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MOLAR EXCESS VOLUMES AND PARTIAL MOLAR EXCESS VOLUMES OF *n*-BUTYLAMINE WITH CHLOROALKANES AT DIFFERENT TEMPERATURES *

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ABSTRACT

Molar excess volumes and partial molar excess volumes are reported for binary mixtures of *n*-butylamine + dichloromethane, trichloromethane and tetrachloromethane at four different temperatures and over the whole concentration range. The Prigogine–Flory–Patterson model of solution thermodynamics has been used to predict the molar excess volumes. This work shows the importance of the three contributions, ΔV_{int}, ΔV_{P^*} and ΔV_F, to V^E.

INTRODUCTION

Molar excess volumes of binary mixtures have been extensively studied from both theoretical and experimental points of view [1,2]. This work reports the molar excess volumes (V^E) and partial molar excess volumes ($\bar{V}^E$) of three binary mixtures at 293.15 , 298.15, 303.15 and 308.15 K where *n*-butylamine is a polar molecule associated in its pure state by hydrogen bonds, and the three chloroalkanes have different polarities. Information can be obtained concerning the interactions between the mixed chemical species. The V^E data were analysed in terms of the Prigogine–Flory–Patterson model. The analysis showed the importance of the three contributions, ΔV_{int}, ΔV_{P^*} and ΔV_F, to V^E.

EXPERIMENTAL

The methods used in our laboratory have been described previously [1,2]. Densities were determined with a digital densimeter AP, DMA 45. A

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thermostatically controlled bath (constant to ±0.01 °C) was used. Calibration was carried out with doubly distilled water and air with an error of ±0.1 kg m^{-3}. All weighings were made on a Mettler H315 balance. Temperatures were read from calibrated thermometers.

n-Butylamine (BA) from Riedel de Häen (puriss.) was dried over potassium hydroxide pellets for three days, refluxed for 2 h, distilled and the middle colourless fraction collected [3]. Dichloromethane (DM), from Merck (puriss.), was distilled over calcium oxide, trichloromethane (CL), from Merck (puriss.), was washed with distilled water, dried over calcium chloride and distilled, and, finally, tetrachloromethane (TC), from Merck (puriss.), was used without further purification.

Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

RESULTS

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison.

Tables 2–4 show the experimental values of the densities of the three systems at four different temperatures.

The excess molar volume was calculated using the following equation:

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

where M_1 and M_2 are the molecular weights of the components, x_1 and x_2 are the mole fractions of components 1 and 2, and ρ, ρ_1 and ρ_2 are the densities of the solutions and of the pure components.

TABLE 1

Densities values of the pure components

Component	Density $\rho \times 10^{-3}$ (kg m^{-3})							
	293.15 K		298.15 K		303.15 K		308.15 K	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
BA	0.7370	–	0.7328	0.73308 [a]	0.7276	–	0.7228	–
DM	1.3231	1.3256 [b]	1.3142	1.3148 [c]	1.3050	1.3077 [b]	1.2960	–
CL	1.4878	1.48911 [b]	1.4785	1.4797 [b]	1.4691	1.4706 [b]	1.4597	–
TC	1.5940	1.59402 [b]	1.5844	1.58439 [b]	1.5748	1.5748 [b]	1.5653	–

[a] Ref. 4.
[b] Ref. 5.
[c] Ref. 6.

TABLE 2

Experimental densities of *n*-butylamine (1) + dichloromethane (2)

x_1	Density $\rho \times 10^{-3}$ (kg m^{-3})			
	293.15 K	298.15 K	303.15 K	308.15 K
0.1020	1.2335	1.2257	1.2172	1.2091
0.1371	1.2052	1.1976	1.1894	1.1814
0.2306	1.1351	1.1280	1.1203	1.1129
0.3081	1.0820	1.0754	1.0681	1.0611
0.4356	1.0031	0.9971	0.9903	0.9839
0.5159	0.9580	0.9523	0.9458	0.9397
0.5926	0.9175	0.9121	0.9060	0.9003
0.6971	0.8660	0.8612	0.8554	0.8500
0.8192	0.8108	0.8063	0.8008	0.7957
0.9041	0.7750	0.7707	0.7654	0.7605

