TEMPERATURE DEPENDENCE OF MOLAR EXCESS VOLUMES AND EXCESS THERMAL EXPANSION COEFFICIENTS FOR BINARY MIXTURES OF CYCLOHEXANE WITH SOME HYDROCABONS BETWEEN 298.15 AND 313.15 K

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SUMMARY

An apparatus for measuring liquid density at various temperatures was constructed using a vibrating-tube densimeter, and using this apparatus, densities were measured for binary mixtures of cyclohexane + benzene, + toluene, + ethylbenzene and + heptane at temperature range from 298.15 to 313.15 K. Molar excess volumes, V^E , for these mixtures were determined from the density data. They show the positive values for all the systems. The temperature dependence of excess volumes was positive for benzene and toluene systems but negative for the other systems. Excess thermal expansion coefficients, α^E , for these mixtures were also evaluated from the temperature dependence of V^E . α^E were obviously negative except for the cyclohexane rich region in the benzene and the toluene systems.

INTRODUCTION

Temperature dependence of molar excess volume, $(\partial V^{E}/\partial T)_{p}$ and the excess thermal expansion coefficient, α^{E} , of binary liquid mixture is very important quantities in consideration of the differences in the P, V, T relation and in the behavior of component molecules between the solution state and the ideal state. However, these data have been scarcely reported because of the difficulty of exact determination. Recently, in order to obtain the accurate solution density at various temperatures, an apparatus equipped with a vibrating-tube densimeter was constructed and tested in our laboratory. This type of densimeter is appropriate to measure liquid density precisely and easily. In this study, $(\partial V^E / \partial T)_P$ and α^E were estimated from the molar excess volumes, I^{E} , found by the density measurement for binary mixtures of cyclohexane(CH) + benzene(BZ), + toluene(TL), + ethylbenzene(EB) and + heptane(HP) between 298.15 and 315.15 K. In addition, the errors included in the estimated quantities were analysed.

EXPERIMENTAL

Materials

All the hydrocarbons, Special-Grade reagents (Wako Pure Chemical Ind. Ltd., Japan), were distilled with a 1.2 m column before use. The purities were estimated to be better than 99.9 moles-%, using a GLC (shimadzu GC-3BT, Japan).

Apparatus and Procedure

An apparatus constructed consists of a vibrating-tube densimeter (Anton Paar DNA-602, Austria) equipped with special sample inlet part for the good thermal exchange, a thermostated water bath controlled within ± 0.0003 K between 278 and 338 K, two thermometers using a quartz sensor (ETA MT-3500, Switzerland), a frequency counter (Iwatsu SC-7102, Japan) with a photocoupler and a schmitt trigger signal input circuit, and a computer system (NEC PC-9801VM, Japan) with GP-IB interface. The details of the apparatus and the result of the performance test are described in the other communication in near future(ref. 1).

The sample solutions for density measurement were prepared in an "Onion Cell" with 10 cm³ in volume by the same manner as described previously (ref. 2). The accuracy of the concentration of solution was believed to be less than $\pm 3 \times 10^{-5}$ in mole fraction, x.

The density of sample liquid, β was calculated from the period of oscillation, γ of an U-shaped sample tube in a densimeter, as follows:

(1)

$$v = a + br^2 + cr^4$$

where, a, b and c are constants characteristic of the oscillator. The constants, a and b had to be always evaluated by measuring τ for two liquids of the well-known densities in a series of measurement. On the other hand, the constant c, necessary for accurate measurement, was once determined by the least-squares method using densities of five organic standard liquids obtained by a 60 cm³ Ostwald type of pycnometer, by which liquid density can be found within the error of less than \pm 1×10^{-5} . The accuracy of the density measurement was believed to be less than \pm 1×10^{-5} g cm⁻³ from the accuracy of ρ in the standard liquids. Normally, the density of the liquid is related to τ by the first two terms of eqn.(1) in use of a vibrating-tube densimeter (refs. 3 and 4). However, it has been found that density measurements with the precision of $\pm 10^{-5}$ can not made, if eqn.(1) would not be used. The densities of all the component liquids were determined from the constants *a* and *b* evaluated by using two standard liquids which cover the density range of interest at each temperature. The density measurement in a series of solution system was made in a way of increasing in order the densities of sample liquids. The sample liquid was injected to the densimeter by the following two manners; one is that the next sample liquid is injected after washing out an old sample liquid by ethanol and drying the tube by an air pump (Drying method), and the other is that the old sample liquid is slowly pushed out by the next one (Push-Out method).

