EXCESS VOLUME OF THE BENZENE–METHANOL–ACETONITRILE TERNARY MIXTURE AT TEMPERATURES OF 25 AND 40°C AND CORRELATION OF ITS CONCENTRATION DEPENDENCE

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Density of the benzene–methanol–acetonitrile ternary mixture was measured by a vibrating-tube densimeter at temperatures of 25 and 40°C. From the measured values, the excess volume of mixture was calculated. The obtained dependences of excess volume on composition were correlated by five empirical correlation functions. Two ways of expressing the binary contributions to the total excess volume of ternary mixture were examined as well.

In our previous work[1] we had dealt with the measurement of excess volume of binary mixtures formed by benzene, methanol and acetonitrile at temperatures of 25 and 40°C. Excess volume of these binary mixtures shows an interesting shape of its dependence on composition:
An S-shaped dependence in case of mixtures benzene–methanol and benzene–acetonitrile and negative excess volume but strongly asymmetrical dependence in case of the methanol–acetonitrile mixture. The nature of components is as well considerably different, *viz.* non-polar benzene, associating methanol and strongly polar acetonitrile. Therefore it is useful to measure excess volume of the ternary mixture consisting of the above-mentioned components, particularly for the reason that the data on excess volume of this ternary system are absent in the literature.

EXPERIMENTAL

Apparatus and measuring method. A vibrating-tube densimeter, whose design had been described previously[1], has been used for the measurement of density. Calibration of the apparatus has been carried out with benzene and cyclohexane whose density has been determined by means of the Ostwald–Sprengel bicapillary pycnometer having inner volume of 4 cm^3. The method of preparation of measured mixtures and the way of measurement have been the same as in previous work[1].

Substances used. The purification of the substances used has been carried out in the same way as in previous work[1]. Densities of the pure substances are as follows: Benzene: $\varrho_4^{25} = 0{\cdot}87349$ (lit. 0·87347—0·87372), $\varrho_4^{40} = 0{\cdot}85718$ (lit. 0·85722—0·85771); Methanol: $\varrho_4^{25} = 0{\cdot}78669$ (lit. 0·78655—0·78676), $\varrho_4^{40} = 0{\cdot}77225$ (lit. 0·77234); Acetonitrile: $\varrho_4^{25} = 0{\cdot}77688$ (lit. 0·77664), $\varrho_4^{40} = 0.76037$ (lit. 0·76127); Cyclohexane: $\varrho_4^{25} = 0{\cdot}77380$ (lit. 0·77322—0·77397), $\varrho_4^{40} = 0{\cdot}75991$ (lit. 0·75999).

RESULTS

Our experimental data on density and excess volume are given in Table 1. Mole fractions and densities are presented with accuracy to five and six decimal places to reduce the effect of rounding errors when calculating excess volume. The measured dependence of excess volume on composition is illustrated in Fig. 1.

By a similar way as in previous paper[1], the estimation of average error (scatter) in the excess volume has been carried out for a set of twenty randomly chosen measurements at the temperature of 25°C and the value $1{\cdot}5 \,.\, 10^{-3}$ cm^3 mol^{-1} has been obtained which approximately corresponds to the root means square deviation in excess volume obtained on correlating the measured data (see below).

Correlation of the Dependence of Excess Volume on Composition

For the purposes of the correlation of ternary data, excess volume is usually expressed by the relation

$$v^{\mathrm{E}} = \sum_{i<j} v_{ij}^{\mathrm{E}}(x_i, x_j) + v_{\mathrm{T}}^{\mathrm{E}}, \qquad (1)$$

where the binary contributions, v_{ij}^{E}, are represented in terms of a correlation relation of the respective binary system and for the ternary contribution, $v_{\mathrm{T}}^{\mathrm{E}}$, some empirical function is used. This way of expressing the excess volume has the disadvantage that the value of the ternary contribution depends on the fact what kinds of correlations are used for correlating binary data. Moreover, the binary contributions are evaluated at a point of composition which have no physical meaning from the point of view of binary system, *i.e.* it does not hold $x_i + x_j = 1$ for a ternary point.

