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Excess Molar and Partial Volumes of 2,2?-Oxybis[Propane] + Ethyl Acrylate, Butyl Acrylate, Methyl Methacrylate, and Styrene at 298.15 K

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EXCESS MOLAR AND PARTIAL VOLUMES OF 2,2'-OXYBIS[PROPANE] + ETHYL ACRYLATE, BUTYL ACRYLATE, METHYL METHACRYLATE, AND STYRENE AT 298.15 K

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Densities of the binary systems of 2,2'-oxybis[propane] with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene have been measured as a function of the composition, at 298.15 K and atmospheric pressure, using an Anton Paar DMA 5000 oscillating U-tube densimeter and used to calculate the partial and excess volumes. The latter were correlated with the Redlich–Kister equation and with a series of Legendre polynomials. The excess volumes are negative for all the systems reported here.

Keywords: Densities; Excess volumes; Partial volumes; Monomers; 2,2'-oxybis[propane]; Acrylates; DIPE

1. INTRODUCTION

The mixing of different compounds gives rise to properties such as volumes, enthalpies, and entropies of mixing, which reflect the extent of the deviations from nonideality. Excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property if the system behaves ideally, and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute–solute, solute–solvent, and solvent–solvent species. For example, a positive value of the excess enthalpy indicates an endothermic process, and a negative value of the excess volume represents a packing effect. Excess volumes represent the first derivative of the excess Gibbs function with respect to the pressure, $V^E = (\partial G^E / \partial P)_{T,n}$; the pertinent partial excess volume corresponds to the variation of the chemical potential with pressure, $\bar{V}_i^E = (\partial \mu_i / \partial P)_{T,n_j}$.

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Information about excess volumes can be also used to test the different mixing rules for equations of state extended to the liquid state.

This work is part of our program to provide data for the characterization of the molecular interactions between solvents and commercially important monomers, in particular, the influence of the chemical structure of the solute in the systems under consideration. 2,2'-oxybis[propane], diisopropyl ether (DIPE), is an excellent solvent and may be useful in polymerization reactions, in the cleaning of polymer surfaces, electronic materials, etc. Acrylic esters and styrene are important industrial chemicals used in the large-scale preparation of useful polymers. The esters are also interesting because they contain both a double bond and an ester group.

Sastry and Dave (1996, 1997) measured the excess volumes, isentropic compressibilities, and dielectric behavior of fifteen binary mixtures of alkyl (methyl, ethyl, and butyl) methacrylate with hexane, heptane, carbon tetrachloride, chlorobenzene, and *o*-dichlorobenzene at 308.15 K and found that with aliphatic hydrocarbons the results were controlled by dispersing interactions; with chlorinated solvents the controlling factors were specific interactions (O–Cl and n – π types). Sastry and Valand (2000) also measured the excess volumes of mixtures of alkyl (methyl, ethyl, and butyl) acrylates in several alkanols at 298.15 and 308.15 K, and found that they were always positive. These results were explained on the basis of nonspecific interactions between the components. Sastry *et al.* (1999) measured the excess volumes of methyl methacrylate (MMA) with ethylbenzene and other aromatic hydrocarbons such as benzene, toluene, and (*o,m,p*)-xylene at 298.15 and 303.15 K and found that except for toluene all exhibited positive excess volumes. Wisniak *et al.* (2001) measured the excess volumes of 2,2'-oxybis[propane] with benzene, toluene, and cyclohexane and found that they were negative for the two aromatics and positive for cyclohexane.

No literature data are available for the excess volumes of the systems studied here.

2. EXPERIMENTAL SECTION

(a) Materials

Diisopropyl ether (99.87 mass%), ethyl acrylate, EA (99.8 mass%), butyl acrylate, BA (99.9 mass%), MMA (99.9 mass%), and styrene (99.9 mass%) were purchased from Aldrich. The provider certified the purity of all the reagents. EA, BA, and MMA were vacuum distilled previous to use to eliminate the stabilizer (about 0.002% mass of hydroquinone monomethyl ether). Styrene, containing 10–15 ppm of 4-*tert*-butylcatechol as stabilizer, was not distilled to avoid polymerization but was degassed by freezing and heating. After purification all reagents were stored under molecular sieves. The purity of the solvents was further ascertained by comparing their densities at 298.15 K with values reported in the literature (Table I).

