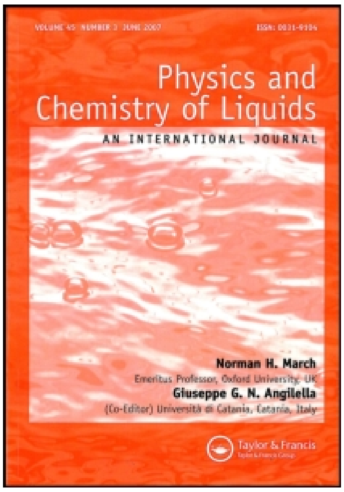

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EXCESS VOLUMES AND EXCESS VISCOSITIES OF BINARY MIXTURES OF 2-CHLOROBUTANE WITH ISOMERIC BUTANOLS AT 298.15 K

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This paper reports excess volumes and excess viscosities for binary mixtures of 2-chlorobutane with isomeric butanols at 298.15 K. Excess properties were correlated by means of a Redlich-Kister type equation. A qualitative interpretation of the results in terms of OH-OH and Cl-OH interactions is presented. The Prigogine-Flory-Patterson and Blomfield-Dewan theories have been used to analyze the results. Experimental isentropic compressibilities are also reported.

KEY WORDS: Excess volumes, excess viscosities, 2-chlorobutane, isomeric butanols, binary mixtures, PFP theory, BD theory.

INTRODUCTION

Following our research program on thermodynamic and transport properties of binary mixtures containing a chloroalkane[1-6], here we present excess volumes and excess viscosities of binary mixtures of 2-chlorobutane with isomeric butanols.

A knowledge of the excess volumes and excess viscosities is fundamental in the understanding of molecular interactions, the working-out of new theoretical models and several industrial applications. With regard to the molecular interactions we carried out a qualitative study of the influence of hydrogen bonding in butanols as with the Cl-OH interactions. From a quantitative point of view we have applied the Prigogine-Flory-Patterson and Bloomfield-Dewan theories to the experimental data.

EXPERIMENTAL

The liquids used, 1-butanol (better than 99.8 mol %), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol %), and 2-butanol and 2-chorobutane (better than 99 mol %) were obtained from Aldrich.

The purity of chemicals has been checked by GLC using a semicapillary methyl silicone column (o.d. 530 μm) and a flame ionization detector. The analysis showed that the major peak area exceeds 99.8%. All isomeric butanols were dried over activated molecular sieves type 0.3 nm from Merk.

Densities of pure components and mixtures were measured using an Anton Paar DMA-58 vibrating tube densitimeter. The densitimeter was calibrated with deionized double distilled water and dry air. The uncertainty of the density measurements was $\pm 1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$. Viscosities were measured with an Ubbelhode viscosimeter with a Scott-Geräte automatic measuring unit model AVS-440. Calibration was carried out with deionized doubly-distilled water. Kinetic energy corrections were applied to the experimental data. The estimated error was $\pm 1 \times 10^{-4}$ cP. Mole fractions were determined directly by weighing.

Table 1 shows the experimental values of density and viscosity for the pure components at 298.15 K, compared with the published values[7,8]. These results agree reasonably well with the values given in literature.

Excess volumes V^E and excess viscosities η^E can be computed from experimental data of density and viscosity, and composition using the following relations:

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

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

where M_i, ρ_i, η_i and x_i designate the molar mass, density, viscosity and the mole fraction of component i. Quantities without subscript refer to the mixture.

RESULTS AND DISCUSSION

The obtained V^E and η^E values are presented in Tables 2 and 3 and plotted in Figures 1 and 2. The results were fitted to a Redlich-Kister type equation.

$$Y^E = x_1(1 - x_1)\sum a_i(2x_1 - 1)^i \tag{3}$$

where a_i is the coefficient for order i obtained from the least square fit of the values presented in Tables 2 and 3. The coefficients a_i are listed in Table 4 along with the

Table 1 Densities, ρ, and viscosities, η, of pure components at 298.15 K and comparison with literature data.

