Densities and Viscosities of the Ternary Mixtures 1-Butanol + 1-Chlorobutane + 1-Butylamine and 2-Methyl-1-propanol + 1-Chlorobutane + 1-Butylamine at 298.15 K

Magdalena Domínguez, Santiago Rodríguez, M. Carmen López, Félix M. Royo, and José S. Urieta*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Sección de Químicas, Universidad de Zaragoza, Ciudad universitaria, Zaragoza 50009, Spain

Densities and viscosities at 298.15 K of the ternary mixtures 1-butanol + 1-chlorobutane + 1-butylamine and 2-methyl-1-propanol + 1-chlorobutane + 1-butylamine and the binary mixtures 1-butanol + 1-butylamine and 2-methyl-1-propanol + 1-butylamine have been measured. Excess molar volumes and viscosity deviations were fitted to the polynomial equation of Cibulka. The experimental results were also compared with those predicted by the empirical equations of Redlich−Kister, Tsao−Smith, Kohler, and Colinet.

Introduction

In previous papers (Lafuente et al., 1993; Cea et al., 1994; Lafuente et al., 1995) we have determined some excess thermodynamic properties of several binary mixtures containing either isomers of butanol or a haloalkane. In this work, besides binary mixtures, the densities and viscosities of the ternary mixtures 1-butanol + 1-chlorobutane + 1-butylamine and 2-methyl-1-propanol + 1-chlorobutane + 1-butylalmine have been measured at the temperature 298.15 K. Such results should give some insight into the interactions among the OH, NH_2, and Cl groups.

Experimental Section

Materials. The liquids used, 1-butanol (better than 99.0 mol % pure), 2-methyl-1-propanol (better than 99.5 mol % pure), 1-chlorobutane (better than 99.0 mol % pure), and 1-butylamine (better than 99.0 mol % pure) were obtained from Aldrich. The purities of the chemicals were checked not only by comparing the measured densities and viscosities with those reported in the literature but also by gas chromatography using a semicapillary methyl silicone column (o.d. 530 μm) and a flame-ionization detector. The analysis shows that the major peak area exceeds 99.8%. No further purification was considered necessary. The butanols were dried with activated molecular sieves, type 0.3 nm, from Merck. Table 1 shows the experimental values of density and viscosity for the pure components at 298.15 K compared with those found in the literature.

Methods. Densities, ρ, of pure components and binary and ternary mixtures were determined with an Anton Paar DMA-58 vibrating tube densimeter, calibrated with deionized doubly distilled water and dry air. The uncertainty for the density measurements was $\pm 1 \times 10^{-5}$ g·cm^{-3}.

Viscosities, η, of pure components and binary and ternary mixtures were determined by using an Ubbelhode viscosimeter with a Schott-Geräte automatic measuring unit, model AVS-440, for which the accuracy of the flow time measurement is ±0.01 s. Details of calibrations and procedures can be found in an earlier paper (Blasco et al., 1993).

The compositions (mole fraction) of binary and ternary blends were determined by mass using a Mettler H20T balance. The uncertainty of the mass was ±0.01 mg, and the precision of the mole fraction is estimated to better than $\pm 1 \times 10^{-4}$.

Table 1. Densities, ρ, and Viscosities, η, of Pure Components at 298.15 K and Comparison with Literature Data

	ρ/(g·cm^{-3})		η/(mPa·s)	
component	exptl	lit.	exptl	lit.
1-butanol	0.805 75	0.805 75[a]	2.5647	2.5710[a]
2-methyl-1-propanol	0.797 81	0.797 80[a]	3.3973	3.3330[a]
				3.3800[c]
1-chlorobutane	0.880 85	0.880 85[a]	0.4273	0.4260[a]
1-butylamine	0.732 25	0.733 00[b]	0.4690	0.4700[b]

[a] Riddick et al. (1986). [b] Davolio et al. (1990). [c] Viswanath et al. (1989).

Results and Discussion

The viscosity deviations, $\Delta\eta$, for binary and ternary mixtures were calculated using

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

where η is the viscosity of the mixture, η_i is the viscosity of pure component i, x_i is the mole fraction of component i, and n is the number of components in the mixture.