(b) Density Measurements

The density of the samples was measured with an Anton Paar Model DMA 5000 oscillating U-tube densimeter, provided with automatic viscosity correction, two integrated Pt 100 platinum thermometers (DKD traceable), and a stated accuracy of

TABLE I Purity and densities of pure components at 298.15 K

Component	Purity (mass%)	Density (g cm ⁻³)	
		Measured	Literature
DIPE (1)	99.87	0.718567	0.71854 ¹
Butyl acrylate (2)	99.9	0.893666	0.8941 ²
Ethyl acrylate (3)	99.8	0.915930	0.9163 ²
Methyl methacrylate (4)	99.9	0.937669	0.93766 ³
Styrene (5)	99.9	0.901972	0.9016 ⁴

¹Riddick *et al.* (1986); ²Sastry and Valand (2000); ³Beichen *et al.* (1986); ⁴Haijun *et al.* (1995).

$5 \times 10^{-6} \text{ g cm}^{-3}$. The temperature in the cell was regulated to $\pm 0.001 \text{ K}$ with a solid-state thermostat. The apparatus was calibrated once a day with dry air and bidistilled freshly degassed water.

All liquids were boiled or heated to remove dissolved air. Solutions of different compositions were prepared by mass in a 10 cm^3 rubber-stoppered vial to prevent evaporation, using a Mettler AG 204 balance accurate to $\pm 10^{-4} \text{ g}$. To minimize the errors in composition, the heavier component was charged first and the sample kept in ice water. Accuracy in the mole fraction is $\pm 5 \times 10^{-5}$, of the density (duplicate) measurement $\pm 2 \times 10^{-6} \text{ g cm}^{-3}$, and of the temperature $\pm 0.002 \text{ K}$.

Proper safety measures were taken when handling all the materials.

3. RESULTS AND DISCUSSION

At least 21 density measurements were performed (with repetition) for each binary system over the full concentration range ($0 \leq x \leq 1$).

The excess volumes V^E of the solutions of molar composition x were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E = [xM_1 + (1-x)M_2]/\rho - [xM_1/\rho_1 + (1-x)M_2/\rho_2] \quad (1)$$

where ρ , ρ_1 , and ρ_2 are the densities of the solution and pure components 1 and 2, respectively, and M_1 and M_2 are the molar masses of the pure components. The corresponding values of ρ and V^E are reported in Tables II–V and Fig. 1. The partial volumes were calculated using the relations (Van Ness and Abbott, 1982)

$$\bar{V}_j = V - x_i \frac{dV}{dx_i} \quad (2)$$

$$\bar{V}_i = V + x_j \frac{dV}{dx_i} \quad (3)$$

The pertinent values of \bar{V}_i appear in Table VI and are necessarily consistent.

TABLE II Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system DIPE (1) + butyl acrylate (2) at 298.15 K

x_1	ρ (g cm ⁻³)	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
			(cm ³ mol ⁻¹)	
0	0.893666	143.420	0	0
0.0248	0.889784	143.323	-67.4240	2.93
0.0506	0.885732	143.220	-138.564	-2.27
0.0998	0.877852	143.048	-250.398	-5.69
0.1500	0.869623	142.903	-334.625	2.49
0.2001	0.861312	142.768	-407.747	7.81
0.2509	0.852877	142.635	-479.307	4.07
0.3003	0.844647	142.504	-549.613	-10.0
0.3498	0.836209	142.402	-591.856	-5.28
0.4000	0.827594	142.309	-623.325	0.930
0.4497	0.819014	142.221	-650.041	1.16
0.4999	0.810269	142.148	-661.792	5.23
0.5499	0.801503	142.082	-666.940	3.66
0.6004	0.792545	142.030	-657.914	3.06
0.6507	0.783601	141.983	-643.246	-5.85
0.6996	0.774776	141.959	-607.074	-6.72
0.7503	0.765524	141.956	-548.465	-1.88
0.8109	0.754310	141.976	-454.748	5.32
0.8503	0.747000	141.997	-385.818	4.24
0.9002	0.737626	142.040	-281.028	2.52
0.9499	0.728258	142.096	-164.384	-8.72
0.9751	0.723381	142.149	-81.2370	-0.200
1.0000	0.718567	142.200	0	0

