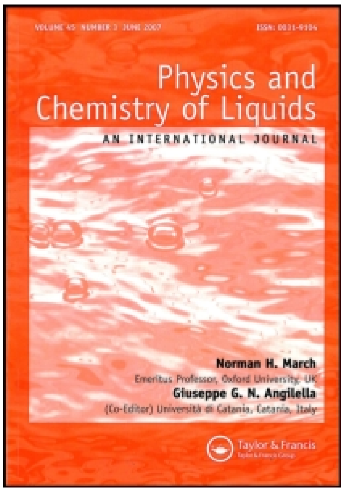

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Excess Dielectric Permittivity and Excess Molar Volumes of Binary Mixtures of *n*-Octane with 1-Alkanol at the Temperature 298.15 K

T. P. Iglesias[a]; J. L. Legido[a]; L. Romani[b]; J. Peleteiro[b]; M. I. Paz Andrade[c]
[a] Departamento de Física Aplicada, Facultad de Ciencias, Apdo 874, Universidad de Vigo, Vigo, Spain [b] Departamento de Física Aplicada, Facultad de Ciencias, Campus de Orense, Universidad de Vigo, Orense, Spain [c] Departamento de Física Aplicada, Facultad de Fisica, Universidad de Santiago, santiago de composa, Spain

To cite this Article Iglesias, T. P. , Legido, J. L. , Romani, L. , Peleteiro, J. and Andrade, M. I. Paz(1995) 'Excess Dielectric Permittivity and Excess Molar Volumes of Binary Mixtures of *n*-Octane with 1-Alkanol at the Temperature 298.15 K', Physics and Chemistry of Liquids, 30: 3, 159 — 168

To link to this Article: DOI: 10.1080/00319109508031650

URL: http://dx.doi.org/10.1080/00319109508031650

Phys. Chem. Liq., 1995, Vol. 30, pp. 159–168
Reprints available directly from the publisher
Photocopying permitted by license only

EXCESS DIELECTRIC PERMITTIVITY AND EXCESS MOLAR VOLUMES OF BINARY MIXTURES OF *n*-OCTANE WITH 1-ALKANOL AT THE TEMPERATURE 298.15 K

T. P. IGLESIAS, J. L. LEGIDO*

Departamento de Física Aplicada, Facultad de Ciencias,
Apdo 874, Universidad de Vigo, 36200 Vigo, Spain

L. ROMANI, J. PELETEIRO

Departamento de Física Aplicada, Facultad de Ciencias,
Campus de Orense, Universidad de Vigo, 32004 Orense, Spain

M. I. PAZ ANDRADE

Departamento de Física Aplicada, Facultad de Fisica,
Universidad de Santiago, 15706 Santiago de Compostela, Spain

(Received 22 March 1995)

Excess dielectric permittivities and excess molar volumes have been measured for the binary liquid mixtures of *n*-octane with (1-hexanol, 1-heptanol, 1-octanol) at the temperature of 298.15 K and at atmospheric pressure. Dielectric permittivity was determined using the short-circuited line method and the excess molar volume was obtained from densities measured by vibrating-tube densimetry.

KEY WORDS: Dielectric permittivity, excess molar volumes, *n*-alkane + 1-alkanol.

INTRODUCTION

Forming part of our studies on properties of binary mixtures (a 1-alkanol + an *n*-alkanes)[1–4], here we inform about the excess dielectric permittivities and excess molar volumes of *n*-octane + (1-hexanol, 1-heptanol, 1-octanol) at the temperature of 298.15 K and at atmospheric pressure. Dielectric permittivities were determined at 1GHz by using the short-circuited line method and the excess molar volume was calculated from the experimental density values measured by vibrating-tube densimetry. Variable-degree polynomials were adjusted to the results.

---

* To whom the correspondence should be addressed.

EXPERIMENTAL SECTION

The chemicals used presented the following commercial characteristics that: *n*-octane (>99.5%), 1-hexanol (>99.5%), 1-heptanol (>99.5%) and 1-octanol (>99%). All these were supplied by Merck and by Fluka. The substances were degassed, and dried on molecular sieves (Union Carbide, type 4Å). The densities values (Tab. 1) were very similar to the values reported in the literature(5,6).

Table 1 Dielectric permittivity, excess dielectric permittivity, densities and excess molar volumes at the temperature 298.15 K.