Component	$\rho/g\,cm^{-3}$		η/cp	
	this paper	*lit.*	*this paper*	*lit.*
2-chlorobutane	0.86743	0.8671[a]	0.3981	–
1-butanol	0.80575	0.80575	2.550	2.5710
2-butanol	0.80241	0.80241	3.084	2.998
2-methyl-1-propanol	0.79784	0.7978	3.363	3.330
2-methyl-2-propanol	0.78100	0.7812	4.394	4.438

[a] Ref. 8

Table 2 Excess volumes V^E of binary mixtures 2-chlorobutane(1) + isomeric butanols(2) at 298.15 K.

x_1	$V^E/cm^3\,mol^{-1}$	x_1	$V^E/cm^3\,mol^{-1}$	x_1	$V^E/cm^3\,mol^{-1}$
2-chlorobutane(1) + 1-butanol(2)					
0.1047	−0.0404	0.4036	−0.0309	0.6950	0.0555
0.2014	−0.0520	0.4954	−0.0047	0.7975	0.0635
0.3100	−0.0521	0.6210	0.0332	0.8642	0.0563
2-chlorobutane(1) + 2-butanol(2)					
0.1066	0.0902	0.4116	0.3167	0.7113	0.3505
0.2070	0.1735	0.5136	0.3512	0.8086	0.3016
0.3096	0.2530	0.6461	0.3673	0.8980	0.1956
2-chlorobutane(1) + 2-methyl-1-propanol(2)					
0.1064	0.0001	0.4109	0.0768	0.7276	0.1393
0.1565	0.0019	0.5196	0.1086	0.8078	0.1229
0.3124	0.0408	0.6280	0.1319	0.8606	0.1091
2-chlorobutane(1) + 2-methyl-2-propanol(2)					
0.1095	0.2950	0.4114	0.6619	0.7104	0.5997
0.2131	0.4991	0.5006	0.6811	0.8131	0.4780
0.3446	0.6347	0.6129	0.6618	0.9064	0.3031

Table 3 Excess viscosites η^E of binary mixtures 2-chlorobutane(1) + isomeric butanols(2) at 298.15 K.

x_1	η^E/cP	x_1	η^E/cP	x_1	η^E/cP
2-chlorobutane(1) + 1-butanol(2)					
0.0923	−0.3532	0.3997	−0.7062	0.7062	−0.4835
0.2012	−0.5792	0.4990	−0.6929	0.7976	−0.3516
0.3028	−0.6903	0.6032	−0.6038	0.9029	−0.1807
2-chlorobutane(1) + 2-butanol(2)					
0.1029	−0.7829	0.4027	−1.1899	0.7035	−0.6926
0.2048	−1.1674	0.5030	−1.0623	0.8032	−0.4754
0.3034	−1.2242	0.6049	−0.8891	0.9161	−0.2125
2-chlorobutane(1) + 2-methyl-1-propanol(2)					
0.0990	−0.6686	0.4075	−1.1836	0.7058	−0.7226
0.2002	−1.0436	0.5051	−1.0877	0.8104	−0.4861
0.3053	−1.2019	0.6091	−0.9201	0.9108	−0.2406
2-chlorobutane(1) + 2-methyl-2-propanol(2)					
0.1018	−1.7393	0.4187	−1.9357	0.7176	−1.0325
0.2213	−2.1590	0.5154	−1.6735	0.8155	−0.6885
0.3134	−2.1205	0.6189	−1.3541	0.9176	−0.3146