Each set of results were fitted using a Redlich–Kister equation of the type

$$V^{\mathrm{E}} = x_1(1 - x_1) \sum_{j=1}^{n} a_j(1 - 2x_1)^{j-1} \tag{2}$$

where a_j are the parameters obtained by a linear squares fitting procedure. In each case, the optimum number of coefficients was ascertained from an

TABLE 3

Experimental densities of *n*-butylamine (1) + trichloromethane (2)

x_1	Density $\rho \times 10^{-3}$ (kg m^{-3})			
	293.15 K	298.15 K	303.15 K	308.15 K
0.0601	1.4337	1.4250	1.4161	1.4071
0.1276	1.3746	1.3664	1.3580	1.3496
0.1585	1.3482	1.3404	1.3319	1.3237
0.2301	1.2881	1.2806	1.2727	1.2649
0.2658	1.2590	1.2517	1.2439	1.2363
0.3360	1.2026	1.1957	1.1882	1.1811
0.4049	1.1489	1.1424	1.1352	1.1282
0.4341	1.1264	1.1201	1.1131	1.1064
0.4542	1.1113	1.1051	1.0981	1.0915
0.4991	1.0776	1.0716	1.0648	1.0584
0.6045	1.0009	0.9953	0.9889	0.9829
0.6156	0.9930	0.9874	0.9810	0.9751
0.6443	0.9727	0.9672	0.9609	0.9550
0.7093	0.9274	0.9222	0.9160	0.9105
0.7325	0.9115	0.9064	0.9004	0.8949
0.8611	0.8256	0.8210	0.8153	0.8102
0.9302	0.7810	0.7767	0.7713	0.7663

TABLE 4

Experimental densities of *n*-butylamine (1) + tetrachloromethane (2)

x_1	Density $\rho \times 10^{-3}$ (kg m^3)			
	293.15 K	298.15 K	303.15 K	308.15 K
0.1017	1.5067	1.4978	1.4887	1.4797
0.1975	1.4246	1.4163	1.4076	1.3990
0.2974	1.3390	1.3313	1.3229	1.3148
0.3676	1.2788	1.2715	1.2635	1.2557
0.4895	1.1744	1.1677	1.1602	1.1530
0.5536	1.1195	1.1132	1.1059	1.0990
0.6318	1.0524	1.0465	1.0396	1.0331
0.6708	1.0190	1.0132	1.0066	1.0002
0.7779	0.9272	0.9220	0.9158	0.9099
0.8299	0.8827	0.8777	0.8717	0.8661
0.9120	0.8123	0.8077	0.8022	0.7969

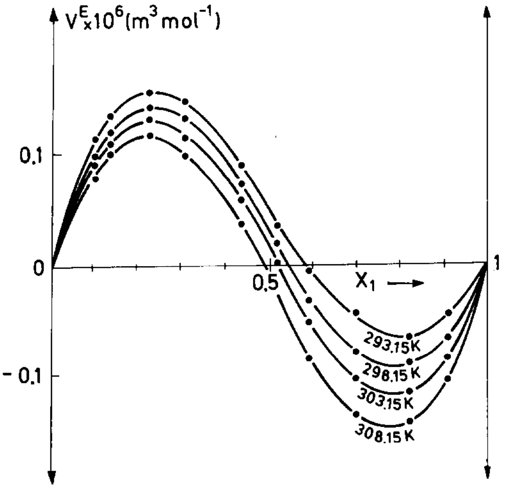

Fig. 1. Excess molar volumes for *n*-butylamine (1) + dichloromethane (2): · · · , experimental results; continuous curves calculated using eqn. (2).

