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Excess Molar Volumes and Excess Molar Heat Capacities for Binary Mixtures of (Ethanol + Benzene, or Toluene, or *o*-Xylene, or Chlorobenzene) at a Temperature of 298.15 K

Reiji Tanaka* and Satoru Toyama

Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku,
Osaka, Japan 558

Excess molar volumes, measured in a vibrating-tube densimeter, and excess molar heat capacities, measured in a flow calorimeter, were made for binary mixtures of (ethanol + benzene, or toluene, or *o*-xylene, or chlorobenzene) at a temperature of 298.15 K. Those experimental results were interpreted in terms of self-association of ethanol and hydrogen bonds formed between ethanol and an aromatic compound.

Introduction

Recently, we have published measurements of excess molar volumes V_m^E and excess molar heat capacities $C_{p,\mathrm{m}}^\mathrm{E}$ for binary mixtures of ethanol with aprotic polar compounds (Tanaka and Toyama, 1996). This paper reports determinations of V_m^E and $C_{p,\mathrm{m}}^\mathrm{E}$ for binary mixtures of (ethanol + benzene, or toluene, or *o*-xylene, or chlorobenzene) at a temperature of 298.15 K in order to provide information about molecular interactions between an alkanol and an aromatic compound.

Experimental Section

Materials. The sample liquids were all Wako Pure Chemical Industries Ltd., Special-Grade Reagents. The purification for ethanol was the same in the previous work (Tanaka *et al.* 1986). Other liquids were fractionally distilled as received. Purities were tested by GLC analysis. Purified ethanol contained water of 0.004 mole fraction as an impurity, and purities of other liquids were better than 0.9995 mole fraction.

Measurements. The mixtures were prepared in specially devised vessels (Takenaka et al., 1980). The error in the mole fraction of ethanol, x, was less than $\pm 2 \times 10^{-5}$ for most of the compositions, but for the range of $x < 0.01$ the uncertainty increased to $\pm 2 \times 10^{-4}$.

The excess molar volumes were determined from density measurements. The densities ρ were measured in a vibrating-tube densimeter (Model 01D, Sodev Inc., Canada). The temperature of the circulating water in the densimeter was controlled within a deviation of ±0.0003 K. The uncertainty in ρ was about $\pm 2 \times 10^{-5}$ g cm^{-3}, while the imprecision was less than $\pm 3 \times 10^{-6}$ g cm^{-3}. The systematic error in V^E was estimated to be ±0.001 cm^3 mol^{-1} for $x > 0.01$ but increased to ±0.003 cm^3 mol^{-1} for $x < 0.01$.

The excess molar heat capacities were calculated from the values of heat capacity divided by volume (C_p/V) determined in a flow calorimeter (Techneurop Inc., Canada). The estimated systematic uncertainty in $C_{p,\mathrm{m}}^\mathrm{E}$ was less than ±0.02 J K^{-1} mol^{-1} for most of the compositions and was about ±0.002 J K^{-1} mol^{-1} for $x < 0.002$. Procedures of preparing mixtures, measurements, and estimation for the experimental error have been described previously (Takenaka *et al.*, 1980; Tanaka, 1982; Tanaka and Toyama, 1996).

Table 1. Densities ρ, Molar Heat Capacities $C_{p,\mathrm{m}}^*$ of the Component Liquids, and Molar Heat Capacities of Ethanol at Infinite Dilution $C_{p,1}^\infty$ in Each Solvent at a Temperature of 298.15 K

	ρ/g cm^{-3}		$C_{p,\mathrm{m}}^*$/J K^{-1} mol^{-1}		$C_{p,1}^\infty$/J K^{-1}mol^{-1}
	obs.	lit.	obs.	lit.	obs.
ethanol	0.785 08	0.785 04[a]	112.30	112.34[c]	
benzene	0.873 65	0.873 64[b]	135.690	135.76[c]	111
toluene	0.862 22	0.862 24[b]	156.971	157.081[d]	113
o-xylene	0.875 86	0.875 82[b]	187.574	187.584[d]	124
chlorobenzene	1.101 08	1.101 10[b]	150.786	150.787[d]	112

[a] Riddick and Bunger (1970). [b] Tanaka and Benson (1976). [c] Fortier *et al.* (1976). [d] Fortier and Benson (1977).