The densities, excess molar volumes, viscosities, and viscosity deviations of the binary mixtures 1-butanol + 1-butylamine and 2-methyl-1-propanol + 1-butylamine are given in Tables 2 and 3. In previous papers (Artigas et al., 1993; Domínguez et al., 1995) we have determined V^E and $\Delta\eta$ of alkanol + 1-chlorobutane and 1-chlorobutane + 1-butylamine mixtures. The excess molar volumes and viscosity deviations were fitted to a Redlich−Kister type equation:

$$R_{ij} = x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p \qquad (2)$$

where $R_{ij} = V^E$/(cm^3·mol^{-1}) or $R_{ij} = \Delta\eta$/(mPa·s), x_i denotes the mole fraction of component i in the $i + j$ mixture with $x_j = 1 - x_i$, and A_p are adjustable parameters obtained by

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Table 2. Experimental Density, ρ, and the Derived Excess Molar Volume V^E of Binary Mixtures at 298.15 K

x_1	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	x_1	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})
1-Butanol (1) + 1-Butylamine (2)					
0.0995	0.742 00	−0.3955	0.5990	0.784 50	−1.1750
0.1994	0.751 41	−0.7127	0.6959	0.790 47	−1.0200
0.2967	0.760 22	−0.9504	0.7936	0.801 13	−0.7733
0.3975	0.768 96	−1.1240	0.8955	0.790 47	−0.4224
0.4999	0.777 24	−1.2050			
2-Methyl-1-propanol (1) + 1-Butylamine (2)					
0.0990	0.741 05	−0.3642	0.5989	0.779 47	−1.1180
0.1946	0.749 26	−0.6548	0.6948	0.784 88	−0.9807
0.2938	0.757 53	−0.9026	0.7951	0.789 78	−0.7398
0.3946	0.765 46	−1.0740	0.8943	0.793 95	−0.4165
0.5017	0.773 20	−1.1520			

Table 3. Experimental Viscosity, η, and Viscosity Deviations, $\Delta\eta$, of Binary Mixtures at 298.15 K

x_1	η/(mPa·s)	$\Delta\eta$/(mPa·s)	x_1	η/(mPa·s)	$\Delta\eta$/(mPa·s)
1-Butanol (1) + 1-Butylamine (2)					
0.0983	0.5497	−0.1253	0.5988	1.2909	−0.4329
0.1986	0.6488	−0.2364	0.7009	1.5182	−0.4197
0.2972	0.7685	−0.3233	0.7974	1.7818	−0.3583
0.4004	0.9222	−0.3859	0.8990	2.1229	−0.2301
0.4976	1.0850	−0.4268			
2-Methyl-1-propanol (1) + 1-Butylamine (2)					
0.1005	0.5513	−0.2117	0.5998	1.3729	−0.8525
0.2000	0.6546	−0.4000	0.7007	1.6737	−0.8473
0.2984	0.7783	−0.5646	0.8122	2.1264	−0.7209
0.3994	0.9361	−0.7025	0.8939	2.5930	−0.4936
0.4997	1.1353	−0.7969			

Table 4. Coefficients A_p of Eq 2 and Standard Deviations, σ, for Excess Molar Volumes, V^E/(cm^3·mol^{-1}), and Viscosity Deviations, $\Delta\eta$/(mPa·s), of Binary Systems

	A_0	A_1	A_2	A_3	σ
1-Butanol (1) + 1-Chlorobutane (2)					
V^E [a]	0.2987	−0.6810	0.2456	−0.1862	0.0014
$\Delta\eta$ [b]	−2.7899	−1.3045	−0.2857	0.2710	0.0043
2-Methyl-1-propanol (1) + 1-Chlorobutane (2)					
V^E [a]	0.6107	−0.5842	0.2849	−0.4410	0.0021
$\Delta\eta$ [b]	−4.3316	−2.6869	−1.4032	−0.2676	0.0034
1-Butanol (1) + 1-Butylamine (2)					
V^E	−4.8090	−0.4437	0.6053	0.6337	0.0050
$\Delta\eta$	−1.6982	−0.5027	−0.4393	−0.3149	0.0024
2-Methyl-1-propanol (1) + 1-Butylamine (2)					
V^E	−4.5990	−0.3835	0.6197	0.2851	0.0032
$\Delta\eta$	−3.2017	−1.6067	−0.9878	−0.3918	0.0049
1-Chlorobutane (1) + 1-Butylamine (2)					
V^E [c]	1.0457	0.1288	0.0773	−0.0024	0.0024
$\Delta\eta$ [c]	−0.0889	−0.0014	−0.0237	0.0220	0.0005

[a] Artigas et al. (1993). [b] Artigas et al. (1995). [c] Domínguez et al. (1995).

the unweighted least-squares method. The coefficients A_p and the standard deviations are given in Table 4. The excess molar volume and viscosity deviation data for the binary mixtures are plotted in Figures 1 and 2.

The excess molar volumes for the ternary mixtures 1-butanol + 1-chlorobutane + 1-butylamine and 2-methyl-1-propanol + 1-chlorobutane + 1-butylamine are shown in Tables 5 and 6. The viscosity deviations for the ternary mixtures are shown in Tables 7 and 8.