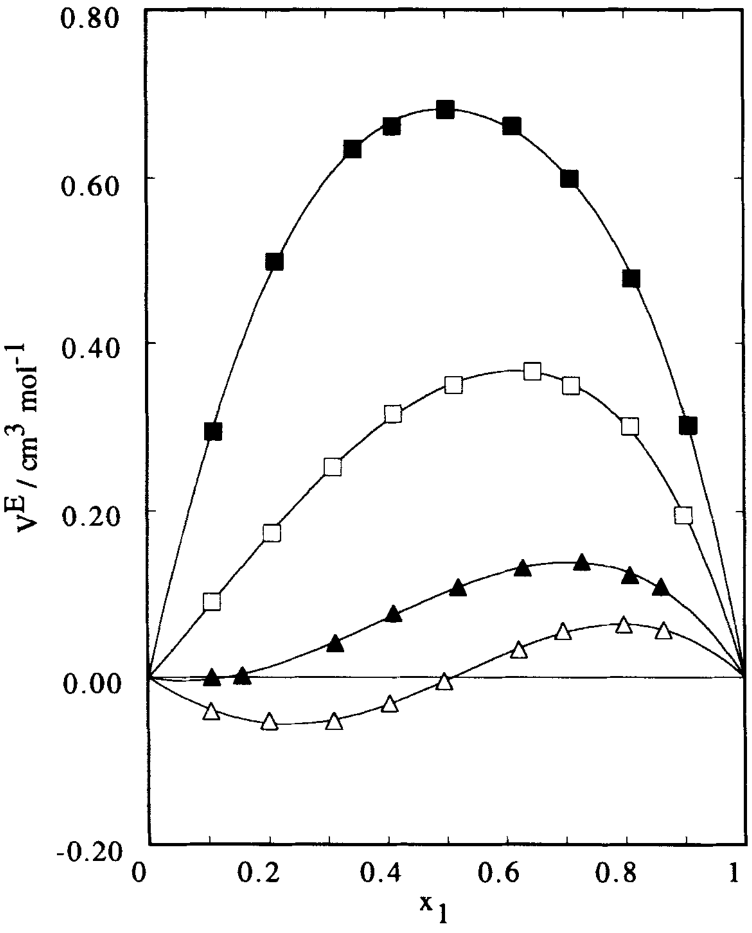

Figure 1 Excess volumes, V^E, of 2-chlorobutane(1) + an isomeric butanol(2) at 298.15 K as a function of mole fraction x_1: (△) 1-butanol; (□) 2-butanol; (▲) 2-methyl-1-propanol; (■) 2-methyl-2-propanol.

standard deviations $\sigma(Y^E)$:

$$\sigma(Y^E) = \left[\sum (Y^E_{\text{exp}} - Y^E_{\text{cal}})^2/(N-p)\right]^{1/2} \tag{4}$$

where N is the number of experimental points and p is the number of coefficients a_i.

Excess volume for the mixture with 1-butanol shows a sigmoid curve and there is an inversion of sign (from negative to positive) at $x_1 = 0.5$. V^E for the mixture with 2-methyl-1-propanol present slightly negative values at low mole fractions of 2-chlorobutane. Finally V^E for the mixtures with 2-butanol and 2-methyl-2-propanol is positive over the whole composition range. V^E follows the sequence: 1-butanol < 2methyl-1-propanol < 2-butanol < 2methyl-2-propanol. This sequence has been previously observed in other mixtures chloroalkane with isomeric butanols[2,5].