The results for the densities of pure liquids ρ, the molar heat capacities $C_{p,\mathrm{m}}^*$ of pure liquids, and the molar heat capacities at infinite dilution $C_{p,1}^\infty$ of ethanol observed in each solvent are listed in Table 1 along with literature values. The values of $C_{p,1}^\infty$ were calculated by extrapolating the apparent molar heat capacity of ethanol to infinite dilution by the least-squares method.

Results and Discussion

The experimental results of V_m^E and $C_{p,\mathrm{m}}^\mathrm{E}$ for all the mixtures are summarized in Table 2. The smoothing function

$$X_\mathrm{m}^\mathrm{E} = x(1-x)\sum c_i x^{(i-1)/2} \tag{1}$$

where x is the mole fraction of ethanol and X_m^E is either V_m^E/cm^3 mol^{-1} or $C_{p,\mathrm{m}}^\mathrm{E}$/J K^{-1} mol^{-1}, was fitted to each set of results by the least-squares method. Several equations with a skewing factor were tried for smoothing experimental values. However, we could not minimize the calculated standard deviations s to the values of estimated experimental error with a set of parameters as also experienced by Marsh and Burfitt (1975) for $V_\mathrm{m}^\mathrm{E}/x(1-x)$ of (ethanol + nonpolar solvent). The values of c_i and s determined from this analysis are given in Tables 3 and 4. The observed values were graphically expressed as $X_\mathrm{m}^\mathrm{E}/x(1-x)$ rather than X_m^E in order to emphasize the characteristic behavior in dilute region.

Figure 1 shows the observed values of $V_\mathrm{m}^\mathrm{E}/x(1-x)$ and the smoothed curves for four systems along with literature values. Our values for (ethanol + benzene) agreed excel-

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* Corresponding author. Phone: 6-605-3126. Fax: 6-605-2522.

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Table 2. Experimental Results for Excess Molar Volumes V_m^E and Excess Molar Heat Capacities $C_{p,m}^E$ at a Temperature of 298.15 K. $V^\circ = 1\ cm^3\ mol^{-1}$; $C^\circ = 1\ J\ K^{-1}\ mol^{-1}$

