Excess Molar Volume and Viscosity Study of Ternary Mixtures of *tert*-butylmethylether and *n*-heptane with Alcohols at 293.15 K

MARIA MAGDALENA BUDEANU*, VASILE DUMITRESCU, OCTAV PANTEA
Petroleum and Gas University of Ploieşti, 39 Bucureşti Blv., 100680, Ploieşti, Romania

Excess values of molar volume and viscosity of the tert-butylmethylether (MTBE) + n-heptane + ethanol, MTBE + n-heptane + n-propanol and MTBE + n-heptane + iso-propanol systems and the corresponding values of binary mixtures were determined at 293.15 K and atmospheric pressure by measuring densities and viscosities, over the whole composition range. Excess molar volumes and excess viscosities of the binary and ternary systems were fitted to Redlich-Kister equation, Hwang equation and a series of Legendre polynomials. Two geometric models (Kohler and general geometric model) for predicting ternary excess properties from experimental binary mixtures were applied.

Keywords: excess properties, binary and ternary liquid mixtures, n-heptane, tert-butylmethylether, alcohols, geometric model.

Excess properties can provide information about intermolecular interactions between components. In this paper we report experimental data of excess molar volumes and excess viscosities for three ternary liquid solution containing MTBE and *n*-heptane as common components and alcohols (ethanol, *n*-propanol and *iso*-propanol) as a function of composition at 293.15 K. The physical properties of such mixtures are important in the petrochemical industry because the ethers and alcohols are used as oxygenating antiknock agents for gasoline. The component selected for marking the ternaries are well known organic liquids and also have wide range of applications in various fields of chemistry besides being used in industries [1,2]. The measured excess properties data have been compared with those predicated from binary data with the use of semi-empirical equations [3,4] and geometric models [5-7].

Experimental part

The chemical MTBE was obtained from Merck (>99.5 mol%), *n*-heptane was supplied by Sigma-Aldrich (>99 mol%), ethanol (>99.3 mol%) and *iso*-propanol (>99.7 mol%) were obtained from Chemical Company and *n*-propanol was supplied by Merck (>99.9 mol%). The chemicals were dried over molecular sieves (Fluka type 4 Å). The purity was checked through chromatographic analysis. The mole fractions were determined by weighing and precision of the mole fraction was ± 0.00005. The densities were determined by hydrostatic weighing method of Kohlrausch with the precision of ± 0.00005 g/cm^3. The experimental technique has been previously described [8], the temperature of thermostatic water bath being controlled to ± 0.05 K. Viscosities of the pure compounds and of the binary mixtures were determined with an Ubbelohde kinematic viscometer [9] that was kept in a vertical position in a water thermostat. A thermostatically controlled bath (constant to ± 0.05 K) was used. The kinematic viscosity was calculated using the relation:

$$\upsilon = At - B/t \qquad (1)$$

where *t* is the flowing time (± 0.1s) of a constant volume liquid through the viscometer capillary; *A* and *B* are characteristic constants of the used viscometer, which were determined by taking water and benzene as the calibrating liquids for correction of kinetic energy deviations. The dynamic viscosity was determined from the equation:

$$\eta = \upsilon\rho \qquad (2)$$

where ρ is the density of the liquid. The precision of the viscosity was estimated to be ± 0.0010 mPa·s. In all determinations, triplicate experiments were performed at each composition and temperature, and the arithmetic average was taken for the calculations of the viscosity.

Results and discussions

The measured densities and viscosities of pure compounds are reported in table 1. The measured values of densities agree within an average absolute percentage deviation less than 0.05 % for all compounds except *iso*-propanol which has average absolute percentage deviation 0.2 %. The measured values of viscosities agree within an average absolute percentage deviation less of 2.2 % for all compounds except MTBE. For MTBE, the viscosity value reported in the literature differs by less than 4 % than our results. These differences can be attributed to the different purity of the reagents used.

The excess molar volumes (V^E) were calculated from the densities of the pure liquids and their mixtures using the equation (3).