The precision of density measurements of mixtures by the Push-out method was estimated to be less than $\pm 5 \times 10^{-6}$ g cm⁻³, and $\pm 1 \times 10^{-5}$ g cm⁻³ by the Drying method. The worse reproducibility in the Drying method is considered to be due to the elastic hysteresis of the oscillator during the drying of the tube.

RESULTS AND DISCUSSION

The density measurements of component liquids and binary mixtures of CH(1) + BZ(2), + TL(2), + EB(2) and + HP(2) were carried out at 298.15, 303.15, 308.15 and 313.15 K. The linear polynomial for the molar volume, U, of the sampl liquids, against temperature, T, was obtained by the least-squares method, and using it, the thermal expansion coefficients for the sample liquids, α , were calculated at each temperature by the thermodynamic relation:

$$\alpha = (1/V)(\partial V/\partial T)_{P}$$

The ρ and α obtained for the pure component liquids are listed in Table 1.

 v^{E} of mixtures were estimated according to the definition:

$$v^{E} = v_{m} - (x_{1}v_{1}^{*} + x_{2}v_{2}^{*})$$
(3)

where $V_{\rm m}$ is the molar volume of mixture, v_i^* and x_i are the molar volume and the mole fraction of the component *i*,

193

(2)

TABLE	1
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Densities, ϕ , and thermal expansion coefficients, α for component liquids between 298.15 and 313.15 K.

0.773882 0.001219 0.873659 0.001225	0.769150 0.001233 0.868299 0.001235	0.764401 0.001248 0.862935 0.001246	0.759611 0.001263 0.857552 0.001256
0.873659 0.001225	0.868299 0.001235	$0.862935 \\ 0.001246$	0.857552
			0.001200
0.862263 0.001083	0.857573 0.001090	0.852920 0.001098	$0.848215 \\ 0.001106$
0.862555 0.001018	0.858131	0.853751 0.001037	$0.849291 \\ 0.001047$
0.679533 0.001251	0.675266 0.001267	0.670977 0.001284	0.666652
	0.001083 0.862555 0.001018 0.679533 0.001251	0.001083 0.001090 0.862555 0.858131 0.001018 0.001027 0.679533 0.675266 0.001251 0.001267	$\begin{array}{ccccccc} 0.001083 & 0.001090 & 0.001098 \\ 0.862555 & 0.858131 & 0.853751 \\ 0.001018 & 0.001027 & 0.001037 \\ 0.679533 & 0.675266 & 0.670977 \\ 0.001251 & 0.001267 & 0.001284 \\ \hline \\ b \ Units: \ F^{-1} \end{array}$

TABLE 2

Densities, ρ and molar excess volumes, $v^{\rm E}$ for cyclohexane(1) + hydrocarbon(2) mixtures between 298.15 and 313.15 K

