EXCESS VOLUMES AND REFRACTIVE INDICES IN THE BENZENE–TERT-AMYL METHYL ETHER AND CYCLOHEXANE–TERT-AMYL METHYL ETHER SYSTEMS AT 298·15 K

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Excess molar volumes in the benzene–tert-amyl methyl ether and cyclohexane–tert-amyl methyl ether systems were measured by a vibrating-tube densimeter at 298·15 K and compared with the data for the methanol–tert-amyl methyl ether system determined previously. Besides, the refractive indices in both the systems were measured at the same temperature.

Tert-amyl methyl ether (TAME, 3,3-dimethyl-2-oxypentane) appears to be an efficient antiknock additive to produce low-leaded or lead-free gasoline. Reassuming the foregoing systematic study[1,2] of systems containing this substance, excess volumes and refractive indices in the benzene–TAME and cyclohexane–TAME systems at 298·15 K have been measured.

EXPERIMENTAL

Preparation of pure substances. TAME was synthesized and purified as described in our preceding work[1] where the comparison of its physico-chemical constants with literature data at the temperature of 293·15 K has also been given. At 298·15 K the measured values of its density $\varrho(298{\cdot}15) = 0{\cdot}76577$ g cm^{-3} and refractive index $n_D(298{\cdot}15) = 1{\cdot}3858$ (literature values for this temperature are not available).

Benzene (pure, thiophene-free, Lachema, Brno) was shaken with H_2SO_4, washed with water and NaOH solution, separated, dried with $CaCl_2$, then with sodium and rectified from sodium on a packed column (60 cm long, 3 cm internal diameter) filled with Pyrex helices (3 mm diameter) at a reflux ratio 15 : 1. The middle fraction was taken for measurement.

Cyclohexane (A. R. grade, Lachema, Brno) was treated with silica gel[3], dried with molecular sieve Nalcit 4A, and rectified from sodium on the column above. The middle fraction was used for measurement.

The physico-chemical constants of benzene and cyclohexane used for the measurement and their comparison with literature values are given in Table I.

Procedure and apparatus. The procedure was essentially the same as that described in our preceding work[2]. Samples of the benzene–TAME and cyclohexane–TAME mixtures were prepared by weighing in vessels ("onion cells") designed and recommended by Takenaka and

coworkers[5] ensuring the composition calculated from weighed amounts of pure substances to correspond most accurately to the true composition of the liquid mixture without being necessary to take into account the amount of substances in the vapour phase. The estimated total error in mole fraction x does not exceed the value $5 \cdot 10^{-4}$ even at the concentration ends.

TABLE I

Physical constants of pure substances at 298·15 K

Substance	Density, g cm^{-3}		Refractive index		Ref.
	measured	literature	measured	literature	
Benzene	0·87362	0·87359—0·87376	1·4979	1·49790—1·49810	4
Cyclohexane	0·77396	0·77370—0·77399	1·4235	1·42354—1·42358	4

TABLE II

Experimental excess molar volumes V^E (cm^3 mol^{-1}) and refractive indices n_D at 298·15 K and their comparison with calculated values[a] in the benzene(1)–TAME(2) system

x_1	V^E_{exp}	$n_{D,exp}$	V^E_{calc}	$n_{D,calc}$	$\Delta V^E \cdot 10^4$	$\Delta n_D \cdot 10^5$
0·0434	−0·0028	1·3890	−0·0007	1·3889	−21	4
0·1230	0·0049	1·3950	0·0049	1·3950	0	3
0·2398	0·0229	1·4046	0·0213	1·4046	16	−5
0·3319	0·0359	1·4130	0·0359	1·4129	0	5
0·4306	0·0486	1·4225	0·0500	1·4225	−14	−4
0·5126	0·0601	1·4311	0·0594	1·4311	7	−6
0·5986	0·0656	1·4408	0·0663	1·4408	−7	4
0·6735	0·0691	1·4498	0·0689	1·4498	2	3
0·7482	0·0671	1·4595	0·0674	1·4594	−3	3
0·8163	0·0625	1·4689	0·0608	1·4688	17	5
0·8780	0·0499	1·4779	0·0489	1·4780	10	−7
0·9113	0·0376	1·4831	0·0394	1·4832	−18	−5
0·9415	0·0272	1·4880	0·0285	1·4880	−13	−1
0·9729	0·0144	1·4933	0·0146	1·4932	−2	1
Deviations:		mean absolute			9	4
		standard			14	5

[a] Constants of Eq. (*1*) for V^E: $A_1 = 0{\cdot}232663$, $A_2 = -0{\cdot}208665$, $A_3 = 0{\cdot}031189$, $A_4 = -0{\cdot}111434$; of Eq. (*2*) for n_D: $B_1 = -0{\cdot}048377$, $B_2 = 0{\cdot}010279$, $B_3 = -0{\cdot}003854$.

