

Densities, Excess Volumes, and Partial Molar Volumes of *m*-Xylene + Ethyl Acrylate, + Butyl Acrylate, + Methyl Methacrylate, and + Styrene at 298.15 K

R. D. Peralta,^{1,2} R. Infante,¹ G. Cortez,¹ G. Cadenas,¹ and J. Wisniak³

Received August 26, 2002

Densities of the binary systems of *m*-xylene with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene have been measured as a function of composition, at 298.15 K and atmospheric pressure, using an Anton Paar DMA 5000 oscillating U-tube densimeter. The calculated excess volumes were correlated with the Redlich–Kister equation and with a series of Legendre polynomials. The excess volumes are positive for the binaries of *m*-xylene with methyl methacrylate, ethyl acrylate, and styrene. The excess volumes for the *m*-xylene + butyl acrylate system are positive for solvent (*m*-xylene) concentrations below 0.3 mole fraction and negative above this concentration.

KEY WORDS: acrylates; densities; excess volumes; *m*-xylene; monomers; styrene.

1. INTRODUCTION

The mixing of different compounds gives rise to solutions that generally do not behave ideally. The deviation from ideality is expressed by many thermodynamic variables, particularly by excess properties. 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

¹ Centro de Investigación en Química Aplicada, Saltillo 25000, Coahuila, México.

² To whom correspondence should be addressed. E-mail: rene@polimex.ciqqa.mx

³ Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

the excess volume represents an intercalation packing effect, that is, an expansion of the mixture. 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, $\bar{V}_i^E = (\partial \mu_i / \partial P)_{T,n_j}$. Excess volumes may be used also to test different mixing rules for equations of state of gases (EOS) applied to the liquid state, although this procedure may remove the EOS from their original theoretical background.

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. *m*-Xylene is an excellent solvent and may be useful in polymerization and other chemical 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 [1,2] 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 $n-\pi$ types). Sastry and Valand [3] 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. [4] measured the excess volumes of methyl methacrylate 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. The excess volumes for the system MMA + *m*-xylene showed a maximum of about $V^E \approx 0.12 \text{ cm}^3 \cdot \text{mol}^{-1}$.

No literature data are available for excess volumes of *m*-xylene with ethyl acrylate, butyl acrylate, and styrene.

2. EXPERIMENTAL

2.1. Materials

m-Xylene (99.78 mass%), ethyl acrylate, EA, (99.8 mass%), butyl acrylate, BA, (99.9 mass%), methyl methacrylate, MMA, (99.9 mass%),

Table I. Purity, Densities, and Molar Masses of Pure Components at 298.15 K

| Component | Molar Masses | Purity (mass %) | Density ($\text{g} \cdot \text{cm}^{-3}$) | |
|-------------------------|--------------|-----------------|---|--------------|
| | | | measured | literature |
| <i>m</i> -Xylene (1) | 106.17 | 99.78 | 0.859796 | 0.85986 [12] |
| Butyl acrylate (2) | 128.17 | 99.9 | 0.893958 | 0.8941 [3] |
| Ethyl acrylate (3) | 100.12 | 99.8 | 0.915930 | 0.9163 [3] |
| Methyl methacrylate (4) | 100.12 | 99.9 | 0.937669 | 0.93766 [13] |
| Styrene (5) | 104.15 | 99.9 | 0.901880 | 0.9016 [14] |

and styrene (99.9 mass%) were acquired from Aldrich. The supplier certified the purity of all the reagents by gas chromatography. EA, BA, and MMA were vacuum distilled prior to use to eliminate the stabilizer (about 0.002% mass of hydroquinone monomethyl ether). Styrene, containing 10 to 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 densities of the purified reagents at 298.15 K were determined, and their values are reported in Table I along with values given in the literature.

2.2. 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 precision of $5 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$. The temperature in the cell was regulated to $\pm 0.001 \text{ K}$ with a solid-state thermostat. The adjustment of the apparatus was verified daily with dry air and bi-distilled 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. To prevent contact between the samples and the rubber stopper, each component was added with a syringe; the mixtures were agitated gently, and the samples for density measurements were also withdrawn with a syringe. The total uncertainty (ISO 9001) in the mole fraction is 5.8×10^{-5} ; the precision of the density (duplicate) measurements is $\pm 2 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$, and of the temperature $\pm 0.002 \text{ K}$. The total uncertainty of density is $1.0 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ and of temperature is 0.01 K .

Proper safety measures were taken when handling all the materials.

