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Volumetric Properties of 1,1-Dimethylethyl Methyl Ether With Ethyl Acrylate, Butyl Acrylate, Methyl Methacrylate, and Styrene at 298.15 K

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Densities of the binary systems of 1,1-dimethylethyl methyl ether (MTBE) 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. The calculated excess volumes were correlated with the Redlich–Kister equation and with a series of Legendre polynomials. The excess volumes are negative for all the systems studied.

KEY WORDS: 1,1-dimethylethyl methyl ether; butyl acrylate; densities; ethyl acrylate; excess volumes; methyl methacrylate; mixtures; monomers; MTBE; styrene.

1. INTRODUCTION

The mixing of different compounds gives rise to excess properties such as volumes of mixing, enthalpies, and entropies, which reflect the extent of the deviations from non-ideality. 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.

This work is part of our program to provide data for the characterization of the molecular interactions between solvents and industrially

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important monomers, in particular, the influence of the chemical structure of the solute in the systems under consideration.

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, and with chlorinated solvents the controlling factors were specific interactions (O-Cl and n-π 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 non-specific interactions between the components. Sastry et al. [4] measured the excess volumes of methyl methacrylate and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and (*o*, *m*, *p*)-xylene at 298.15 and 303.15 K and found that except for toluene all exhibited positive excess volumes.

There is ample literature on measurements of the excess volume of MTBE with a large number of compounds, but none on the solutes considered here. Linek [5] measured the excess volumes of mixtures of ethers such as MTBE, ethyl propyl ether, butyl methyl ether, and butyl ethyl ether with esters such as ethyl ethanoate, ethyl propanoate, and propyl ethanoate at 298.15 K and found that they were almost zero over the entire range of composition.

No literature data are available for the excess volumes of the systems studied in this work.

2. EXPERIMENTAL

2.1. Materials

MTBE, (99+mass%), ethyl acrylate, EA, (99+mass%), butyl acrylate, BA, (99+mass%), methyl methacrylate, MMA, (99+mass%), and styrene (99 mass%) were purchased from Aldrich.

The purity of the reagents was certified by the provider

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 to 15 ppm of 4-tert-butylcatechol as stabilizer, was not distilled to avoid polymerization but was degassed by freezing and heating. The purity of the solvents was further ascertained by comparing their densities at 298.15 K with values reported in the literature [3, 6, 7] (Table I).

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

Component	Purity (mass%)	Density ($g \cdot cm^{-3}$)	
		measured	lit.
MTBE (1)	99+	0.735356	0.7353 [6]
Butyl acrylate (2)	99+	0.893666	0.8941 [3]
Ethyl acrylate (3)	99	0.915930	0.9163 [3]
Methyl methacrylate (4)	99	0.937669	0.93766 [7]
Styrene (5)	99	0.901972	0.9016 [13]

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), a stated safe uncertainty given by the supplier of 5×10^{-6} $g \cdot cm^{-3}$ and a precision of 1×10^{-6}. The temperature in the cell was regulated to 0.001 K with a solid-state thermostat. The apparatus was calibrated once a day 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 10^{-4} g. To minimize the errors in composition, the heavier component was charged first and the sample kept in ice water. Total uncertainty (ISO 9001) in the mole fraction is 7.1×10^{-5}; precision of the density (duplicate) measurement 2×10^{-6} $g \cdot cm^{-3}$, and of the temperature ± 0.002 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 ($0 \leqslant x \leqslant 1$).

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:

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

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

Table II. Experimental Densities, Volumes, Calculated Excess Volumes, and Deviations dV^E for the System MTBE (1) + Butyl Acrylate (2) at 298.15 K

x_1	$\rho(\mathrm{g\cdot cm^{-3}})$	V (mol·cm^{-3})	V^E (mol·cm^{-3})	$\delta V^E \times 10^{3a}$
0	0.893666	143.420	0	0
0.0308	0.889964	142.632	−0.06320	−5
0.0502	0.887579	142.139	−0.09870	−6
0.1000	0.881288	140.894	−0.1720	−2
0.1499	0.874754	139.663	−0.2277	10
0.2005	0.868069	138.407	−0.2927	3
0.2522	0.861018	137.137	−0.3453	1
0.3002	0.854341	135.959	−0.3924	−5
0.3503	0.847167	134.745	−0.4274	−5
0.4005	0.839787	133.536	−0.4541	−4
0.4506	0.832208	132.342	−0.4676	4
0.5012	0.824425	131.134	−0.4837	1
0.5499	0.816730	129.985	−0.4871	3
0.5998	0.808666	128.811	−0.4856	1
0.6505	0.800227	127.636	−0.4679	5
0.7001	0.791797	126.487	−0.4486	−1
0.7502	0.783045	125.342	−0.4147	−4
0.7999	0.774117	124.216	−0.3693	−9
0.8502	0.764705	123.110	−0.2897	5
0.9002	0.755215	122.012	−0.2125	1
0.9500	0.745433	120.938	−0.1132	3
0.9748	0.740469	120.408	−0.05930	1
1	0.735356	119.874	0	0

[a] $\delta V^E = V^E_{\exp tl} - V^E_{calc}$.

components. The corresponding values of ρ and V^E are reported in Tables II to V and Fig. 1. The values of V^E were correlated with composition using two methods:

(a) The Redlich–Kister expression [8]

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

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.

Table III. Experimental Densities, Volumes, Calculated Excess Volumes, and Deviations dV^E for the System MTBE (1) + Ethyl Acrylate (3) at 298.15 K

x_1	ρ (g·cm^{-3})	V	V^E	$\delta V^E \times 10^3$ [a]
		(cm^3·mol^{-1}		
0	0.915930	109.310	0	0
0.0253	0.911121	109.554	−0.02320	1
0.0509	0.906300	109.799	−0.04830	−1
0.1007	0.896906	110.285	−0.08840	−1
0.1502	0.887585	110.774	−0.1225	0
0.2039	0.877543	111.309	−0.1548	1
0.2500	0.868970	111.773	−0.1781	2
0.3003	0.859696	112.279	−0.2031	0
0.3507	0.850431	112.792	−0.2228	0
0.4000	0.841444	113.296	−0.2393	−2
0.4503	0.832298	113.817	−0.2495	−1
0.5011	0.823112	114.349	−0.2543	0
0.5498	0.814353	114.862	−0.2559	0
0.5998	0.805404	115.396	−0.2501	2
0.6503	0.796443	115.936	−0.2439	−1
0.7000	0.787649	116.475	−0.2298	−2
0.7534	0.778235	117.062	−0.2064	−1
0.8000	0.770029	117.585	−0.1769	2
0.8501	0.761296	118.147	−0.1434	1
0.8998	0.752650	118.713	−0.1030	0
0.9500	0.743973	119.290	−0.05520	0
0.9753	0.739644	119.579	−0.03320	−5
1	0.735356	119.874	0	0

[a] $\delta V^E = V^E_{\exp tl} - V^E_{calc}$.

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

$$V^E = x_1 x_2 \sum_{k=0}^{N} a_k L_k(x_1) \tag{3}$$

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

$$V^E = x_1 x_2 [a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1)] \tag{4}$$

Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel, and Chebyshev, which have the important 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

Table IV. Experimental Densities, Volumes, Calculated Excess Volumes, and Deviations dV^E for the System MTBE (1) + Methyl Methacrylate (4) at 298.15 K