$$\delta V^E = V_{\text{expt}}^E - V_{\text{calc}}^E.$$

TABLE III Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system DIPE(1) + butyl acrylate (3) at 298.15 K

x_1	ρ (g cm ⁻³)	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
			(cm ³ mol ⁻¹)	
0	0.915930	109.310	0	0
0.0257	0.909714	110.115	-40.4230	-2.28
0.0525	0.903248	110.964	-73.0460	2.10
0.1011	0.891822	112.498	-136.350	-1.15
0.1496	0.880622	114.042	-187.665	-0.970
0.2009	0.869007	115.688	-229.234	3.22
0.2503	0.858141	117.272	-270.599	-2.10
0.2994	0.847499	118.864	-293.223	3.71
0.3512	0.836575	120.543	-317.194	2.13
0.4002	0.826499	122.135	-336.157	-2.56
0.4510	0.816249	123.797	-345.451	-3.87
0.5025	0.806076	125.491	-345.234	-2.46
0.5496	0.796960	127.048	-339.202	-1.29
0.6001	0.787410	128.721	-324.890	1.59
0.6507	0.778068	130.400	-309.739	-1.16
0.7000	0.769104	132.052	-278.985	5.92
0.7503	0.760212	133.733	-254.227	0.0700
0.8004	0.751492	135.422	-211.437	5.87
0.8501	0.743085	137.092	-175.718	-1.80
0.8999	0.734801	138.777	-130.163	-6.70
0.9501	0.726559	140.494	-65.8650	-0.560
0.9747	0.722632	141.328	-40.1780	-6.08
1.0000	0.718567	142.200	0	0

$$\delta V^E = V_{\text{expt}}^E - V_{\text{calc}}^E.$$

TABLE IV Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system DIPE (1) + methyl methacrylate (4) at 298.15 K

x_1	ρ (g cm ⁻³)	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
0	0.937669	106.775	0	0
0.0252	0.930904	107.607	-60.1560	-9.24
0.0508	0.923954	108.474	-101.513	-4.33
0.0999	0.910857	110.144	-170.751	1.42
0.1506	0.897720	111.873	-237.089	-3.47
0.2018	0.884633	113.647	-278.009	4.41
0.2507	0.872506	115.342	-315.526	3.17
0.2998	0.860660	117.047	-347.382	-0.760
0.9506	0.848607	118.833	-362.755	5.12
0.4001	0.837230	120.569	-380.892	0.920
0.4502	0.826033	122.328	-393.594	-4.06
0.5001	0.815090	124.097	-393.746	-2.74
0.5510	0.804222	125.904	-390.743	-4.80
0.6007	0.793839	127.680	-375.375	-1.05
0.6508	0.783636	129.474	-355.152	0.390
0.7005	0.773766	131.258	-332.491	-3.07
0.7498	0.764117	133.048	-288.378	7.37
0.8003	0.754505	134.881	-243.302	9.62
0.8495	0.745404	136.664	-202.623	0.220
0.8989	0.736416	138.470	-148.804	-4.62
0.9495	0.727442	140.322	-90.0910	-14.2
0.9750	0.722890	141.278	-36.0480	2.44
1.0000	0.718567	142.200	0	0

$$\delta V^E = V_{\text{exptl}}^E - V_{\text{calc}}^E$$

TABLE V Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system DIPE (1) + styrene (5) at 298.15 K

