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Excess Volumes and Excess Viscosities of Binary Mixtures of 1-Bromo-2-Methylpropane + an Isomer of Butanol at 298.15 and 313.15 K

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Excess volumes V^E, excess viscosities η^E, and excess free energies of activation of flow G^{*E} at 298.15 and 313.15 K are reported for binary mixtures of 1-bromo-2-methylpropane and each of the alcoholic isomers of 1-butanol. The results were obtained from density and viscosity measurements and show positive values for V^E and negative values for both η^E and G^{*E} for all mixtures over the entire composition range.

KEY WORDS: activation energy; binary mixtures; free energy; 1-bromo-2-methylpropane; butanols; viscosity; excess volume.

1. INTRODUCTION

Previous works reported indicate our interest in the development of a research program based on the measurement of excess properties of binary mixtures involving the alcoholic isomers of butanol as one of the components together with an alkane or haloalkane [1–7]. At this time, we present the results obtained for V^E, η^E, and G^{*E} at 298.15 and 313.15 K for 1-bromo-2-methylpropane. No literature data were found for these mixtures to compare our values.

2. EXPERIMENTS

All pure components used were provided by Aldrich, and their purities were 1-butanol (better than 99.8 mol%), 2-methyl-1-propanol and

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Table I. Densities, ρ, and Viscosities, η, of Pure Compounds at 298.15 K Compared with Literature Data [9]

Liquid	ρ (g·cm^{-3})		η (cP)	
	Expt.	Lit.	Expt.	Lit.
1-Bromo-2-methylpropane	1.25622	1.2571	0.4859	—
1-Butanol	0.80576	0.8060	2.5702	2.571
2-Butanol	0.80241	0.8026	2.9973	2.998
2-Methyl-1-propanol	0.79777	0.7978	3.3328	3.333
2-Methyl-2-propanol	0.78078	0.7812	4.4356	4.438

2-methyl-2-propanol (better than 99.5 mol%), and 2-butanol and 1-bromo-2-methylpropane (better than 99.0 mol%). All isomeric butanols were stored over activated molecular sieve type 0.3 nm from Merck. The purity of chemicals used was checked by GLC and was considered sufficient, so no further purification was attempted.

Details of the calibrate and measurement procedure can be found in an earlier paper [8]. Denisties of pure liquids and mixtures were measured with an Anton-Paar DMA-58 vibrating-tube density meter. The corresponding viscosities were determined by means of an Ubbelhode viscometer with a Schott-Geräte automatic measuring unit Model AVS-440. The experimental values for density and viscosity of the pure components at 298.15 K are listed and compared with literature values [9] in Table I.

3. RESULTS AND DISCUSSION

The excess were calculated from our measurements according to the following equations:

$$V^{E} = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \tag{1}$$

$$\eta^{E} = \eta - (x_1\eta_1 + x_2\eta_2) \tag{2}$$

$$G^{*E} = RT \ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2) \tag{3}$$

where ρ, ρ_1, and ρ_2 are the densities (g·cm^{-3}); η, η_1, and η_2 are the absolute viscosities (cP); V, V_1, and V_2 are the molar volumes (cm^3·mol^{-1}); and x_i is the mole fraction of component i in the mixture.

Subscript 1 for 1-bromo-2-methylpropane, 2 for isomeric butanol, without subscript for the mixture.

The values of each excess property at each temperature were correlated with a Redlich–Kister polynomial equation:

$$Y^{E} = x_1(1 - x_1) \sum A_i(2x_1 - 1)^i \tag{4}$$

where a_i, are adjustable parameters and x_1 is the mole fraction of 1-bromo-2-methylpropane.

The excess functions for the mixtures are presented in Tables II to IV and graphically represented in Figs. 1 to 6. Table V lists the values of the parameters A_i together with the standard deviations $\sigma(Y^{E})$.