The excess molar volumes and viscosity deviations for the ternary mixtures were fitted to the polynomial equation proposed by Cibulka (1982):

$$R_{123} = (R_{123})_{\text{Redlich-Kister}} + x_1x_2x_3[B_1 + B_2x_1 + B_3x_2] \quad (3)$$

The B_i parameters were calculated by the least-squares

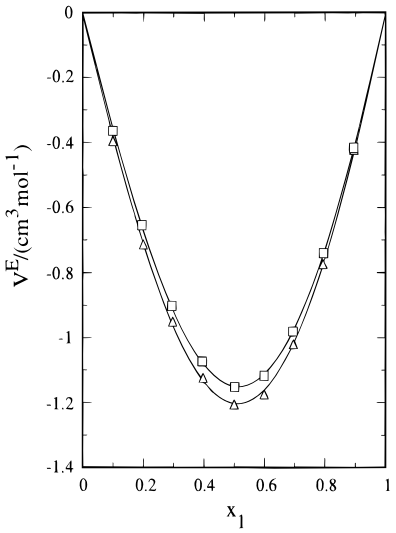


Figure 1. Excess molar volumes V^E/(cm^3·mol^{-1}) at 298.15 K of the binary mixtures (△) 1-butanol (1) + 1-butylamine (2) and (□) 2-methyl-1-propanol (1) + 1-butylamine (2).

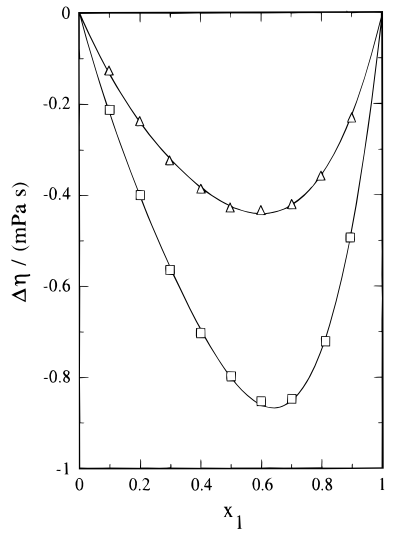


Figure 2. Viscosity deviations $\Delta\eta$/(mPa·s) at 298.15 K of the binary mixtures (△) (1-butanol (1) + 1-butylamine (2) and (□) 2-methyl-1-propanol (1) + 1-butylamine (2).

method. Table 9 presents the values of the B_i coefficients of eq 3 and the corresponding standard deviations, σ, for the ternary systems. Curves of constant V^E_{123} and $\Delta\eta_{123}$ for the ternary systems have been plotted in Figures 3 and 4.

Also the V^E_{123} and $\Delta\eta_{123}$ for ternary systems have been calculated by using the empirical equations proposed by Redlich−Kister, Tsao−Smith, Kohler, and Colinet (Acree, 1984), which only take binary contributions into account.

Redlich and Kister (1948)

$$R_{123} = x_1x_2\sum_{v=0}^{r}(A_v)_{12}(x_1 - x_2)^v + x_1x_3\sum_{v=0}^{r}(A_v)_{13}(x_1 - x_3)^v + x_2x_3\sum_{v=0}^{r}(A_v)_{23}(x_2 - x_3)^v \quad (4)$$

where x_i is the mole fraction of component i and $(A_v)_{ij}$ are adjustable coefficients for the binary mixture $i + j$ obtained

Table 5. Experimental Densities and Excess Molar Volumes of the Ternary Mixture 1-Butanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3) at 298.15 K

x_1	x_2	ρ/(g·cm^{-3})	V^E_{123}/(cm^3·mol^{-1})	x_1	x_2	ρ/(g·cm^{-3})	V^E_{123}/(cm^3·mol^{-1})
0.1007	0.1021	0.757 57	−0.3262	0.3926	0.3009	0.812 89	−0.7105
0.1004	0.2035	0.772 42	−0.2152	0.3896	0.4077	0.827 55	−0.5161
0.1010	0.3030	0.787 48	−0.1841	0.3921	0.5019	0.840 11	−0.2767
0.1023	0.3998	0.802 30	−0.1881	0.4954	0.1033	0.791 88	−1.0005
0.1001	0.4968	0.816 19	−0.1225	0.4887	0.2067	0.806 29	−0.8152
0.1029	0.5955	0.831 11	−0.1268	0.4865	0.3086	0.820 27	−0.5932
0.1030	0.6978	0.845 79	−0.0797	0.4962	0.4004	0.832 79	−0.3006
0.0994	0.7995	0.859 60	0.0082	0.5902	0.1046	0.798 58	−0.9121
0.1962	0.1055	0.767 09	−0.6141	0.5927	0.2018	0.812 18	−0.6586
0.1936	0.2058	0.781 97	−0.5379	0.5911	0.3077	0.826 03	−0.3365
0.1953	0.3059	0.797 15	−0.4870	0.6886	0.1075	0.804 86	−0.7007
0.1978	0.3997	0.811 15	−0.4223	0.6895	0.2038	0.817 63	−0.3784
0.2007	0.4941	0.825 35	−0.3854	0.7916	0.1040	0.809 68	−0.3900
0.2009	0.5949	0.839 79	−0.3042	0.0484	0.0516	0.744 81	−0.1612
0.1984	0.6974	0.853 27	−0.1236	0.0494	0.1011	0.752 26	−0.1177
0.2946	0.1071	0.776 32	−0.8496	0.0503	0.8489	0.862 70	0.0490
0.2963	0.2066	0.791 36	−0.7578	0.0510	0.8978	0.869 72	0.0540
0.2926	0.3045	0.805 45	−0.6517	0.0975	0.0531	0.749 62	−0.3174
0.2947	0.4009	0.819 57	−0.5538	0.0977	0.8522	0.866 80	0.0419
0.2941	0.4972	0.833 34	−0.4455	0.8506	0.0506	0.805 49	−0.3745
0.2900	0.6036	0.847 01	−0.2051	0.8464	0.1015	0.811 92	−0.1967
0.2971	0.1030	0.784 41	−0.9957	0.8991	0.0501	0.807 60	−0.1853
0.3972	0.2023	0.799 01	−0.8566				

