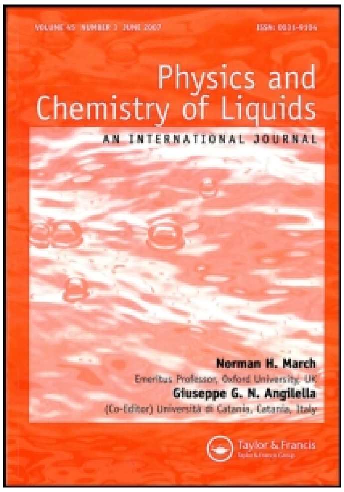

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Excess Volumes and Excess Viscosities of Binary Mixtures of an Halohydrocarbon With 1-Butanol at the Temperatures 298.15 and 313.15 K

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EXCESS VOLUMES AND EXCESS VISCOSITIES OF BINARY MIXTURES OF AN HALOHYDROCARBON WITH 1-BUTANOL AT THE TEMPERATURES 298.15 AND 313.15 K

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Excess volumes, excess viscosities and excess energies of activation for viscous flow have been determined at 298.15 K and 313.15 K by means of density and viscosity measurements for the binary mixtures of a halogenated (Br, Cl) benzene or cyclohexane with 1-butanol. The results show the influence of both the type of cyclic system and the halogen atom. At 298.15 K, the mixtures with aromatic derivatives present negative values of V^E in a wide composition range mainly corresponding to the zone rich in 1-butanol. This region diminishes at 313.15 K. The values for η^E and G^{*E} are negative for all mixtures at two temperatures.

Keywords: Binary mixtures; bromobenzene; bromocyclohexane; chlorobenzene; chlorocyclohexane; 1-butanol

INTRODUCTION

Previous papers have been concerned with the systematic study of excess thermodynamic and excess flow properties for binary mixtures involving associated organic liquids together with several halocompounds [1–3]. In this work, we present the values of V^E, η^E and G^{*E} obtained at 298.15 and 313.15 K for the mixtures (chlorobenzene or chlorocyclohexane or

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bromobenzene or bromocyclohexane) with 1-butanol, in order to show the effect of both the change from cyclic alkane to analogous aromatic and the substitution from one to another halogen atom (chlorine or bromine) on the association in the mixtures.

EXPERIMENTAL

The pure components used were: 1-butanol (better than 99.8 mol %) and chlorocyclohexane (better than 99 mol %) provided by Aldrich, chlorobenzene, bromobenzene (both better than 99.5 mol %), and bromocyclohexane (better than 99 mol %) provided by Fluka. The purity of the chemicals was checked by GLC chromatography and no further purification was considered necessary. The pure components were stored over activated molecular sieve.

Table I shows the experimental values of density and viscosity for the pure components compared with literature data [4, 5]. Density measurements were carried out by means of an Anton Paar DMA-58 vibrating tube densimeter. Viscosities were obtained with a Schott-Geräte automatic measuring model AVS-440 connected with an Ubbelhode viscosimeter. The procedure has been previously described [6].

RESULTS AND DISCUSSION

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

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

TABLE I Densities ρ, and viscosities η, of pure compounds at $T = 298.15$ K and comparison with literature data [4, 5].

Component	$\rho/g\ cm^{-3}$		η/cP	
	Lit.[4]	*This paper*	*Lit.*	*This paper*
Chlorobenzene	1.1009	1.10100	0.7530[5]	0.7519
Chlorocyclohexane	–	0.99323	–	1.5600
Bromobenzene	1.48820	1.48818	1.074[5]	1.0715
Bromocyclohexane	–	1.32796	–	2.0441
1-Butanol	0.8060	0.80568	2.571[4]	2.5702

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

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

where ρ, ρ_1 and ρ_2 are the densities (g.cm^{-3}) of the mixture and of the pure components, respectively; in the same way, η, η_1 and η_2 are the absolute viscosities (*cP*) of the mixture and of the pure components while V, V_1 and V_2 are the molar volumes (cm^3·mol^{-1}) of the mixture and of the pure components; x_i is the mole fraction of component i in the mixture. Subscript 1 corresponds to the halocompound and 2 to the 1-butanol.

The experimental values of excess functions for the mixtures at their correspondent temperatures are given in Tables II–IV. They are also represented in Figures 1–6.

The values of V^E, η^E and G^{*E} at each temperature were fitted to a Redlich-Kister type equation by the least squares method:

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

where a_i are adjustable parameters. The values of the parameters a_i together with the standard deviations $\sigma(Y^E)$ are gathered in Table V.