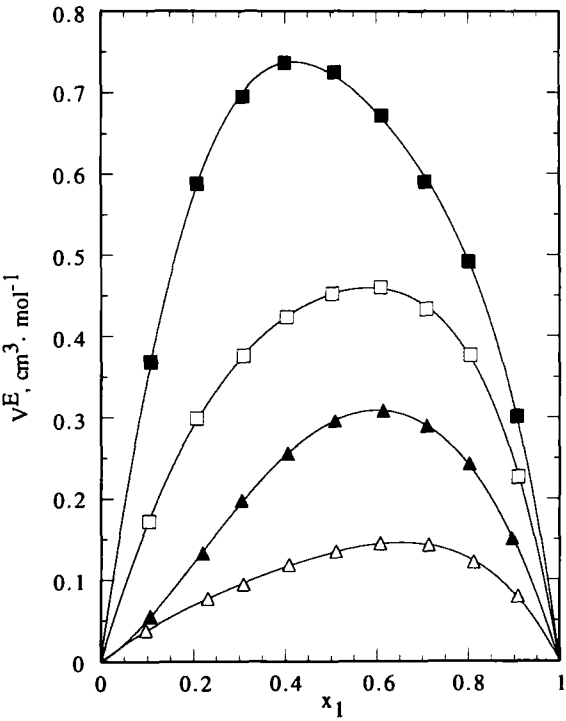

Fig. 1. Excess volumes, V^{E}, of 1-bromo-2-mthylpropane (1) + 1 butanol (2) at 298.15 K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■).

Table II. Excess Molar Volumes V^E of Binary Mixtures 1-Bromo-2-Methylpropane (1) + an Isomer of Butanol (2) at 298.15 and 313.15 K

	$cm^3 \cdot mol^{-1}$					
T (K)	x_1	V^E	x_1	V^E	x_1	V^E
	1-Bromo-2-methylpropane + 1-butanol					
298.15	0.0975	0.0383	0.4080	0.1185	0.7129	0.1432
	0.2314	0.0772	0.5103	0.1354	0.8110	0.1220
	0.3091	0.0951	0.6067	0.1448	0.9084	0.0798
	1-Bromo-2-methylpropane + 2-butanol					
298.15	0.1043	0.1724	0.4032	0.4232	0.7081	0.4331
	0.2076	0.2991	0.5022	0.4524	0.8050	0.3768
	0.3095	0.3761	0.6084	0.4602	0.9087	0.2268
	1-Bromo-2-methylpropane + 2-methyl-1-propanol					
298.15	0.1066	0.0555	0.4047	0.2555	0.7097	0.2895
	0.2199	0.1328	0.5086	0.2956	0.8020	0.2430
	0.3048	0.1981	0.6142	0.3083	0.8954	0.1511
	1-Bromo-2-methylpropane + 2-methyl-2-propanol					
298.15	0.1074	0.3686	0.3999	0.7366	0.7058	0.5903
	0.2083	0.5882	0.5085	0.7253	0.8010	0.4920
	0.3072	0.6955	0.6112	0.6723	0.9062	0.3014
	1-Bromo-2-methylpropane + 1-butanol					
313.15	0.1001	0.0483	0.4042	0.2331	0.7057	0.2937
	0.2067	0.1250	0.5065	0.2637	0.8106	0.2882
	0.3036	0.1883	0.6039	0.2818	0.8763	0.2453
	1-Bromo-2-methylpropane + 2-butanol					
313.15	0.1061	0.2282	0.4067	0.5540	0.7002	0.5644
	0.2098	0.3739	0.5049	0.5824	0.7809	0.4928
	0.3090	0.4797	0.6024	0.5987	0.9037	0.2967
	1-Bromo-2-methylpropane + 2-methyl-1-propanol					
313.15	0.1029	0.0918	0.4086	0.3365	0.7077	0.4369
	0.2062	0.2017	0.5114	0.3660	0.8153	0.4288
	0.3101	0.2790	0.6117	0.4012	0.9073	0.3281
	1-Bromo-2-methylpropane + 2-methyl-2-propanol					
313.15	0.1076	0.3746	0.4110	0.8167	0.7163	0.6601
	0.2169	0.6372	0.5080	0.8224	0.8024	0.5349
	0.3097	0.7522	0.6120	0.7730	0.8961	0.3418