Table 6. Experimental Densities and Excess Molar Volumes of the Ternary Mixture 2-Methyl-1-propanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3) at 298.15 K

x_1	x_2	ρ/(g·cm^{-3})	V^E_{123}/cm^3·mol^{-1})	x_1	x_2	ρ/(g·cm^{-3})	V^E_{123}/cm^3·mol^{-1})
0.1021	0.1035	0.757 02	−0.3060	0.3954	0.3023	0.810 10	−0.6844
0.1023	0.2037	0.771 98	−0.2305	0.3984	0.3968	0.823 39	−0.5041
0.0981	0.3033	0.786 49	−0.1681	0.3933	0.5010	0.836 60	−0.2262
0.1034	0.3976	0.801 04	−0.1559	0.4970	0.1022	0.787 97	−0.9883
0.0992	0.4982	0.815 65	−0.1282	0.5001	0.2013	0.802 17	−0.7772
0.1019	0.5958	0.829 93	−0.0786	0.4949	0.3000	0.815 63	−0.5778
0.1031	0.6967	0.844 63	−0.0518	0.5013	0.3964	0.828 50	−0.2800
0.1037	0.7974	0.858 79	0.0129	0.5962	0.1059	0.794 53	−0.8946
0.1950	0.1019	0.764 54	−0.5486	0.5981	0.2018	0.807 93	−0.6541
0.1981	0.2070	0.780 84	−0.5114	0.5975	0.3039	0.821 15	−0.3221
0.1976	0.3030	0.795 24	−0.4638	0.6866	0.1074	0.799 62	−0.7314
0.2068	0.4092	0.811 65	−0.4133	0.6970	0.2038	0.812 71	−0.3724
0.2010	0.4982	0.824 21	−0.3524	0.7969	0.1033	0.803 80	−0.3984
0.2021	0.5967	0.838 07	−0.2385	0.0500	0.0519	0.744 61	−0.1592
0.1995	0.7004	0.851 75	−0.0618	0.0499	0.0966	0.751 34	−0.1294
0.2984	0.1056	0.773 96	−0.8212	0.0518	0.8503	0.862 53	0.0599
0.2918	0.2065	0.788 51	−0.7143	0.0512	0.8992	0.869 56	0.0521
0.2958	0.3025	0.802 95	−0.6246	0.0984	0.0518	0.748 78	−0.3151
0.3024	0.3914	0.816 36	−0.5401	0.0997	0.8516	0.866 02	0.0516
0.2969	0.4971	0.830 75	−0.3829	0.8515	0.0518	0.799 20	−0.3906
0.2978	0.5994	0.844 48	−0.1807	0.8512	0.0982	0.805 14	−0.2071
0.3977	0.1043	0.781 40	−0.9578	0.8958	0.0516	0.800 88	−0.2278
0.3972	0.2040	0.795 98	−0.8186				

by the least-squares method.

Tsao and Smith (1953)

$$R_{123} = x_2(1 - x_1)^{-1}R_{12} + x_3(1 - x_1)^{-1}R_{13} + (1 - x_1)R_{23} \quad (5)$$

in which x_i is the mole fraction of component i and R_{ij} refers to the excess properties for the binary mixtures at compositions (x_i^o, x_j^o) such that $x_i^o = x_1$ for the 1 + 2 and 1 + 3 binary systems and $x_j^o = x_2/(x_2 + x_3)$ for the 2 + 3 binary system.

Kohler (1960)

$$R_{123} = (x_1 + x_2)^2R_{12} + (x_1 + x_3)^2R_{13} + (x_2 + x_3)^2R_{23} \quad (6)$$

in which x_i is the mole fraction of component i and R_{ij} refers to the excess properties of the binary mixtures at a composition (x_i^o, x_j^o) such that $x_i^o = 1 - x_j^o = x_i/(x_i + x_j)$.