x_1	ρ (g cm ⁻³)	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
0	0.901972	115.469	0	0
0.0256	0.896948	116.060	-93.1990	5.46
0.0503	0.892182	116.625	-188.102	3.15
0.1010	0.882467	117.796	-374.384	-2.82
0.1507	0.872951	118.968	-530.899	1.99
0.2003	0.863581	120.146	-677.485	-0.860
0.2505	0.854139	121.358	-807.907	-4.53
0.3008	0.844667	122.601	-909.005	1.07
0.3501	0.835490	123.832	-995.849	-1.56
0.4003	0.826172	125.109	-1061.92	-2.90
0.4503	0.816864	126.414	-1093.14	8.90
0.4997	0.807828	127.707	-1118.86	4.61
0.5498	0.798718	129.040	-1125.76	-2.10
0.6008	0.789481	130.423	-1104.79	-3.46
0.6513	0.780341	131.823	-1056.13	0.140
0.7002	0.771626	133.187	-998.972	-8.71
0.7502	0.762635	134.628	-895.761	2.96
0.8002	0.753782	136.079	-780.996	0.500
0.8501	0.744940	137.562	-630.645	5.95
0.9002	0.736117	139.077	-454.908	5.12
0.9498	0.727452	140.599	-258.261	-7.27
0.9745	0.723101	141.378	-140.214	-7.46
1.0000	0.718567	142.200	0	0

$$\delta V^E = V_{\text{exptl}}^E - V_{\text{calc}}^E$$

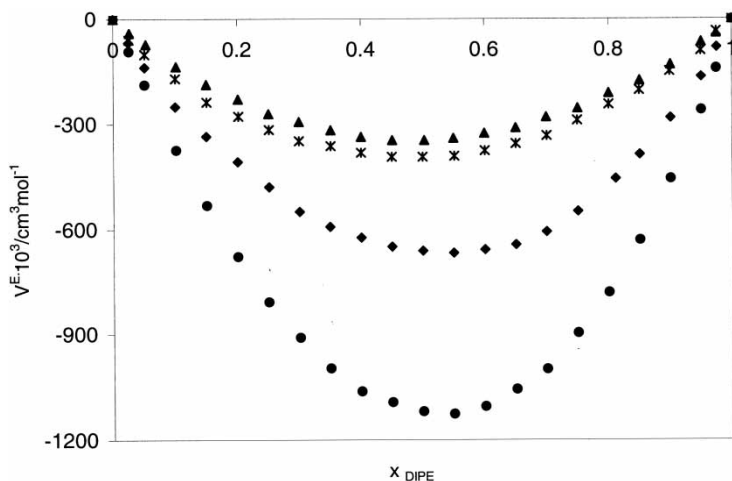


FIGURE 1 Excess volumes at 298.15 K: * DIPE + MMA; ▲ DIPE + EA; ◆ DIPE + BA; ● DIPE + styrene.

TABLE VI Partial volumes \bar{V}_i , $\text{cm}^{-3} \text{mol}^{-1}$

x_1	DIPE (1) + BA(2)		DIPE (1) + EA(3)		DIPE (1) + MMA(4)		DIPE (1) + styrene(5)	
	\bar{V}_2	\bar{V}_1	\bar{V}_3	\bar{V}_1	\bar{V}_4	\bar{V}_1	\bar{V}_5	\bar{V}_1
0	143.420	139.201	109.310	140.671	106.775	140.062	115.469	138.294
0.05	143.407	139.761	109.305	140.860	106.765	140.480	115.464	138.503
0.10	143.375	140.149	109.291	141.030	106.739	140.803	115.442	138.761
0.15	143.333	140.420	109.270	141.181	106.704	141.051	115.401	139.047
0.20	143.282	140.616	109.241	141.317	106.664	141.242	115.337	139.348
0.25	143.221	140.763	109.206	141.438	106.621	141.391	115.249	139.650
0.30	143.144	140.879	109.165	141.546	106.576	141.509	115.137	139.946
0.35	143.048	140.976	109.118	141.642	106.530	141.606	115.001	140.229
0.40	142.930	141.061	109.067	141.729	106.481	141.687	114.842	140.495
0.45	142.788	141.136	109.010	141.805	106.427	141.759	114.660	140.741
0.50	142.623	141.206	108.948	141.874	106.368	141.825	114.455	140.967
0.55	142.439	141.275	108.880	141.935	106.299	141.887	114.227	141.173
0.60	142.241	141.345	108.807	141.989	106.220	141.945	113.973	141.361
0.65	142.035	141.423	108.728	142.037	106.129	142.000	113.690	141.530
0.70	141.828	141.514	108.642	142.078	106.025	142.050	113.372	141.683
0.75	141.620	141.621	108.548	142.114	105.906	142.095	113.011	141.820
0.80	141.409	141.746	108.445	142.144	105.776	142.133	112.595	141.941
0.85	141.181	141.886	108.333	142.167	105.635	142.163	112.110	142.043
0.90	140.908	142.028	108.210	142.185	105.488	142.184	111.539	142.124
0.95	140.543	142.147	108.075	142.196	105.341	142.196	110.858	142.179
1	140.014	142.200	107.926	142.200	105.202	142.200	110.043	142.200