Table 1
COMPARISON OF EXPERIMENTAL DENSITIES AND VISCOSITIES OF PURE LIQUIDS WITH LITERATURE VALUES AT 293.15K

Component	Density (g·cm^{-3})		Viscosity (mPa·s)	
	Exp.	Lit.	Exp.	Lit.
MTBE	0.7408	0.7404[10] 0.74065[11]	0.3706	0.3861[12]
n-Heptane	0.6842	0.6839[13]	0.4197	-
Ethanol	0.7895	0.78945[14]	1.2206	1.1940[15]
n-Propanol	0.8044	0.80428[16]	2.2304	2.1970[16]
iso-Propanol	0.7871	0.78535[16]	2.4064	2.4140[16]

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* *email: m19magda@yahoo.com; Tel.: 0724/853 844*

$$V^E = \sum_{i=1}^{n} x_i M_i \left(\rho^{-1} - \rho_i^{-1}\right) \qquad (3)$$

where x, M and ρ are the mole fraction, molar mass and density, respectively; n is the number of the components in the mixture and the subscript i indicates values for the pure components.

The experimental values of viscosity (η) are used to calculate the excess viscosity (η^E) defined by the equation:

$$\eta^E = \eta - \sum_{i=1}^{n} x_i \eta_i \qquad (4)$$

where η is the viscosity of the mixture and η_i is the viscosity of the pure component.

Experimental values of V^E and η^E for all the binary systems are listed in table 2.

The experimental excess volumes for the binary systems MTBE + *n*-heptane, and for *n*-heptane + alcohol (ethanol, *n*-propanol, *iso*-propanol) are positive over the whole range of composition. A different situation is found for the binary systems MTBE + alcohol (ethanol, *n*-propanol, *iso*-propanol), the experimental values are negative over the whole range of composition. The results of this study are in close agreement with the work of Rodriques et al. [17] with regard to the system composed of MTBE with *n*-heptane, with the work of Hoga and Torres [18] for mixtures MTBE and alcohol and with the work of Jimenez et al. [19] for the system composed of *n*-heptane with *n*-propanol. No experimental data were found for the mixtures of *n*-heptane with ethanol and *n*-heptane with *iso*-propanol in order to compare with our values. Several effects may contribute to the values of V^E, such as breaking of liquid order on mixing, contribution to the difference in size and shape of the components, difference in free volumes, and dipole-dipole interactions [20]. The positive values of the excess molar volumes indicate that the two former effects are dominant over the latter effects, implying that dispersions forces are dominant in MTBE + *n*-heptane system [21]. Negative values of excess molar volume for the binary systems MTBE + alcohol were associated with hydrogen bonding and complex formation between ether (non-self-associating component) and alcohol (strong self-associating component) as well as with structural effects [18; 22-25]. Important parameters that should be taken into consideration in order to explain the behaviour of the interactions in the mixture are the length of the alcohol chain, as well as the position of the hydroxyl group. The more negative values of the excess molar volumes for MTBE + *n*-propanol mixtures than those for MTBE + *iso*-propanol mixtures can be understood by considering that the sterically hindered *iso*-propanol molecules can restrict the interstitial accommodation resulting in less negative contribution to the V^E [18].

The experimental excess viscosities are negative over the whole range of composition for all binary systems. Negative deviations of viscosities occur when dispersion forces are preponderant, which is in complete agreement with the conclusion reached for the V^E behaviour [21]. The negative excess viscosity was explained by many authors through different forms [26-29]. By the addition of MTBE molecules, the alcohol molecules dissociate and have greater mobility than the pure alcohols due to the reduced cohesive forces of alcohol molecules upon mixing [30-32].

Experimental data for the ternary systems are shown in table 3. No literature data are available for the excess properties of the ternary systems which are studied in this work at 293.15 K.

The values of the excess molar volumes for the studied ternary systems, indicate both positive and negative values. Positive values are obtained for low alcohol concentrations ($x_3 \leq 0.45$) and for increased *n*-heptane and MTBE concentrations and negative values are noticed for decreased concentrations of *n*-heptane and increased concentrations of alcohol and MTBE. The negative ternary excess volume data in the present study may be due to the intermolecular OH - O bonds created between alcohol and MTBE molecules. It is well established that alcohols are self-associated through hydrogen bonding. Dipole-dipole interactions too affect the properties of alcohols [32]. The negative values of V^E can be explained due to a closer approach of the unlike molecules in the liquid mixtures, indicating the existence of specific interaction between the liquid components [33].

The experimental excess viscosities are negative over the whole range of composition for all ternary systems. A negative excess viscosity shows a greater facility to flow for the real mixture with respect to the ideal behaviour.