Table III. Excess Molar Viscosites η^E of Binary Mixtures 1-Bromo-2-Methylpropane (1) + an Isomer of Butanol (2) at 298.15 and 313.15 K

	cP					
T (K)	x_1	η^E	x_1	η^E	x_1	η^E
	1-Bromo-2-methylpropane + 1-butanol					
298.15	0.1067	−0.2943	0.4058	−0.6225	0.7037	−0.4404
	0.2056	−0.4784	0.5013	−0.6037	0.7977	−0.3241
	0.3012	−0.5809	0.5989	−0.5416	0.8888	−0.1942
	1-Bromo-2-methylpropane + 2-butanol					
298.15	0.0998	−0.6753	0.3990	−1.0417	0.7010	−0.6329
	0.1938	−0.9728	0.4960	−0.9512	0.8018	−0.4402
	0.2971	−1.0768	0.5939	−0.8138	0.8984	−0.2378
	1-Bromo-2-methylpropane + 2-methyl-1-propanol					
298.15	0.1020	−0.5499	0.4028	−1.0425	0.7046	−0.6640
	0.1987	−0.8797	0.4944	−0.9772	0.7994	−0.4755
	0.2960	−1.0253	0.5929	−0.8461	0.9000	−0.2525
	1-Bromo-2-methylpropane + 2-methyl-2-propanol					
298.15	0.1064	−1.6457	0.4076	−1.8763	0.7001	−1.0562
	0.2104	−2.0417	0.5005	−1.6527	0.7830	−0.7810
	0.3043	−2.0421	0.5919	−1.3937	0.8974	−0.3833
	1-Bromo-2-methylpropane + 1-butanol					
313.15	0.1067	−0.1752	0.4058	−0.3929	0.7037	−0.2811
	0.2056	−0.2940	0.5013	−0.3816	0.7977	−0.2070
	0.3012	−0.3631	0.5989	−0.3434	0.8888	−0.1259
	1-Bromo-2-methylpropane + 2-butanol					
313.15	0.0998	−0.3312	0.3990	−0.5306	0.7010	−0.3327
	0.1938	−0.4825	0.4960	−0.4889	0.8018	−0.2342
	0.2971	−0.5377	0.5939	−0.4239	0.8984	−0.1303
	1-Bromo-2-methylpropane + 2-methyl-1-propanol					
313.15	0.1020	−0.3042	0.4028	−0.5583	0.7046	−0.3832
	0.1987	−0.4916	0.4944	−0.5536	0.7994	−0.2755
	0.2960	−0.5772	0.5929	−0.4864	0.9000	−0.1495
	1-Bromo-2-methylpropane + 2-methyl-2-propanol					
313.15	0.1064	−0.5613	0.4076	−0.7143	0.7001	−0.4246
	0.2104	−0.7303	0.5005	−0.6413	0.7830	−0.3137
	0.3043	−0.7551	0.5919	−0.5509	0.8974	−0.1619

Table IV. Excess Free Energies of Activation of Flow G^{*E} of Binary Mixtures 1-Bromo-2-Methylpropane (1) + an Isomer of Butanol (2) at 298.15 and 313.15 K