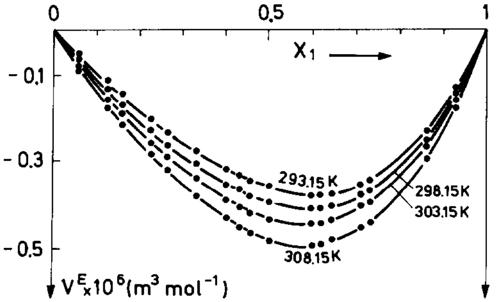

Fig. 2. Excess molar volumes for *n*-butylamine (1) + trichloromethane (2): · · · , experimental results; continuous curves calculated using eqn. (2).

TABLE 5

Coefficients a_j and standard deviations determined by the method of least-squares

System	T (K)	a_1	a_2	a_3	a_4	a_5	$\sigma \times 10^3$
BA (1) + DM (2)	293.15	0.200	1.200	0.260	−0.20	–	5
	298.15	0.146	1.296	0.015	−0.23	–	2
	303.15	0.052	1.385	−0.081	−0.24	–	2
	308.15	−0.050	1.500	−0.180	−0.30	–	5
BA (1) + CL (2)	293.15	−1.440	0.66	−0.08	–	–	4
	298.15	−1.560	0.64	−0.17	–	–	5
	303.15	−1.740	0.67	−0.20	−0.6	0.8	5
	308.15	−1.910	0.66	−0.21	–	–	5
BA (1) + TC (2)	293.15	−1.970	0.73	−0.18	0.10	–	3
	298.15	−2.060	0.77	−0.19	–	–	3
	303.15	−2.120	0.76	−0.20	0.10	−0.20	3
	308.15	−2.174	0.79	−0.25	–	–	2

examination of the variation of the standard error estimate with n (calculated with a VAX 11/780 computer)

$$\sigma = \left(\sum \left(V^{\mathrm{E}}_{\mathrm{obs}} - V^{\mathrm{E}}_{\mathrm{cal}}\right)^2 / \left(n_{\mathrm{obs}} - n\right)\right)^{1/2} \tag{3}$$

The values adopted for the coefficients a_j and the standard error of estimates associated with the use of eqn. (3) are summarized in Table 5.

Figures 1–3 show the experimental values of V^{E} as a function of the mole fraction of component 1. The continuous curves were calculated from eqn. (2) using the adopted values for the coefficients.

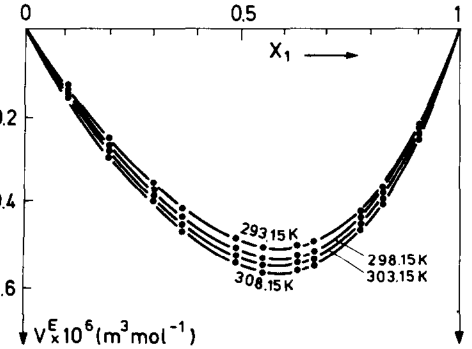

Fig. 3. Excess molar volumes for n-butylamine (1) + tetrachloromethane (2): · · · , experimental results; continuous curves calculated using eqn. (2).

DISCUSSION

Figure 1 shows the molar excess volume for the BA (1) + DM (2) system over the whole concentration range. This is a sigmoid curve showing a volume contraction at high concentrations of BA, which can be explained by the fact that BA is a hydrogen-bonded associated liquid. The addition of dichloromethane which is polar but not an associated liquid, reduces the number of intermolecular hydrogen bonds between *n*-butylamine molecules with the result that $V^{\mathrm{E}} < 0$. On the other hand, the addition of *n*-butylamine to dichloromethane produces a positive V^{E}, which can be explained (according to Prigogine [7]) by an interaction of the dipole–dipole type with intermolecular complex formation. The same kind of curve has been observed by other authors [8–10].