Table 2.
EXPERIMENTAL BINARY EXCESS PROPERTIES AT 293.15 K

x_1	V^E (cm^3/mol)	η^E (mPa·s)	x_1	V^E (cm^3/mol)	η^E (mPa·s)	x_1	V^E (cm^3/mol)	η^E (mPa·s)
MTBE (1) + *n*-heptane (2)								
0.1004	0.1954	-0.0031	0.3982	0.4372	-0.0094	0.7018	0.3055	-0.0048
0.2006	0.2878	-0.0059	0.4986	0.4504	-0.0097	0.7948	0.2481	-0.0031
0.2994	0.3957	-0.0077	0.5985	0.3817	-0.0086	0.8995	0.1194	-0.0013
n-heptane (1) + ethanol (2)								
0.1005	0.1174	-0.1544	0.4016	0.4336	-0.2705	0.7041	0.3954	-0.1909
0.2020	0.2912	-0.2332	0.5079	0.4491	-0.2469	0.8008	0.3356	-0.1364
0.3022	0.3885	-0.2637	0.5967	0.4365	-0.2267	0.8935	0.2515	-0.0820
MTBE (1) + ethanol (2)								
0.1005	-0.2821	-0.1383	0.3979	-0.5674	-0.2858	0.7005	-0.5296	-0.1895
0.1986	-0.4535	-0.2291	0.4969	-0.6227	-0.2736	0.8024	-0.4899	-0.1386
0.3015	-0.5333	-0.2751	0.5968	-0.5792	-0.2411	0.9005	-0.3148	-0.0760
n-heptane (1) + *n*-propanol (2)								
0.1020	0.1016	-0.4048	0.4005	0.2309	-0.6626	0.7025	0.2623	-0.4457
0.2018	0.1361	-0.5744	0.5017	0.2493	-0.6225	0.8010	0.2373	-0.3007
0.2990	0.1945	-0.6368	0.6033	0.2973	-0.5481	0.8918	0.1737	-0.1681
MTBE (1) + *n*-propanol (2)								
0.0960	-0.3006	-0.3521	0.4043	-0.6121	-0.7001	0.6989	-0.5911	-0.4350
0.2003	-0.4396	-0.6280	0.5088	-0.6596	-0.6236	0.7966	-0.5271	-0.3094
0.3005	-0.5605	-0.7025	0.5958	-0.6048	-0.5505	0.8983	-0.3718	-0.1646
n-heptane (1) + *iso*-propanol (2)								
0.1003	0.1432	-0.6107	0.3980	0.3005	-0.8720	0.6981	0.3496	-0.5264
0.2009	0.1926	-0.8297	0.5002	0.3978	-0.7906	0.8014	0.2637	-0.3536
0.3009	0.2910	-0.8844	0.5961	0.3670	-0.6742	0.9084	0.1859	-0.1657
MTBE (1) + *iso*-propanol (2)								
0.1007	-0.1910	-0.5399	0.3981	-0.3781	-0.8465	0.6993	-0.3601	-0.5056
0.1995	-0.2730	-0.7996	0.4991	-0.3877	-0.7709	0.8005	-0.3523	-0.3394
0.3030	-0.3614	-0.8700	0.5992	-0.3766	-0.6577	0.8987	-0.2912	-0.1640