		V	V^E	$\delta V^E \times 10^3$ [a]
x_1	ρ (g·cm^{-3})	(cm^3·mol^{-1})		
0	0.937608	106.782	0	0
0.0262	0.931889	107.101	−0.02510	−4
0.0501	0.926652	107.398	−0.04000	1
0.1003	0.915793	108.015	−0.08110	−1
0.1500	0.905097	108.634	−0.1128	4
0.2000	0.894547	109.247	−0.1540	−3
0.2500	0.883985	109.875	−0.1803	1
0.2501	0.883973	109.875	−0.1814	0
0.3009	0.873354	110.515	−0.2065	1
0.3506	0.863050	111.145	−0.2264	2
0.4010	0.852706	111.785	−0.2473	−3
0.4498	0.842724	112.416	−0.2557	−1
0.4996	0.832639	113.062	−0.2608	−2
0.5503	0.822431	113.727	−0.2594	−2
0.6000	0.812468	114.389	−0.2487	1
0.6500	0.802575	115.055	−0.2365	0
0.7003	0.792649	115.736	−0.2140	3
0.7504	0.782882	116.414	−0.1920	1
0.8001	0.773228	117.096	−0.1612	2
0.8500	0.763685	117.779	−0.1311	−3
0.9000	0.754130	118.476	−0.08900	0
0.9501	0.744687	119.174	−0.04710	−1
0.9753	0.739984	119.524	−0.02590	−3
1	0.735356	119.874	0	0

[a] $\delta V^E = V^E_{\exp tl} - V^E_{calc}$.

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.

The series of Legendre polynomials have the important characteristic that the structure of the first three terms is the same as the first three terms of the Redlich–Kister expression.

Equations (2) and (3) were fitted using a least-squares optimization procedure, with all points weighted equally and minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{1}^{N} (V^E_{i,\exp t} - V^E_{i,calc})^2 \tag{5}$$

Table V. Experimental Densities, Volumes, Calculated Excess Volumes, and Deviations dV^E for the System MTBE (1) + Styrene (5) at 298.15 K

x_1	ρ (g·cm^{-3})	V (cm^3·mol^{-1})	V^E (cm^3·mol^{-1})	$\delta V^E \times 10^3$ [a] (cm^3·mol^{-1})
0	0.901972	115.469	0	0
0.0258	0.898012	115.519	−0.06350	4
0.0512	0.894112	115.568	−0.1265	6
0.1036	0.886098	115.667	−0.2584	−1
0.1512	0.878715	115.773	−0.3620	−1
0.2003	0.870982	115.898	−0.4531	5
0.2516	0.862932	116.028	−0.5496	−2
0.3008	0.855075	116.173	−0.6212	1
0.3565	0.846159	116.345	−0.6942	−3
0.4020	0.838784	116.499	−0.7414	−6
0.4498	0.830936	116.680	−0.7706	−2
0.5005	0.822521	116.887	−0.7864	3
0.5499	0.814299	117.097	−0.7946	0
0.6002	0.805803	117.333	−0.7801	3
0.6497	0.797382	117.579	−0.7524	2
0.7002	0.788695	117.850	−0.7034	4
0.7503	0.779997	118.135	−0.6390	2
0.7999	0.771343	118.431	−0.5612	−5
0.8499	0.762455	118.764	−0.4491	2
0.9000	0.753490	119.112	−0.3210	2
0.9500	0.744534	119.471	−0.1830	−10
0.9747	0.740014	119.666	−0.09710	−7
1	0.735356	119.874	0	0

[a] $\delta V^E = V^E_{\exp tl} - V^E_{calc}$.

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

$$s = \left[\sum (V^E_{i,\exp t} - V^E_{i,calc})^2 / (N-k) \right]^{1/2} \tag{6}$$

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 [9]. It was not deemed necessary to perform a step-wise regression.

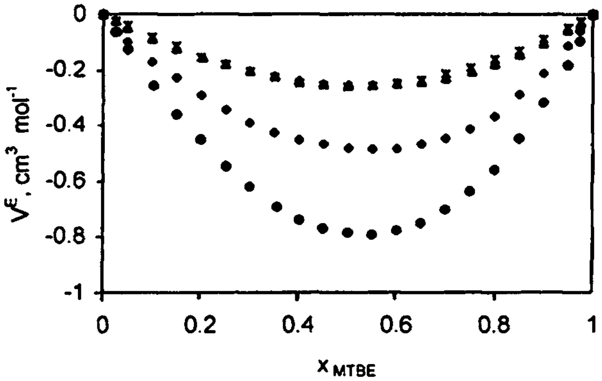

Fig. 1. Excess volumes at 298.15 K: ∗ MTBE + MMA; ▲ MTBE + EA; ◆ MTBE + BA; • MTBE + styrene.