	J · mol^{-1}					
T (K)	x_1	G^{*E}	x_1	G^{*E}	x_1	G^{*E}
	1-Bromo-2-methylpropane + 1-butanol					
298.15	0.1067	−155.2	0.4058	−529.8	0.7037	−531.8
	0.2056	−300.0	0.5013	−580.6	0.7977	−434.0
	0.3012	−423.6	0.5989	−581.7	0.8888	−295.9
	1-Bromo-2-methylpropane + 2-butanol					
298.15	0.0998	−499.6	0.3990	−1119.4	0.7010	−853.1
	0.1938	−837.9	0.4960	−1111.5	08018	−637.1
	0.2971	−1056.4	0.5939	−1019.2	0.8984	−372.9
	1-Bromo-2-methylpropane + 2-methyl-1-propanol					
298.15	0.1020	−273.9	0.4028	−836.0	0.7046	−716.7
	0.1987	−532.8	0.4944	−864.6	0.7994	−562.0
	0.2960	−718.9	0.5929	−811.9	0.9000	−335.6
	1-Bromo-2-methylpropane + 2-methyl-2-propanol					
298.15	0.1064	−1004.4	0.4076	−1661.6	0.7001	−1108.7
	0.2104	−1489.2	0.5005	−1555.7	0.7830	−857.4
	0.3043	−1659.4	0.5919	−1380.9	0.8974	−457.0
	1-Bromo-2-methylpropane + 1-butanol					
313.15	0.1067	−150.2	0.4058	−532.1	0.7037	−511.5
	0.2056	−300.2	0.5013	−572.0	0.7977	−408.1
	0.3012	−427.9	0.5989	−564.8	0.8888	−278.5
	1-Bromo-2-methylpropane + 2-butanol					
313.15	0.0998	−440.3	0.3990	−953.2	0.7010	−720.1
	0.1938	−724.1	0.4960	−938.7	0.8018	−538.5
	0.2971	−891.1	0.5939	−865.0	0.8984	−325.2
	1-Bromo-2-methylpropane + 2-methyl-1-propanol					
313.15	0.1020	−270.0	0.4028	−780.7	0.7046	−654.5
	0.1987	−516.1	0.4944	−796.1	0.7994	−503.6
	0.2960	−687.1	0.5929	−758.5	0.9000	−305.4
	1-Bromo-2-methylpropane + 2-methyl-2-propanol					
313.15	0.1064	−707.9	0.4076	−1190.4	0.7001	−827.3
	0.2104	−1044.8	0.5005	−1129.0	0.7830	−625.0
	0.3043	−1173.8	0.5919	−1018.8	0.8974	−360.2

Table V. Coefficients, A_i, in Eq. (4) and Standard Deviations, Determined by the Method of Least Squares

	A_0	A_1	A_2	A_3	A_4	σ
1-Bromo-2-methylpane + 1-butanol at 298.15 K						
V^E (cm^3 · mol^{-1}))	0.5334	0.2921	0.2205	0.0309		0.0015
η^E (cP)	−2.4150	0.8473	−0.1671	−0.2102		0.0009
G^{*E} (J · mol^{-1})	−2304.3	−576.5	65.1	−464.5		5.2
1-Bromo-2-methylpropane + 2-butanol at 298.15 K						
V^E (cm^3 · mol^{-1})	1.8070	0.3676	0.7658	0.2611		0.0031
η^E (P)	−3.7690	2.4691	−1.9633	0.9507		0.0034
G^{*E} (J · mol^{-1}	−4430.9	1268.5	−666.5	−495.3		6.4
1-Bromo-2-methylpropane + 2-methyl-1-propanol at 298.15 K						
V^E (cm^3 · mol^{-1})	1.1756	0.5770	−0.1180	0.1516		0.0022
η^E (cP)	−3.8891	2.1798	−0.9088	−0.2346		0.0057
G^{*E} (J · mol^{-1})	−3442.2	242.3	76.5	−1098.6		6.3
1-Bromo-2-methylpropane + 2-methyl-2-propanol at 298.15 K						
V^E (cm^3 · mol^{-1})	2.8959	−0.6583	1.2042	0.6693		0.0047
η^E (cP)	−6.6250	5.0423	−4.0250	5.1879	−4.1786	0.0120
G^{*E} (J · mol^{-1})	−6209.8	3156.0	−2420.3	662.1		5.2
1-Bromo-2-methylpropane + 1-butanol at 313.15 K						
V^E (cm^3 · mol^{-1})	1.0409	0.4671	0.6792	1.1398		0.0019
η^E (cP)	−1.5298	0.5184	−0.0414	−0.2521		0.0008
G^{*E} (J · mol^{-1})	−2279.3	−387.9	204.2	−637.6		5.2
1-Bromo-2-methylpropane + 2-butanol at 313.15 K						
V^E (cm^3 · mol^{-1})	2.3425	0.5150	0.8008	0.1525		0.0056
η^E (cP)	−1.9383	1.1535	−0.9253	0.4188		0.0025
G^{*E} (J · mol^{-1})	−3740.9	1082.5	−735.0	−313.2		5.0
1-Bromo-2-methylpropane + 2-methyl-1-propanol at 313.15 K						
V^E (cm^3 · mol^{-1})	1.1756	0.5770	−0.1180	0.1516		0.0022
η^E (cP)	−2.2113	1.1702	−0.4955	−0.1642		0.0038
G^{*E} (J · mol^{-1})	−3197.3	362.9	5.5	−932.5		6.2
1-Bromo-2-methylpropane + 2-methyl-2-propanol at 313.15 K						
V^E (cm^3 · mol^{-1})	3.2856	−0.4365	0.7815	0.3855		0.0060
η^E (cP)	−2.5730	1.7468	−1.2214	1.4134	−1.2853	0.0025
G^{*E} (J · mol^{-1})	−4499.9	2012.6	−1672.1	475.7		14.0