<i>x</i> ₁	$(\stackrel{\rho}{g} \text{ cm}^{-3})$	v ^E (cm ³ mol ⁻¹) ^x 1	$(g \text{ cm}^{-3})$	v ^E (cm ³ mol ⁻¹)
CH + BZ					
T=298.15	K				
Run1					
0.06715	0.864090	0.1613	0.10970	0.858312	0.2498
0.16373	0.851231	0.3521	0.19293	0.847549	0.3993
0.23745	0.842073	0.4663	0.29010	0.835835	0.5339
0.33867	0.830346	0.5798	0.38632	0.825152	0.6151
0.44139	0.819394	0.6415	0.49508	0.814006	0.6544
0.54141	0.809553	0.6525	0.59476	0.804636	0.6360
0.64663	0.800062	0.6053	0.69906	0.795641	0.5593
0.74481	0.791941	0.5073	0.79838	0.787801	0.4306
0.84643	0.784230	0.3512	0.89726	0.780638	0.2501
0.94726	0.777273	0.1353			
Run2					
0.06559	0.864304	0.1581	0.09862	0.859777	0.2298
0.15283	0.852619	0.3343	0.20956	0.845462	0.4275
0.25148	0.840375	0.4867	0.30197	0.834469	0.5467
0.36834	0.827075	0.6046	0.39858	0.823828	0.6246
0.44409	0.819101	0.6443	0.49163	0.814336	0.6552
0.55746	0.808040	0.6504	0.59658	0.804462	0.6363
0.65117	0.799654	0.6040	0.70311	0.795300	0.5562
0.75353	0.791245	0.4970	0.80003	0.787653	0.4312
0.85426	0.783663	0.3369	0.90057	0.780415	0.2424
0.94639	0.777325	0.1381			
T=303.15	К				
0.04371	0.862062	0.1070	0.08428	0.856466	0.1980
0.13734	0.849420	0.3047	0.18724	0.843073	0.3913