x	V_m^E/V°	$C_{p,m}^E/C^\circ$	x	V_m^E/V°	$C_{p,m}^E/C^\circ$	x	V_m^E/V°	$C_{p,m}^E/C^\circ$
xEthanol + (1 − x)Benzene								
0.002 08	0.0041	0.0083	0.035 48	0.0497	3.36	0.290 34	0.0798	13.97
0.004 10	0.0080	0.0039	0.039 98	0.0532	3.95	0.365 94	0.0621	14.51
0.006 03		0.0856	0.057 28	0.0650	5.93	0.479 72	0.0290	13.80
0.007 61	0.0153	0.1410	0.076 67	0.0740	7.59	0.582 57	−0.0018	12.27
0.009 25	0.0182	0.2157	0.099 58	0.0825	9.11	0.695 91	−0.0302	9.77
0.011 72	0.0215	0.362	0.130 30	0.0882	10.59	0.789 13	−0.0430	7.17
0.023 26	0.0377	1.64	0.155 74	0.0907	11.53	0.898 77	−0.0370	3.60
xEthanol + (1 − x)Toluene								
0.000 99	0.0012	0.003	0.032 40		3.33	0.304 99	0.0075	15.29
0.001 96	0.0028	0.019	0.038 98	0.0338	4.32	0.405 55	−0.0283	15.44
0.004 01	0.0059	0.059	0.060 96	0.0452	6.93	0.501 62	−0.0624	14.70
0.005 97	0.0094	0.121	0.080 58	0.0470	8.66	0.599 11	−0.0908	13.14
0.007 90	0.0118	0.206	0.102 29	0.0499	10.08	0.669 04	−0.1104	10.86
0.009 36	0.0136	0.289	0.132 88	0.0481	11.65	0.797 75	−0.1091	7.91
0.019 88	0.0222	1.44	0.200 78	0.0375	13.78	0.898 65	−0.0777	4.24
xEthanol + (1 − x)o-Xylene								
0.000 94		0.012	0.020 39	0.0327	1.58	0.302 11	0.0260	15.80
0.001 88		0.045	0.024 32	0.0367	2.19	0.397 31	−0.0067	16.00
0.004 08	0.0089	0.092	0.029 72	0.0405	3.10	0.501 44	−0.0438	15.23
0.006 19	0.0122	0.164	0.040 84	0.0492	4.78	0.603 67	−0.0762	13.65
0.008 27	0.0154	0.264	0.058 32	0.0554	6.97	0.701 49	−0.0972	11.38
0.009 85	0.0184	0.365	0.091 93	0.0633	9.82	0.800 98	−0.1010	8.36
0.014 90	0.0253	0.84	0.196 98	0.0545	14.19	0.900 71	−0.0751	4.56
xEthanol + (1 − x)Chlorobenzene								
0.001 05		0.0070	0.049 17		5.79	0.305 87	−0.1113	15.89
0.002 03	0.0019	0.0200	0.063 64	0.0215	7.42	0.404 28	−0.1749	16.10
0.003 69	0.0040	0.046	0.077 10	0.0160	8.63	0.506 89	−0.2341	15.37
0.005 99	0.0061	0.103	0.099 38	0.0086		0.601 08	−0.2756	13.92
0.007 98	0.0084	0.186	0.099 64	0.0091	10.24	0.699 85	−0.2939	11.63
0.009 92	0.0106	0.30	0.112 52	0.0030		0.800 86		8.47
0.019 93	0.0161	1.41	0.124 25	−0.0009	11.63	0.901 60	−0.1786	4.53
0.032 29		3.39	0.212 90	−0.0511	14.57			

Table 3. Coefficients c_i and Standard Deviation s for Representation of $V_m^E/cm^3\ mol^{-1}$ by Eq 1 for {xEthanol + (1 − x)Aromatic Compound} at a Temperature of 298.15 K

	benzene	toluene	o-xylene	chlorobenzene
c_1	2.8010	1.9390	3.0003	1.6706
c_2	−9.9423	−6.4216	−13.010	−7.1176
c_3	17.372	7.7665	26.904	7.8814
c_4	−17.934	−4.3181	−34.162	−2.8942
c_5	9.7182		24.437	−1.9112
c_6	−2.5616		−8.240	
s	0.0005	0.0008	0.0007	0.0005

lently with those reported by Marsh and Burfitt (1975). The values for this system reported by Kato (1980) are in good agreement with ours for middle range in x. Letcher and his co-workers reported experimental values for (ethanol + o-xylene) (Letcher *et al.*, 1990) and for (ethanol + chlorobenzene) (Letcher and Nevines, 1994). In both cases their results are in good agreement with our results.

In all cases the V_m^E curves are s-shaped, and their sign changes from positive to negative with increasing x. The positive values of V_m^E in a range of small x is due to the breaking of hydrogen bonds formed among ethanol molecules. Tamres (1952) showed spectroscopic and calorimetric evidences of complex formation between methanol and aromatic compounds due to hydrogen bondings where alkylbenzene behaves as an electron donor. More recently, Ioki *et al.* (1978) have theoretically clarified the nature of the intramolecular hydrogen bond in 2-hydroxybiphenyl acting between the hydroxyl group and aromatic ring (OH−π interaction) by using MO calculations. They found that the hydrogen bond is formed mainly from resonance energy between the hydroxyl group and carbon atoms, and a charge transfer structure of ($OH^-\cdots C^+$) contributes to the intramolecular hydrogen bond formation to some extent at an O−H distance below 1.4 Å. They concluded that OH−π interaction occurs essentially between the 1s orbital of the hydrogen atom and the $2p_z$ orbital of a carbon atom. They assumed that this molecule is twisted around the central single bond by 50° so that the delocalization of π-electron between two benzene rings can be neglected. We may consider, therefore, that a similar OH−π interaction occurs between separated molecules of phenol and benzene. The negative values in V_m^E at larger x are reasonably at-

