_6$H$_6$				
0.02501	0.222	0.211	0.55014	–0.284	–0.257
0.05003	0.405	0.365	0.60013	–0.354	–0.330
0.10005	0.547	0.537	0.65013	–0.415	–0.393
0.15007	0.534	0.575	0.70012	–0.429	–0.445
0.20009	0.504	0.526	0.75010	–0.462	–0.482
0.25010	0.428	0.426	0.80009	–0.488	–0.499
0.30012	0.315	0.300	0.85007	–0.464	–0.483
0.35012	0.161	0.169	0.90005	–0.419	–0.415
0.40013	0.101	0.043	0.95003	–0.283	–0.266
0.45014	–0.076	–0.071	0.97501	–0.204	–0.150
0.50013	–0.171	–0.171			
	xC$_6$H$_6$ + (1 – x) (CH$_3$)$_2$NCHO				
0.02501	–0.096	–0.091	0.55008	0.331	0.298
0.05002	–0.169	–0.155	0.60008	0.413	0.405
0.10003	–0.228	–0.221	0.65008	0.544	0.518
0.15004	–0.234	–0.230	0.70007	0.625	0.631
0.20005	–0.198	–0.204	0.75006	0.724	0.729
0.25006	–0.107	–0.157	0.80005	0.766	0.793
0.30007	–0.112	–0.099	0.85004	0.783	0.795
0.35008	–0.023	–0.034	0.90003	0.714	0.698
0.40008	–0.013	0.037	0.95002	0.485	0.453
0.45008	0.124	0.115	0.97501	0.236	0.256
0.50008	0.174	0.201			
	xCH$_3$CN + (1 – x)(CH$_3$)$_2$NCHO				
0.02502	0.019	0.022	0.65020	–0.160	–0.141
0.05004	–0.004	0.007	0.70019	–0.103	–0.111
0.10008	–0.042	–0.058	0.75017	–0.087	–0.081
0.15011	–0.122	–0.113	0.80014	–0.018	–0.050
0.20014	–0.129	–0.141	0.85011	–0.028	–0.014
0.25017	–0.161	–0.151	0.90008	0.001	0.029
0.30019	–0.159	–0.157	0.90008	0.033	0.029
0.35020	–0.174	–0.165	0.90008	0.039	0.029
0.40021	–0.165	–0.177	0.95004	0.033	0.057
0.45022	–0.189	–0.188	0.97502	0.054	0.047
0.50022	–0.179	–0.192	0.97502	0.093	0.047
0.55022	–0.195	–0.185	0.97502	0.046	0.047

Table 3 The values and errors of coefficients and *s* of Eq. (1)

property	A_1	A_2	A_3	A_4	A_5	A_6	A_7	*s*
$x\mathrm{CH_3CN} + (1-x)\mathrm{C_6H_6}$								
$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	1792.5	–648.9	184.3	87.3	170.4	–	–	0.77
	(1.5)	(4.9)	(15.6)	(12.5)	(26.6)			
$C^{\mathrm{E}}_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1}	–0.682	3.711	2.127	4.528	–	–	–	0.028
	(0.046)	(0.175)	(0.208)	(0.441)				
$x\mathrm{C_6H_6} + (1-x)(\mathrm{CH_3})_2\mathrm{NCHO}$								
$C^{\mathrm{E}}_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1}	0.804	–3.665	2.883	–4.245	–	–	–	0.026
	(0.042)	(0.159)	(0.188)	(0.399)				
$x\mathrm{CH_3CN} + (1-x)(\mathrm{CH_3})_2\mathrm{NCHO}$								
$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	–807.7	–39.59	8.83	–	–	–	–	0.83
	(1.4)	(2.70)	(6.19)					
$C^{\mathrm{E}}_{p,\mathrm{m}}$ / J·K^{-1}·mol^{-1}	–0.770	–0.041	1.518	–1.617	–5.474	1.166	7.165	0.019
	(0.041)	(0.178)	(0.688)	(0.985)	(2.455)	(1.157)	(2.255)	

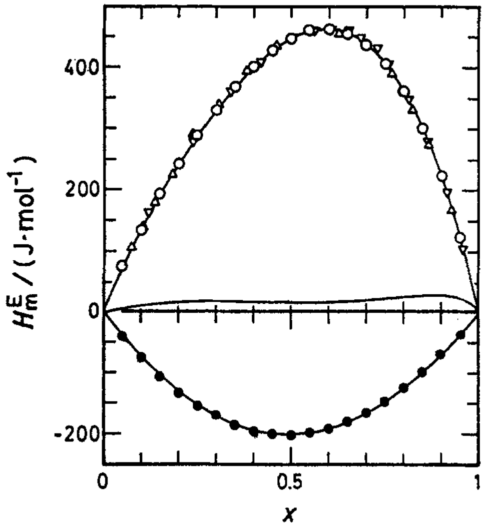

Fig. 1 Excess enthalpies of the mixtures of xAN + (1–x)benzene, $x$benzene + (1–x)DMF, and xAN + (1–x)DMF at 298.15 K
—O— : $x\mathrm{CH_3CH} + (1-x)\mathrm{C_6H_6}$, Δ : same above [8], ∇ : same above [9], — : $x\mathrm{C_6H_6} + (1-x)(\mathrm{CH_3})_2\mathrm{NCHO}$ [1], —●— : $x\mathrm{CH_3CN} + (1-x)(\mathrm{CH_3})_2\mathrm{NCHO}$