3. RESULTS AND DISCUSSION

At least twenty-one density measurements were performed (with repetition) for each binary system over the full concentration range ($0 \leq x_1 \leq 1$).

The excess volumes V^E of the solutions of mole fraction x_1 were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E = [x_1 M_1 + (1 - x_1) M_2] / \rho - [x_1 M_1 / \rho_1 + (1 - x_1) M_2 / \rho_2] \quad (1)$$

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 Table II and Fig. 1. The values of the measured volumes were used to calculate the partial volumes of the components using well-known relations reported elsewhere [5]. The excess volumes calculated by Eq. 1 were correlated using the analytical expression of Redlich–Kister and a series of Legendre polynomials $L_k(x_1)$, as described in a previous publication [6]. The pertinent values of \bar{V}_i appear in Table III and are necessarily consistent.

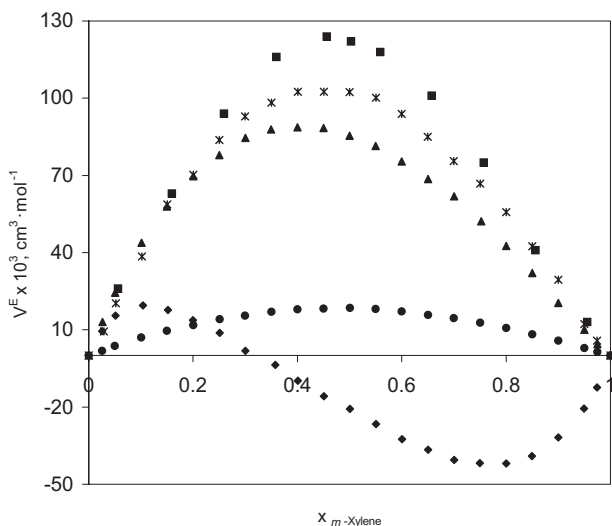


Fig. 1. Excess volumes at 298.15 K: *, *m*-xylene + MMA; ▲, *m*-xylene + EA; ◆, *m*-xylene + BA; ●, *m*-xylene + styrene; ■, *m*-xylene + MMA, Sastry et al. [4].

Table II. Experimental Densities, Volumes, and Excess Volumes for All Systems at 298.15 K