These shortcomings can be removed in such a way that the total binary contribution is expressed as a combination of values of excess volume of individual binary systems evaluated at binary points of composition[2]. For instance, if the binary contributions are expressed in terms of values of excess volume evaluated at the binary points which are obtained by projecting a ternary point from the vertex of the triangle diagram to the axis of the respective binary system, then on keeping the condition of the solution regularity conservation[2] we obtain the relation

$$v^{\mathrm{E}} = \sum_{i<j} (x_i + x_j)^2 \, v_{ij}^{\mathrm{E}} \left(\frac{x_i}{x_i + x_j}, \frac{x_j}{x_i + x_j} \right) + v_{\mathrm{T}}^{\mathrm{E}} \,. \qquad (2)$$

For correlation of the ternary contribution, $v_{\mathrm{T}}^{\mathrm{E}}$, it is possible to use the relations which result from extending the relations used for binary correlations. By extending the Redlich–Kister relation[3] we obtain

$$v_{\mathrm{T}}^{\mathrm{E}} = x_1 x_2 x_3 \left[\sum_{s=1}^{n} A_s (x_i - x_j)^{s-1} + \sum_{s=n+1}^{n+m} A_s (x_i - x_k)^{s-n} \right], \qquad (3)$$

where $m = n - 1$ for an odd number of adjustable parameters A_s, $m = n - 2$ for an even number of parameters and the total number of parameters is $N = m + n$. A short form of this relation had been used by Radojkovic and coworkers[4]:

$$v_T^E = x_1 x_2 x_3 \sum_{s=1}^{N} A_s (x_i - x_j)^{s-1} . \qquad (4)$$

A correlation relation similar to that proposed by Jones and coworkers[5] for correlating binary data could be used for ternary correlations, *e.g.* in the form

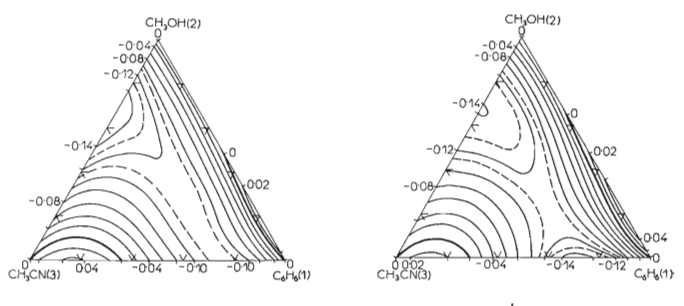
$$v_T^E = x_1 x_2 x_3 (A_1 + A_2 x_i^{1/2} + A_3 x_j^{1/2} + A_4 x_k^{1/2} + A_5 x_i + A_6 x_j + A_7 x_i^{3/2} + \ldots) . \qquad (5)$$

Further relation, which, however, has not its binary version, can be written in the form

$$v_T^E = x_1 x_2 x_3 \left\{ \sum_{s=1}^{n} A_s [(x_i - x_j) x_k]^{s-1} + \sum_{s=n+1}^{n+m} A_s [(x_i - x_k) x_j]^{s-n} \right\} , \qquad (6)$$

where for n, m hold the same relations as in Eq. (*3*). This relation had been used by Rastogi and coworkers[6] in the short form

$$v_T^E = x_1 x_2 x_3 \sum_{s=1}^{N} A_s [(x_i - x_j) x_k]^{s-1} . \qquad (7)$$



a *b*

FIG. 1

Dependence of Excess Volume of the Benzene(1)–Methanol(2)–Acetonitrile(3) Mixture on Composition

a 25°C, *b* 40°C. Lines connect places of identical values of excess volume (in $cm^3 . mol^{-1}$). Dashed line for —0·11 and —0·13 $cm^3\ mol^{-1}$. Mixture composition in mole fractions.