The density measurements were made with a DMA 60 + 602 vibrating-tube densimeter (A. Paar, Austria). The densimeter measuring cell was tempered with a Heto type CB7 ultrathermostat maintaining the temperature of vibrating cell with the accuracy of ±0·01 K. Testing of the apparatus was described in detail in our preceding work[2]. The accuracy of the excess volume determination is better than $5 \cdot 10^{-3}$ cm^3 mol^{-1}.

The refractive index measurements were made with an Abbe-type refractometer (Carl Zeiss, Jena). The n_D determination was accurate to 0·0001.

RESULTS AND DISCUSSION

Excess volumes V^E at 298·15 K, calculated from the measured density values of samples weighed, are given in Tables II and III, along with the experimental values of n_D of the same samples at the same temperature. To fit the results, the equation of the Redlich–Kister type was used. Then we can write for excess molar volume V^E

$$V^E = x_1(1 - x_1)\sum_{i=1}^{n} A_i(1 - 2x_1)^{i-1}, \qquad (1)$$

TABLE III

Experimental excess molar volumes V^E (cm^3 mol^{-1}) and refractive indices n_D at 298·15 K and their comparison with calculated values[a] in the cyclohexane(1)–TAME(2) system

x_1	V^E_{exp}	$n_{D,exp}$	V^E_{calc}	$n_{D,calc}$	$\Delta V^E \cdot 10^4$	$\Delta n_D \cdot 10^5$
0·0666	0·0913	1·3874	0·0910	1·3875	3	−14
0·1268	0·1647	1·3890	0·1650	1·3891	−3	−11
0·2156	0·2578	1·3918	0·2586	1·3916	−8	16
0·2938	0·3239	1·3940	0·3244	1·3940	−5	−2
0·3799	0·3790	1·3969	0·3771	1·3968	19	8
0·4510	0·4050	1·3993	0·4039	1·3993	11	−2
0·5630	0·4112	1·4034	0·4130	1·4034	−18	−3
0·6318	0·3960	1·4061	0·3973	1·4062	−13	−7
0·7129	0·3567	1·4095	0·3565	1·4096	2	−8
0·7777	0·3073	1·4125	0·3058	1·4125	15	4
0·8295	0·2533	1·4150	0·2532	1·4149	1	13
0·9120	0·1454	1·4189	0·1464	1·4189	−10	−1
0·9573	0·0759	1·4212	0·0753	1·4212	6	−3
Deviations:		mean absolute			9	7
		standard			12	10

[a] Constants of Eq. (*1*) for V^E: $A_1 = 1{\cdot}652083$, $A_2 = -0{\cdot}212722$, $A_3 = -0{\cdot}005323$; of Eq. (*2*) for n_D: $B_1 = -0{\cdot}014408$, $B_2 = 0{\cdot}001615$, $B_3 = -0{\cdot}000185$.

and for refractive index of binary mixture n_D

$$n_D = x_1 n_{D1} + (1 - x_1) n_{D2} + x_1(1 - x_1) \sum_{i=1}^{n} B_i (1 - 2x_1)^{i-1}, \qquad (2)$$

where x_1 is the mole fraction of the first component, A_i, B_i are constants whose values are to be determined from experimental data, and n_{D1}, n_{D2} are refractive indices of pure components 1 and 2 at the temperature of measurement. The optimum number of constants in Eqs (*1*) and (*2*) was sought, and for our systems, $n = 3$ was found with the exception of V^E in the benzene–TAME system where an S-shaped form of concentration dependence requires four constants to describe well the concentration dependence $V^E(x_1)$.

The evaluation of constants A_i and B_i was carried out by the maximum likelihood method by using the procedure described in the book from our laboratory[6]. On inserting the estimated experimental errors in x_1, V^E, and n_D, the calculated values of x_1 agree within the given four decimal places with the experimental x_1. Therefore, the calculated values of x_1 are not given in Tables II and III, and the evaluation of constants reduces to simple least-squares method. The mean and standard deviations of the fit are also given in Tables II and III. Comparison of V^E values in the systems benzene–TAME, cyclohexane–TAME and methanol–TAME (presented in our previous work[2]) is illustrated in Fig. 1. Whereas the methanol–TAME system exhibits negative and numerically rather high values of V^E, those for cyclohexane–TAME are positive and of nearly the same height. V^E values for the system benzene–TAME are numerically substantially lower and the inspection of the shape of the V^E curve reveals an S-shaped form at a concentration end.

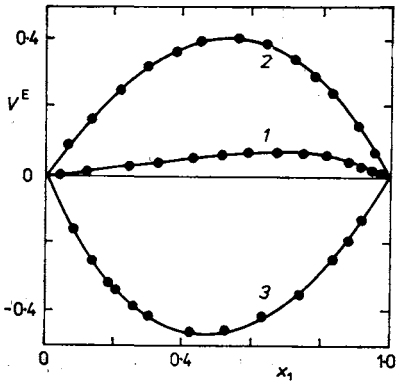

FIG. 1

Comparison of excess molar volumes V^E ($cm^3\ mol^{-1}$) in systems containing TAME: *1* benzene(1)–TAME(2), *2* cyclohexane(1)–TAME(2), *3* methanol(1)–TAME(2)

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