| <i>m</i> -xylene (1) + butyl acrylate (2) | | | <i>m</i> -xylene (1) + ethyl acrylate (3) | | | <i>m</i> -xylene (1) + methyl methacrylate (4) | | | <i>m</i> -xylene (1) + styrene (5) | | | | | |
|---|---------------------------------|--|---|---------------------------------|--|--|---------------------------------|--|------------------------------------|---------------------------------|--|----------|---------------------------------|--|
| x_1 | ρ (g·cm ⁻³) | V (cm ³ ·mol ⁻¹) | x_1 | ρ (g·cm ⁻³) | V (cm ³ ·mol ⁻¹) | x_1 | ρ (g·cm ⁻³) | V (cm ³ ·mol ⁻¹) | x_1 | ρ (g·cm ⁻³) | V (cm ³ ·mol ⁻¹) | x_1 | ρ (g·cm ⁻³) | V (cm ³ ·mol ⁻¹) |
| 0 | 0.893958 | 143.3736 | 0 | 0.915930 | 109.3097 | 0 | 0.937669 | 106.7754 | 0 | 0.901880 | 115.4810 | 0 | 0.901880 | 115.4810 |
| 0.0253 | 0.893151 | 142.8794 | 0.00948 | 0.914163 | 109.6946 | 0.01305 | 0.935002 | 107.2666 | 0.00939 | 0.0257 | 0.900713 | 115.6882 | 0.0257 | 0.900713 |
| 0.0516 | 0.892333 | 142.3636 | 0.01549 | 0.912556 | 110.0476 | 0.02441 | 0.932842 | 107.6656 | 0.02026 | 0.0500 | 0.899607 | 115.8851 | 0.0500 | 0.899607 |
| 0.1042 | 0.890724 | 141.3201 | 0.01947 | 0.909222 | 110.7910 | 0.04379 | 0.928323 | 108.5133 | 0.03843 | 0.1004 | 0.897338 | 116.2916 | 0.1004 | 0.897338 |
| 0.1517 | 0.889288 | 140.3746 | 0.01765 | 0.906122 | 111.4951 | 0.05792 | 0.923951 | 109.3446 | 0.05878 | 0.1497 | 0.895139 | 116.6884 | 0.1497 | 0.895139 |
| 0.1995 | 0.887834 | 139.4193 | 0.01373 | 0.902993 | 112.2172 | 0.06971 | 0.92004 | 0.919587 | 0.101931 | 0.2002 | 0.892906 | 117.0944 | 0.2002 | 0.892906 |
| 0.2510 | 0.886250 | 138.3900 | 0.00885 | 0.899922 | 112.9384 | 0.07788 | 0.915295 | 111.0392 | 0.08378 | 0.2510 | 0.890671 | 117.5036 | 0.2510 | 0.890671 |
| 0.3002 | 0.884731 | 137.4050 | 0.00182 | 0.896929 | 113.6514 | 0.08452 | 0.911130 | 111.8756 | 0.09287 | 0.2998 | 0.888546 | 117.8956 | 0.2998 | 0.888546 |
| 0.3573 | 0.882921 | 136.2629 | -0.00370 | 0.894020 | 114.3561 | 0.08785 | 0.906973 | 112.7256 | 0.09822 | 0.3503 | 0.886364 | 118.3008 | 0.3503 | 0.886364 |
| 0.4006 | 0.881541 | 135.3951 | -0.00982 | 0.891121 | 115.0694 | 0.08869 | 0.902886 | 113.5747 | 0.10256 | 0.4001 | 0.884228 | 118.7003 | 0.4001 | 0.884228 |
| 0.4505 | 0.879924 | 134.3973 | -0.01587 | 0.888296 | 115.7742 | 0.08839 | 0.898966 | 114.4040 | 0.10256 | 0.4498 | 0.882115 | 119.0985 | 0.4498 | 0.882115 |
| 0.5005 | 0.878271 | 133.3985 | -0.02070 | 0.885498 | 116.4833 | 0.08542 | 0.895092 | 115.2357 | 0.10237 | 0.5006 | 0.879973 | 119.5050 | 0.5006 | 0.879973 |
| 0.5504 | 0.876601 | 132.3991 | -0.02660 | 0.882766 | 117.1850 | 0.08148 | 0.891252 | 116.0734 | 0.10024 | 0.5502 | 0.877898 | 119.9016 | 0.5502 | 0.877898 |
| 0.6005 | 0.874901 | 131.3970 | -0.03251 | 0.880068 | 117.8883 | 0.07539 | 0.887548 | 116.8960 | 0.09394 | 0.6001 | 0.875830 | 120.2997 | 0.6001 | 0.875830 |
| 0.6501 | 0.873178 | 130.4051 | -0.03664 | 0.877397 | 118.5937 | 0.06858 | 0.883898 | 117.7199 | 0.08497 | 0.6502 | 0.873769 | 120.6994 | 0.6502 | 0.873769 |
| 0.7003 | 0.871411 | 129.4043 | -0.04062 | 0.874744 | 119.3026 | 0.06182 | 0.880304 | 118.5430 | 0.07558 | 0.7000 | 0.871733 | 121.0967 | 0.7000 | 0.871733 |
| 0.7499 | 0.869615 | 128.4155 | -0.04485 | 0.872079 | 120.0260 | 0.05219 | 0.876681 | 119.3838 | 0.06680 | 0.7501 | 0.869704 | 121.4955 | 0.7501 | 0.869704 |
| 0.8000 | 0.867765 | 127.4183 | -0.04817 | 0.869646 | 120.6948 | 0.04259 | 0.873218 | 120.2005 | 0.05576 | 0.8001 | 0.867690 | 121.8940 | 0.8001 | 0.867690 |
| 0.8499 | 0.865878 | 126.4301 | -0.03905 | 0.867154 | 121.3881 | 0.03202 | 0.869802 | 121.0188 | 0.04244 | 0.8499 | 0.865703 | 122.2900 | 0.8499 | 0.865703 |
| 0.9003 | 0.863907 | 125.4343 | -0.03174 | 0.864684 | 122.0843 | 0.02040 | 0.866420 | 121.8397 | 0.02945 | 0.9005 | 0.863698 | 122.6921 | 0.9005 | 0.863698 |
| 0.9494 | 0.861929 | 124.4684 | -0.02060 | 0.862232 | 122.7820 | 0.01009 | 0.863101 | 122.6593 | 0.01225 | 0.9500 | 0.861748 | 123.0859 | 0.9500 | 0.861748 |
| 0.9746 | 0.860887 | 123.9764 | -0.01238 | 0.861001 | 123.1357 | 0.00446 | 0.861471 | 123.0643 | 0.00586 | 0.9751 | 0.860768 | 123.2849 | 0.9751 | 0.860768 |
| 1 | 0.859796 | 123.4828 | 0 | 1 | 0.859796 | 123.4828 | 0 | 1 | 0.859796 | 123.4828 | 0 | 1 | 0.859796 | 123.4828 |