Table 3
EXPERIMENTAL TERNARY EXCESS PROPERTIES AT 293.15 K

x_1	x_2	V^E (cm^3/mol)	η^E (mPa·s)	x_1	x_2	V^E (cm^3/mol)	η^E (mPa·s)
MTBE (1) + *n*-heptane (2)+ ethanol (3)							
0.1002	0.1007	-0.2675	-0.2441	0.2982	0.3941	-0.1169	-0.1990
0.151	0.1482	-0.2524	-0.2904	0.3942	0.2032	-0.2315	-0.2376
0.2017	0.2035	-0.2068	-0.2900	0.4619	0.095	-0.5153	-0.2545
0.2965	0.2965	-0.1250	-0.2440	0.7951	0.1006	-0.2934	-0.0777
0.3968	0.3963	0.0400	-0.1472	0.7052	0.142	-0.2170	-0.1112
0.4551	0.4472	0.3963	-0.0784	0.5983	0.2054	-0.2649	-0.1312
0.0978	0.7992	0.0762	-0.0790	0.3987	0.2969	-0.1177	-0.1980
0.1455	0.7041	0.0772	-0.1115	0.2024	0.3956	0.0298	-0.2396
0.2125	0.599	0.1331	-0.1317	0.1029	0.4504	0.1021	-0.2507
MTBE (1) + *n*-heptane (2) + *n*-propanol (3)							
0.1009	0.1013	-0.4111	-0.6246	0.301	0.3939	0.0591	-0.4369
0.1477	0.1503	-0.2709	-0.6793	0.3958	0.2027	-0.4333	-0.5619
0.2051	0.2031	-0.2773	-0.6912	0.4406	0.1008	-0.6409	-0.5966
0.3063	0.3018	-0.2409	-0.5340	0.8019	0.0995	-0.2999	-0.1570
0.3948	0.3976	0.0420	-0.3122	0.6996	0.1459	-0.3437	-0.2378
0.4586	0.4552	0.0381	-0.1366	0.6045	0.2014	-0.2456	-0.2975
0.0997	0.7994	0.0329	-0.1500	0.3969	0.3005	-0.2172	-0.4402
0.1509	0.7001	0.0939	-0.2378	0.2065	0.3931	0.0356	-0.5606
0.2016	0.5957	0.1487	-0.3034	0.1018	0.4518	0.0891	-0.6006
MTBE (1) + *n*-heptane (2) +*iso*-propanol (3)							
0.0933	0.1015	-0.0127	-0.8263	0.3039	0.4038	0.2438	-0.5082
0.1498	0.1498	-0.0228	-0.8898	0.3974	0.204	0.0179	-0.6657
0.2037	0.2053	0.3252	-0.8768	0.4582	0.0991	-0.1857	-0.7124
0.2956	0.3039	0.1007	-0.6620	0.8090	0.0979	-0.1043	-0.1715
0.4068	0.4028	0.2198	-0.3414	0.7077	0.1417	-0.1023	-0.2731
0.4569	0.4488	0.2649	-0.1759	0.6078	0.2072	-0.0527	-0.3303
0.1000	0.8011	0.0982	-0.1819	0.4059	0.3032	0.1273	-0.5063
0.1396	0.708	0.2443	-0.2833	0.2027	0.4073	0.1590	-0.6587
0.2051	0.6066	0.2671	-0.3442	0.0939	0.4539	0.2714	-0.7427

This occurs when interactions between the molecules are stronger for the pure compounds than for their mixtures [34].

The values of excess properties for binary systems were correlated with composition using three methods:

a) The Redlich-Kister [10] expression:

$$X^E = x_i x_j \sum_{k=0}^{3} A_k (2x_i - 1)^k \tag{5}$$

b) The Hwang expression [4]:

$$X^E = x_i x_j \left(A_0 + A_1 x_i^3 + A_2 x_j^3\right) \tag{6}$$

c) A series of Legendre polynomials $L_k(x_i)$:

$$X^E = x_i x_j \sum_{k=0}^{3} a_k L_k(x_i)$$

which for the first terms is:

$$X^E = x_i x_j \left[A_0 + A_1(x_i - x_j) + A_2(6x_i^2 - 6x_i + 1) + A_2(20x_i^3 - 30x_i^2 + 12x_i - 1)\right] \tag{7}$$

In eqs. (5) - (7) X^E represents any of the following properties: V^E, η^E; x_i, x_j are the mole fractions of the components *i* and *j*, respectively, and A_0, A_1, A_2 and A_k denotes the polynomial coefficients. Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel and Chebyshev, which have the important characteristic that for a continuous series of observations, the values of the coefficients do not change as the number of terms in the series is increased [35].

The values of these coefficients are indicated in table 4 along with the standard deviation, σ, defined by:

$$\sigma = \left[\frac{\sum (X^E_{obs.} - X^E_{calc.})^2}{m - n}\right]^{1/2} \tag{8}$$

where *m* is the number of data points and *n* is the number of estimated parameters.

For the binary systems, all proposed equations correlate well the experimental data, except Hwang equation for *n*-heptane + ethanol mixture in the case of excess volumes and *n*-heptane + *n*-propanol mixture for excess viscosities.