Table VI. Coefficients A_k (Eq. (2)), Standard Deviation (Eq. (6)), Durbin–Watson Statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

							$(V^E)_{x=0.5}$	$V_1^{E,\infty}$	$V_2^{E,\infty}$
System	A_0	A_1	A_2	A_3	$s \times 10^3$	d^a	$(\mathrm{cm^3 \cdot mol^{-1}})$		
1+2	−1.939	−3.839	−3.073	1.250	4.853	1.50	−4.846	−1.987	−2.505
1+3	−1.018	−1.588	−5.623	6.763	1.807	1.72	−2.546	−9.835	−1.166
1+4	−1.036	−0.061	−0.1550		0.0022	2.32	−0.259	−0.819	−0.942
1+5	−3.157	−0.5140	0.03000		0.0042	1.56	−0.789	−2.673	−3.702

^{a} $d = \sum_{u=2}^{N} (e_u - e_{u-1})^2 / \sum_{u=1}^{N} e_u^2$
$e_u = V^E_{u,\,calc} - V^E_{u,\,\exp tl}$

Table VII. Coefficients a_k (Eq. (3)), Standard Deviation (Eq. (6)), Durbin–Watson Statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

							$(V^E)_{x=0.5}$	$V_1^{E,\infty}$	$V_2^{E,\infty}$
System	A_0	A_1	A_2	A_3	$s \times 10^3$	d^a	$(\mathrm{cm^3 \cdot mol^{-1}})$		
1+2	−2.0410	−0.30885	−0.20486	0.05004	4.99	1.50	−0.481	−2.504	−1.987
1+3	−1.0371	−0.11817	−0.037490	0.02705	1.86	1.72	−0.255	−1.165	−0.983
1+4	−0.9846	−0.06157	0.10374		2.30	2.32	−0.259	−0.942	−0.819
1+5	−3.1675	−0.51405	−0.02040		4.36	1.56	−0.789	−3.702	−2.673

^{a} $d = \sum_{u=2}^{N} (e_u - e_{u-1})^2 / \sum_{u=1}^{N} e_u^2$
$e_u = V^E_{u,\,calc} - V^E_{u,\,\exp tl}$

The values of the function V^E/x_1x_2 at infinite dilution represent the values of the partial excess volume at infinite dilution, $\bar{V}_i^{E,\infty}$ [10], and can be calculated from the adjustable parameters as follows:

(a) *Redlich–Kister*

$$\bar{V}_1^{E,\infty} = A_0 - A_1 + A_2 - \cdots = \bar{V}_1^{\infty} - V_1^0 \tag{7}$$

$$\bar{V}_2^{E,\infty} = A_0 + A_1 + A_2 + \cdots = \bar{V}_2^{\infty} - V_2^0 \tag{8}$$

(b) *Legendre*

$$\bar{V}_1^{E,\infty} = a_0 - a_1 + a_2 - \cdots = \bar{V}_1^{\infty} - V_1^0 \tag{9}$$

$$\bar{V}_2^{E,\infty} = a_0 + a_1 + a_2 + \cdots = \bar{V}_2^{\infty} - V_2^0 \tag{10}$$

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 VI. Equations (7) and (8) or (9) and (10) yield the same values of $\bar{V}_i^{E,\infty}$. Figure 2 shows a typical distribution of the residuals, which is random as determined by the Durbin–Watson statistic.

Inspection of the results of Tables II to V and Fig. 1 indicates that the excess volumes for the four systems MTBE + monomer are negative for the complete composition range. The results for MTBE + styrene are consistent with those reported in the literature for the systems of cyclohexane and toluene with MTBE, ETBE, and TAME, that is, mixtures of branched ethers with cyclohexane expand on mixing, while those with toluene contract [11].

