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Excess Molar Volumes and Excess Molar Heat Capacities for Binary Mixtures of Ethanol with Chlorocyclohexane, 1-Nitropropane, Dibutyl Ether, and Ethyl Acetate at the Temperature of 298.15 K

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Determinations of excess molar volumes in a vibrating densimeter and excess molar heat capacities in a flow calorimeter were carried out at the temperature of 298.15 K for binary mixtures of ethanol with chlorocyclohexane, 1-nitropropane, dibutyl ether, and ethyl acetate.

Introduction

Previously, we published the experimental results of excess molar heat capacities $C_{p,\mathrm{m}}^{\mathrm{E}}$ for binary mixtures of 1-alkanols with heptane (Tanaka *et al*., 1986). This paper reports determinations of excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$ and $C_{p,\mathrm{m}}^{\mathrm{E}}$ for binary mixtures of ethanol with chlorocyclohexane, 1-nitropropane, dibutyl ether, and ethyl acetate at the temperature of 298.15 K. The measurements were carried out to provide information about thermodynamic properties of (an alkanol + an aprotic polar compound) systems. We are not aware of any previous investigations of $V_{\mathrm{m}}^{\mathrm{E}}$ and directly measured $C_{p,\mathrm{m}}^{\mathrm{E}}$ for the present systems.

Experimental Section

Materials. The sample liquids were all Wako Pure Chemical Industries Ltd., Special-Grade Reagents. The purification for ethanol was the same as in the previous work (Tanaka *et al*., 1986). Chlorocyclohexane and 1-nitropropane were distilled under reduced pressure at a temperature controlled between 333 K and 353 K. Dibutyl ether was used as received. Ethyl acetate was dried over 4A molecular sieves and distilled. The mole fraction purities tested by glc analysis were 0.991 for chlorocyclohexane, 0.999 for 1-nitropropane, and 0.999 for dibutyl ether. No impurity was detected for ethyl acetate.

Measurements. The mixtures were prepared in specially devised vessels (Takenaka *et al*., 1980). The error in the mole fraction of ethanol, x, was within $\pm 2 \times 10^{-5}$ 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}, but the imprecision was less than $\pm 3 \times 10^{-6}$ g cm^{-3}. The systematic error in $V_{\mathrm{m}}^{\mathrm{E}}$ was estimated to be ±0.001 cm^3 mol^{-1} for the compositions of $x > 0.01$, while it increased to ±0.003 cm^3 mol^{-1} in the range of $x < 0.01$. The procedure and the test for density measurements have been described previously (Tanaka, 1979; Takenaka *et al*., 1980).

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

	ρ^*/g cm^{-3}		$C_{p,\mathrm{m}}^{*}$/J K^{-1} mol^{-1}		$C_{p,\mathrm{m}}^{\infty}$/J K^{-1} mol^{-1} obs
	obs	lit.	obs	lit.	
C_2H_5OH	0.785 08	0.785 04[a]	112.30	112.68[b] 112.34[c] 112.4[d]	
$C_6H_{11}Cl$	0.993 99	0.985 71[e]	179.55		111
$C_3H_7NO_2$	0.995 95	0.996 09[a]	160.46	175[a]	119
$(C_4H_9)_2O$	0.763 76	0.764 1[a]	279.46	252[a]	146
$CH_3CO_2C_2H_5$	0.894 42	0.894 55[a]	170.52		108

[a] Riddick and Bunger (1970). [b] Tanaka *et al*. (1986). [c] Fortier and Benson (1976). [d] Hwa and Ziegler (1966). [e] Letcher (1972).