Experimental values of the binary systems were used to test several equations that have been suggested for predicting excess properties of ternary mixtures. Empirical correlations of Redlich-Kister, Hwang et al. and Legendre polynomials were used as follows:

Redlich and Kister proposed an expression for the excess volumes of a ternary mixture:

$$\begin{aligned} X^E_{123} &= x_1 x_2\left(A_0^{12} + A_1^{12}(x_1 - x_2) + A_2^{12}(x_1 - x_2)^2 + A_3^{12}(x_1 - x_2)^3\right) + \\ &+ x_1 x_3\left(A_0^{13} + A_1^{13}(x_1 - x_3) + A_2^{13}(x_1 - x_3)^2 + A_3^{13}(x_1 - x_3)^3\right) + \\ &+ x_2 x_3(A_0^{23} + A_1^{23}(x_2 - x_3) + A_2^{23}(x_2 - x_3)^2 + A_3^{23}(x_2 - x_3)^3) \end{aligned} \tag{9}$$

Hwang et al. [4] developed the relation for binary system and Acree et al. [36] extended the predictive approach to ternary system and employed the equation:

$$\begin{aligned} X^E_{123} &= x_1 x_2\left(A_0^{12} + A_1^{12} x_1^3 + A_2^{12} x_2^3\right) + \\ &+ x_1 x_3\left(A_0^{13} + A_1^{13} x_1^3 + A_2^{13} x_3^3\right) + x_2 x_3\left(A_0^{23} + A_1^{23} x_2^3 + A_2^{23} x_3^3\right) \end{aligned} \tag{10}$$

Legendre polynomials for ternary system:

$$\begin{aligned} X^E_{123} &= x_1 x_2\left(A_0^{12} + A_1^{12}(x_1 - x_2) + A_2^{12}(6x_1^2 - 6x_1 + 1) + A_3^{12}(20x_1^3 - 30x_1^2 + 12x_1 - 1)\right) + \\ &+ x_1 x_3\left(A_0^{13} + A_1^{13}(x_1 - x_2) + A_2^{13}(6x_1^2 - 6x_1 + 1) + A_3^{13}(20x_1^3 - 30x_1^2 + 12x_1 - 1)\right) + \\ &+ x_2 x_3\left(A_0^{23} + A_1^{23}(x_2 - x_3) + A_2^{23}(6x_2^2 - 6x_2 + 1) + A_3^{23}(20x_2^3 - 30x_2^2 + 12x_2 - 1)\right) \end{aligned} \tag{11}$$

In eqs. (9) – (11) X^E_{123} is V^E or η^E for ternary mixtures, x_1, x_2 and x_3 are mole fractions of the component 1, 2 and 3 and A_{j0}, A_1 and A_2 are the binary parameters.

We tested two models geometric: Kohler [5] and general geometric model [6,7]. The expressions for the models used are:

Table 4
VALUES OF PARAMETERS A_k FOR EQS. (5), (6) AND (7) AND STANDARD DEVIATION σ

Mixture	Parameters and σ	Equation					
		V^E, cm³/mol			η^E, mPa·s		
		(5)	(6)	(7)	(5)	(6)	(7)
MTBE + *n*-Heptane	A_0	1.74111	1.77145	1.68458	-0.03737	-0.04628	-0.02846
	A_1	-0.46214	-0.67551	-0.38457	0.0154	0.05272	0.01342
	A_2	-0.12916	0.32692	-0.08621	0.02672	0.0186	0.0178
	A_3	0.12932	-	0.05203	-0.0026	-	-0.00127
	σ	0.015	0.015	0.0156	0.0005	0.0005	0.0005
n-Heptane + ethanol	A_0	1.80221	1.68014	1.92228	-1.01031	-0.86914	-1.15165
	A_1	-0.19564	0.87458	0.71574	0.41974	0.01061	0.52711
	A_2	0.36012	0.09695	0.24019	-0.42402	-1.14056	-0.28255
	A_3	1.51907	-	0.6075	0.17875	-	0.07168
	σ	0.008	0.022	0.0081	0.002	0.0026	0.0027
MTBE + ethanol	A_0	-2.36789	-1.87747	-2.85914	-1.08729	-1.03196	-1.14302
	A_1	0.00982	-2.13065	-0.25048	0.51513	0.3395	0.43584
	A_2	-1.47368	-1.79705	-0.98234	-0.16711	-0.78445	-0.11153
	A_3	-0.43415	-	-0.17355	-0.13174	-	-0.05311
	σ	0.0168	0.0168	0.0168	0.0016	0.0044	0.0016
n-Heptane + *n*-propanol	A_0	1.03145	0.85818	1.20488	-2.48186	-2.21667	-2.74719
	A_1	0.52803	1.28113	0.46245	1.00314	0.58341	1.65418
	A_2	0.52025	0.10553	0.34672	-0.79575	-2.7051	-0.53057
	A_3	-0.10929	-	-0.04418	1.08458	-	0.43408
	σ	0.0122	0.012	0.0122	0.0023	0.0121	0.0074
MTBE+ *n*-propanol	A_0	-2.50591	-1.95914	-3.05161	-2.56671	-2.30563	-2.82601
	A_1	-0.10586	-2.56348	-0.4766	1.709	0.86124	1.4963
	A_2	-1.63703	-1.80455	-1.09116	-0.77771	-2.93984	-0.51831
	A_3	-0.61742	-	-0.24722	-0.35421	-	-0.14178
	σ	0.020	0.0207	0.0205	0.012	0.0167	0.012
n-Heptane + *iso*-propanol	A_0	1.44812	1.34312	1.5537	-3.12109	-2.53743	-3.70602
	A_1	0.45744	0.8964	0.35218	1.91981	0.61234	2.87324
	A_2	0.3167	-0.05518	0.21106	-1.75504	-5.28341	-1.16996
	A_3	-0.17599	-	-0.07025	1.58838	-	0.63598
	σ	0.0242	0.023	0.024	0.0117	0.0169	0.0117
MTBE + *iso*-propanol	A_0	-1.50329	-1.00251	-2.00545	-3.07647	-2.6445	-3.50822
	A_1	0.14184	-2.39351	-0.67432	2.00605	1.08022	2.60192
	A_2	-1.50645	-1.61883	-1.00456	-1.29541	-4.53493	-0.86334
	A_3	-1.36073	-	-0.54416	0.99288	-	0.39729
	σ	0.0143	0.0233	0.0143	0.0039	0.0057	0.0039