TABLE I

Density and Excess Volume of the Benzene(1)–Methanol(2)–Acetonitrile(3) Mixture

x_1	x_2	ϱ / g cm^{-3}	v^E / cm^3 mol^{-1}	x_1	x_2	ϱ / g cm^{-3}	v^E / cm^3 mol^{-1}
		25°C		0·20652	0·74965	0·818362	—0·0562
				0·21095	0·38323	0·813641	—0·0997
0·03413	0·32813	0·786111	—0·0925	0·21497	0·65627	0·818580	—0·0997
0·03877	0·63378	0·791902	—0·1421	0·21511	0·19557	0·810568	—0·0371
0·04185	0·90460	0·794549	—0·0566	0·21547	0·19238	0·810579	—0·0377
0·04601	0·85692	0·795172	—0·0862	0·22032	0·70234	0·819789	—0·0796
0·04863	0·37037	0·789717	—0·0968	0·23130	0·40995	0·816762	—0·1052
0·05427	0·20738	0·788081	—0·0448	0·23496	0·60205	0·820404	—0·1063
0·06007	0·85265	0·797560	—0·0826	0·24032	0·30901	0·815982	—0·0798
0·06862	0·20803	0·790371	—0·0479	0·24074	0·09344	0·811844	0·0001
0·07448	0·58697	0·797134	—0·1310	0·25537	0·51817	0·821706	—0·1144
0·07496	0·11989	0·789801	—0·0063	0·25977	0·39502	0·820114	—0·1069
0·08068	0·72609	0·800008	—0·1260	0·28579	0·58709	0·826472	—0·1015
0·08282	0·78546	0·800867	—0·1043	0·29870	0·35675	0·824066	—0·1010
0·08742	0·86803	0·801986	—0·0522	0·32053	0·48036	0·828857	—0·1130
0·10477	0·31937	0·797590	—0·0776	0·32132	0·30159	0·825713	—0·0978
0·10778	0·08511	0·794085	0·0060	0·32713	0·55422	0·830655	—0·0935
0·12800	0·80296	0·807923	—0·0719	0·33121	0·62893	0·831903	—0·0523
0·13268	0·40191	0·803051	—0·0956	0·34393	0·24585	0·827155	—0·0860
0·13437	0·25239	0·800704	—0·0532	0·35516	0·41929	0·831627	—0·1101
0·13711	0·21490	0·800440	—0·0406	0·35729	0·11876	0·826005	—0·0416
0·14147	0·06478	0·798334	0·0239	0·36094	0·16741	0·827451	—0·0647
0·14393	0·54264	0·807091	—0·1210	0·37099	0·07241	0·826589	—0·0305
0·14463	0·14018	0·800171	—0·0125	0·37129	0·60710	0·835739	—0·0332
0·14983	0·25260	0·802848	—0·0508	0·37363	0·13140	0·828018	—0·0492
0·15118	0·07293	0·79802	0·0204	0·37912	0·51073	0·835532	—0·0858
0·15191	0·09617	0·800348	0·0081	0·39167	0·55266	0·837301	—0·0605
0·15241	0·67515	0·810255	—0·1126	0·39240	0·09307	0 829255	—0·0415
0·15414	0·50313	0·807940	—0·1182	0·39993	0·21139	0·832496	—0·0863
0·15799	0·45077	0·807530	—0·1058	0·40313	0·33398	0·835160	—0·1059
0·16349	0·11428	0·802231	0·0011	0·41294	0·53869	0·839164	—0·0526
0·17112	0·66827	0·812809	—0·1087	0·41809	0·35361	0·837073	—0·1094
0·17272	0·54940	0·811314	—0·1199	0·42592	0·43806	0·839186	—0·0944
0·17836	0·62513	0·813273	—0·1172	0·43385	0·34878	0·838537	—0·1072
0·17920	0·74203	0·814745	—0·0799	0·43551	0·49746	0·840845	—0·0639
0·17997	0·48715	0·811268	—0·1137	0·44632	0·12589	0·835498	—0·0722
0·18780	0·26835	0·808378	—0·0617	0·46518	0·16065	0·838027	—0·0848
0·19736	0·17664	0·807963	—0·0321	0·46596	0·32078	0·841153	—0·1067
0·20000	0·08084	0·806480	0·0090	0·50992	0·11160	0·841295	—0·0829
0·20202	0·75250	0·817820	—0·0585	0·51281	0·43513	0·846833	—0·0440
0·20514	0·10302	0·807507	0·0028	0·51647	0·08826	0·841431	—0·0782