The heat capacity divided by volume (C_p/V) for each mixture was determined in a Picker flow calorimeter (Techneurop Inc., Canada). The standard liquid for measurements was heptane for which 1.523 97 J K^{-1} cm^{-3} was adopted for C_p/V as in our earlier work (Tanaka, 1982). The values of C_p/V for aprotic polar solvents were firstly determined relatively to heptane and then the measurements for mixtures were carried out with the stepwise reference method by using the aprotic solvent as the first reference liquid. All the measurements were carried out in increasing and decreasing sequences of x to cancel out the flow rate change due to the mixing of liquids in contact in the cell tube. The operational procedure of measurements has been described in detail previously (Tanaka, 1982). The experimental values of C_p/V were converted to the molar heat capacities $C_{p,\mathrm{m}}$, and the excess quantities $C_{p,\mathrm{m}}^{\mathrm{E}}$ were calculated with the help of determined density values. The estimated uncertainty in $C_{p,\mathrm{m}}$ varied depending on x: it decreased from ±0.07 J K^{-1} mol^{-1} to ±0.02 J K^{-1} mol^{-1} with decreasing x from 1 to 0.04 and decreased to about ±0.002 J K^{-1} mol^{-1} at $x \approx 0.001$. The estimated systematic error 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 $x < 0.002$. The results for the densities of pure liquid ρ^*, the molar heat capacities $C_{p,\mathrm{m}}^{*}$ of pure liquids, and the molar heat capacities at infinite dilution $C_{p,\mathrm{m}}^{\infty}$ of ethanol in each solvent are listed in Table 1 along with literature values. The values of $C_{p,\mathrm{m}}^{\infty}$ were calculated by extrapolating the apparent molar heat capacities of ethanol to infinite dilution by the least squares method.

Results and Discussion

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

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

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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 the Temperatue of 298.15 K: $V° = 1$ cm³ mol⁻¹; $C° = 1$ J K⁻¹ mol⁻¹

x	$V^E/V°$	$C_{p,m}^E/C°$	x	$V^E/V°$	$C_{p,m}^E/C°$	x	$V^E/V°$	$C_{p,m}^E/C°$
			$xC_2H_5OH + (1 - x)C_6H_{11}Cl$					
0.001 06	0.0021	0.002	0.038 43	0.0655	4.34	0.497 81	0.0756	14.40
0.002 05	0.0036	0.018	0.059 47	0.0829	6.99	0.595 19	0.0510	12.84
0.003 98	0.0093	0.055	0.080 77	0.0971	8.90	0.696 02	0.0257	10.54
0.005 99	0.0134	0.117	0.100 91	0.1062	10.28	0.797 80	0.0053	7.58
0.007 95	0.0179	0.202	0.125 74	0.1151	11.57	0.855 02	−0.0028	
0.009 93	0.0221	0.321	0.197 62	0.1202	13.90	0.871 00	−0.0043	
0.020 94	0.0419	1.60	0.300 38	0.1119	15.23	0.893 69	−0.0051	4.23
0.030 36	0.0556	3.10	0.398 53	0.0968	15.26	0.931 06	−0.0058	
						0.950 19	−0.0044	
			$xC_2H_5OH + (1 - x)C_3H_7NO_2$					
0.001 08	0.0014	0.009	0.029 65	0.0281	0.61	0.301 99	0.0400	13.29
0.001 54	0.0019	0.013	0.039 33	0.0360	1.00	0.400 67	0.0083	14.68
0.002 03	0.0027	0.020	0.049 81	0.0428	1.49	0.500 96	−0.0268	14.86
0.004 04	0.0043	0.043	0.059 02	0.0471	1.97	0.601 50	−0.0617	14.01
0.006 12	0.0067	0.068	0.069 41	0.0521	2.60	0.701 32	−0.0902	12.19
0.007 86	0.0086	0.090	0.077 13	0.0560	3.07	0.799 87	−0.1042	9.42
0.009 24	0.0101	0.101	0.100 45	0.0611	4.51	0.901 73	−0.0863	5.39
0.019 86	0.0203	0.32	0.202 39	0.0619	10.32			
			$xC_2H_5OH + (1 - x)(C_4H_9)_2O$					
0.000 90	−0.0028	0.03	0.031 58	−0.0221	1.66	0.197 58	−0.0871	8.31
0.001 89	−0.0035	0.08	0.036 40	−0.0275	1.90	0.228 09	−0.0934	8.80
0.003 12	−0.0045	0.14	0.043 31	−0.0325	2.29	0.268 35	−0.0975	9.33
0.004 11	−0.0051	0.19	0.050 22	−0.0353	2.70	0.309 10	−0.0984	9.76
0.004 77	−0.0037	0.24	0.054 31	−0.0397	2.92	0.340 46	−0.1012	9.82
0.006 05	−0.0065	0.29	0.063 40	−0.0424	3.44	0.405 33	−0.0999	9.97
0.008 12	−0.0082	0.39	0.070 54	−0.0471	3.80	0.507 61	−0.0953	9.46
0.011 02	−0.0082	0.56	0.089 52	−0.0567	4.74	0.605 73	−0.0854	8.41
0.015 17	−0.0131	0.75	0.108 99	−0.0644	5.63	0.703 15	−0.0699	6.89
0.018 78	−0.0134	0.96	0.129 17	−0.0718	6.38	0.800 23	−0.0493	4.98
0.025 15	−0.0202	1.28	0.169 29	−0.0834	7.60	0.901 06	−0.0243	2.62
			$xC_2H_5OH + (1 - x)CH_3CO_2C_2H_5$					
0.001 39	0.001	−0.002	0.029 08	0.025	0.366	0.228 74		4.72
0.002 01	0.002	−0.000	0.040 32	0.031	0.539	0.257 74		5.28
0.003 06	0.003	0.009	0.050 45	0.038	0.723	0.298 10	0.142	6.01
0.005 00	0.005	0.032	0.060 34	0.049	0.902	0.398 62	0.153	7.17
0.007 08	0.007	0.059	0.069 58	0.050	1.075	0.497 19	0.153	7.56
0.009 73	0.007	0.107	0.090 09	0.062	1.518	0.595 96	0.144	7.25
0.012 02	0.011	0.118	0.100 72		1.76	0.695 89	0.126	6.31
0.016 05	0.015	0.174	0.129 42	0.081	2.43	0.798 83	0.096	4.70
0.020 87	0.016	0.253	0.149 26	0.088	2.90	0.892 63	0.060	2.74
0.023 33	0.021	0.276	0.199 91		4.12			