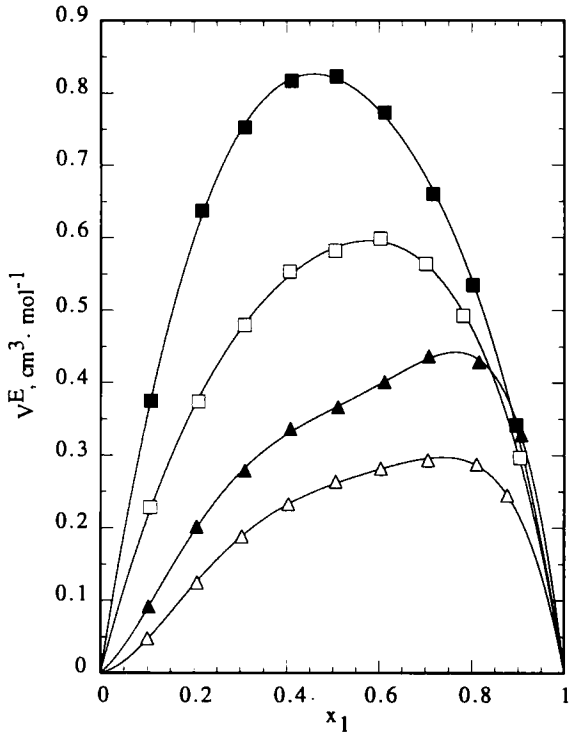

Fig. 2. Excess volumes, V^E, of 1-bromo-2-methylpropane (1) + a butanol (2) at 313.15 K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■).

Studies made in other works on the excess properties of mixtures containing isomers of butanol have shown that the prevailing effect is the breaking of the association due to hydrogen bonding in alkanols. When an OH group moves from a primary carbon atom to a secondary or tertiary one, the breaking of self-association occurs to a greater extent and their respective values (maximum for V^E, minimum for η^E or G^{*E}) are obtained smaller molar fractions in butanol for each case. Other effects with minor influence on the values of the excess properties are related to the breaking of the characteristic interactions of the pure component that is mixed with butanol and the formation of new interactions between the components of the mixture. In the case of mixtures with 1-bromo-2-methylpropane, besides the interaction Br–OH the conformational equilibrium of brominated compound must be taken into account as some authors have pointed out [10].

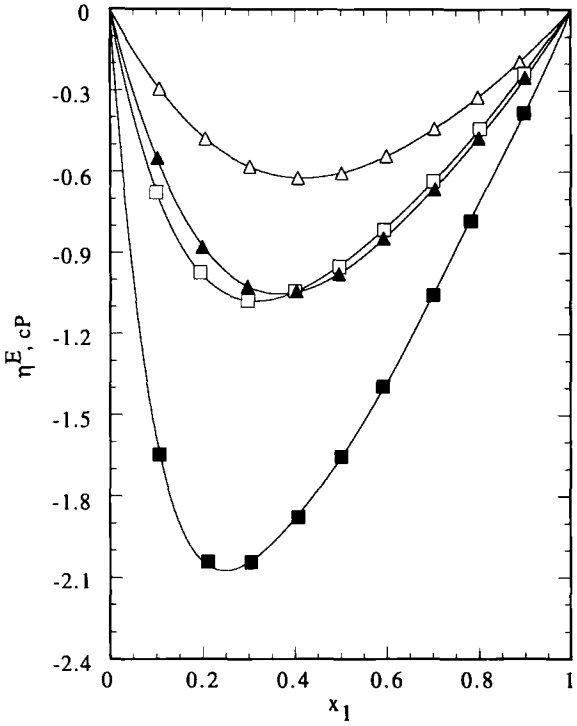

Fig. 3. Excess viscosities, η^E, of 1-bromo-2-methylpropane (1) + a butanol (2) at 298.15 K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■)