The other two systems, in Figs. 2 and 3, show negative V^{E} values over the whole concentration range. Several effects may contribute to the values of V^{E}, such as the breaking of liquid order on mixing, unfavourable interactions between groups, differences in molecular volumes and differences in free volumes between liquid components [11]. The first two effects produce a positive excess volume. Negative values of V^{E} indicate the presence of strong specific interactions in the binary mixtures containing *n*-butylamine. The negative values may be attributed to the formation of charge transfer complexes between the π-electrons of the chlorine atoms of trichloromethane and tetrachloromethane with the lone pair electrons in *n*-butylamine. The presence of three and four chlorine atoms and one hydrogen atom which acts as a σ-acceptor may be involved in the formation of hydrogen bonds which are stronger with tetrachloromethane.

The variation in the magnitude of V^{E} with increasing temperature is found to be small. The results indicate that the extent of complex formation in these systems does not change significantly with increasing temperature over the range studied.

The negative V^{E} lobes in the *n*-butylamine-rich regions also suggest that occupation by the chloroalkanes of the cavities among the hydrogen-bonded structure of pure *n*-butylamine has taken place.

From a theoretical standpoint, examination of the partial derivative excess properties at infinite dilution appears to be of particular interest. At the limit of infinite dilution, solute–solute interactions disappear; thus, the values of the infinite dilution partial molar excess properties provide insight into the relationships between solute–solvent interactions and the respective thermodynamic properties, independent of composition effects.

The partial molar excess volume of a component in a binary mixture can be determined from excess volume data, as follows

$$\overline{V}_i^{\mathrm{E}} = V^{\mathrm{E}} + (1 - x_i)\frac{\partial V^{\mathrm{E}}}{\partial x_i} \tag{4}$$

At the limit of infinite dilution, V^{E} and x_i become zero; then

$$\bar{V}_i^{\mathrm{E}\infty} = \left(\frac{\partial V^{\mathrm{E}}}{\partial x_i} \right)_{x_i = 0} \tag{5}$$

or the infinite dilution partial molar excess volume is the slope of the excess volume versus mole fraction curve at infinite dilution. Thus, $\bar{V}_i^{\mathrm{E}}$ can be obtained by fitting V^{E} versus composition data to a curve and obtaining the slope of the curve at $x_i = 0$.

Typically, five or six data points at mole fractions ranging from approximately 0.005 to 0.05 were used to determine $\bar{V}_i^{\mathrm{E}}$. The curves are linear and from the slope we obtained the $\bar{V}_i^{\mathrm{E}\infty}$ values shown in Table 6.

Figures 4 and 5 show $\bar{V}_1^{\mathrm{E}}$ and $\bar{V}_2^{\mathrm{E}}$ at 298.15 K for the three systems. The maximum uncertainties in $\bar{V}^{\mathrm{E}}$ were estimated as $\pm 0.1 \times 10^{-6}$ m^3 mol^{-1}.

An error analysis indicates that V^{E} tends to be slightly less accurate for systems in which the solvent has a large molar volume or in which the densities of the two components differ greatly (such as *n*-butylamine and tetrachloromethane). Conversely, greater accuracy in V^{E} is obtained when the solvent has a small molar volume and when the two components have similar densities. $\bar{V}_i^{\mathrm{E}}$ values are negative for BA + CL and BA + TC, as are V^{E} values. For the BA + DM system, there is a minimum in $\bar{V}_1^{\mathrm{E}}$ and a

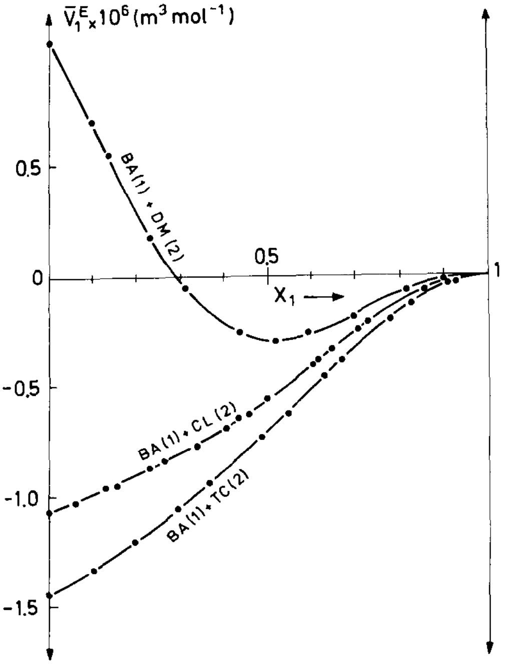

Fig. 4. Partial molar excess volumes of component 1 vs. mole fraction of component 1.