Table 3. Coefficients c_j and Standard Deviation s for Representation of V_m^E/cm³ mol⁻¹ by Eq 1 for {x Ethanol + (1 − x) Aprotic Polar Compound} at the Temperature of 298.15 K

	$C_6H_{11}Cl$	$C_3H_7NO_2$	$(C_4H_9)_2O$	$CH_3CO_2C_2H_5$
c_1	2.8215	0.89135	−0.38213	1.2171
c_2	−4.9535	4.9136	−0.14075	−3.2551
c_3	−7.9164	−38.745	−0.14052	8.3314
c_4	32.242	103.76	−0.17700	−10.230
c_5	−34.309	−149.62		4.6092
c_6	11.977	114.80		
c_7		−37.402		
s	0.0006	0.0004	0.0009	0.001

where X_m^E is either V_m^E/cm³ mol⁻¹ or $C_{p,m}^E$/J K⁻¹ mol⁻¹ was fitted to each set of results by the least squares method. The values of c_i and the calculated standard deviations s obtained from this analysis are given in Tables 3 and 4.

Figure 1 shows the observed values of V_m^E and the smoothed curves expressed by eq 1 for four systems. The values are positive over the whole composition range in the system with ethyl acetate while the values are all negative in the system with 1-nitropropane. The curves are sigmoid for other systems and the sign changes from positive to negative with increasing x.

All the experimental results of $C_{p,m}^E$ and their representations by eq 1 are plotted in Figure 2a and the results in the very dilute region are shown enlarged in Figure 2b. Nagata *et al.* (1975) reported excess molar enthalpies of mixing H_m^E for the mixture of ethanol with ethyl acetate at the temperatures of 298 K and 308 K. The heat capacity calculated from their results reaches about 10 J K⁻¹ mol⁻¹ accompanying double maxima. The disagreement found between two sets of results is attributed to the deviation in H_m^E measurements. Except for the values in the system with ethyl acetate at mole fractions less than 0.002, $C_{p,m}^E$ values were all positive. In each case the curve has an inflection point in the region of $x < 0.15$ so that the present systems exhibit similar shapes of $C_{p,m}^E$ with those found for the mixtures of 1-alkanol + n-alkane (Costas and Patterson, 1985; Tanaka *et al.*, 1986; Roux *et al.*, 1993). The values of $C_{p,m}^E$ for the systems consisting of associated species are essentially positive, unless the attractive force is extremely strong, since they are characterized with thermal relaxation exerted in the equilibrium between monomers and associated molecules. In the present systems positive contributions arise from the complex formations between alkanol−alkanol and also alkanol−solvent molecules. A very sharp peak appeared at $x \approx 0.008$ in the partial molar heat capacities $C_{p,1}$ of 1-alkanols in heptane mixture and they were attributed to a characteristic aggregation of alkanols in inert solvents. Such behavior of aggregation resembles micelle formations in aqueous media. Whereas, in the present systems, the sharpness of the peak in $C_{p,1}$ is much more mild because