From the results of excess volumes obtained, it can be immediately seen that mixtures containing aromatic halocompounds show smaller values than those containing the corresponding cyclohexane derivative. In this way, at 298.15 K the mixtures containing halocyclohexane have positive V^E values over the entire composition range (except the slightly negative values for the mixture chlorocyclohexane + 1-butanol in the region richest in alkanol) while V^E is negative until the molar fraction $x_1 = 0.6$ for mixtures with chlorobenzene and bromobenzene at the same temperature. When the temperature rises, the V^E values become more positive although the negative values subsist for the mixtures with aromatic derivatives in a more restricted zone (until $x_1 = 0.2$).

On the other side, the values are very similar for the mixtures with chlorocyclohexane and bromocyclohexane at both temperatures while the extreme points are more accentuated for the mixtures containing chlorobenzene than they are for the ones containing bromobenzene.

Referring to the results provided by the viscosity measurements it can be observed that η^E and G^{*E} are negative over the whole composition range for all the mixtures at both temperatures. Values of η^E are

TABLE II Excess volumes V^E of binary mixtures halohydrocarbon (1) + 1-butanol (2) at indicated temperature.

x_1	$V^E/cm^3\ mol^{-1}$	x_1	$V^E/cm^3\ mol^{-1}$	x_1	$V^E/cm^3\ mol^{-1}$
Chlorobenzene + 1-butanol at 298.15 K					
0.1057	−0.0951	0.4107	−0.1066	0.7044	0.0021
0.2110	−0.1282	0.5046	−0.0770	0.7991	0.0366
0.3066	−0.1281	0.5998	−0.0410	0.8954	0.0469
Chlorocyclohexane + 1-butanol at 298.15 K					
0.1120	−0.0053	0.4091	0.0937	0.7006	0.1495
0.2031	0.0206	0.5012	0.1200	0.8045	0.1441
0.3108	0.0607	0.6039	0.1403	0.9022	0.1080
Bromobenzene + 1-butanol at 298.15 K					
0.1093	−0.1043	0.4052	−0.1392	0.7039	0.0025
0.2073	−0.1459	0.5049	−0.1057	0.8265	0.0618
0.3071	−0.1522	0.6029	−0.0557	0.9017	0.0703
Bromocyclohexane + 1-butanol at 298.15 K					
0.0978	0.0167	0.4010	0.0745	0.6963	0.1359
0.2128	0.0380	0.4957	0.0927	0.8039	0.1373
0.3057	0.0572	0.6032	0.1173	0.8903	0.1127
Chlorobenzene + 1-butanol at 313.15 K					
0.1071	−0.0772	0.4076	−0.0504	0.7034	0.0603
0.2045	−0.0927	0.5027	−0.0177	0.8044	0.0841
0.3092	−0.0798	0.6033	0.0231	0.8971	0.0778
Chlorocyclohexane + 1-butanol at 313.15 K					
0.1041	0.0252	0.4151	0.1556	0.7062	0.2285
0.2058	0.0646	0.4998	0.1884	0.8061	0.2136
0.3065	0.1128	0.6073	0.2137	0.9004	0.1498
Bromobenzene + 1-butanol at 313.15 K					
0.1030	−0.0553	0.4061	−0.0378	0.7032	0.1014
0.2059	−0.0817	0.5034	0.0145	0.7997	0.1041
0.3019	−0.0741	0.5967	0.0642	0.9096	0.0667
Bromocyclohexane + 1-butanol at 313.15 K					
0.1030	0.0284	0.4066	0.1500	0.6960	0.2109
0.2082	0.0755	0.4980	0.1730	0.7943	0.2164
0.3078	0.1184	0.5919	0.1924	0.8891	0.1757

very similar for three of the mixtures and differ for the one containing chlorobenzene that shows bigger absolute values. As the temperature increases, bigger values are obtained being less noticeable the differences between the mixtures with chlorobenzene and the rest.

TABLE III Excess viscosites η^E of binary mixtures halohydrocarbon (1) + 1-butanol (2) at indicated temperature.