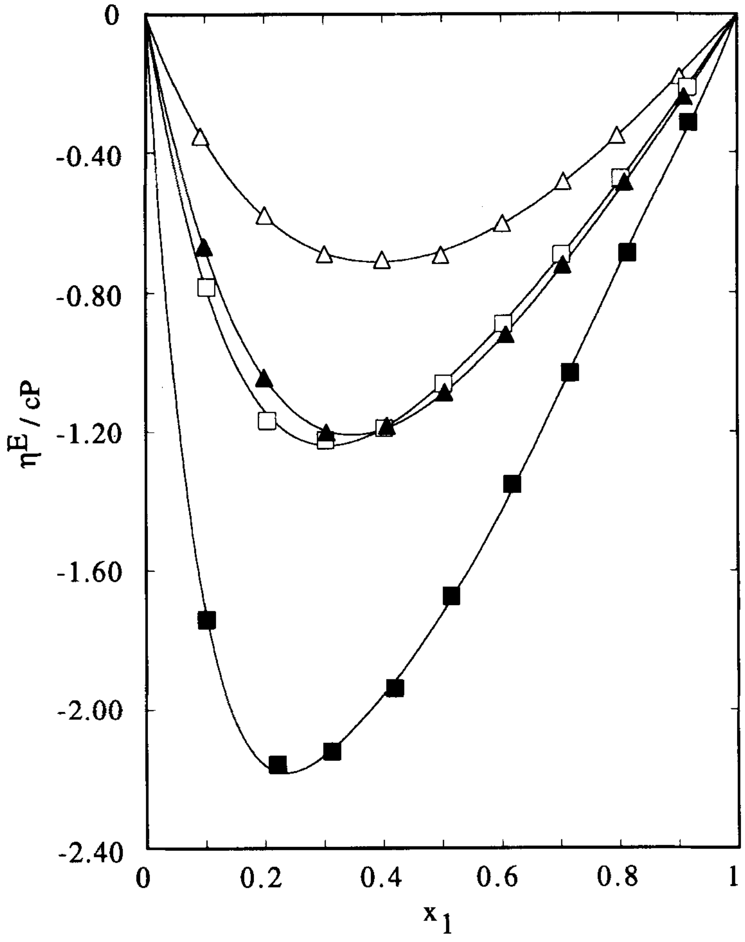

Figure 2 Excess viscosities, η^E, of 2-chlorobutane(1) + an isomeric butanol(2) at 298.15 K as a function of mole fraction x_1: (△) 1-butanol; (□) 2-butanol; (▲) 2-methyl-1-propanol; (■) 2-methyl-2-propanol.

Excess volumes observed can be interpreted as a consequence of various effects. The changes in the association of butanols, the breaking of the dipole-dipole interactions between chloroalkane molecules and the steric hindrance, which could result in a worse molecular packaging in the mixture than in the pure compounds, have a positive effect on V^E. While the specific interaction between the Cl-group of the chloroalkane and the OH-group of the butanol, the changes in the free volume and interstitial acommodation have a negative effect on V^E. In the mixture with 1-butanol these effects are compensated for and small excess volume is obtained. In mixtures with 2-butanol and 2-methyl-1-propanol, the effects which contribute positively to V^E are preponderant. Finally, with 2-methyl-2-propanol the association by hydrogen bonds are broken to a greater extent and therefore the excess volume is greater.

Excess viscosities are negative over the entire composition range. Absolute η^E values follow the sequence: 1-butanol < 2-methyl-1-propanol < 2-butanol < 2-methyl-2-propanol,

Table 4 Coefficients, a_i, and standard deviations, σ, for eq. (3).

Function	a_0	a_1	a_2	a_3	a_4	σ
			2-chlorobutane(1) + 1-butanol(2)			
$V^E/\text{cm}^3\,\text{mol}^{-1}$	−0.0122	0.6427	0.1126	−0.0774		0.0021
η^E/cp	−2.7304	1.0791	−0.5162	0.3641		0.0070
			2-chlorobutane(1) + 2-butanol(2)			
$V^E/\text{cm}^3\,\text{mol}^{-1}$	1.3981	0.6122	0.2321	0.2560		0.0029
η^E/cp	−4.2576	3.0492	−2.2639	0.9659		0.0120
			2-chlorobutane(1) + 2-methyl-1-propanol(2)			
$V^E/\text{cm}^3\,\text{mol}^{-1}$	0.4113	0.5903	0.0730	0.0357		0.0026
η^E/cp	−4.3789	2.6952	−1.3385	0.2071		0.0036
			2-chlorobutane(1) + 2-methyl-2-propanol(2)			
$V^E/\text{cm}^3\,\text{mol}^{-1}$	2.7268	−0.0191	0.8886	0.4539		0.0049
η^E/cp	−6.8870	5.2230	−4.0741	6.2090	−5.2866	0.0200

although η^E values for the mixtures containing 2-methyl-1-propanol and 2-butanol are similar.