TABLE I
(*Continued*)

x_1	x_2	ϱ / g cm^{-3}	v^E / cm^3 mol^{-1}	x_1	x_2	ϱ / g cm^{-3}	v^E / cm^3 mol^{-1}
0·54088	0·10618	0·843984	—0·0872	0·12501	0·11665	0·780663	—0·0014
0·54638	0·35530	0·848664	—0·0685	0·14189	0·29789	0·786427	—0·0631
0·55810	0·15297	0·846430	—0·1004	0·16836	0·02274	0·785019	0·0222
0·55898	0·08982	0·845315	—0·0918	0·21896	0·43220	0·799690	—0·1083
0·56478	0·10242	0·846022	—0·0917	0·22132	0·75589	0·804965	—0·0358
0·56559	0·20413	0·847988	—0·1020	0·22923	0·66217	0·804989	—0·0894
0·56772	0·15626	0·847295	—0·0995	0·23748	0·48578	0·803105	—0·1137
0·57227	0·24156	0·849201	—0·1000	0·23809	0·39650	0·801355	—0·0966
0·61657	0·36018	0·854013	—0·0116	0·23954	0·57128	0·804868	—0·1080
0·67048	0·25915	0·856826	—0·0466	0·24734	0·14400	0·797471	—0·0318
0·67878	0·23572	0·857119	—0·0542	0·28259	0·11795	0·801267	—0·0338
0·68246	0·20725	0·857009	—0·0656	0·28889	0·34403	0·806666	—0·0994
0·68784	0·25998	0·857980	—0·0303	0·33922	0·41460	0·813840	—0·1076
0·72887	0·10209	0·858816	—0·0896	0·35184	0·23269	0·811601	—0·0851
0·73310	0·14399	0·859697	—0·0737	0·36276	0·54017	0·818456	—0·0747
0·75734	0·12571	0·861030	—0·0678	0·37905	0·31946	0·816357	—0·1067
0·77402	0·20297	0·862834	0·0024	0·38463	0·11026	0·812636	—0·0617
0·79303	0·16543	0·863625	—0·0124	0·39838	0·46556	0·821008	—0·0918
0·80331	0·09934	0·863630	—0·0589	0·45289	0·18991	0·821365	—0·1054
0·87426	0·10050	0·867664	0·0015	0·46497	0·51471	0·827720	—0·0139
0·90135	0·03412	0·868616	—0·0409	0·47513	0·26381	0·824878	—0·1067
				0·47593	0·44678	0·827923	—0·0560
		40°C		0·53448	0·07920	0·826787	—0·1035
				0·54341	0·24183	0·830585	—0·1010
0·03431	0·57728	0·774688	—0·1312	0·54409	0·31521	0·831896	—0·0856
0·06974	0·21503	0·774287	—0·0386	0·55910	0·14832	0·830274	—0·1107
0·07365	0·50161	0·779948	—0·1177	0·58002	0·23466	0·833524	—0·0955
0·07475	0·77440	0·784325	—0·1119	0·59774	0·20383	0·834479	—0·1021
0·08251	0·63279	0·783539	—0·1274	0·62566	0·35098	0·838472	0·0028
0·09569	0·67305	0·786244	—0·1224	0·71119	0·06766	0·840837	—0·1139
0·11200	0·79025	0·790328	—0·0879	0·71939	0·11564	0·842124	—0·0925
0·12331	0·40016	0·785649	—0·0892	0·90687	0·07542	0·852799	0·0233

In Eqs (3)–(7) the mole fractions of individual components are denoted generally by subscripts i, j, k for, as it has been shown when applying these relations, a change in standard deviation of excess volume can take place in some cases by cyclic exchange of components, *i.e.* $i, j, k = 1, 2, 3$ or 2, 3, 1, or 3, 1, 2.

The measured ternary data of the benzene–methanol–acetonitrile mixture have been correlated by means of correlation relations (3)–(7), the binary contributions have been expressed in terms of Eq. (1) or (2). The correlation relations given in paper[1] have been used for binary systems, only for the methanol(2)–acetonitrile(3) system at 40°C we have used the Redlich–Kister relation in the form ($cm^3 . mol^{-1}$)

$$v_{23}^E = x_2 x_3 [-0{\cdot}49220 - 0{\cdot}35021(x_2 - x_3) - 0{\cdot}15946(x_2 - x_3)^2 - 0{\cdot}12317(x_2 - x_3)^3] ; \quad \sigma(v^E) = 0{\cdot}0011 \text{ cm}^3 . \text{mol}^{-1} . \qquad (8)$$

The parameters A_s (Eqs (3)–(7)) have been evaluated by the least squares method, the number of parameters has been assessed by the F-test.