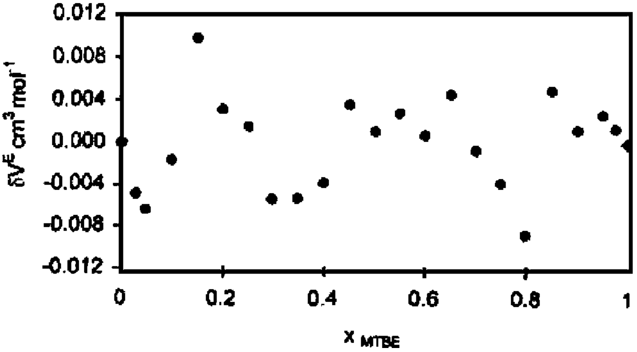

Fig. 2. Residual distribution plot for the system MTBE + BA according to the fit given in Table VI.

As regards to the symmetry of the excess function, it appears that an almost symmetric $V^E(x)$ function is observed for all the systems studied here. The curves in Fig. 5 show the presence of a clear minimum, which becomes more negative and is always centered at $x \approx 0.5$ confirming that the maximum specific interaction occurs at about the equimolar composition.

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 (originating from non-chemical or chemical interactions such as hydrogen bonding or complex-forming interactions such as self-association) and (b) a negative effect due to physical interactions (for example, heteroassociation) 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 sphericicity of the solute molecule and higher molar volume of the solvent.

Structurally, MTBE 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-π interaction [11].

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 $(V^E)_{x=0.5}$ ranging from about -0.28 to $-0.8\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ (the pertinent value of V^E is given by $A_0/4$).

For the systems studied here the V^E curves are all negative, the relative magnitude depending on the nature of the solute (monomer) and the solvent. While the overall magnitude of V^E is a result of the effect of breaking the ether's dipole-dipole association, the negative sign indicates a net packing effect contributed by structural effects arising from interstitial accommodation. These results are similar to those obtained by Pal and Kumar [12] for the excess volumes of mixtures of polyethers and ester. In addition, the curves are almost symmetrical, reflecting lack of self-association of each component.

Interactions between an aromatic hydrocarbon (such as styrene) and an ether have been described as much stronger than those between a cyclic hydrocarbon (such as cyclohexane) and an ether. For example, the inductive action of the vinyl group in styrene enhances the n-π interaction and leads to mixing volumes larger than for benzene. The large negative values for the system MTBE + styrene indicate that the disruption of the dipolar association of the ether is considerably less than the additional specific interaction between its pairs of electrons and the π electrons of the aromatic ring. In addition, the substitution of a vinyl group on the benzene ring constitutes an obstacle to n-π specific interactions because of the bulkiness of the *t*-butyl radical.

Anyhow, it is clear that there is a substantial difference in packing of MTBE with the esters and with styrene. The value of $(V^E)_{x=0.5}$ for the latter is about 2 to 3 times larger than for the former.

The observed molar excess volumes exhibit an interesting dependence with respect to the structure of the unsaturated ester: their values increase as the length of the ester chain increases from methyl to butyl, signaling an increase of the contribution of the interstitial accommodation.

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. J. Linek, *Int. Electron. J. Phys.-Chem. Data* **1**:43 (1995).
6. *TRC Thermodynamic Tables–Non-hydrocarbons* (Thermodynamics Research Center, The Texas A&M University System, College Station, Texas, extant 2001).
7. L. Beichen, S. E. M. Hamam, and B. C.-Y Lu, *J. Chem. Thermodyn.* **18**:1043 (1986).
8. O. Redlich and A. T. Kister, *Ind. Eng. Chem.* **40**:345 (1948).
9. J. Wisniak and A. Polishuk, *Fluid Phase Equil.* **164**:61 (1999).
10. H. C. Van Ness and M. M. Abbott, *Classical Thermodynamics of Nonelectrolyte Solutions* (McGraw–Hill, New York, 1982).
11. S. C. Sharma, R. Kaur, and J. Singh, *J. Chem. Thermodyn.* **24**:1171 (1992).
12. A. Pal and H. Kumar, *Fluid Phase Equil.* **181**:17 (2001).
13. W. Haijun, C. Mingzhi, and Z. Gokang, *J. Chem. Thermodyn.* **27**:457 (1995).