Viscosities of the liquids are function of the intermolecular interactions and the size and shape of the molecules. Negative excess viscosities indicate a greater fluidity of the mixture compared with the pure liquids. This confirms the breaking of both the association and the dipole-dipole interactions in the pure liquids. That is to say, η^E values can be explained in a similar way to the V^E.

THEORETICAL ANALYSIS

1-Prigogine-Flory-Patterson Theory

According to Prigogine-Flory-Patterson model of solutions[9,10] V^E can be calculated from the equation:

$$\frac{V^E}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}}{(4/3)\tilde{V}^{-1/3}-1}\Psi_1\theta_2\frac{X_{12}}{P_1^*} - \frac{(\tilde{V}_1-\tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3}-1]}{[(4/3)\tilde{V}^{-1/3}-1]\tilde{V}}\Psi_1\Psi_2$$

$$+\frac{(\tilde{V}_1-\tilde{V}_2)}{P_1^*\Psi_2+P_2^*\Psi_1}(P_1^*-P_2^*)\Psi_1\Psi_2 \tag{5}$$

where the contact energy fraction Ψ_1 is given by

$$\Psi_1 = 1-\Psi_2 = \frac{\phi_1P_1^*}{\phi_1P_1^*+\phi_2P_2^*} \tag{6}$$

and all other parameters pertain to the Flory theory[11,12].

The first term in Eq. (5) is the interactional contribution, ΔV_{int}, the second term is the free volume contribution, ΔV_{fv}, and the third one is the internal pressure contribution, ΔV_P^*.

Flory parameters of the pure components along with their physical properties are listed in Table 5. Expansion coefficient, α, was derived from the densities determined in the laboratory. Isothermal compressibilities, κ_T, were calculated from α, isentropic compressibilites, κ_S, and molar heat capacities, C_p[13,14]. Values of κ_S were calculated from the experimental densities, ρ, and ultrasonic velocities, u. (through the relation $\kappa_S = (\rho u^2)^{-1}$). An Anton Paar DSA-48 density and sound analyzer was used to determine ρ and u.

To solve Eq. (5) it is necessary to obtain values for the interaction parameter X_{12} which is usually done using experimental values from excess enthalpy. For these mixtures, values of H^E are not available, thus values of X_{12} were derived by fitting the theory to experimental equimolecular V^E values for each one the four systems. Table 6 gives the interaction parameters, the calculated values of the three contributions to the equimolecular excess volume according to Eq. (5) and the experimental and theoretical V^E values.

In all cases, the interactional contribution was found to be positive, for mixtures involing 1-butanol and 2-methyl-1-propanol this contribution is small, however for mixtures involving 2-butanol and 2-methyl-2-propanol it is large and is the dominant term. The free volume contribution is negative for the four systems, in mixtures for which the reduced volumes of the components are similar this contribution is small, such as for mixtures with 2-butanol and 2-methyl-2-propanol. The third contribution, the internal pressure contribution is positive and large for mixtures with 1-butanol and 2-methyl-1-propanol and small for mixtures with 2-butanol and 2-methyl-2-propanol.

Table 5 Physical properties and Flory parameters of the pure components at 298.15 K.

Component	V_m^a	$\alpha \times 10^{3b}$	C_p^c	κ_s^d	κ_T^d	$\tilde{V}$	V^{*a}	P^{*e}
2-chlorobutane	106.72	1.313	160.9	1014.6	1355.5	1.3085	81.56	494.5
1-butanol	91.99	0.928	177.2	807.4	940.7	1.2328	74.62	447.0
2-butanol	92.37	1.059	196.9	848.4	1005.3	1.2597	73.33	498.4
2-methyl-1-propanol	92.90	0.978	181.5	888.2	1034.2	1.2432	74.73	435.8
2-methyl-2-propanol	94.90	1.387	218.6	1018.0	1267.0	1.3220	71.79	570.4

[a] Units: $cm^3 mol^{-1}$. [b] Units: K^{-1}. [c] Units: $JK^{-1} mol^{-1}$. [d] Units: TPa^{-1}. [e] Units: $J cm^{-3}$.