x_1	η^E/cP	x_1	η^E/cP	x_1	η^E/cP
Chlorobenzene + 1-butanol at 298.15 K					
0.0994	−0.2279	0.4044	−0.5622	0.7033	−0.4124
0.2022	−0.4096	0.5062	−0.5485	0.7704	−0.3389
0.3004	−0.5163	0.6010	−0.4960	0.8960	−0.1730
Chlorocyclohexane + 1-butanol at 298.15 K					
0.1049	−0.2149	0.4058	−0.4852	0.7058	−0.3970
0.2062	−0.3579	0.5062	−04895	0.8082	−0.3105
0.3144	−0.4543	0.6073	−0.4570	0.9024	−0.1844
Bromobenzene + 1-butanol at 298.15 K					
0.1006	−0.1601	0.3944	−0.4761	0.6983	−0.3798
0.1994	−0.3158	0.4961	−0.4811	0.7966	−0.2879
0.3003	−0.4253	0.6003	−0.4365	0.8960	−0.1657
Bromocyclohexane + 1-butanol at 298.15 K					
0.1003	−0.1836	0.3997	−0.4579	0.7028	−0.4028
0.2011	−0.3212	0.5003	−0.4698	0.8051	−0.3232
0.3037	−0.4131	0.5964	−0.4522	0.9063	−0.1992
Chlorobenzene + 1-butanol at 313.15 K					
0.0994	−0.1614	0.4044	−0.3605	0.7033	−0.2645
0.2022	−0.2721	0.5062	−0.3503	0.7704	−0.2185
0.3004	−0.3337	0.6010	−0.3151	0.8960	−0.1144
Chlorocyclohexane + 1-butanol at 313.15 K					
0.1049	−0.1440	0.4058	−0.3229	0.7058	−0.2674
0.2062	−0.2457	0.5062	−0.3247	0.8082	−0.2149
0.3144	−0.3008	0.6073	−0.3032	0.9024	−0.1325
Bromobenzene + 1-butanol at 313.15 K					
0.1006	−0.1168	0.3944	−0.3056	0.6983	−0.2467
0.1994	−0.2140	0.4961	−0.3065	0.7966	−0.1867
0.3003	−0.2787	0.6003	−0.2834	0.8960	−0.1168
Bromocyclohexane + 1-butanol at 313.15 K					
0.1003	−0.1393	0.3997	−0.3183	0.7028	−0.2830
0.2011	−0.2298	0.5003	−0.3255	0.8051	−0.2306
0.3037	−0.2874	0.5964	−0.3137	0.9063	−0.1381

With regard to G^{*E}, the values for the chlorinated derivatives are more negative than those for the brominated compounds. Anyway, the changes with the temperature are not significant. The minima of both excess properties, namely η^E and G^{*E}, appear very centred (x_1

TABLE IV Excess energies of activation for viscous flow G^{*E} of binary mixtures halohydrocarbon (1) + 1-butanol (2) at indicated temperature.

x_1	$G^{*E}/J\ mol^{-1}$	x_1	$G^{*E}/J\ mol^{-1}$	x_1	$G^{*E}/J\ mol^{-1}$
Chlorobenzene + 1-butanol at 298.15 K					
0.0994	−127.4	0.4044	−509.1	0.7033	−513.4
0.2022	−277.5	0.5062	−556.6	0.7704	−449.6
0.3004	−406.9	0.6010	−552.4	0.8960	−261.8
Chlorocyclohexane + 1-butanol at 298.15 K					
0.1049	−192.3	0.4058	−535.8	0.7058	−507.5
0.2062	−346.4	0.5062	−572.3	0.8082	−414.5
0.3144	−475.6	0.6073	−560.6	0.9024	−251.8
Bromobenzene + 1-butanol at 298.15 K					
0.1006	−101.8	0.3944	−472.1	0.6983	−487.1
0.1994	−244.7	0.4961	−524.8	0.7966	−397.1
0.3003	−379.6	0.6003	−512.2	0.8960	−244.5
Bromocyclohexane + 1-butanol at 298.15 K					
0.1003	−171.7	0.3997	−492.2	0.7028	−463.3
0.2011	−317.6	0.5003	−520.1	0.8051	−375.3
0.3037	−428.6	0.5964	−511.4	0.9063	−231.6
Chlorobenzene + 1-butanol at 313.15 K					
0.0994	−171.6	0.4044	−532.0	0.7033	−502.9
0.2022	−324.6	0.5062	−565.3	0.7704	−438.2
0.3004	−442.3	0.6010	−545.1	0.8960	−258.5
Chlorocyclohexane + 1-butanol at 313.15 K					
0.1049	−202.6	0.4058	−540.3	0.7058	−498.3
0.2062	−371.8	0.5062	−566.8	0.8082	−414.1
0.3144	−481.8	0.6073	−547.8	0.9024	−259.2
Bromobenzene + 1-butanol at 313.15 K					
0.1006	−139.5	0.3944	−485.1	0.6983	−476.5
0.1994	−287.1	0.4961	−521.1	0.7966	−379.2
0.3003	−411.4	0.6003	−513.6	0.8960	−256.7
Bromocyclohexane + 1-butanol at 313.15 K					
0.1003	−202.7	0.3997	−506.8	0.7028	−463.4
0.2011	−347.1	0.5003	−526.2	0.8051	−376.6
0.3037	−447.3	0.5964	−511.5	0.9063	−221.6

approximately 0.5) moving slightly toward regions richer in 1-butanol in the case of excess viscosity for the mixtures with chlorobenzene.