TABLE 6

Partial molar excess volumes at infinite dilution at 298.15 K

System	$\bar{V}_1^{E\infty} \times 10^6$ (m^3 mol^{-1})	$\bar{V}_2^{E\infty} \times 10^6$ (m^3 mol^{-1})
BA (1) + DM (2)	1.07	−0.78
BA (1) + CL (2)	−1.06	−2.11
BA (1) + TC (2)	−1.44	−2.69

maximum in $\bar{V}_2^E$, in agreement with the sigmoid curve; this means that there are strong interactions between the two components.

The original Prigogine–Flory theory [7,12] includes three contributions in order to explain the thermodynamic behaviour of the liquid mixtures: an interactional contribution to V^E (ΔV_{int}^E) which is proportional to the interaction parameter X_{12}; the free volume contribution, which arises from the dependence of the reduced volume upon the reduced temperature as a result of the differences between the degrees of expansion of the two components (ΔV_F); and the internal pressure contribution (ΔV_{P^*}) which depends on

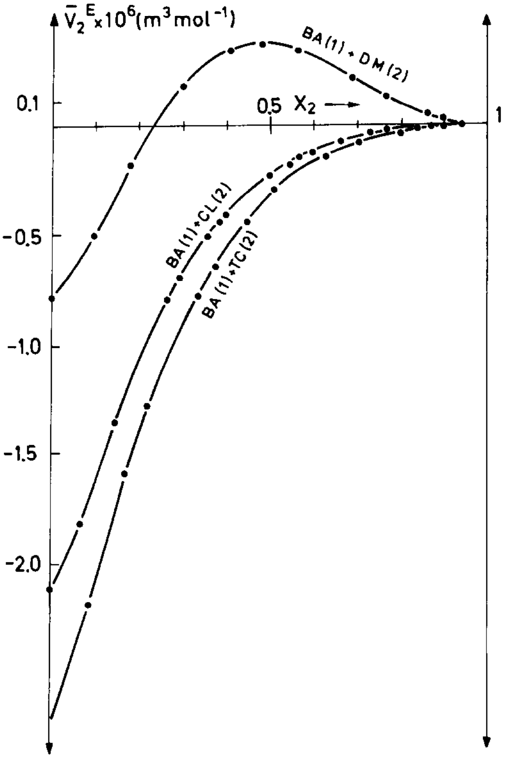

Fig. 5. Partial molar excess volumes of component 2 vs. mole fraction of component 2.

TABLE 7

Equation of state parameters for the pure components at 298.15 K

Component	$\alpha \times 10^3$ (K^{-1})	$\kappa \times 10^7$ (kPa^{-1})	$V \times 10^6$ ($m^3\ mol^{-1}$)	$\tilde{V}$	$\tilde{T}$	$V^\star \times 10^6$ ($m^3\ mol^{-1}$)	$P^\star \times 10^{-6}$ ($J\ m^{-3}$)	$T^\star$ (K)
BA	1.256 [a]	11.99 [c]	99.8035	1.2979	0.06414	76.896	526	4648
DM	1.391 [b]	10.26 [b]	64.6325	1.3227	0.06730	48.864	707	4430
CL	1.26 [b]	9.98 [b]	80.7426	1.2987	0.06424	62.172	635	4641
TC	1.229 [c]	10.80 [b]	97.0954	1.2929	0.06347	75.099	567	4698

[a] From density measurements.

[b] Ref. 5.

[c] From surface tension data (unpublished data).

both the differences of the characteristic pressures and of the reduced volumes of the components.

Some new effects not treated by this theory have been discussed for the case of mixtures of molecules of different shape [13,14].