Table 4. Coefficients c_j and Standard Deviation s for Representation of $C^{E}_{p,m}$/J K^{-1} mol^{-1} by Eq 1 for {x Ethanol + (1 − x) Aprotic Polar Compound} at the Temperature of 298.15 K

	$C_6H_{11}Cl$	$C_3H_7NO_2$	$(C_4H_9)_2O$	$CH_3CO_2C_2H_5$
	$0 < x < 0.01$	$0 < x < 0.1$	$0 < x < 0.1$	$0 < x < 0.1$
c_1	14.698	6.3491	34.742	−14.754
$c_2/10^3$	−0.38115	0.1206	0.15830	0.4977
$c_3/10^3$	5.6575	−1.7843	−0.26886	−3.7826
$c_4/10^3$		15.234		14.801
$c_5/10^3$		−41.220		−27.922
$c_6/10^3$		36.132		21.775
$c_7/10^3$				−2.6834
s	0.004	0.006	0.02	0.005
	$0.01 < x < 0.1$	$0.1 < x < 1$	$0.1 < x < 1$	$0.1 < x < 1$
c_1	147.62	655.61	−9.1171	26.114
$c_2/10^3$	−5.3603	−9.1169	0.65745	−0.19885
$c_3/10^3$	69.359	52.754	−2.2565	1.0087
$c_4/10^3$	−339.11	−156.68	3.4049	−1.8387
$c_5/10^3$	731.22	264.59	−2.4670	1.4797
$c_6/10^3$	−589.31	−257.77	0.69856	−0.44943
$c_7/10^3$		135.279		
$c_8/10^3$		−29.645		
s	0.03	0.03	0.04	0.01
	$0.1 < x < 1$			
c_1	126.31			
$c_2/10^3$	0.40459			
$c_3/10^3$	−2.6005			
$c_4/10^3$	4.9407			
$c_5/10^3$	−4.1232			
$c_6/10^3$	1.2976			
s	0.03			

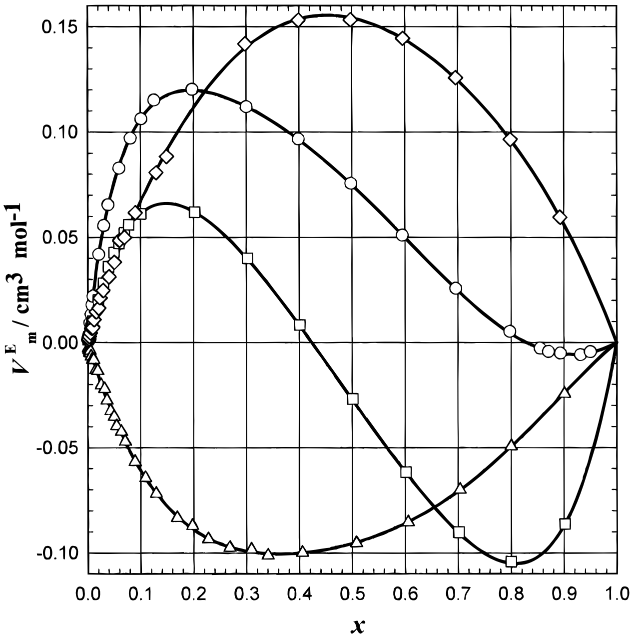

Figure 1. Excess molar volumes V^{E}_{m} of {x alkanol + (1 − x) aprotic polar compound} at the temperature of 298.15 K: (○) chlorocyclohexane; (△) 1-nitropropane; (□) dibutyl ether; (◇) ethyl acetate; (curves) least squares representations by eq 1.