Table 4. Coefficients c_i and Standard Deviation s for Representation of $C_{p,m}^E/J\ K^{-1}\ mol^{-1}$ by Eq 1 for {xEthanol + (1 − x)Aromatic Compound} at a Temperature of 298.15 K

	benzene	toluene	o-xylene	chlorobenzene
	$0 < x < 0.01$	$0 < x < 0.01$	$0 < x < 0.01$	$0 < x < 0.01$
c_1	−1.4988	15.958	−20.632	−21.394
$c_2/10^2$	0.47289	−3.8583	17.798	17.045
$c_3/10^3$	1.1373	5.6448	−24.754	−35.251
$c_4/10^3$	11.257		126.553	323.87
$c_5/10^3$				−895.32
s	0.0006	0.004	0.013	0.0006
	$0.001 < x < 0.1$	$0.01 < x < 0.1$	$0.01 < x < 0.1$	$0.01 < x < 0.1$
c_1	132.52	143.44	319.50	161.73
$c_2/10^3$	−4.6411	−5.2098	−9.542	−5.8123
$c_3/10^3$	57.256	68.160	107.91	73.737
$c_4/10^3$	−264.3	−337.98	−504.61	−357.81
$c_5/10^3$	528.57	741.91	−1060.2	768.15
$c_6/10^3$	−384.73	−611.08	−828.80	−616.65
s	0.03	0.03	0.02	0.03
	$0.1 < x < 1$	$0.1 < x < 1$	$0.1 < x < 1$	$0.1 < x < 1$
c_1	−252.02	149.16	−69.265	131.31
$c_2/10^3$	4.4869	0.13382	2.620	0.3117
$c_3/10^3$	−21.125	−1.5682	−12.657	−2.1126
$c_4/10^3$	48.599	3.1459	28.557	3.9000
$c_5/10^3$	−60.105	−2.6248	−34.392	−3.1007
$c_6/10^3$	38.365	0.80939	21.422	0.9203
$c_7/10^3$	−9.935		−5.433	
s	0.08	0.03	0.07	0.03

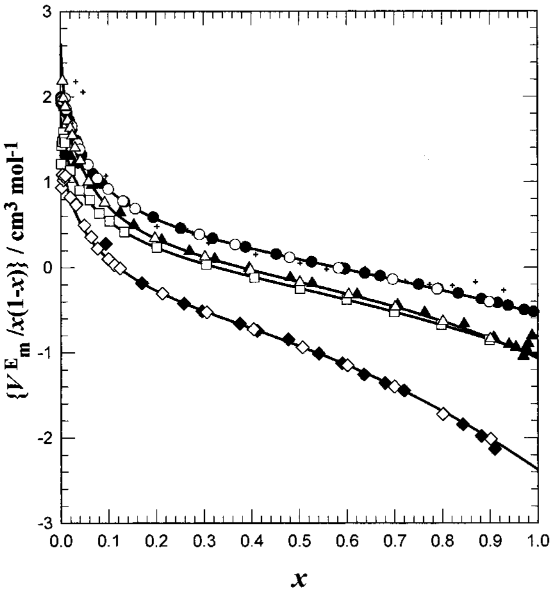

Figure 1. Excess molar volumes V^E_m of {$x$ethanol + (1 − x)aromatic compound} at a temperature of 298.15 K. Present work: (○) benzene; (□) toluene; (△) o-xylene; (◇) chlorobenzene. Literature value: (●) benzene, Marsh and Burfitt (1975); (+) benzene, Kato (1980); (▲) o-xylene, Letcher *et al.* (1990); (◆) chlorobenzene, Letcher and Nevines (1994).