The equation is

$$\frac{V^E}{x_1V_1^\star + x_2V_2^\star} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}}{\frac{4}{3}\tilde{V}^{-1/3}-1}\psi_1\theta_2\frac{X_{12}}{P_1^\star} - \frac{(\tilde{V}_1-\tilde{V}_2)(\frac{14}{9}\tilde{V}^{-1/3}-1)}{(\frac{4}{3}\tilde{V}^{-1/3}-1)\tilde{V}}\psi_1\psi_2$$
$$+\frac{(\tilde{V}_1-\tilde{V}_2)(P_1^\star-P_2^\star)}{P_1^\star\psi_2+P_2^\star\psi_1}\psi_1\psi_2 = \Delta V_{\text{int}} + \Delta V_F + \Delta F_{P^\star} \qquad (6)$$

The various parameters involved in eqn. (6) for the pure components (with subscript) and the mixture (without subscript) are obtained from the Flory theory [15] and are shown in Table 7.

The interactional contribution to V^E contains the interaction parameter X_{12}, which is usually calculated using experimental values of the excess enthalpy H^E. As there are no values of H^E for these systems, X_{12} values were derived by fitting the theory to experimental values of V^E for each one of the three systems at 298.15 K.

Table 8 gives the calculated equimolecular values of the three contributions to V^E, according to eqn. (6) together with X_{12} and the experimental and calculated V^E values.

TABLE 8

Experimental and theoretical molar excess volumes, eqn. (6), at 298.15 K

System	X_{12} ($J\ m^{-3}$)	ΔV_{int}	ΔV_F	$\Delta V_{P^\star}$	$V^E_{\text{exp}} \times 10^6$ ($m^3\ mol^{-1}$)	$V^E_{\text{cal}} \times 10^6$ ($m^3\ mol^{-1}$)
BA (1) + DM (2)	−3.68	-8.1×10^{-4}	2.2×10^{-4}	1.2×10^{-3}	0.034	0.047
BA (1) + CL (2)	−26.23	-5.7×10^{-3}	2.4×10^{-7}	3.8×10^{-5}	−0.392	−0.395
BA (1) + TC (2)	−31.38	-6.9×10^{-3}	9.2×10^{-6}	-9.3×10^{-5}	−0.511	−0.533

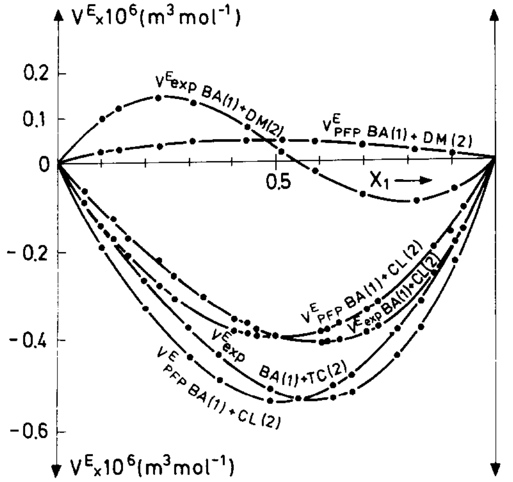

Fig. 6. Experimental and theoretical excess molar volumes at 298.15 K.

An analysis of each of the three contributions to V^E shows that the interactional contribution is always negative and increases from BA + CL to BA + DM. In this last system, the internal pressure contribution, ΔV_{P^*}, and the free volume differences contributions, ΔV_F, are positive and higher than in the other two systems where both contributions have little significance compared to ΔV_{int}.

The total theoretical V^E values for $x_1 = 0.5$ are found to be in excellent agreement with the experimental ones (Table 8).

Figure 6 shows a comparison of theoretical and experimental V^E values throughout the composition range at 298.15 K. It may be observed that the theory reproduces the main features of the experimental data, although quantitative agreement is not achieved in all the mixtures. This is not surprising considering that the PFP theory does not take into account all the possible interactions which give values different from the observed behaviour.

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