The values of V^E were correlated with composition using two methods:

(a) The Redlich–Kister expression (1948)

$$V^E = x_1 x_2 \sum_{k=0}^n A_k (x_1 - x_2)^k \quad (4)$$

where the A_k 's are the adjustable parameters of the model.

The Redlich–Kister regressor is very powerful and frequently used to correlate vapor–liquid equilibrium data and excess properties. Notwithstanding, it suffers from the important drawback that the values of the adjustable parameters change as the number of terms in the series is increased.

(b) A series of Legendre polynomials $L_k(x_1)$

$$V^E = x_1 x_2 \sum_{k=0}^n a_k L_k(x_1) \quad (5)$$

which for the four first terms ($k=0, 1, 2, 3$) is

$$V^E = x_1 x_2 [a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1) + a_3(20x_1^3 - 30x_1^2 + 12x_1 - 1)] \quad (6)$$

Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel, and Chebyshev, which have the valuable characteristic that for a continuous series of observations (infinite) the values of the coefficients do not change as the number of terms in the series is increased. This is an important property because if a physical interpretation can be assigned to one of its coefficients, its value remains constant. For the case of discrete measurements, such as determination of volumes of mixing, the values of the coefficients will vary, but only slightly. In addition, as shown in Table VII, the series of Legendre polynomials have the important characteristic that the structure of its first four terms is the same as that of the first four terms of the Redlich–Kister expression. The mathematical procedure to transform a power expansion, such as that of Redlich–Kister, into an orthogonal series has been described in detail by Tomiska (1981, 1984). Tomiska provides the iteration formulas for Legendre or Chebyshev's series of any order as well as the proof that the procedure is independent of the conversion coefficients from the actual excess property.

Equations (4) and (5) were fitted using a least-squares optimization procedure, with all points weighted equally and minimizing the following objective function (OF):

$$\text{OF} = \sum_1^N (V_{i,\text{exptl}}^E - V_{i,\text{calc}}^E)^2 \quad (7)$$

where N is the number of observations.

The standard deviation s was calculated as

$$s = \left[\sum (V_{i,\text{exptl}}^E - V_{i,\text{calc}}^E)^2 / (N - k) \right]^{1/2} \quad (8)$$

where k is the number of adjustable parameters. The statistical significance of adding one or more terms after the third was examined using a χ^2 -based test, coupled to the

TABLE VII Expressions for Legendre polynomials and the Redlich–Kister expression

Polynomial order, k	L_k (see Eq. (5))	Redlich–Kister (see Eq. (4))
0	1	1
1	$2x_1 - 1$	$2x_1 - 1$
2	$6(x_1^2 - x_1 + (1/6))$	$4(x_1^2 - x_1 + (1/4))$
3	$20(x_1^3 - (3/2)x_1^2 + (3/5)x_1 - (1/20))$	$8(x_1^3 - (3/2)x_1^2 + (3/4)x_1 - (1/8))$
4	$70(x_1^4 - 2x_1^3 + (9/7)x_1^2 - (2/7)x + (1/70))$	$16(x_1^4 - 2x_1^3 + (3/2)x_1^2 - (1/2)x + (1/16))$

requirement that the residues be randomly distributed, as suggested by Wisniak and Polishuk (1999). It was not deemed necessary to perform a step-wise regression. The values of the different adjustable parameters, A_k and a_k , are reported in Tables VIII and IX, together with the pertinent statistics.