The values of these excess properties depend basically on structural effects and on the molecular forces operating between solvent and solute

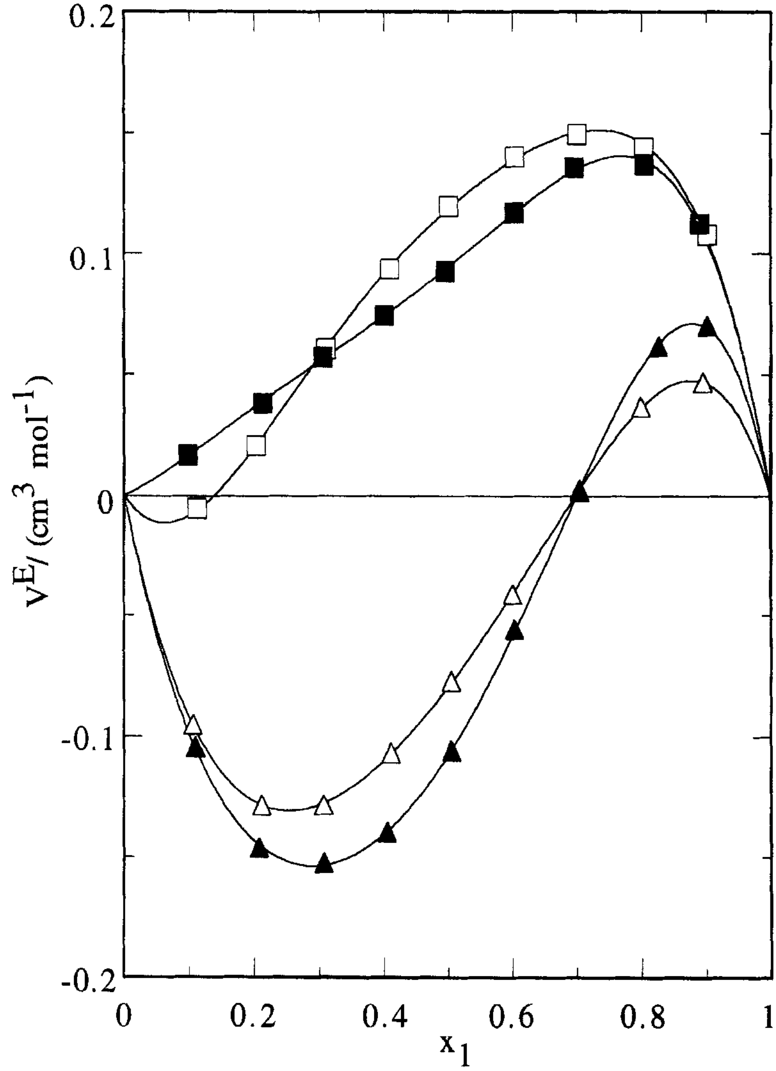

FIGURE 1 Excess volumes, V^E, of halohydrocarbon (1) + 1-butanol (2) at 298.15 K as a function of mole fraction x_1: chlorobenzene (△); chlorocyclohexane (□); bromobenzene (▲); bromocyclohexane (■).