Colinet (1967)

$$R_{123} = 0.5\left[\frac{x_2}{1 - x_1}R_{12}(x_1, 1 - x_1) + \frac{x_1}{1 - x_2}R_{12}(1 - x_2, x_2) + \frac{x_3}{1 - x_1}R_{13}(x_1, 1 - x_1) + \frac{x_1}{1 - x_3}R_{13}(1 - x_3, x_3) + \frac{x_3}{1 - x_2}R_{23}(x_2, 1 - x_2) + \frac{x_2}{1 - x_3}R_{23}(1 - x_3, x_3)\right] \quad (7)$$

The standard deviations for eqs 4−7 are shown in Table 10.

The results of V^E for the binary mixtures 1-butanol + 1-butylamine and 2-methyl-1-propanol + 1-butylamine are negative over the entire composition range. The experi-

Table 7. Experimental Viscosities and Viscosity Deviations of the Ternary Mixture 1-Butanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3) at 298.15 K

x_1	x_2	η/(mPa·s)	$\Delta\eta_{123}$/(mPa·s)	x_1	x_2	η/(mPa·s)	$\Delta\eta_{123}$/(mPa·s)
0.0995	0.0995	0.5362	−0.1372	0.4015	0.2967	0.7970	−0.5010
0.0992	0.2003	0.5243	−0.1442	0.4056	0.3938	0.7621	−0.5405
0.0989	0.3013	0.5130	−0.1507	0.4036	0.4964	0.7184	−0.5757
0.0992	0.3988	0.5059	−0.1544	0.4970	0.0989	1.0233	−0.4831
0.0990	0.5011	0.4981	−0.1574	0.5073	0.2013	0.9660	−0.5577
0.0992	0.6006	0.4912	−0.1607	0.5020	0.2989	0.9162	−0.5924
0.0999	0.7003	0.4854	−0.1637	0.5016	0.3980	0.8647	−0.6389
0.0994	0.8014	0.4768	−0.1673	0.6007	0.0979	1.2032	−0.5205
0.1985	0.0984	0.6274	−0.2535	0.5984	0.2001	1.1173	−0.5974
0.1961	0.2006	0.6096	−0.2619	0.5990	0.3006	1.0508	−0.6610
0.1978	0.2998	0.5975	−0.2735	0.7000	0.0969	1.4032	−0.5288
0.1968	0.4012	0.5836	−0.2811	0.6998	0.2003	1.3105	−0.6167
0.1972	0.5017	0.5711	−0.2902	0.7991	0.1001	1.6587	−0.4808
0.1974	0.6021	0.5582	−0.2994	0.0495	0.0506	0.5001	−0.0704
0.1982	0.7028	0.5442	−0.3108	0.0491	0.0980	0.4940	−0.0738
0.2958	0.1008	0.7350	−0.3496	0.0504	0.8500	0.4444	−0.0948
0.2970	0.2014	0.7142	−0.3688	0.0491	0.9005	0.4406	−0.0938
0.2959	0.3015	0.6907	−0.3858	0.0993	0.0507	0.5411	−0.1339
0.2965	0.4005	0.6696	−0.4040	0.0997	0.8487	0.4651	−0.1775
0.2952	0.5036	0.6454	−0.4213	0.8482	0.0512	1.8706	−0.3738
0.2950	0.6046	0.6180	−0.4440	0.8472	0.1000	1.8099	−0.4304
0.4018	0.0918	0.8700	−0.4372	0.8967	0.0503	2.0481	−0.2980
0.3996	0.1969	0.8308	−0.4674				

Table 8. Experimental Viscosities and Viscosity Deviations of the Ternary Mixture 2-Methyl-1-propanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3) at 298.15 K

x_1	x_2	η/(mPa·s)	$\Delta\eta_{123}$/(mPa·s)	x_1	x_2	η/(mPa·s)	$\Delta\eta_{123}$/(mPa·s)
0.0990	0.0995	0.5367	−0.2180	0.3988	0.3025	0.8195	−0.8047
0.0999	0.2014	0.5246	−0.2285	0.3971	0.4027	0.7751	−0.8399
0.0984	0.3031	0.5146	−0.2299	0.3995	0.5002	0.7346	−0.8834
0.0986	0.4001	0.5062	−0.2348	0.4994	0.0997	1.0640	−0.8632
0.1050	0.4701	0.5058	−0.2510	0.4992	0.2013	1.0009	−0.9215
0.0989	0.6032	0.4928	−0.2406	0.4984	0.3017	0.9416	−0.9743
0.0997	0.7012	0.4873	−0.2444	0.4973	0.4023	0.8812	−1.0272
0.1000	0.8001	0.4791	−0.2493	0.5993	0.0999	1.2684	−0.9514
0.2005	0.1005	0.6328	−0.4191	0.5978	0.2017	1.1772	−1.0339
0.1975	0.2007	0.6133	−0.4297	0.5927	0.3006	1.0892	−1.1028
0.1987	0.3008	0.6032	−0.4351	0.6992	0.0986	1.5334	−0.9789
0.1983	0.4029	0.5880	−0.4448	0.6995	0.2010	1.4167	−1.0923
0.2001	0.5006	0.5789	−0.4551	0.8004	0.1004	1.8972	−0.9114
0.2106	0.6401	0.5622	−0.4968	0.0487	0.0500	0.5002	−0.1092
0.1990	0.7012	0.5445	−0.4780	0.0492	0.0992	0.4948	−0.1141
0.2939	0.1006	0.7414	−0.5840	0.5000	0.8508	0.4507	−0.1292
0.2980	0.2016	0.7237	−0.6095	0.0492	0.9008	0.4466	−0.1289
0.2978	0.3027	0.7008	−0.6276	0.0987	0.0521	0.5413	−0.2146
0.2985	0.4008	0.6791	−0.6473	0.0995	0.8503	0.4710	−0.2540
0.2970	0.5029	0.6536	−0.6642	0.8479	0.0515	2.2064	−0.7433
0.2966	0.6037	0.6222	−0.6902	0.8494	0.1010	2.1262	−0.8259
0.4003	0.0996	0.8974	−0.7396	0.8989	0.0508	2.5038	−0.5953
0.3993	0.2008	0.8555	−0.7744				