A plot of the function $V^E/x_i x_j$ against composition was used in every case to test the quality of the data; this function is extremely sensitive to experimental errors, particularly in the dilute ranges and helps detecting outliers. In addition, its values at infinite dilution represent the values of the partial excess volume at infinite dilution, $\bar{V}_i^{E,\infty}$, which can be also calculated from the adjustable parameters as follows (Van Ness and Abbott, 1982):

(a) Redlich–Kister

$$\bar{V}_1^{E,\infty} = A_0 - A_1 + A_2 - \dots = \bar{V}_1^\infty - V_1^0 \quad (9)$$

$$\bar{V}_2^{E,\infty} = A_0 + A_1 + A_2 + \dots = \bar{V}_2^\infty - V_2^0 \quad (10)$$

(b) Legendre

$$\bar{V}_1^{E,\infty} = a_0 - a_1 + a_2 - \dots = \bar{V}_1^\infty - V_1^0 \quad (11)$$

$$\bar{V}_2^{E,\infty} = a_0 + a_1 + a_2 + \dots = \bar{V}_2^\infty - V_2^0 \quad (12)$$

where V_i^0 is the molar volume of pure component i . The pertinent values of $\bar{V}_i^{E,\infty}$ are also shown in Tables VIII and IX. In addition, it should be realized that in the absence of homoassociation, the value of the partial excess volume at infinite dilution reflects the true solute–solvent interaction. Equations (9) and (10) or (11) and (12) yield the same values of $\bar{V}_i^{E,\infty}$.

TABLE VIII Coefficients A_k (Eq. (4)), standard deviation s (Eq. (8)), Durbin–Watson statistic d , $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System	$A_0 \times 10^2$	$A_1 \times 10^2$	$A_2 \times 10^2$	$A_3 \times 10^2$	$A_4 \times 10^2$	$s \times 10^4$	d^a	$(V^E)_{x=0.5} \times 10^2$	$\bar{V}_1^{E,\infty} \times 10^2$	$\bar{V}_2^{E,\infty} \times 10^2$
(cm ³ mol ⁻¹)										
1+2	-266.8	-39.13	-22.92	18.75	-30.46	55.40	1.52	-66.70	-299.80	-340.6
1+3	-137.1	7.350	-9.060			35.01	2.00	-34.29	-153.60	-138.9
1+4	-156.4	6.680	-29.14	21.53		58.20	1.57	-39.10	-213.70	-157.3
1+5	-449.4	-43.69	-17.18	-32.36		50.38	1.83	-112.4	-390.50	-542.6

$$^a d = \sum_{u=2}^N (e_u - e_{u-1})^2 / \sum_{u=1}^N e_u^2; e_u = V_{u,\text{calc}}^E - V_{u,\text{exptl}}^E.$$

TABLE IX Coefficients a_k (Eq. (5)), standard deviation s (Eq. (8)), Durbin–Watson statistic d , $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$a_4 \times 10^2$	$s \times 10^4$	d^a	$(V^E)_{x=0.5} \times 10^2$	$\bar{V}_1^{E,\infty} \times 10^2$	$\bar{V}_2^{E,\infty} \times 10^2$
(cm ³ mol ⁻¹)										
1+2	-280.5	-27.890	-32.693	7.4990	-6.963	57.10	1.52	66.70	-299.81	-340.60
1+3	-140.2	7.2540	-5.3950			36.32	1.97	-34.40	-152.83	-138.33
1+4	-166.1	19.598	-19.426	8.6120		59.89	1.57	-39.10	-213.75	-157.33
1+5	-455.1	-63.101	-11.456	-12.944		51.84	1.82	-112.0	-390.55	-542.64

$$^a d = \sum_{u=2}^N (e_u - e_{u-1})^2 / \sum_{u=1}^N e_u^2; e_u = V_{u,\text{calc}}^E - V_{u,\text{exptl}}^E.$$