Kohler model:

$$X_{123}^E = (x_1 + x_2)^2 X_{12}^E + (x_1 + x_3)^2 X_{13}^E + (x_2 + x_3)^2 X_{23}^E \qquad (12)$$

where: $X_{ij}^E = x_i^{'} x_j^{'} \left(A_0^{ij} + A_1^{ij}(x_i^{'} - x_j^{'}) + A_2^{ij}(x_i^{'} - x_j^{'})^2 + A_3^{ij}(x_i^{'} - x_j^{'})^3\right)$

The molar fractions in binary contributions were evaluated with:

$$x_i^{'} = 1 - x_j^{'} = \frac{x_i}{x_i + x_j}.$$

General geometric model developed by Chou et al.:

$$\begin{aligned} X_{123}^E &= x_1 x_2 \sum_{i=0}^{n} A_{12}^i (x_1 - x_2 + (2\xi_{12} - 1)x_3)^i + \\ &+ x_2 x_3 \sum_{i=0}^{n} A_{23}^i (x_2 - x_3 + (2\xi_{23} - 1)x_1)^i + \\ &+ x_3 x_1 \sum_{i=0}^{n} A_{31}^i (x_3 - x_1 + (2\xi_{31} - 1)x_2)^i \end{aligned} \qquad (13)$$

where ξ is the similarity coefficient which is defined as:

$$\xi_{12} = \frac{\eta_I}{\eta_I + \eta_{II}}$$

$$\xi_{23} = \frac{\eta_{II}}{\eta_{II} + \eta_{III}}$$

$$\xi_{13} = \frac{\eta_I}{\eta_I + \eta_{III}}$$

where η is called as „deviation sum of squares” which can be calculated as follows:

$$\begin{aligned} \eta_I &= \sum_{i=0}^{n} \frac{1}{2(2i+1)(2i+3)(2i+5)} (A_{12}^i - A_{13}^i)^2 + \\ &+ \sum_{j=0}^{n} \sum_{k>j}^{n} \frac{1}{(j+k+1)(j+k+3)(j+k+5)} (A_{12}^j - A_{13}^j)(A_{12}^k - A_{13}^k) \end{aligned} \qquad (14)$$

$$\begin{aligned} \eta_{II} &= \sum_{i=0}^{n} \frac{1}{2(2i+1)(2i+3)(2i+5)} (A_{21}^i - A_{23}^i)^2 + \\ &+ \sum_{j=0}^{n} \sum_{k>j}^{n} \frac{1}{(j+k+1)(j+k+3)(j+k+5)} (A_{21}^j - A_{23}^j)(A_{21}^k - A_{23}^k) \end{aligned} \qquad (15)$$

$$\begin{aligned} \eta_{III} &= \sum_{i=0}^{n} \frac{1}{2(2i+1)(2i+3)(2i+5)} (A_{31}^i - A_{32}^i)^2 + \\ &+ \sum_{j=0}^{n} \sum_{k>j}^{n} \frac{1}{(j+k+1)(j+k+3)(j+k+5)} (A_{31}^j - A_{32}^j)(A_{31}^k - A_{32}^k) \end{aligned} \qquad (16)$$