Table 6 Contributions to equimolecular V^E according with PFP theory along with the interaction parameter (X_{12}) and theoretical and experimental V^E values.

System	X_{12}^a	ΔV_{int}	ΔV_{fv}	ΔV_P^*	V_{th}^E	V_{exp}^E
2-chlorobutane +						
1-butanol	0.76	0.0131	−0.1647	0.1485	−0.0031	−0.0031
2-butanol	23.86	0.4249	−0.0680	−0.0074	0.3495	0.3495
2-methyl-1-propanol	3.57	0.0647	−0.1221	0.1602	0.1028	0.1028
2-methyl-2-propanol	33.53	0.6499	−0.0051	0.0369	0.6817	0.6817

[a] Units: $J cm^{-3}$.

Table 7 Contributions to the excess viscosity and comparison between theoretical and experimental excess viscosity.

System	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_{fv}$	$\Delta \ln \eta_{th}$	$\Delta \ln \eta_{exp}$	δ^a
2-chlorobutane +						
1-butanol	0.003	−0.023	−0.096	−0.116	−0.241	−0.125
2-butanol	−0.188	0.040	−0.096	−0.241	−0.493	−0.249
2-methyl-1-propanol	−0.022	−0.010	−0.087	−0.119	−0.387	−0.268
2-methyl-2-propanol	−0.268	0.077	−0.082	−0.273	−0.674	−0.401

[a] $\delta = \Delta \ln \eta_{\text{exp}} - \Delta \ln \eta_{\text{th}}$.

2-Bloomfield-Dewan Theory

Several definitions have been used for the excess viscosity, in order to apply the Bloomfield-Dewan theory the more appropriate is :

$$\Delta \ln \eta_{\text{exp}} = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{7}$$

Following Bloomfield-Dewan theory[15], the theoretical excess viscosity $\Delta \ln \eta_{\text{th}}$ is:

$$\Delta \ln \eta_{\text{th}} = -\frac{\Delta H_M}{RT} + \frac{\Delta S^R}{R} + \left(\frac{1}{\tilde{V}-1} - \frac{x_1}{\tilde{V}_1 - 1} - \frac{x_2}{\tilde{V}_2 - 1}\right) \tag{8}$$

This equation displays explicitly the various contributions to the excess viscosities: the enthalpy of mixing, ln η_H, the residual entropy of mixing, ln η_S, and the free volume contribution, ln η_{fv}.

Reduced volumes of the mixture, $\tilde{V}$, and the pure components, $\tilde{V}_1$ and $\tilde{V}_2$, the enthalpy of mixing, ΔH_M, and the residual entropy of mixing, ΔS^R, are calculated using the Flory theory. For this purpose knowledge of the interaction parameter is essential. In the present work we have used the V^E values, to derive X_{12}. Table 7 shows the contributions to the equimolecular excess viscosity, the theoretical and experimental excess viscosities and the difference $\delta = \Delta \ln \eta_{\text{exp}} - \Delta \ln \eta_{\text{th}}$.

From study of Table 7, it is observed that the agreement between the experimental and the theoretical excess viscosity is poor. The calculated $\Delta \ln \eta_{\text{th}}$ values are lower in absolute value than the $\Delta \ln \eta_{\text{exp}}$ values. The difference δ varies from −0.125 for 1-butanol to −0.401 for 2-methyl-2-propanol.

The failure of Bloomfield-Dewan theory to estimate the excess viscosity can be principally attributed to the presence of strong self-association in butanols.

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