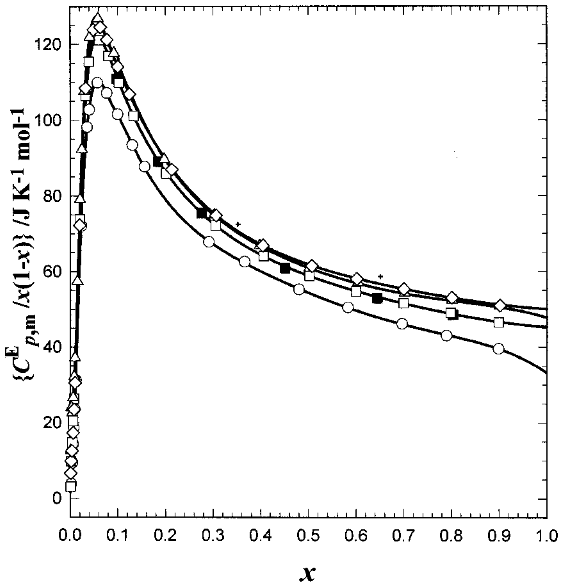

Figure 2. Excess molar heat capacities $C^E_{p,m}$ of {$x$ethanol + (1 − x)aromatic compound} at a temperature of 298.15 K. Present work: (○) benzene; (□) toluene; (△) o-xylene; (◇) chlorobenzene. Literature value: (■) toluene, Hwa and Ziegler (1966); (+) toluene, Michael (1975).

tributed to the OH−π interaction between ethanol and alkylbenzene. However, a more negative V^E_m in the chlorobenzene system cannot be explained consistently if one assumes that the aromatic ring of chlorobenzene acts as an electron donor because the electron-donating ability of chlorobenzene is much weaker than that of alkylbenzene (Tamres, 1952). In this system a contribution due to the formation of a hydrogen bond of OH−Cl type would be a major molecular interaction. Similar changes in V^E_m for mixtures of 1-alkanols with trichloroethylene have been reported by Hossein Iloukhani *et al.* (1984).

Recently, Letcher *et al.* (1995) analyzed excess molar enthalpy H^E_m and V^E_m for binary mixtures of (1-alkanol + 1-alkene, or 1-alkyne) by using an association model. They concluded that no association between 1-alkanol and 1-alkene was necessary for describing H^E_m and V^E_m; however, for (1-alkanol + 1-alkyne) systems the corresponding association has to be taken into account. Their interpretation of association between alkanol and alkyne is based on the picture that the acidic H atom of the 1-alkynes interacts as a proton donor with free OH groups of the alkanol molecules.

Figure 2 shows the present results for $C^E_{p,m}/x(1 - x)$ along with literature values. The agreement between our results and those of Hwa and Ziegler (1966) is excellent. However, the four points reported by Michael (1975) are considerably higher than those two sets of measurements. In each system the values of $C^E_{p,m}$ are positive in the whole range of x. The s-shaped curves in the dilute region of x were commonly observed for mixtures of (alkanol + alkane), and it was explained in terms of thermal relaxation exerted in the equilibrium between monomer and associated alkanols (Costas and Patterson, 1985; Tanaka et al., 1986). The characteristic behavior due to association of alkanol is clearly shown as a sharp peak appeared at small x in the plots of $C^E_{p,m}/x(1 - x)$. A very sharp peak was observed at $x \approx 0.008$ in the partial molar heat capacities $C_{p,1}$ of 1-alkanols in heptane (Tanaka *et al.*, 1986). In the present systems, the sharpness of the peak in $C_{p,1}$ is much more mild because of stabilization of alkanol with aromatic solvents, and they are shifted to higher concentrations as follows: benzene, 0.028; toluene, 0.029; o-xylene, 0.027; chlorobenzene, 0.029. The limiting values $C^\infty_{p,1}$ of ethanol observed at 298.15 K in inert solvents were 107 J K^{-1} mol^{-1} (n-heptane) (Tanaka et al., 1986); 100 J K^{-1} mol^{-1} (n-decane) (Andreoli-Ball *et al.*, 1985). The limiting values observed in the present aromatic solvents are higher than those by 4 to 20 J K^{-1} mol^{-1}. This difference supports the existence of OH−π interaction between ethanol and aromatics.

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