^x 1	$(g \text{ cm}^{-3})$	$(\text{cm}^{3}\text{mol}^{-1})$	^x 1	(g cm ⁻³)	(cm^3mol^{-1})
$\begin{array}{c} 0.23700\\ 0.34256\\ 0.44254\\ 0.54955\\ 0.64878\\ 0.74738\\ 0.80478\\ 0.90227\end{array}$	0.836986 0.824853 0.814258 0.803857 0.794987 0.786892 0.782496 0.775525	0.4662 0.5839 0.6459 0.6524 0.6066 0.5072 0.4238 0.2402	$\begin{array}{c} 0.29064 \\ 0.38753 \\ 0.49381 \\ 0.59347 \\ 0.69313 \\ 0.79359 \\ 0.85251 \end{array}$	0.830696 0.819990 0.809154 0.799831 0.791263 0.783328 0.779005	0.5325 0.6170 0.6572 0.5397 0.5681 0.4426 0.3409
$\begin{array}{c} T=308.15\\ 0.04333\\ 0.13669\\ 0.23923\\ 0.33601\\ 0.44900\\ 0.54770\\ 0.64700\\ 0.75161\\ 0.85257\\ 0.94621 \end{array}$	K 0.856791 0.844258 0.831555 0.820460 0.808593 0.799060 0.790221 0.781689 0.774186 0.767806	$\begin{array}{c} 0.1065\\ 0.3052\\ 0.4716\\ 0.5838\\ 0.6501\\ 0.6571\\ 0.6124\\ 0.5065\\ 0.3431\\ 0.1409 \end{array}$	$\begin{array}{c} 0.05061\\ 0.18411\\ 0.29371\\ 0.39146\\ 0.49206\\ 0.59140\\ 0.70755\\ 0.80490\\ 0.90142 \end{array}$	$\begin{array}{c} 0.855778\\ 0.838243\\ 0.825202\\ 0.814510\\ 0.804343\\ 0.795072\\ 0.785191\\ 0.777636\\ 0.770793 \end{array}$	$\begin{array}{c} 0.1238\\ 0.3899\\ 0.5407\\ 0.6233\\ 0.6588\\ 0.6448\\ 0.5581\\ 0.4286\\ 0.2433 \end{array}$
$\begin{array}{c} T=313.15\\ 0.04914\\ 0.17568\\ 0.25453\\ 0.35479\\ 0.45949\\ 0.54946\\ 0.65007\\ 0.75366\\ 0.84743\\ 0.94514 \end{array}$	K 0.850637 0.834064 0.824566 0.813328 0.802514 0.793908 0.785028 0.776648 0.769692 0.763076	$\begin{array}{c} 0.1214\\ 0.3770\\ 0.4949\\ 0.5994\\ 0.6550\\ 0.6600\\ 0.6128\\ 0.5058\\ 0.3567\\ 0.1431 \end{array}$	$\begin{array}{c} 0.10462\\ 0.20403\\ 0.30975\\ 0.39856\\ 0.47091\\ 0.60984\\ 0.70448\\ 0.80137\\ 0.90396 \end{array}$	0.843157 0.830582 0.818260 0.808693 0.801365 0.788490 0.780527 0.773030 0.765782	$\begin{array}{c} 0.2438 \\ 0.4227 \\ 0.5593 \\ 0.6298 \\ 0.6605 \\ 0.6381 \\ 0.5647 \\ 0.4369 \\ 0.2413 \end{array}$
$\begin{array}{l} \text{CH} \ \ + \ \ \text{TL} \\ \textbf{\textit{T}=298.15} \\ \textbf{0.03349} \\ \textbf{0.11803} \\ \textbf{0.18687} \\ \textbf{0.31174} \\ \textbf{0.40417} \\ \textbf{0.51566} \\ \textbf{0.61591} \\ \textbf{0.71880} \\ \textbf{0.83517} \\ \textbf{0.94110} \end{array}$	K 0.858744 0.850031 0.843070 0.830825 0.822082 0.811915 0.803190 0.794661 0.785585 0.777899	$\begin{array}{c} 0.0633\\ 0.2063\\ 0.3103\\ 0.4594\\ 0.5348\\ 0.5824\\ 0.5746\\ 0.5123\\ 0.3662\\ 0.1541 \end{array}$	0.06922 0.16113 0.25963 0.35026 0.45696 0.55805 0.66063 0.77063 0.88740	0.855046 0.845646 0.835885 0.827131 0.817225 0.808179 0.799431 0.790534 0.781720	$\begin{array}{c} 0.1250\\ 0.2743\\ 0.4023\\ 0.4968\\ 0.5623\\ 0.5849\\ 0.5541\\ 0.4585\\ 0.2722 \end{array}$
$\begin{array}{c} T=303.15\\ 0.03502\\ 0.11421\\ 0.21064\\ 0.29880\\ 0.40925\\ 0.51151\\ 0.61189\\ 0.72437\\ 0.84210\\ \end{array}$	K 0.853892 0.845716 0.836011 0.827368 0.816915 0.807587 0.798827 0.789494 0.780344	$\begin{array}{c} 0.0667\\ 0.2029\\ 0.3441\\ 0.4499\\ 0.5406\\ 0.5847\\ 0.5793\\ 0.5113\\ 0.3572 \end{array}$	$\begin{array}{c} 0.07115\\ 0.15647\\ 0.25883\\ 0.35540\\ 0.45410\\ 0.55555\\ 0.65673\\ 0.78487\\ 0.88572 \end{array}$	$\begin{array}{c} 0.850139\\ 0.841434\\ 0.831262\\ 0.821974\\ 0.812792\\ 0.803708\\ 0.795054\\ 0.784709\\ 0.777124 \end{array}$	0.1310 0.2676 0.4043 0.5003 0.5636 0.5867 0.5589 0.4434 0.2766