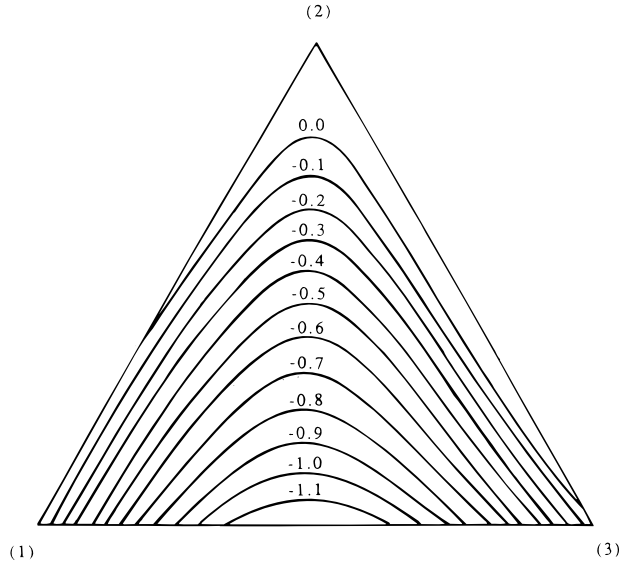
Table 9. Coefficients B_i of Eq 3 and Standard Deviations, σ, for Ternary Systems at 298.15 K

	B_1	B_2	B_3	σ
	1-Butanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3)			
V^E_{123}	−3.2946	2.4427	−14.8836	0.0163
$\Delta\eta_{123}$	1.1729	0.4659	1.8350	0.0038
	2-Methyl-1-propanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3)			
V^E_{123}	−2.0183	−4.1622	−15.1841	0.0159
$\Delta\eta_{123}$	2.1411	4.8505	0.9233	0.0037

mental ternary excess volumes are negative over the whole composition range except for mixtures with a high mole fraction of chlorinated compound in which V^E_{123} shows positive values. The diagrams in which the excess volumes for the ternary systems (Figure 3) are represented have the same shape.

In light of the results included in Tables 9 and 10, it can be observed that only the V^E_{123} obtained by applying the equation of Cibulka fit to the experimental values, while the equations of Redlich and Kister (1948), Tsao and Smith (1953), Kohler (1960), and Colinet (1967) (that only take binary contributions into account) predict V^E_{123} values that are quite different from the experimental ones for the ternary mixtures 1-butanol + 1-chlorobutane + 1-butylamine and 2-methyl-1-propanol + 1-chlorobutane + 1-butylamine; consequently the existence of strong interactions of OH−Cl−NH_2 (all the groups simultaneusly contributing) in the ternary systems under study could be deduced.

Knowing that excess volume is the result of a sum of several effects, chemical, structural, and physical, it would be the breaking of the associated species, cyclic and noncyclic multimers in alkanols and noncyclic trimers in the amine (Shung et al., 1971) (all of them being species formed through hydrogen bonds), and the subsequent formation of bonds of the same type between OH and NH_2 groups that will yield a greater packing and therefore a negative excess volume for the mixture alkanol + 1-butylamine. On the contrary, if a nonassociated compound (such as a chlorinated derivative) is added to either the alkanols or the amine, the forceful association of these