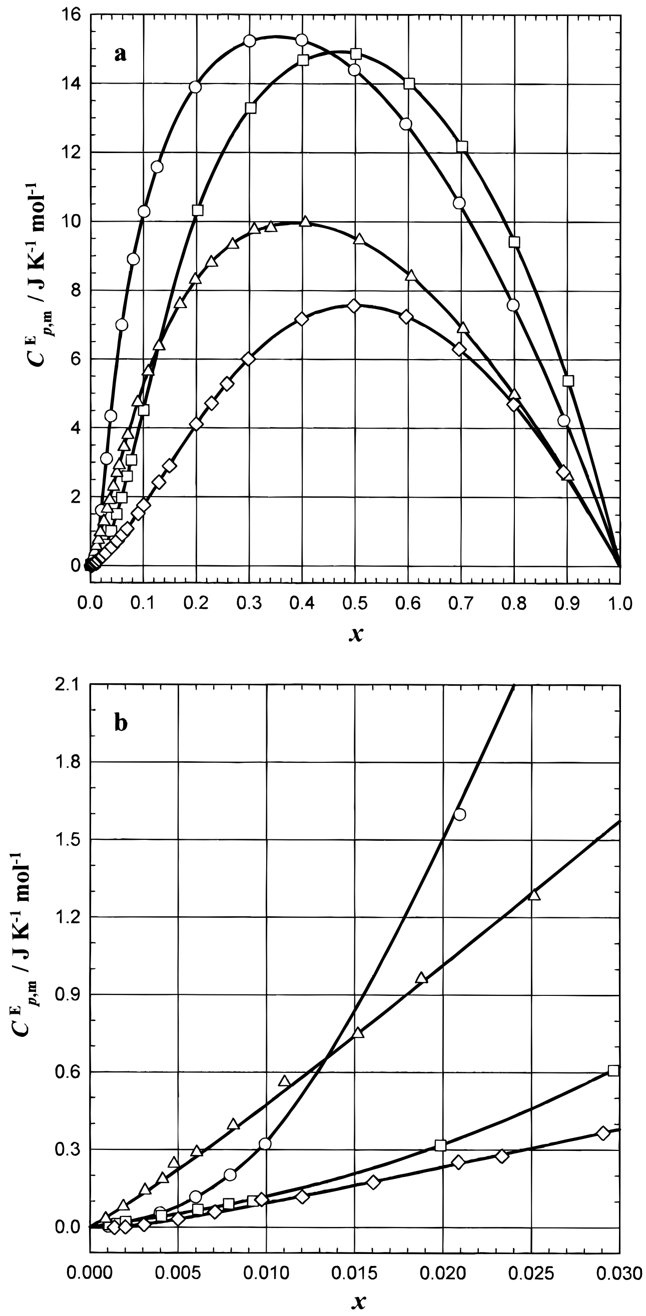

Figure 2. Excess molar heat capacities $C^{E}_{p,m}$ of {x alkanol + (1 − x) aprotic polar compound} at the temperature of 298.15 K: (○) chlorocyclohexane; (△) 1-nitropropane; (□) dibutyl ether; (◇) ethyl acetate; (curves) least squares representations by eq 1.

of stabilization of alkanol with solvent molecules, and they are shifted to higher concentrations as follows: chlorocyclohexane, 0.03; 1-nitropropane, 0.08; dibutyl ether, 0.04; ethyl acetate, 0.15. It is interesting that, although the magnitude is very small, negative values in $C^{E}_{p,m}$ were found in the mixture of (ethanol + ethyl acetate) at low mole fractions. H^{E}_{m} of this system is positive for the entire range of mole fraction with a maximum value exceeding 1200 J K^{-1} mol^{-1} (Nagata *et al.*, 1975). Very small or negative $C^{E}_{p,m}$ values at nearly infinite dilution imply that there exist no complexes which may exhibit a thermal relaxation effect to the heat capacity. From those experimental results we may conclude that the attractive interaction between ethyl acetate and ethanol is moderate. Relatively large values and a monotonous increment of $C^{E}_{p,m}$ with increasing x in the dilute region of ethanol found for the 1-nitropropane system show that ethanol molecules are stabilized due to the complex formation with solvent molecules.

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