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Ŧ	J	v

x ₁	(g cm ⁻³)	l ^{,E} (cm ³ mol-1	, ^x 1	(g cm ⁻³)	v^{E} (cm ³ mol ⁻¹)
0.94226	0.773084	0.1533			
$\begin{array}{c} T=308.15\\ 0.03644\\ 0.11735\\ 0.21306\\ 0.30058\\ 0.41452\\ 0.51220\\ 0.61265\\ 0.72502\\ 0.87930\\ 0.94588 \end{array}$	K 0.849108 0.840752 0.831107 0.822537 0.811763 0.802853 0.794071 0.784741 0.772840 0.768103	$\begin{array}{c} 0.0670\\ 0.2067\\ 0.3483\\ 0.4517\\ 0.5439\\ 0.5850\\ 0.5806\\ 0.5115\\ 0.2935\\ 0.1433 \end{array}$	$\begin{array}{c} 0.08107\\ 0.16781\\ 0.26222\\ 0.35766\\ 0.45317\\ 0.55524\\ 0.65782\\ 0.77255\\ 0.88774 \end{array}$	0.814475 0.835646 0.826280 0.817085 0.808191 0.799047 0.790266 0.780947 0.772230	$\begin{array}{c} 0.1465\\ 0.2831\\ 0.4076\\ 0.5041\\ 0.5658\\ 0.5886\\ 0.5886\\ 0.5600\\ 0.4620\\ 0.2758\end{array}$
T=313.15 0.04311 0.14723 0.23430 0.35289 0.45225 0.55892 0.65140 0.75125 0.85470 0.94382	K 0.843699 0.833006 0.824296 0.812817 0.803556 0.793980 0.786038 0.777866 0.769883 0.763441	$\begin{array}{c} 0.0804\\ 0.2540\\ 0.3765\\ 0.5019\\ 0.5666\\ 0.5923\\ 0.5690\\ 0.4905\\ 0.3424\\ 0.1531 \end{array}$	0.12286 0.20260 0.31332 0.40411 0.49300 0.59857 0.70596 0.80026 0.89799	$\begin{array}{c} 0.835480\\ 0.827446\\ 0.816603\\ 0.808010\\ 0.799837\\ 0.790541\\ 0.781525\\ 0.774027\\ 0.766703 \end{array}$	0.2163 0.3339 0.4648 0.5390 0.5841 0.5867 0.5324 0.4283 0.2578
CH + EB					
T = 298.15 0.04047 0.14371 0.23649 0.32886 0.44815 0.54665 0.64547 0.75135 0.85323 0.95055	K 0.858926 0.849637 0.841232 0.832854 0.822050 0.813147 0.804278 0.794899 0.786066 0.777913	0.0632 0.2089 0.3229 0.4136 0.4911 0.5198 0.5090 0.4445 0.3196 0.1266	$\begin{array}{c} 0.08768\\ 0.17720\\ 0.29005\\ 0.38988\\ 0.48517\\ 0.58934\\ 0.68721\\ 0.80782\\ 0.90139 \end{array}$	0.854690 0.846601 0.836390 0.827333 0.818699 0.809288 0.800558 0.789981 0.781995	0.1318 0.2533 0.3762 0.4578 0.5061 0.5229 0.4912 0.3827 0.2334
$\begin{array}{c} 7=303.15\\ 0.03866\\ 0.14874\\ 0.23045\\ 0.34283\\ 0.44019\\ 0.54940\\ 0.64880\\ 0.74568\\ 0.85394\\ 0.94756\end{array}$	K 0.854664 0.844735 0.837318 0.827117 0.818260 0.808358 0.799409 0.790773 0.781343 0.773450	0.0592 0.2139 0.3136 0.4196 0.4840 0.5167 0.5046 0.4490 0.3178 0.1339	$\begin{array}{c} 0.07936\\ 0.18204\\ 0.28790\\ 0.38443\\ 0.48833\\ 0.59194\\ 0.69229\\ 0.79868\\ 0.89974 \end{array}$	$\begin{array}{c} 0.850993\\ 0.841714\\ 0.832108\\ 0.823312\\ 0.813895\\ 0.804501\\ 0.795512\\ 0.786137\\ 0.777443 \end{array}$	0.1202 0.2565 0.3718 0.4536 0.5030 0.5193 0.4864 0.3925 0.2372
T=308.15 0.04239 0.13575 0.23213 0.34317	K 0.849941 0.841500 0.832750 0.822625	0.0642 0.1952 0.3103 0.4162	0.07991 0.18626 0.29024 0.38561	0.846559 0.836912 0.827451 0.818741	0.1182 0.2591 0.3702 0.4490