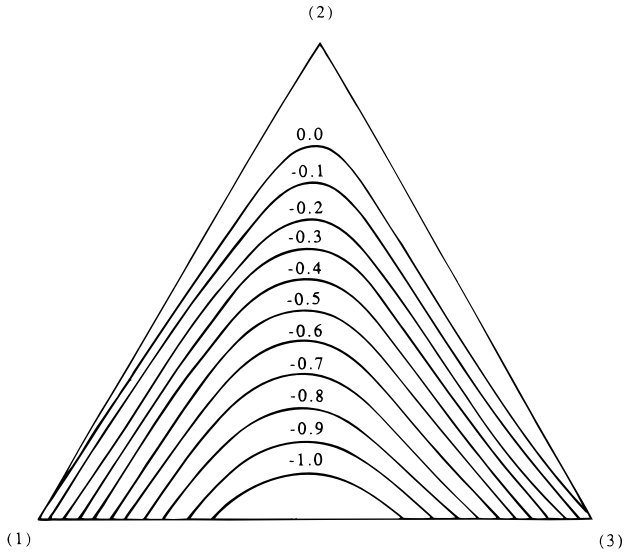
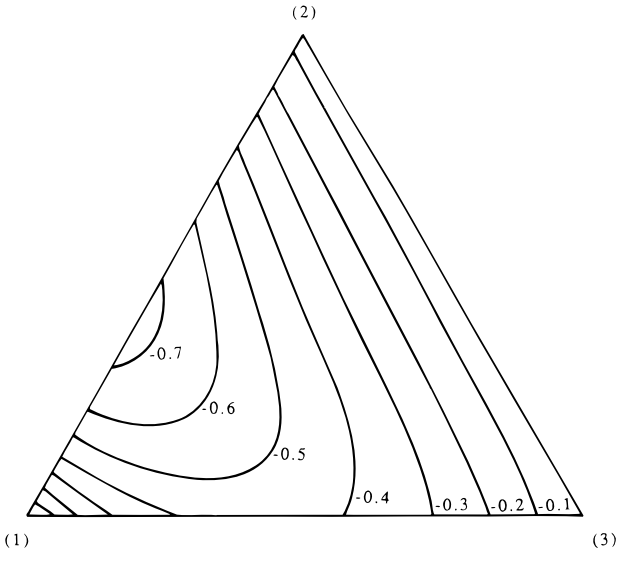


Figure 3. Curves of constant $V^E_{123}/(cm^3 \cdot mol^{-1})$ of the ternary systems (a, top) 1-butanol (1) + 1-chlorobutane (2) + 1-butylamine (3) and (b, bottom) 2-methyl-1-propanol (1) + 1-chlorobutane (2) + 1-butylamine (3).



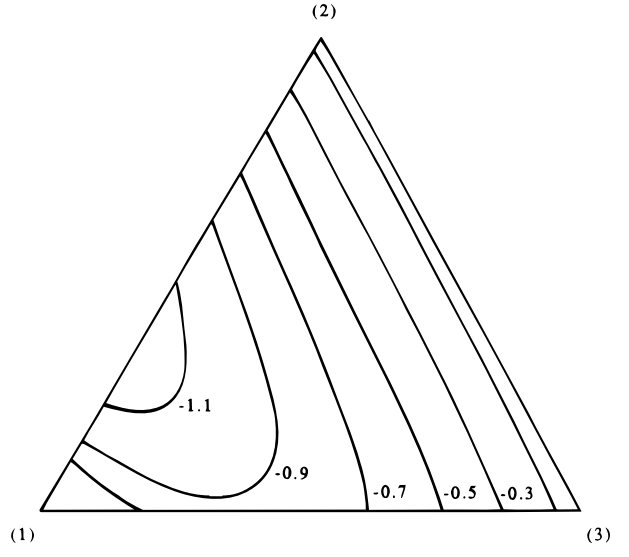


Figure 4. Curves of constant $\Delta\eta_{123}/(mPa \cdot s)$ of the ternary systems (a, top) 1-butanol (1) + 1-chlorobutane (2) + 1-butylamine (3) and (b, bottom) 2-methyl-1-propanol (1) + 1-chlorobutane (2) + 1-butylamine (3).

compounds is broken in such a way that an increasing disorder takes place, leading to positive excess volume values. This same argument can be applicable to the V^E_{123} of ternary mixtures. So, the smaller the ratio of chlorinated derivative, the more negative V^E_{123} will be, while the increase in the amount of 1-chlorobutane will be accompanied by a destruction of hydrogen bonds and a rise in excess volume that will become positive in the zone corresponding to a high mole fraction of chlorinated compound and low mole fractions for the other two components. These results agree with those obtained in a previous paper (Domínguez et al., 1995) for the ternary mixtures 2-butanol + 1-chlorobutane + 1-butylamine and 2-methyl-2-propanol + 1-chlorobutane + 1-butylamine. Structural effects can justify why the V^E_{123} values obtained for the ternary systems with 1-butanol are very similar to those obtained with 2-methyl-1-propanol (given that they are both primary alkanols).