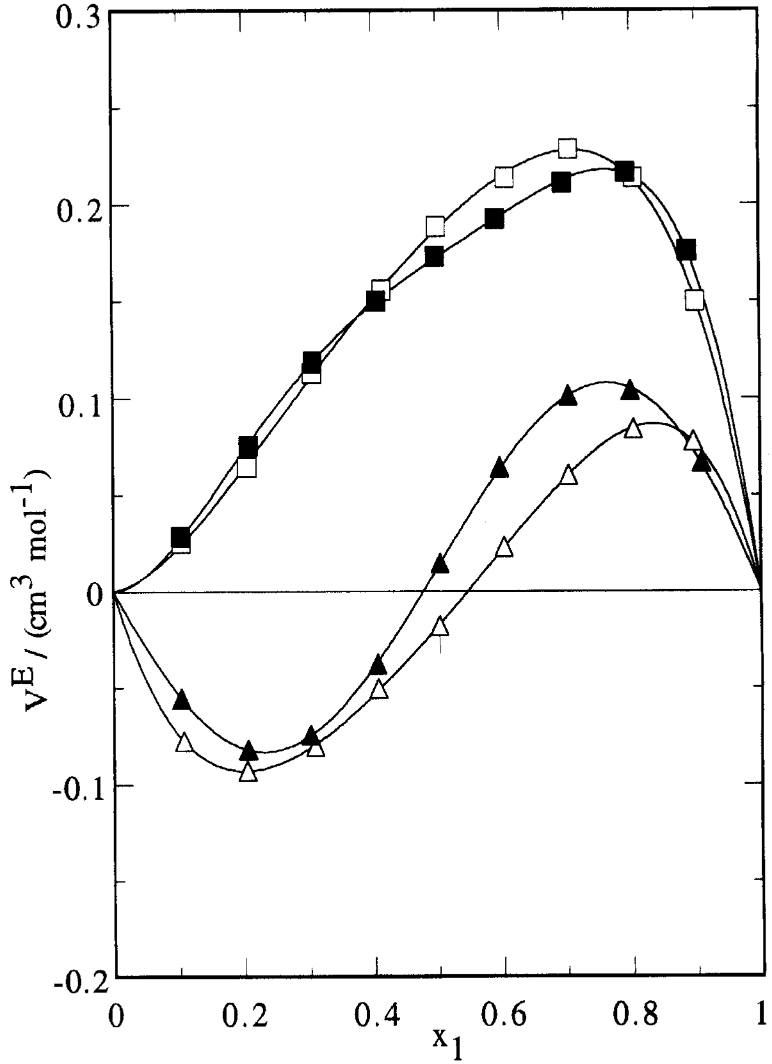

FIGURE 2 Excess volumes, V^E, of halohydrocarbon (1) + 1-butanol (2) at (313.15) K as a function of mole fraction x_1: chlorobenzene (△); chlorocyclohexane (□); bromobenzene (▲); bromocyclohexane (■).

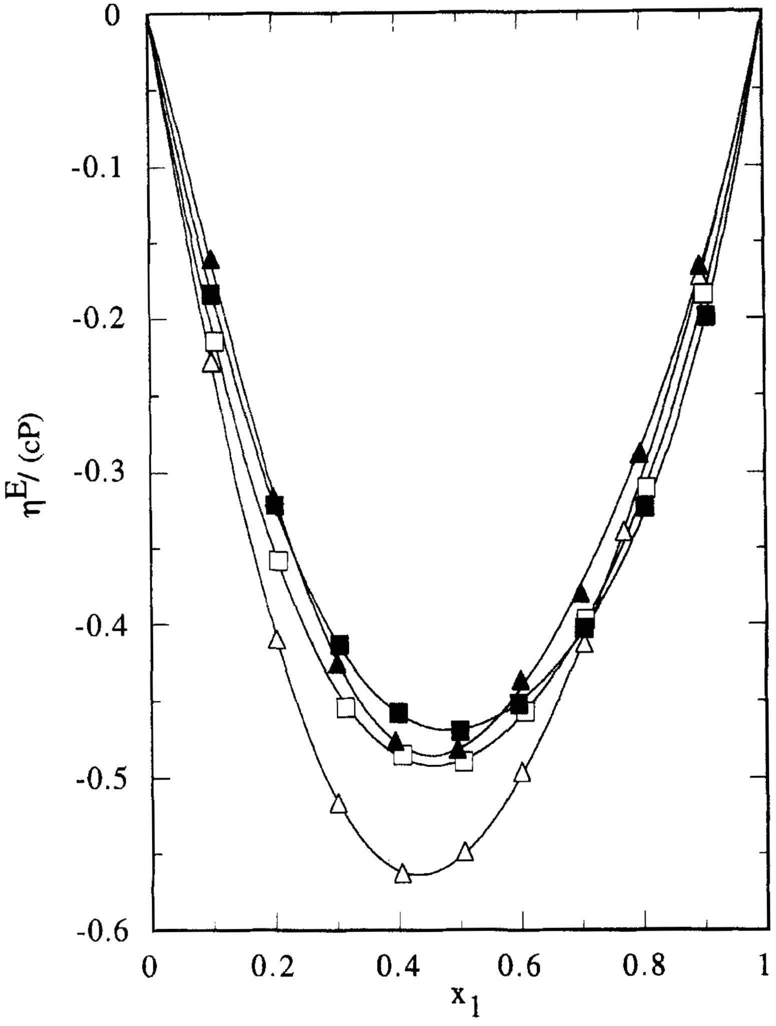

FIGURE 3 Excess viscosities, η^E, halohydrocarbon (1) + 1-butanol (2) at 298.15 K as a function of mole fraction x_1: chlorobenzene (△); chlorocyclohexane (□); bromobenzene (▲); bromocyclohexane (■).

in the mixing process. In our case, the breaking of the association of 1-butanol is the main effect that leads to positive values of V^E and negative values of η^E and G^{*E}. However, two specific interactions contribute in an opposite way: 1) the interaction between the π-electronic