x ₁	ب (g cm ⁻³)	v^{E} (cm ³ mol ⁻¹)	^x 1	د (g. cm ⁻³)	v^{E} (cm ³ mol ⁻¹)
0.42800 0.55230 0.64475 0.74726 0.84835 0.94836	0.814872 0.803564 0.795195 0.786024 0.777159 0.768653	0.4749 0.5133 0.5037 0.4444 0.3249 0.1330	0.48930 0.59347 0.69211 0.79067 0.90016	0.809295 0.799836 0.790952 0.782204 0.772718	0.4999 0.5126 0.4816 0.3994 0.2349
$\begin{array}{c} T=313.15\\ 0.04421\\ 0.17507\\ 0.28604\\ 0.40631\\ 0.48213\\ 0.59366\\ 0.68326\\ 0.68326\\ 0.77855\\ 0.87036\\ 0.95302 \end{array}$	K 0.845302 0.833427 0.823304 0.812311 0.805376 0.795199 0.787093 0.778582 0.770541 0.763502	$\begin{array}{c} 0.0673 \\ 0.2449 \\ 0.3654 \\ 0.4581 \\ 0.4945 \\ 0.5117 \\ 0.4857 \\ 0.4122 \\ 0.2883 \\ 0.1217 \end{array}$	$\begin{array}{c} 0.11163\\ 0.23558\\ 0.33584\\ 0.43760\\ 0.53025\\ 0.63253\\ 0.73332\\ 0.81762\\ 0.91213 \end{array}$	$\begin{array}{c} 0.839192\\ 0.827908\\ 0.818755\\ 0.809445\\ 0.800967\\ 0.791675\\ 0.782607\\ 0.775134\\ 0.766958 \end{array}$	$\begin{array}{c} 0.1635\\ 0.3149\\ 0.4086\\ 0.4758\\ 0.5095\\ 0.5047\\ 0.4532\\ 0.3670\\ 0.2111 \end{array}$
СН + НР					
$\begin{array}{c} T=298.15\\ 0.07702\\ 0.25160\\ 0.40067\\ 0.50970\\ 0.61526\\ 0.69616\\ 0.78396\\ 0.85051\\ 0.91493\\ 0.97275 \end{array}$	K 0.684699 0.697338 0.709294 0.718829 0.728811 0.737028 0.746608 0.754376 0.762401 0.770087	$\begin{array}{c} 0.0641 \\ 0.1857 \\ 0.2599 \\ 0.2932 \\ 0.3021 \\ 0.2907 \\ 0.2526 \\ 0.2049 \\ 0.1350 \\ 0.0489 \end{array}$	$\begin{array}{c} 0.17584\\ 0.32729\\ 0.46115\\ 0.58286\\ 0.65765\\ 0.74484\\ 0.82358\\ 0.88551\\ 0.94655 \end{array}$	$\begin{array}{c} 0.691691\\ 0.703261\\ 0.714496\\ 0.725667\\ 0.733056\\ 0.742246\\ 0.751169\\ 0.758673\\ 0.766550 \end{array}$	0.1362 0.2276 0.2803 0.3013 0.2976 0.2737 0.2275 0.1696 0.0901
T=303.15 0.04497 0.13912 0.24176 0.33643 0.44045 0.53653 0.63366 0.72530 0.84472 0.95584	K 0.678227 0.684719 0.692237 0.699613 0.708275 0.716854 0.726148 0.735584 0.749067 0.763087	$\begin{array}{c} 0.0410\\ 0.1136\\ 0.1809\\ 0.2323\\ 0.2726\\ 0.2931\\ 0.2970\\ 0.2790\\ 0.2081\\ 0.0769 \end{array}$	$\begin{array}{c} 0.09512\\ 0.19487\\ 0.28388\\ 0.38715\\ 0.48736\\ 0.56792\\ 0.68695\\ 0.78777\\ 0.88169 \end{array}$	$\begin{array}{c} 0.681639\\ 0.688745\\ 0.695463\\ 0.703767\\ 0.712387\\ 0.719783\\ 0.731554\\ 0.742456\\ 0.753556 \end{array}$	0.0809 0.1513 0.2053 0.2529 0.2855 0.2968 0.2890 0.2492 0.1726
T=308.15 0.04526 0.14515 0.24202 0.33365 0.44024 0.52946 0.56644 0.68348 0.84696 0.95433	K 0.673964 0.680854 0.687936 0.695048 0.703876 0.711770 0.715206 0.726700 0.744733 0.758189	0.0367 0.1091 0.1713 0.2193 0.2608 0.2832 0.2857 0.2794 0.1989 0.0760	0.09438 0.19369 0.28530 0.38518 0.48822 0.55803 0.64291 0.78956 0.88103	0.677302 0.684347 0.691246 0.699239 0.708062 0.714420 0.722597 0.738098 0.748846	$\begin{array}{c} 0.0735\\ 0.1422\\ 0.1948\\ 0.2410\\ 0.2741\\ 0.2846\\ 0.2855\\ 0.2398\\ 0.1672 \end{array}$