Table III. Partial Molar Volumes V_j in $\text{cm}^3 \cdot \text{mol}^{-1}$

| x_1 | m -Xylene (1) + BA (2) \bar{V}_1 | m -Xylene (1) + EA (3) \bar{V}_3 | m -Xylene (1) + MMA (4) \bar{V}_4 | m -Xylene (1) + Styrene (5) \bar{V}_5 | | | | |
|-------|---|---|--|--|---------|---------|---------|---------|
| 0 | 143.374 | 123.892 | 109.310 | 124.015 | 106.775 | 123.925 | 115.481 | 123.558 |
| 0.05 | 143.379 | 123.667 | 109.312 | 123.914 | 106.776 | 123.885 | 115.481 | 123.551 |
| 0.10 | 143.390 | 123.531 | 109.319 | 123.833 | 106.780 | 123.843 | 115.482 | 123.544 |
| 0.15 | 143.402 | 123.455 | 109.328 | 123.766 | 106.786 | 123.801 | 115.483 | 123.537 |
| 0.20 | 143.413 | 123.419 | 109.340 | 123.712 | 106.794 | 123.761 | 115.484 | 123.531 |
| 0.25 | 143.422 | 123.409 | 109.353 | 123.667 | 106.806 | 123.721 | 115.486 | 123.525 |
| 0.30 | 143.431 | 123.413 | 109.366 | 123.630 | 106.820 | 123.684 | 115.488 | 123.519 |
| 0.35 | 143.441 | 123.427 | 109.381 | 123.600 | 106.837 | 123.649 | 115.491 | 123.513 |
| 0.40 | 143.453 | 123.444 | 109.396 | 123.575 | 106.856 | 123.618 | 115.494 | 123.508 |
| 0.45 | 143.467 | 123.464 | 109.412 | 123.554 | 106.877 | 123.589 | 115.497 | 123.503 |
| 0.50 | 143.483 | 123.484 | 109.428 | 123.536 | 106.899 | 123.564 | 115.501 | 123.499 |
| 0.55 | 143.498 | 123.503 | 109.444 | 123.521 | 106.923 | 123.543 | 115.505 | 123.496 |
| 0.60 | 143.509 | 123.521 | 109.460 | 123.509 | 106.947 | 123.525 | 115.509 | 123.492 |
| 0.65 | 143.511 | 123.535 | 109.476 | 123.500 | 106.971 | 123.511 | 115.514 | 123.490 |
| 0.70 | 143.498 | 123.544 | 109.491 | 123.493 | 106.993 | 123.500 | 115.518 | 123.488 |
| 0.75 | 143.466 | 123.547 | 109.505 | 123.487 | 107.014 | 123.492 | 115.523 | 123.486 |
| 0.80 | 143.408 | 123.542 | 109.516 | 123.484 | 107.031 | 123.487 | 115.527 | 123.485 |
| 0.85 | 143.321 | 123.529 | 109.523 | 123.482 | 107.045 | 123.484 | 115.531 | 123.484 |
| 0.90 | 143.206 | 123.511 | 109.526 | 123.482 | 107.053 | 123.483 | 115.535 | 123.483 |
| 0.95 | 143.064 | 123.492 | 109.521 | 123.482 | 107.055 | 123.483 | 115.539 | 123.483 |
| 1 | 142.908 | 123.483 | 109.506 | 123.483 | 107.048 | 123.483 | 115.541 | 123.483 |

Although the Redlich–Kister equation was originally developed to correlate the excess Gibbs function [7], it is also used to correlate the excess volumes:

$$V^E = x_1 x_2 \sum_{k=0}^n A_k (x_1 - x_2)^k \quad (2)$$

For the four first terms the series of Legendre polynomials becomes

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

Legendre polynomials, unlike the Redlich–Kister expression, 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 the determination of volumes of mixing, the values of the coefficients will vary, but only slightly. In addition, as shown in Table IV, 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. Tomiska [8, 9] has described the mathematical procedure to transform a power expansion, such as that of Redlich–Kister, into an orthogonal series. In addition, Tomiska has provided 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 (2) and (3) were fitted using a least-squares optimization procedure, with all points weighted equally and minimizing the following objective function (OF):

$$\text{OF} = \sum_{i=1}^N (V_{i, \text{exp } t}^E - V_{i, \text{calc}}^E)^2 \quad (4)$$