Table II gives a survey of the best correlations of each type, Table III the values of parameters A_s of correlations selected. It is evident that the shortened forms yield rather worse results than the more general ones (3) and (6). As the most successful for correlating the experimental ternary data have proved relations (3) and (5). From the point of view of the possibility of estimating the excess volume of ternary system only from binary data, *i.e.* $v_T^E = 0$ in Eqs (1) and (2), Eq. (2) is more advantageous

TABLE II

Survey of the Best Correlations of Each Type for the Benzene(1)–Methanol(2)–Acetonitrile(3) Mixture

Binary contributions (Eq.)	Ternary contribution (Eq.)	25°C			40°C		
		i j k	*N*	$\sigma(v^E) . 10^3$ $cm^3 . mol^{-1}$	*i j k*	*N*	$\sigma(v^E) . 10^3$ $cm^3 . mol^{-1}$
(1)	$v_T^E = 0$	—	—	18·8	—	—	21·0
	(3)	2 3 1	5	2·2	2 3 1	4	2·6
	(4)	3 1 2	4	2·6	3 1 2	2	3·1
	(5)	3 1 2	5	2·0	2 3 1	3	2·4
	(6)	2 3 1	6	3·0	1 2 3	4	3·5
	(7)	1 2 3	2	3·9	1 2 3	3	4·2
(2)	$v_T^E = 0$	—	—	10·7	—	—	10·8
	(3)	2 3 1	4	2·0	2 3 1	4	2·5
	(3)	1 2 3	2	2·1			
	(4)	1 2 3	2	2·1	1 2 3	2	2·8
	(5)	1 2 3	5	2·0	1 2 3	5	2·5
	(6)	2 3 1	4	2·9	2 3 1	6	2·7
	(7)	1 2 3	2	3·4	1 2 3	2	3·4

TABLE III

Parameters of Selected Correlations for the Concentration Dependence of Excess Volume of the Benzene(1)–Methanol(2)–Acetonitrile(3) Mixture

t, °C	Binary contributions (Eq.)	Ternary contribution (Eq.)	i j k	A_1	A_2	A_3	A_4	A_5	$\sigma(v^E)$
						$cm^3\ mol^{-1}$			
25	(*1*)	(*3*)	2 3 1	—0·76508	—1·8487	—0·91195	2·0717	0·51986	0·0022
	(*1*)	(*5*)	3 1 2	—1·6303	4·3102	—2·0168	0·37740	—1·9764	0·0020
	(*2*)	(*3*)	2 3 1	—0·49835	—0·01200	0·44808	0·82773	—	0·0020
	(*2*)	(*3*)	1 2 3	—0·46229	—0·86626	—	—	—	0·0021
	(*2*)	(*5*)	1 2 3	1·5066	0·88883	—0·80576	—1·6902	—3·2184	0·0020
40	(*1*)	(*3*)	2 3 1	—0·76173	—1·9425	—0·77291	1·7672	—	0·0026
	(*1*)	(*5*)	2 3 1	—4·0016	1·6479	4·0157	—	—	0·0024
	(*2*)	(*3*)	2 3 1	—0·45775	—0·19554	0·51946	0·65445	—	0·0025
	(*2*)	(*5*)	1 2 3	1·3724	1·8675	—1·2134	—1·5225	—3·9217	0·0025

for expressing the binary contributions, where the standard deviation in excess volume is approximately one half compared with Eq. (*1*). The use of Eq. (*2*) has resulted in reducing the ternary contribution, v_T^E. It has been found that the ratio $|(v_T^E)_{max}|/|v_{max}^E|$ is about 0·15 for Eq. (*2*) and about 0·4 for Eq. (*1*). However, it is to be emphasized that the value of the ternary term in Eq. (*1*) depends on the type of correlation functions used for binary systems.

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