x ₁	$(g \text{ cm}^{-3})$	v ^E (cm ³ mol ⁻	¹) ^x 1	ρ (g cm ⁻³)	$(\text{cm}^3 \text{mol}^{-1})$	
T=313.15	K					
0.04704	0.669752	0.0362	0.09533	0.673025	0.0714	
0.14622	0.676572	0.1069	0.19390	0.680006	0.1356	
0.24756	0.683977	0.1685	0.28644	0.686947	0.1883	
0.34133	0.691262	0.2148	0.39012	0.695233	0.2342	
0.45269	0.700517	0.2543	0.19457	0.704177	0.2656	
0.55807	0.709936	0.2767	0.57538	0.711559	0.2773	
0.63664	0.717457	0.2770	0.68927	0.722752	0.2694	
0.73054	0.727065	0.2580	0.79155	0.733723	0.2305	
0.84818	0.740237	0.1913	0.88421	0.744566	0.1585	
0.95838	0.753983	0.0681				

TABLE 3

 ${\bf A}_i$ coefficients and standard deviation, s, of the fits for least-squares representation for mixtures.

<i>T</i> (K)		CH+BZ	CH+TL	CH+EB	СН+НР
298.15	$\begin{array}{c}A_1\\A_2\\A_3\\A_4\\s\end{array}$	2.6176 -0.096 0.028 0.010 0.0009	2.3131 -0.481 0.067 0.008 0.0009	2.0458 -0.572 0.159 -0.041 0.0010	1.1616 -0.438 0.219 -0.093 0.0006
303.15	$\substack{\substack{A_1\\A_2\\A_3\\A_4\\s}}$	2.6270 -0.116 0.026 0.028 0.0006	2.3226 -0.493 0.083 0.029 0.0009	2.0319 -0.575 0.171 -0.049 0.0011	1.1493 -0.418 0.257 -0.085 0.0007
308.15	A ₁ A ₂ A ₃ A ₄ s	2.6426 -0.118 0.040 0.027 0.0009	2.3281 -0.494 0.083 -0.011 0.0010	2.0144 -0.572 0.170 -0.071 0.0007	1.1050 -0.420 0.220 -0.096 0.0006
313.15	$\begin{smallmatrix} A_1\\ A_2\\ A_3\\ A_4\\ s \end{smallmatrix}$	$\begin{array}{c} 2.6523 \\ -0.128 \\ 0.056 \\ 0.035 \\ 0.0007 \end{array}$	2.3385 -0.513 0.102 -0.006 0.0007	2.0041 -0.579 0.190 -0.041 0.0006	$\begin{array}{c} 1.0668 \\ -0.415 \\ 0.214 \\ -0.081 \\ 0.0005 \end{array}$

respectively. V^E and ρ obtained are shown in Table 2.