Table IV. Terms of Legendre Polynomials and the Redlich–Kister Expression

| Polynomial order, <i>k</i> | L_k , Eq. (7) | Redlich–Kister, Eq. (6) |
|----------------------------|---|---|
| 0 | 1 | 1 |
| 1 | $2x_1 - 1$ | $2x_1 - 1$ |
| 2 | $6(x_1^2 - x_1 + \frac{1}{6})$ | $4(x_1^2 - x_1 + \frac{1}{4})$ |
| 3 | $20(x_1^3 - \frac{3}{2}x_1^2 + \frac{3}{5}x_1 - \frac{1}{20})$ | $8(x_1^3 - \frac{3}{2}x_1^2 + \frac{3}{4}x_1 - \frac{1}{8})$ |
| 4 | $70(x_1^4 - 2x_1^3 + \frac{9}{7}x_1^2 - \frac{2}{7}x_1 + \frac{1}{70})$ | $16(x_1^4 - 2x_1^3 + \frac{3}{2}x_1^2 - \frac{1}{2}x_1 + \frac{1}{16})$ |

where N is the number of observations. The values of the different adjustable parameters, A_k and a_k , are reported in Table V for different values of k , together with the pertinent statistics. The standard deviation s was calculated as

$$s = \left[\sum (V_{i, \text{exp } t}^E - V_{i, \text{calc}}^E)^2 / (N - k) \right]^{1/2} \quad (5)$$

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 requirement that the residues be randomly distributed, as suggested by Wisniak and Polishuk [10]. It was not deemed necessary to perform a step-wise regression.

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 to detect 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 [5]:

(a) *Redlich-Kister*

$$\bar{V}_1^{E, \infty} = A_0 - A_1 + A_2 - \dots = \bar{V}_1^\infty - V_1^0 \quad (6)$$

$$\bar{V}_2^{E, \infty} = A_0 + A_1 + A_2 + \dots = \bar{V}_2^\infty - V_2^0 \quad (7)$$

(b) *Legendre*

$$\bar{V}_1^{E, \infty} = a_0 - a_1 + a_2 - \dots = \bar{V}_1^\infty - V_1^0 \quad (8)$$

$$\bar{V}_2^{E, \infty} = a_0 + a_1 + a_2 + \dots = \bar{V}_2^\infty - V_2^0 \quad (9)$$

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 Table V. In addition, it should be realized that in the absence of self-association, the value of the partial excess volume at infinite dilution reflects the true solute-solvent interaction. Equations (6) and (7) or (8) and (9) yield the same values of $\bar{V}_i^{E, \infty}$. In all systems, the distribution of the residuals (not shown) was random as confirmed by the Durbin-Watson statistic.

Figure 1 compares the results of this work with those of Sastry et al. [4] for the system *m-xylene* + methyl methacrylate. It is seen that in the mid-concentration range Sastry's results are somewhat larger than those reported here. The difference between the two sets of measurements may be due to the different experimental technique (Sastry used a pycnometer) and to a different level of purity of the reagents (not specified by Sastry).

Table V. Coefficients A_k (Eq. (4)), a_k (Eq. (5)), Standard Deviation s (Eq. (8)), Durbin-Watson Statistic d , 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 ($\text{cm}^3 \cdot \text{mol}^{-1}$) | d^a | $\bar{V}_1^{E,\infty} \times 10^2$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) | $\bar{V}_2^{E,\infty} \times 10^2$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) |
|--------|-------------------|-------------------|-------------------|-------------------|-------------------|--|-------|---|---|
| 1+2 | -8.49 | -21.7 | -4.54 | -22.1 | 10.2 | 0.000769 | 1.49 | 40.45 | -46.56 |
| 1+3 | 34.2 | -12.9 | 2.15 | -3.82 | | 0.000446 | 1.58 | 53.17 | 19.62 |
| 1+4 | 41.1 | -8.49 | -5.29 | | | 0.00148 | 1.61 | 44.27 | 27.28 |
| 1+5 | 7.31 | -0.720 | -0.560 | | | 0.000168 | 1.71 | 7.470 | 6.030 |
| | $a_0 \times 10^2$ | $a_1 \times 10^2$ | $a_2 \times 10^2$ | $a_3 \times 10^2$ | $a_4 \times 10^2$ | | | | |
| 1+2 | 7.96 | -34.9 | 2.81 | -8.83 | 2.34 | 0.00079 | 1.49 | 40.94 | -46.56 |
| 1+3 | 35.0 | -15.2 | 1.43 | -1.53 | | 0.000459 | 1.58 | 53.17 | 19.62 |
| 1+4 | 39.3 | -8.49 | -3.53 | | | 0.00152 | 1.61 | 44.27 | 27.28 |
| 1+5 | 7.13 | -0.722 | -0.373 | | | 0.000173 | 1.71 | 7.47 | 6.03 |