The $\Delta\eta$ values obtained for the binary systems alkanol + 1-butylamine plotted in Figure 2 are negative in the entire composition range. The $\Delta\eta_{123}$ achieved for the studied ternary systems (Figure 4) are also negative throughout the entire composition range. It can be observed in the plots that those for both ternary systems have

Table 10. Standard Deviations, σ, of Eqs 4−7 in Estimating Excess Molar Volumes V^E_{123} and Viscosity Deviations $\Delta\eta_{123}$ for Ternary Mixtures at 298.15 K

	σ			
	eq 4 (Redlich−Kister)	eq 5 (Tsao−Smith)	eq 6 (Kohler)	eq 7 (Colinet)
	1-Butanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3)			
V^E_{123}	0.1681	0.2285	0.1740	0.1745
$\Delta\eta_{123}$	0.0412	0.0152	0.0464	0.0467
	2-Methyl-1-propanol (1) + 1-Chlorobutane (2) + 1-Butylamine (3)			
V^E_{123}	0.1857	0.2497	0.1906	0.1932
$\Delta\eta_{123}$	0.0866	0.0150	0.1087	0.1031

the same shape for $\Delta\eta_{123}$. The viscosity deviations obtained for mixtures containing 2-methyl-1-propanol are more negative than those achieved for mixtures with 1-butanol in both binary and ternary mixtures. On the other hand, the ternary system containing 2-methyl-1-propanol is very similar to the one corresponding to 2-butanol + 1-chlorobutane + 1-butylamine that was reported in a previous paper (Domínguez et al., 1995).

The equation of Tsao and Smith (1953) leads to a good agreement with experimental values of $\Delta\eta_{123}$ as can be seen in Table 10, whereas the same equation for the V^{E}_{123} does not predict good values, as we have pointed out above.

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Literature Cited

Acree, W. E., Jr. *Thermodynamic properties of non-electrolyte solutions*; Academic Press: Orlando, FL, 1984; Chapter 4, pp 64−65.

Artigas, H.; Santafé, J.; López, M. C.; Royo, F. M.; Urieta, J. S. Excess volumes of (an alkanol + a haloalkane) at the temperatures 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1993**, *25*, 1403−1407.

Artigas, H. Doctoral Thesis, Universidad de Zaragoza, Spain, 1995.

Blasco, D.; Lafuente, C.; Santafé, J.; Royo, F. M.; Urieta, J. S. Excess volumes and excess viscosities of binary mixtures of cyclohexane + picolines. *Thermochim. Acta*, **1993**, *230*, 55−63.

Cea, P.; Lafuente, C.; Artigas, H.; Royo, F. M.; Urieta, J. S. Excess volumes and excess viscosities of 2-chloro-2-methylpropane with isomeric butanols at 298.15 K. *Can. J. Chem.* **1994**, *72*, 1921−1925.

Cibulka, I. Estimation excess volume and density of ternary liquid mixtures of non electrolites from binary data. *Collect. Czech. Commun.* **1982**, *47*, 1414−1419.

Colinet, C. Ph.D. Thesis, University of Grenoble, France, 1967.

Davolio, F.; Schaefer, C. R.; Ruiz, M. F.; Katz, M. Molar excess volumes and viscosities of ternary system n-Butylamines + 1,4-Dioxane + Acetonitrile at 298.15 K. *J. Solution Chem.* **1990**, *19*, 1085−1094.

Domínguez, M.; Camacho, A.; López, M. C.; Royo, F. M.; Urieta, J. S. Excess molar volumes and excess viscosoties of ternary mixtures (2-butanol + 1-chlorobutane + 1-butylamine) and (2-methyl-2-propanol + 1-chlorobutane + 1-Butylamine) at 298.15 K. *Can. J. Chem.*, 1995, in press.

Kohler, F. Estimation of the thermodynamic data for a ternary system from the corresponding binary systems. *Monatsh. Chem.* **1960**, *91*, 738−740.

Lafuente, C.; Pardo, J.; Rodríguez, V.; Royo, F. M.; Urieta, J. S. Excess Volumes of Binary Mixtures of 1,3-Dichloropropane with Isomeric Butanols at 298.15 and 313.15 K. *J. Chem. Eng. Data* **1993**, *38*, 554−555.

Lafuente, C.; Pardo, J.; Santafé, J.; Royo, F. M.; Urieta, J. S. Excess isoentropic compressibilities of (an isomer of chlorobutane + an isomer of butanol) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 541−549.

Redlich, O.; Kister, A. T. Thermodynamic of non electrolytic solutions. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification (Techniques of Chemistry)*, 4th ed.; Wiley-Interscience: New York, 1986.

Schug, J. C.; Chang, W. M. Self-association of butylamines *J. Phys. Chem.* **1971**, *75*, 938−941.

Tsao, C. C.; Smith, J. M. Heat of mixing of liquids. Appied thermodynamics. *Chem. Eng. Prog., Symp. Ser.* **1953**, *49*, 107−117.

Viswanath, D. S.; Natarajan, G. *Data book on the viscosity of liquids*; Wiley: New York, 1989.

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