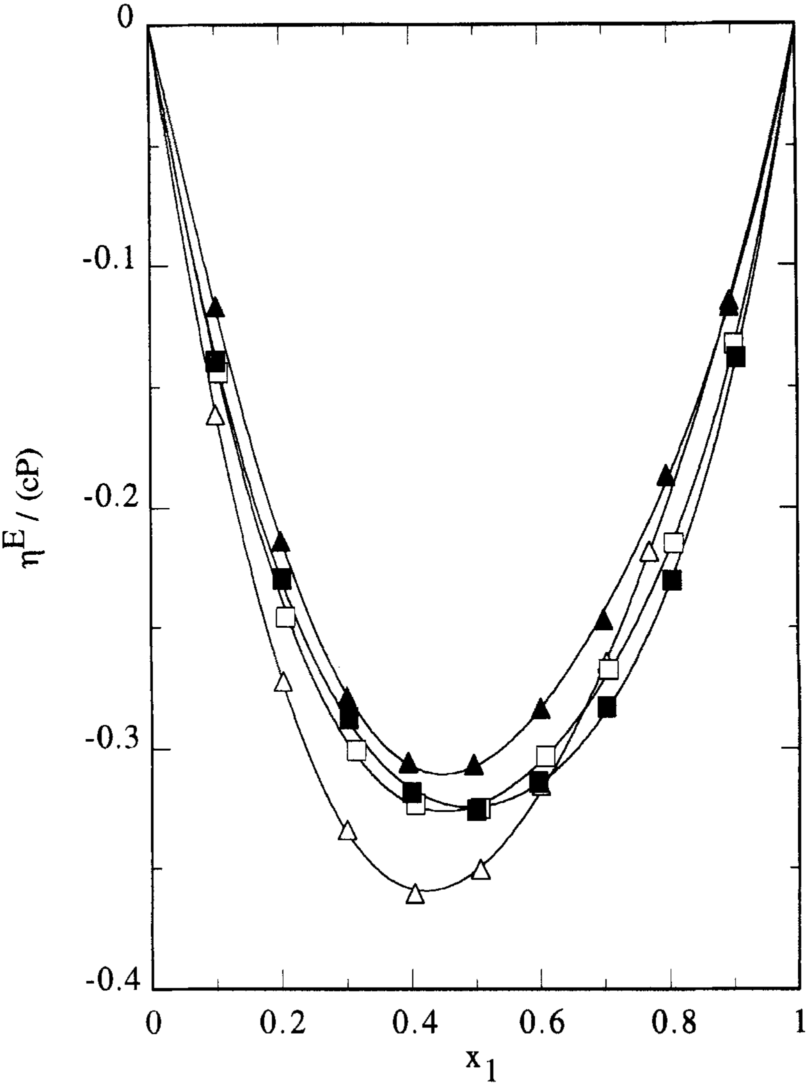

FIGURE 4 Excess viscosities, η^E, of halohydrocarbon (1) + 1-butanol (2) at 313.15 K as a function of mole fraction x_1: chlorobenzene (△); chlorocyclohexane (□); bromobenzene (▲); bromocyclohexane (■).