$$^a d = \frac{\sum_{i=2}^N (e_i - e_{i-1})^2 / \sum_{i=1}^N e_{i+1}^2}{\sum_{i=1}^N e_{i+1}^2} = V_{i, \text{calc}}^E - V_{i, \text{exp}}^E$$

Further, calculation of the excess volumes will normally involve taking the difference between two very large numbers that may result in a *very* large error in their difference. As an example, for the point $x_1 = 0.5003$ in Table II, $V^E = 0.103 \text{ cm}^3 \cdot \text{mol}^{-1}$ and the overall uncertainty is about $\pm 6 \times 10^{-4}$. Hence, the importance of making the measurements very carefully and using equipment that will provide enough significant figures must be emphasized.

Inspection of the results of Table II and Fig. 1 indicates that the excess volumes are positive for the binaries of *m*-xylene with methyl methacrylate, ethyl acrylate, and styrene. The excess volumes for the system *m*-xylene + butyl acrylate are positive for solvent concentrations below 0.3 mole fraction and negative above this concentration.

The function $V^E(x_1)$ is almost symmetric for the binaries of *m*-xylene with MMA, EA, and styrene, suggesting that the maximum specific interaction occurs near the equimolar composition and there is little or no self-association of the solute or solvent.

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 and maximum values of V^E ranging from about -0.040 to $+0.10 \text{ cm}^3 \cdot \text{mol}^{-1}$ (the pertinent value of V^E is given by $A_0/4$). The overall positive magnitude of V^E indicates a net dislocation effect that increases as the structure becomes more branched from EA to MMA, and caused by an intercalation effect of *m*-xylene that breaks dipole-dipole associations. $n-\pi$ 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) positive values for the system *m*-xylene + MMA indicate that the disruption of the dipolar association of the ester is considerably larger 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 [11].

The positive values of V^E for the system *m*-xylene + BA in the range $0 < x_1 < 0.3$ are due to the same reasons as for the solutes MMA and EA. As the concentration of *m*-xylene increases, disruption of the dipole association of the ester becomes smaller than the specific attraction between its pair of electrons and the π electrons of the aromatic ring. There is also the possibility of some complexation between both compounds.

REFERENCES

1. N. V. Sastry and P. N. Dave, *Int. J. Thermophys.* **17**:1289 (1996).
2. N. V. Sastry and P. N. Dave, *Proc. Indian Acad. Sci. (Chem. Sci.)* **109**:211 (1997).

3. N. V. Sastry and M. K. Valand, *Phys. Chem. Liq.* **38**:61 (2000).
4. N. V. Sastry, S. R. Patel, and M. C. Patel, *J. Chem. Thermodyn.* **31**:797 (1999).
5. H. C. Van Ness and M. M. Abbott, *Classical Thermodynamics of Nonelectrolyte Solutions* (McGraw-Hill, New York, 1982).
6. R. D. Peralta, R. Infante, G. Cortez, R. R. Ramirez, and J. Wisniak, *J. Chem. Thermodyn.* **35**:239 (2003).
7. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**:345 (1948).
8. J. Tomiska, *CALPHAD* **5**:93 (1981).
9. J. Tomiska, *CALPHAD* **8**:283 (1984).
10. J. Wisniak and A. Polishuk, *Fluid Phase Equilib.* **164**:61 (1999).
11. S. C. Sharma, R. Kaur, and J. Singh, *J. Chem. Thermodyn.* **2**:1171 (1972).
12. *TRC Thermodynamic Tables, extant 2002. Hydrocarbons*, Thermodynamics Research Center, The Texas A&M University System, College Station, Texas, TX, table db-3300.0 (2001).
13. L. Beichen, S. E. M. Hamam, and B. C.-Y. Lu, *J. Chem. Thermodyn.* **18**:1043 (1986).
14. J. A. Riddick, W. Bunger, and T. Sakano, *Organic Solvents Physical Properties and Methods of Purification*, 4th Ed. (Wiley, New York, 1986).