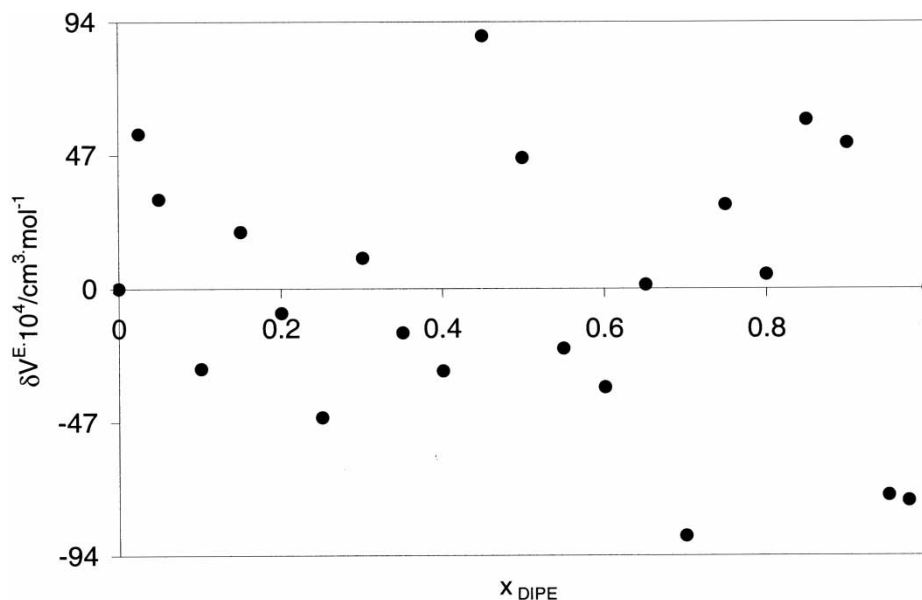


FIGURE 2 Residual distribution plot for the system DIPE + styrene, according to the fit given in Table VIII.

Figure 2 shows a typical distribution of the residuals, which is random as determined by the Durbin–Watson statistic.

An important observation in the calculation is obtained by considering the numerical value of the two terms that compose the right hand side of Eq. (1). Consider for example the point $x=0.5499$ in Table II. For this concentration the molar volumes of the solution and of the equivalent ideal solution (rounded) are 142.082 and 142.749 cm^3/mol , respectively. Hence, calculation of the excess volumes will normally involve taking the difference between two very large numbers of about the same size and yielding, for the specific concentration, $V^E = -0.6669 \text{ cm}^3/\text{mol}$. It is clear that a small error in each of the two large volumes may reflect in a *very* large error in their difference. Hence the importance of making the measurements very carefully and using an equipment that will provide enough significant figures. This is the same problem present in the calculation of heats of reaction; they can be calculated from heats of formation or from heats of combustion. The second case is usually in large error for the same reason; we are taking the difference between large numbers to obtain a number smaller in one order of magnitude (at least) of the original figures.

The sign and intensity of the volume changes that take place during mixing is the result of several effects that operate in the same or opposite directions. The most important ones are: (a) a positive effect caused by the break-up of the structure of one or both components (originated from nonchemical or chemical interactions such as hydrogen bonding or complex-forming interactions such as self-association) and (b) a negative effect due to physical interactions or geometric fitting of one component into the second, leading to a more compact packing (interstitial accommodation). The second contribution becomes more and more important with increasing sphericity of the solute molecule and higher molar volume of the solvent (Sharma *et al.*, 1992).

Structurally DIPE may be considered the homomorph of 2,4-dimethylpentane, aprotic and almost nonpolar. Interactions between a polar component and such

ether are considered to occur via complex formation between the two species or $n-\pi$ interaction (Sharma *et al.*, 1972).