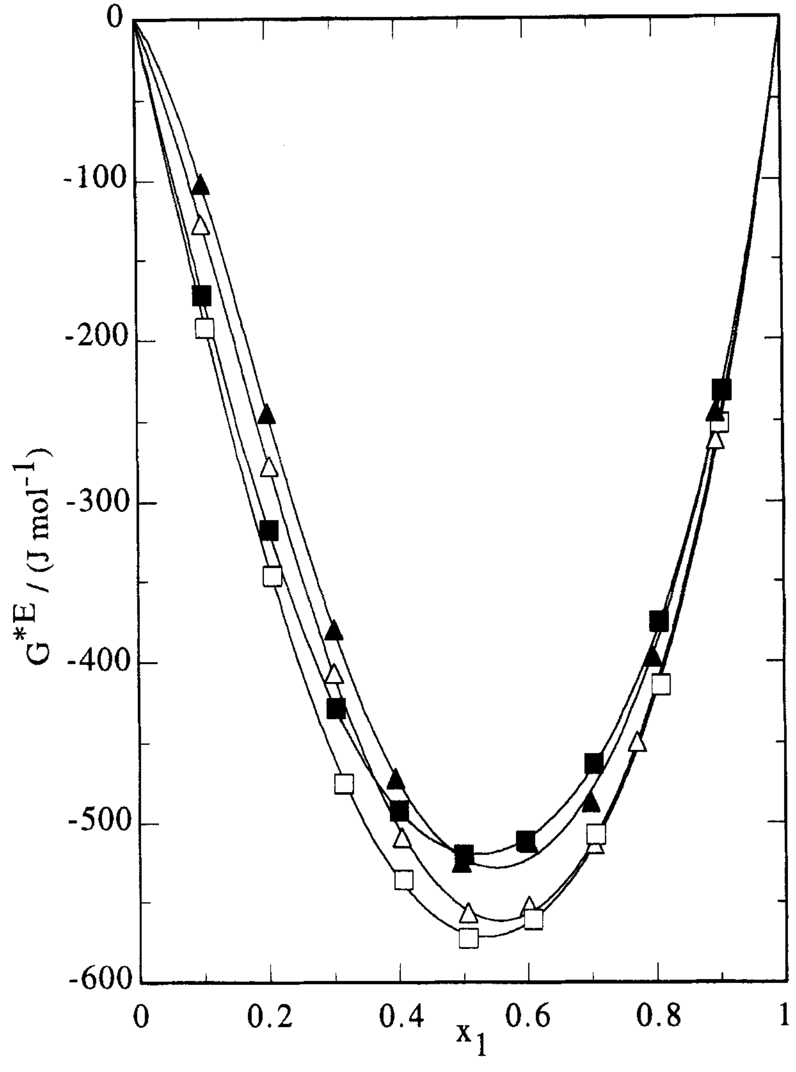

FIGURE 5 Excess energies of activation for viscous flow, G^{*E}, of halohydrocarbon (1) + 1-butanol (2) at 298.15 K as a function of mole fraction x_1: chlorobenzene (△); chlorocyclohexane (□); bromobenzene (▲); bromocyclohexane (■).

cloud of the aromatic ring and the OH group described by Stokes [7], and 2) the interaction of the halogen atom with the OH group, interaction that other authors have pointed out [8,9] when they have compared

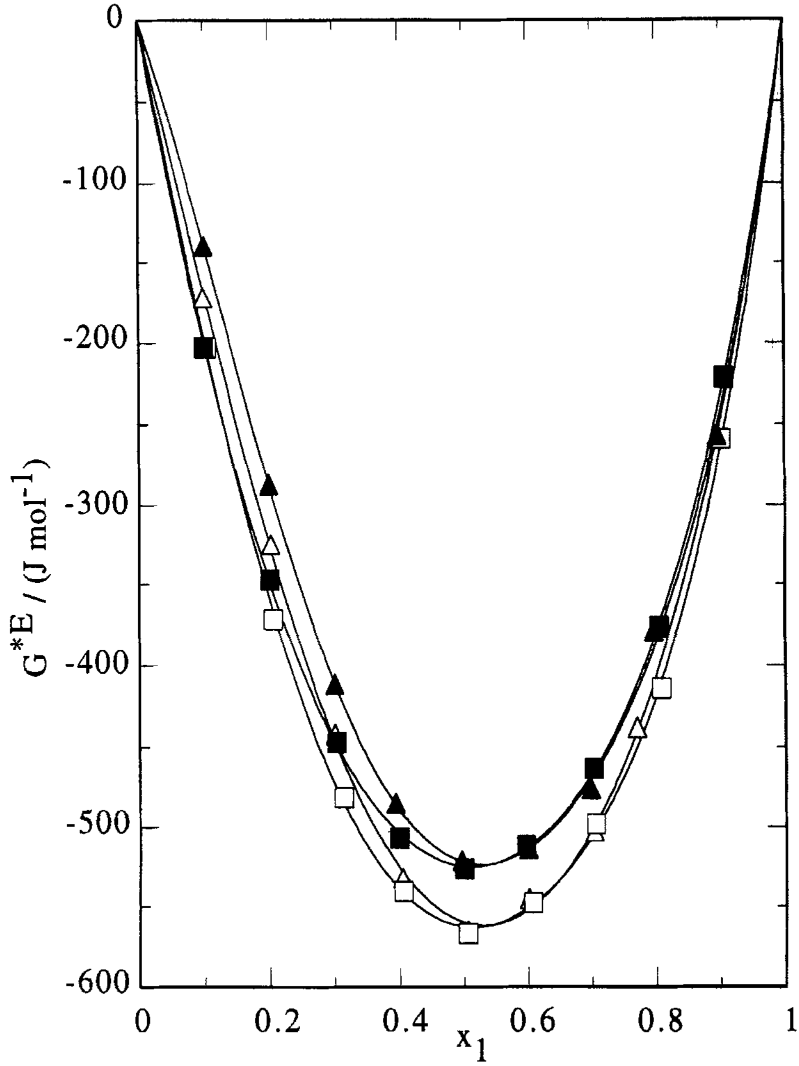

FIGURE 6 Excess energies of activation for viscous flow, G^{*E}, of halohydrocarbon (1) + 1-butanol (2) at 313.15 K as a function of mole fraction x_1: chlorobenzene (△); chlorocyclohexane (□); bromobenzene (▲); bromocyclohexane (■).