The parameters of Redlich-Kister polynomial appearing in the above equations (13) – (16) observe the following regulation:

$$A_{ij}^k = (-1)^k A_{ji}^k.$$

The values of standard deviation between experimental and estimated values of excess properties calculated with eqs. 9-13 are indicated in table 5.

Among the three empirical correlations used the best agreement with the experimental data was achieved by the equation suggested by Redlich-Kister for excess volumes and Hwang equation for excess viscosities for all ternary mixtures. The best results between the geometric models used to predict ternary excess properties from

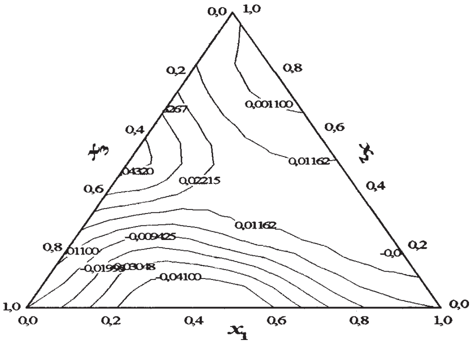

Fig.1. Isolines of excess molar volumes for the ternary system MTBE (1) + *n*-heptane (2) + *iso*-propanol (3) at 293.15 K, calculated with eq. 12

Equation	σ , cm^3/mol	σ , mPa·s
MTBE (1) + *n*-heptane (2) + ethanol (3)		
Redlich-Kister	0.013	0.029
Hwang	0.040	0.016
Legendre	0.040	0.038
Kohler	0.026	0.036
General geometric model	0.034	0.021
MTBE (1) + *n*-heptane (2) + *n*-propanol (3)		
Redlich-Kister	0.014	0.106
Hwang	0.048	0.051
Legendre	0.051	0.120
Kohler	0.021	0.130
General geometric model	0.040	0.040
MTBE (1) + *n*-heptane (2) + *iso*-propanol (3)		
Redlich-Kister	0.033	0.150
Hwang	0.076	0.046
Legendre	0.060	0.180
Kohler	0.010	0.208
General geometric model	0.039	0.058

Table 5
STANDARD DEVIATION (Eq.8) OF EXCESS PROPERTIES FOR TERNARY SYSTEMS AT 293.15K

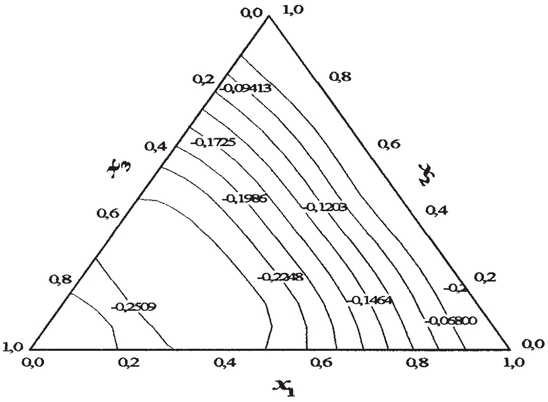

Fig.2 Isolines of excess viscosities for the ternary system MTBE (1) + *n*-heptane (2) + ethanol (3) at 293.15 K, calculated with eq. 13

binary contributions were obtained with Kohler model for the excess volumes and with the general geometric model for the excess viscosities. As an illustration, figures 1 and 2 show calculated values of V^E (eq. 12) and of η^E (eq. 13).

Conclusions

New data of excess molar volume and excess viscosities of ternary mixtures of the MTBE + *n*-heptane + ethanol, MTBE + *n*-heptane + *n*-propanol and MTBE + *n*-heptane + *iso*-propanol were determined at 293.15 K. These results have been computed and fitted to the Redlich-Kister equation, Hwang equation and a series of Legendre polynomials. The Redlich-Kister equation is the best to correlate excess molar volumes, while Hwang equation is adequate to correlate excess viscosities. Between the two geometric models used the Kohler model is better to correlate excess molar volumes while the general geometric model is most appropriate to estimate excess viscosities.

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