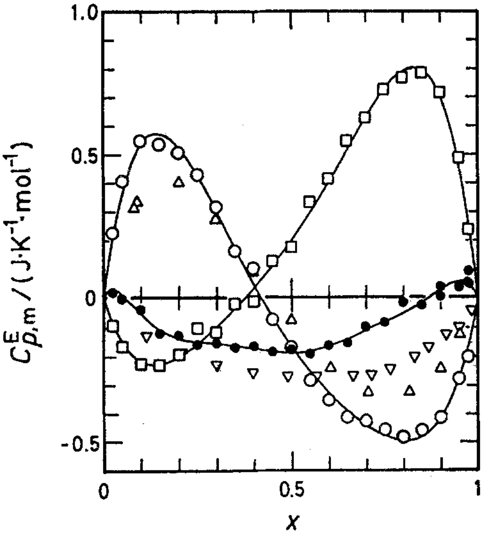

Fig. 2 Excess heat capacities of xAN + (1–x)benzene, $x$benzene + (1–x)DMF, and xAN + (1–x)DMF at 298.15 K
—O— : $xCH_3CN + (1-x)C_6H_6$, Δ : same above [11], —□— : $xC_6H_6 + (1-x)(CH_3)_2NCHO$, —•—: $xCH_3CN + (1-x)(CH_3)_2NCHO$, ∇: same above [11]

cibility of AN + cyclohexane [10] and then another attractive interaction between AN and benzene must be considered. $C^E_{p,m}$ of this system is anomalous and changes the sign from negative to positive with the decrease of mole fraction x. The result reported by Grolier *et al.*[11] is slightly smaller in the absolute value than ours. It also suggests that any molecular orientation is newly formed by mixing or dipolar interaction in the pure AN liquid is left unbroken in the benzene rich solution and the non-randomness effect [12] due to these structures makes $C^E_{p,m}$ in the benzene rich mixture positive. Cibulka *et al.* [13] have reported V^E_m of this system changes the sign from positive to negative with increase of benzene, which agrees our result of density measurement to be published in near future. Brown and Fox [14] have reported for the excess entropy of this system to be negative at 318 K. It is concluded that an attractive interaction of molecular correlated orientation is newly formed between AN and benzene molecules in the mixture.

The $xC_6H_6 + (1-x)(CH_3)_2NCHO$ *system*

H^E_m of this system previously reported [1] is anomalous and approximately 15–30 J·mol^{-1} in almost the whole region of mole fraction, as shown in Fig. 1. This suggests that the exothermic interaction which produces a new associated structure between DMF molecules and benzene molecules cancel the endothermic effect due to the breaking of dipolar interactions of DMF molecules by

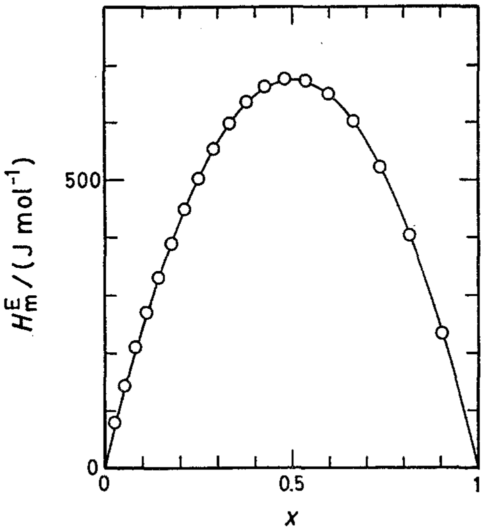

Fig. 3 The excess enthalpies of a hypothetical mixture of $x(CH_3CN)_2$ + $(1-x)C_6H_6$

mixing with benzene, as similar to AN + benzene system. The smaller endothermic effect of DMF + benzene system than AN + benzene is ascribed to the random orientation of DMF molecules in the pure state on contrary to the antiparallel orientation of AN molecules. This explanation is supported by $C^E_{p,m}$ curve which changes sign from negative to positive with increase of benzene, as similar to the AN + benzene system.

The $xCH_3CN + (1-x)(CH_3)_2NCHO$ *system*

H^E_m of the mixture is negative in the whole range of concentration. The curve is almost parabolic and the minimum is –220 J·mol^{-1}. It is reasonable to consider that the unlike intermolecular interaction between AN and DMF is dominantly formed and makes H^E_m negative.

$C^E_{p,m}$ is, however, not simple and it shows small positive parts in both ends of mole fraction x and negative and flat in the middle of mole fraction.

Grolier *et al.*[11] also have reported $C^E_{p.m}$ which is more negative and then no positive part which we found in both ends of mole fraction of AN. The curve is, however, very similar to our ones as a whole. Three contributions must be considered. One is the negative contribution due to the further formation of AN and DMF pair as suggested by Radnai *et al.*[4], at higher temperature. The other is the positive contribution due to that AN-dimer as diluent is left unbroken in extremely high x, and an AN molecule disturbs the random orientation of DMF molecules in the pure state [5] in extremely low x and makes DMF to rearrange in some ordered one.

The further discussion will be given together with volumetric properties, molar volume, isentropic and isothermal compressibilities in near future.

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Zusammenfassung — An binären Gemischen aus Acetonitril, Dimethylformamid und Benzol wurden bei 298.15 K die Überschußenthalpien und die isobaren Überschußwärmekapazitäten gemessen. Die Überschußenthalpie von Acetonitril + Benzol ist positiv, die von Acetonitril + Dimethylformamid ist negativ. Die Überschußenthalpie ist bei Dimethylformamid positiv und wie bereits berichtet [1] annähernd Null. Die Überschußwärmekapazität von Acetonitril + Benzol und Benzol + Dimethylformamid wechselt bei Zunahme von Benzol das Vorzeichen von negativ zu positiv. Die von Acetonitril + Dimethylformamid ist nicht einfach. An beiden Enden der Molenbruchskale ist sie leicht positiv und nicht allzu negativ in der Mitte der Molenbruchskale. Die Kurve flacht in dieser Region ab.