A comparisation between the results for V^E reported in this paper and those achieved for mixtures of the same alkanols with 1-bromobutane [2], that is, an isomer of 1-bromo-2-methylpropane and also carries the Br atom on a primary carbon, shows close similarities in both the values of the property and the molar fraction corresponding to the maxima. For both temperatures, the values secured with 1-bromo-2-methylpropane are slightly higher than the ones for 1-bromobutane, the greatest difference being observed for mixtures with 2-methyl-1-propanol. The only exception is the mixture with 1-butanol at 298.15 K whose V^E is a little lower. This could be explained considering that the structure of the branched brominated compound leads to a larger breaking than that caused by the linear brominated isomer. Moreover, an easier interstitial accommodation of 1-bromo-2-methylpropane in 1-butanol is expected because this alkanol has the greatest degree of association [11]. On the other hand, the present

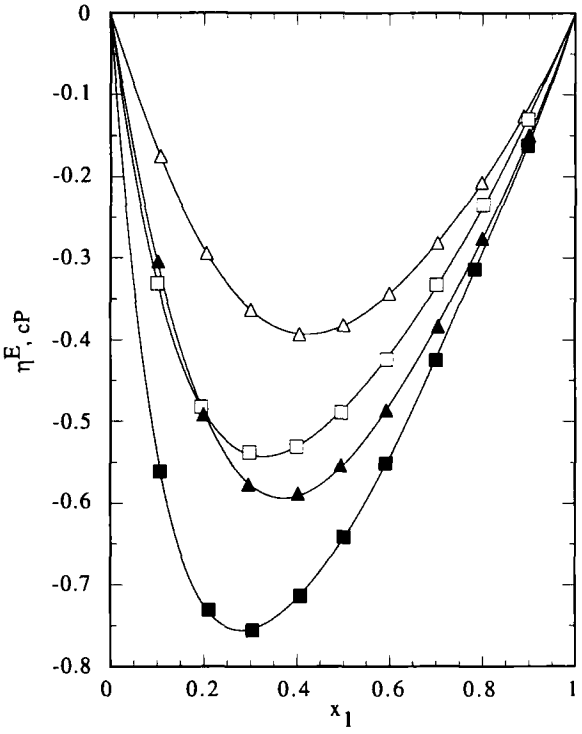

Fig. 4. Excess viscosities, η^E, of 1-bromo-2-methylpropane (1) + a butanol (2) at 313.15 K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■).

results are appreciably larger than those obtained if the butanols are mixed with another halogenated compound like 1-chlorobutane [1] suggesting that the greater size of bromine atom induces a larger breaking in the association of alcohols. With rising temperature the excess volume increases too. This behavior has been observed for other mixtures containing haloalkanes [3, 5–7].

With respect to the viscosity, we must emphasize that the values of η^E are strongly negative as was expected according to Fort and Moore [12] or Meyer et al. [13] and Nigam et al. [14] for G^{*E}. All these authors have stated that negative values in the mentioned properties are characteristic for systems in which dispersive forces like the rupture of the self-association in alkanols are prevailing. Pure butanols have high viscosities and the addition of the other component brings about the breaking of their structure, giving rise to a minor degree of association that facilitates the flow of the