The magnitude and sign of V^E is a reflection of the type of interactions taking place in the mixture. This is very well exhibited by the mixtures studied here with the minimum value of V^E ranging from about -0.345 to -1.12 cm^3/mol (the pertinent value of V^E is given by $A_0/4$). In every case the overall negative magnitude of V^E indicates a net packing effect that increases as the structure becomes more branched or aromatic. $n-\pi$ interactions between an aromatic hydrocarbon (such as styrene) and an ester are much stronger than those between a cyclic hydrocarbon and an aromatic. The (largest) negative values for the system DIPE + styrene indicates that the disruption of the dipolar association of the ether is considerably less than the specific interaction between its pairs of electrons and the π electrons of the aromatic ring. In addition, the substitution by an ethenyl group in the benzene ring constitutes an obstacle to $n-\pi$ specific interactions because of its bulkiness. As shown in Fig. 1, the system DIPE + styrene presents the largest packing effect. This fact is the result of the inductive effect of the vinyl group in styrene enhancing the electron density of its ring and the electrostatic interaction with the benzene ring, and of the steric effect of the vinyl group, which operates in the opposite direction. The net result is a smaller dislocation of the structure of DIPE.

It is also clear that there is a substantial difference in DIPE dislocation between EA and styrene. The value of $(V^E)_{x=0.5}$ for the latter is about three times larger than that of EA. In addition, there is clear effect of the side of the alkyl group of the ester. The chains with the smallest size have the smallest negative excess volumes.

It is interesting to compare the influence of the structure of the aromatic or cyclic hydrocarbon solute on the value of the excess volume with DIPE as a common solvent. Figure 3 reports the excess volumes for the systems DIPE + benzene, toluene,

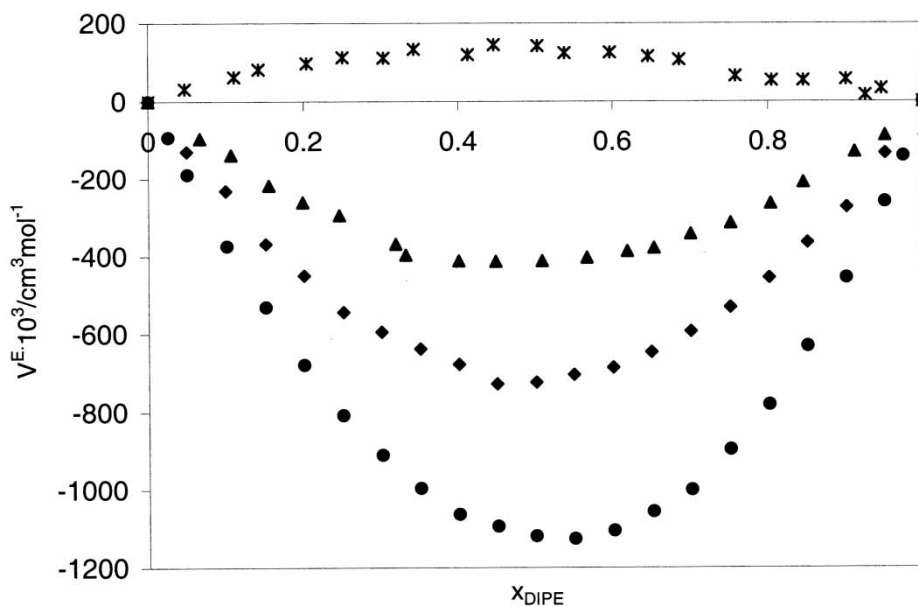


FIGURE 3 Influence of the structure of the solute on the excess volumes at 298.15 K; * DIPE + cyclohexane; \blacktriangle DIPE + benzene; \blacklozenge DIPE + toluene; \bullet DIPE + styrene.

cyclohexane (Wisniak *et al.*, 2001), and styrene, at 298.15 K. It is seen that disappearance of the aromatic character switches the sign of V^E from negative to positive and that the more branched the aromatic solute the more negative the excess volume becomes.

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