As shown in Table 2, v^E are positive for all the mixtures over the entire range of composition and at the temperature range investigated. This is attributed to the difference of molecular packing between the pure state and the solution one. Results of v^E at each temperature were respectively fitted to a RedlichKister type of polynomial by the least-squares method:

$$v^{\mathbf{E}} = x_1 x_2 \sum_{i=1}^{4} A_i (1 - 2x_1)^{i-1}$$
(4)

The A_j coefficients are given in Table 3, along with the standard deviation, s, of the fits for each mixture. The deviation of t^E from that at 298.15 K for these mixtures, calculated by eqn.(3) using A_j coefficients, were plotted in Fig. 1.

As shown in this figure, l^E is more positive for CH + Bz and + TL mixtures but more negative for the CH + EB and + HP mixtures with increase of temperature.

Eqn.(4) can be extented to representing v^E as a function of temperature as well as of composition by considering the coefficients A_i to be polynomial functions of temperature:

$$v^{E} = x_{1}x_{2} \sum_{i=1}^{4} (a_{i} + b_{i} T) (1 - 2x_{1})^{i-1}$$
(5)

where T is temperature. By differentiating eqn.(5), the temperature dependence of l^{E} , $(\partial l^{E}/\partial T)_{p}$, is given as follows:

$$(\exists v^{E}/\partial T)_{p} = x_{1}x_{2} \sum_{i=1}^{4} b_{i} (1 - 2x_{1})^{i-1}$$
 (6)

Excess thermal expansion coefficient, α^{E} , is calculated from the following equation:

$$\alpha^{\mathbf{E}} = \alpha - \alpha^{\mathbf{id}} = \frac{(\partial v^{\mathbf{E}} / \partial T)_{P} - v^{\mathbf{E}} \alpha^{\mathbf{id}}}{v^{\mathbf{id}} + v^{\mathbf{E}}}$$
(7)

where the superscript id denotes the ideal state.

Figs. 2 and 3 show the composition dependence of $(\partial v^E / \partial T)_P$ and α^E for the present mixtures. $\mathcal{E}^2(\alpha^E)$, the mean square error in α^E was estimated as follows:

$$\epsilon^{2}(\alpha^{E}) = \alpha^{2}\epsilon^{2}(v^{E})/v^{2} + \epsilon^{2}(r^{E})/v^{2}$$
(8)

where $\mathcal{E}^2(X)$ is the mean square error of property X and f^E is $(\partial v^E/\partial T)_P$, respectively. As indicated in eqn.(7), α^E is functions of v^{id} , v^E and their temperature dependences, $(\partial v^{id}/\partial T)_P$ and $(\partial v^E/\partial T)_P$. However, errors in v^{id} and $(\partial v^{id}/\partial T)_P$ were neglected, because these errors were very small in the present mixtures. The errors were calculated from the most





Fig.1. Deviation of ι^E from that at 298.15 K, calculated by eqn.(3) using A_j coefficients. (a) CH + BZ, (b) CH + TL, (c) CH + EB and (d) CH + HP. (c) and (•): Run1 and Run2 at 298.15 K, (Δ): at 303.15 K, (\Box): at 308.15 K and (+): at 313.15 K.



provable errors in the coefficients A_i and b_j in eqns.(4) and (5), and shown as errors bars in Figs. 2 and 3.

Generally, it is considered that the composition dependence of $(\partial V^E/\partial T)_P$ will be similar to that of α^E . However, we found $(\partial V^E/\partial T)_P > 0$ and $\alpha^E < 0$ for the CH rich region of BZ and TL systems, as shown in Figs. 2 and 3. This means that t^E increases with temperature, but the ratio of increase in t^E is smaller than that of volume in the ideal state.

In conclusion, the apparatus for measuring $\alpha^{\rm E}$ was constructed by using the vibrating-tube densimeter(DMA-602) and the significant values of $\alpha^{\rm E}$ for the mixtures of CH with BZ, TL, EB and HP were found.



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