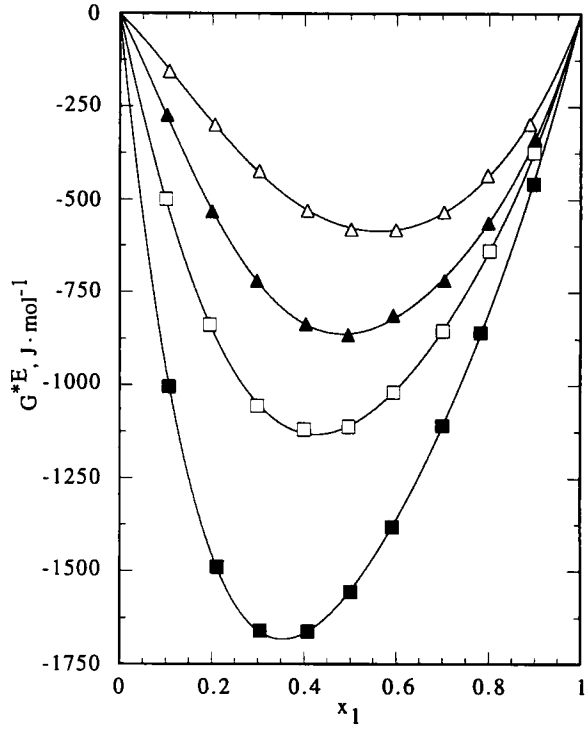

Fig. 5. Excess free energies of activation of flow, G^{*E}, of 1-bromo-2-methylpropane (1) + a butanol (2) at 298.15 K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■).

mixture, so a noticeable decrease in viscosity occurs and, consequently, the excess flow properties present negative values, the most negative being those corresponding to the mixtures with 2-methyl-2-propanol, while the mixtures with 1-butanol show the least negative ones.

The minima of η^E and G^{*E} shift toward regions richer in halogenated compound following the sequence:

2-methyl-2-propanol < 2-butanol < 2-methyl-1-propanol < 1-butanol

being very similar to the molar fractions for 2-methyl-1-propanol and 1-butanol for η^E. The values of minima increase in the same order.

When the temperature rises, the values of the excess flow properties become less negative, and the less their values at 298.15 K, the more pronounced is the increase. This phenomenon is especially remarkable in the case of excess viscosities of 2-butanol mixtures, whose values are higher

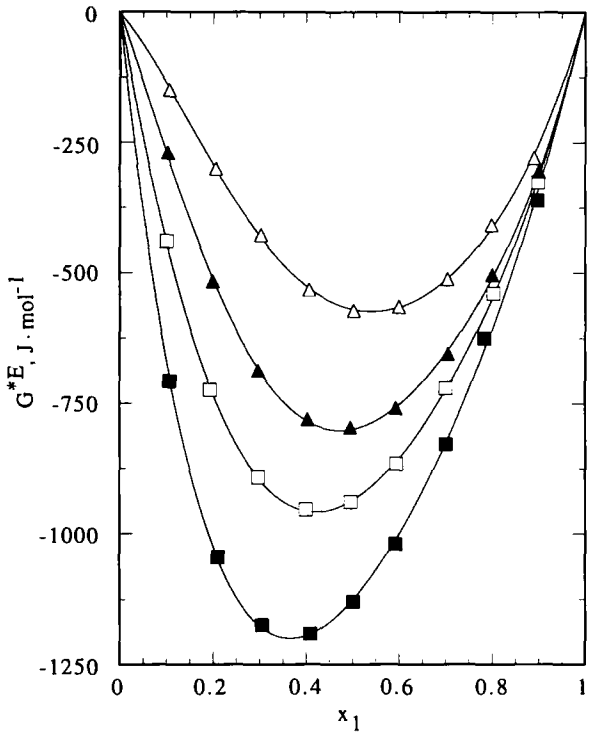

Fig. 6. Excess free energies of activation of flow, G^{*E}, of 1-bromo-2-methylpropane (1) + a butanol (2) at 313.15 K as a function of mole fraction x_1: 1-butanol (△); 2-butanol (□); 2-methyl-1-propanol (▲); 2-methyl-2-propanol (■).

than those of the mixture with 2-methyl-1-propanol. Then an inversion in the order of curves of η^E at 313.15 K can be observed with respect to the sequence at 298.15 K indicated above. The values of G^{*E} change in the same way: an increase in the temperature produces an increase in G^{*E}, a considerable increase (471 $J \cdot mol^{-1}$) in mixtures with 2-methyl-2-propanol, and a less significant one (10 $J \cdot mol^{-1}$) in mixtures with 1-butanol.

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