TABLE V Coefficients a_i of equation (4) and standard deviations determined by the method of least squares.

Function	a_0	a_1	a_2	a_3	σ
Chlorobenzene + 1-butanol at 298.15 K					
V^E/cm^3 mol^{-1}	−0.3174	0.7034	0.0971	0.4054	0.0007
η^E/cP	−2.2073	0.6665	−0.0198	−0.3703	0.0020
G^{*E}/J mol^{-1}	−2215.4	−536.5	153.7	−540.8	2.9
Chlorocyclohexane + 1-butanol at 298.15 K					
V^E/cm^3 mol^{-1}	0.4747	0.4705	0.1231	0.5231	0.0013
η^E/cP	−1.9561	0.2802	−0.3728	−0.2624	0.0023
G^{*E}/J mol^{-1}	−2276.4	−268.4	−277.3	−411.1	3.7
Bromobenzene + 1-butanol at 298.15 K					
V^E/cm^3 mol^{-1}	−0.4299	0.8308	0.4150	0.5317	0.0011
η^E/cP	−1.9235	0.4021	0.1667	−0.6499	0.0044
G^{*E}/J mol^{-1}	−2090.1	−470.3	286.4	−782.9	6.3
Bromocyclohexane + 1-butanol at 298.15 K					
V^E/cm^3 mol^{-1}	0.3779	0.4283	0.4754	0.2997	0.0012
η^E/cP	−1.8743	0.1063	−0.4436	−0.4366	0.0019
G^{*E}/J mol^{-1}	−2074.5	−151.5	−317.9	−534.3	2.2
Chlorobenzene + 1-butanol at 313.15 K					
V^E/cm^3 mol^{-1}	−0.0726	0.7635	0.1274	0.4428	0.0008
η^E/cP	−1.4026	0.4321	−0.1648	−0.1251	0.0016
G^{*E}/J mol^{-1}	−2239.4	−258.9	−122.6	−469.1	5.4
Chlorocyclohexane + 1-butanol at 313.15 K					
V^E/cm^3 mol^{-1}	0.7465	0.6491	0.3428	0.3784	0.0018
η^E/cP	−1.2942	0.1954	−0.3704	−0.2624	0.0022
G^{*E}/J mol^{-1}	−2250.5	−96.5	−498.6	−610.5	4.5
Bromobenzene + 1-butanol at 313.15 K					
V^E/cm^3 mol^{-1}	0.0498	1.1039	0.0707	−0.3680	0.0009
η^E/cP	−1.2280	0.2626	−0.0716	−0.3534	0.0022
G^{*E}/J mol^{-1}	−2087.4	−220.7	−49.7	−797.8	6.0
Bromocyclohexane + 1-butanol at 313.15 K					
V^E/cm^3 mol^{-1}	0.6892	0.4465	0.5856	0.8196	0.0012
η^E/cP	−1.2967	0.0352	−0.4227	−0.1409	0.0018
G^{*E}/J mol^{-1}	−2098.0	−79.2	−487.7	−249.0	2.9

the values of excess thermodynamic properties of the mixtures with the halogenated derivative with those of systems with the corresponding nonhalogenated compound, and that can be observed comparing the presented results with those obtained for the cyclohexane [10].

The obtained V^E values seems to indicate that the plain structure of the aromatic compounds causes a smaller breaking of association in 1-butanol than the steric arrangement of the cyclohexane derivatives. Besides, if we take the π-OH interaction into account the values for the mixtures with chloro and bromobenzene will be prevailingly negative although not very different from zero. When the chlorine atom is substituted with a bromine one, no remarkable changes can be observed, although the slight negative value of the mixture with chlorocyclohexane at 298.15 K could be attributed to the minor size of chlorine that would lead to a smaller breaking.

It has been stated above that breaking of the association in the alkanol yields negative η^E. This effect is the main which works in relation with this property. Effectively, some authors [11–13] have pointed out that negative values of η^E and G^{*E} are characteristic of mixtures in which the dispersion forces, like the disruption of hydrogen bonds of 1-butanol, are predominant.

According with the data of pure compounds the aromatic rings flow better than the cycloalkylic ones and the chlorinated derivatives faster than the brominated. The superposition of both effects would be important enough to explain the smaller values of η^E for the mixture containing chlorobenzene while the overall result of both structural and interaction factors would cause the similarity of η^E for the other systems.

The possibility of a greater strength of the Br-OH bond compared with the Cl-OH one cited [3] in relation to the excess compressibility for similar mixtures seems to have no significant effect this time.

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