x	ε'	ε''	ρ $g \cdot cm^{-3}$	ε'^E	ε''^E	v^E $cm^3 \cdot mol^{-1}$
			x *n*-octane + (1 − x) 1-hexanol			
0.0000	3.498	1.846	0.81507	0.000	0.000	0.0000
0.0417	3.416	1.717	0.80892	−0.017	−0.053	−0.0181
0.1028	3.329	1.512	0.80008	−0.009	−0.144	−0.0274
0.1588	3.234	1.358	0.79215	−0.017	−0.195	−0.0199
0.1858	3.187	1.288	0.78841	−0.022	−0.215	−0.0155
0.2448	3.104	1.134	0.78041	−0.013	−0.260	0.0013
0.2907	3.036	1.010	0.77436	−0.009	−0.300	0.0148
0.3364	2.966	0.891	0.76850	−0.008	−0.334	0.0272
0.3836	2.895	0.769	0.76258	−0.006	−0.369	0.0444
0.4368	2.812	0.645	0.75611	−0.007	−0.395	0.0597
0.4574	2.779	0.589	0.75365	−0.007	−0.412	0.0655
0.5099	2.689	0.471	0.74752	−0.016	−0.434	0.0797
0.5354	2.644	0.415	0.74461	−0.021	−0.442	0.0845
0.5853	2.563	0.327	0.73903	−0.025	−0.438	0.0951
0.6344	2.479	0.236	0.73365	−0.032	−0.439	0.1110
0.6924	2.373	0.167	0.72751	−0.048	−0.401	0.1214
0.7539	2.278	0.085	0.72119	−0.047	−0.370	0.1308
0.8075	2.188	0.046	0.71587	−0.053	−0.309	0.1336
0.8623	2.106	0.022	0.71063	−0.050	−0.232	0.1237
0.9243	2.033	0.001	0.70497	−0.027	−0.139	0.0884
1.0000	1.942	0.000	0.69847	0.000	0.000	0.0000
			x *n*-octane + (1 − x) 1-heptanol			
0.0000	3.290	1.340	0.81897	0.000	0.000	0.0000
0.0580	3.227	1.234	0.81120	0.015	−0.028	−0.0322
0.1741	3.081	1.024	0.79570	0.026	−0.083	−0.0519
0.2353	3.014	0.905	0.78767	0.041	−0.120	−0.0478
0.2746	2.974	0.828	0.78258	0.054	−0.144	−0.0401
0.3229	2.903	0.717	0.77640	0.048	−0.190	−0.0342
0.3699	2.849	0.646	0.77047	0.057	−0.198	−0.0242
0.4645	2.719	0.470	0.75877	0.055	−0.248	−0.0089
0.4693	2.714	0.455	0.75818	0.056	−0.257	−0.0060
0.5189	2.634	0.369	0.75217	0.043	−0.276	0.0046
0.5654	2.570	0.299	0.74661	0.043	−0.284	0.0163
0.6717	2.395	0.149	0.73413	0.010	−0.291	0.0470
0.7766	2.240	0.060	0.72216	−0.003	−0.239	0.0828
0.8837	2.028	0.002	0.71042	−0.071	−0.154	0.0914
0.9365	2.017	0.020	0.70487	−0.011	−0.065	0.0673
1.0000	1.942	0.000	0.69847	0.000	0.000	0.0000

(Table 1 Continued)

x	ε'	ε''	ρ $g \cdot cm^{-3}$	ε'^E	ε''^E	v^E $cm^3 \cdot mol^{-1}$
			x *n*-octane + (1 − x) 1-octanol			
0.0000	3.096	1.010	0.82162	0.000	0.000	0.0000
0.0547	3.032	0.949	0.81481	−0.001	−0.006	−0.0264
0.1051	3.001	0.885	0.80852	0.026	−0.019	−0.0404
0.1397	2.972	0.840	0.80420	0.037	−0.029	−0.0489
0.2378	2.886	0.706	0.79196	0.064	−0.064	−0.0683
0.2886	2.836	0.636	0.78564	0.073	−0.082	−0.0746
0.3538	2.769	0.549	0.77754	0.081	−0.104	−0.0772
0.3903	2.729	0.495	0.77301	0.083	−0.121	−0.0776
0.4393	2.674	0.423	0.76693	0.085	−0.143	−0.0768
0.4907	2.614	0.351	0.76055	0.084	−0.163	−0.0691
0.5415	2.544	0.280	0.75424	0.073	−0.183	−0.0559
0.5921	2.484	0.217	0.74794	0.071	−0.195	−0.0372
0.6394	2.410	0.165	0.74206	0.052	−0.199	−0.0132
0.6957	2.334	0.112	0.73506	0.041	−0.195	0.0152
0.7348	2.280	0.081	0.73021	−0.032	−0.187	0.0372
0.7702	2.229	0.058	0.72584	0.022	−0.174	0.0581
0.8028	2.189	0.042	0.72183	0.019	−0.157	0.0713
0.8349	2.143	0.025	0.71791	0.010	−0.142	0.0844
0.8697	2.102	0.013	0.71369	0.010	−0.119	0.0882
0.8929	2.076	0.009	0.71091	0.010	−0.100	0.0869
0.9186	2.040	0.003	0.70786	0.004	−0.079	0.0817
1.0000	1.942	0.000	0.69847	0.000	0.000	0.0000

Dielectric permittivities were determined through the use of the standing wave technique for short-circuited termination(1). The sample is located at the end of a coaxial line where electromagnetic standing waves with fixed wavelength λ are established. Since the sample impedance, as calculated from the characteristics of the standing wave, can be measured, one obtains the transcendental equation on the complex form.

$$-j\lambda(1-jS\tan(2\pi D_m/\lambda))/(2\pi d(S-j\tan(2\pi D_m/\lambda)))=\tan\mathrm{h}(\gamma d)/(\gamma d) \qquad (1)$$

The l.h.s. of this equation is known from experiment: S is the voltage standing wave ratio (VSWR); D_m is the distance the surface of the dielectric and first minimum of the standing wave pattern and d is the sample thickness.

The complex relative permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$ can be expressed as a function of the complex propagation coefficient, γ, for electromagnetic waves inside a non-magnetic sample.

$$\varepsilon^* = -(\gamma\lambda/2\pi)^2 \qquad (2)$$

The excess complex dielectric permittivities were calculated from the expression:

$$\varepsilon^{*E} = \varepsilon^* - (x\,\varepsilon^*_{al} + (1-x)\,\varepsilon^*_{ol}) \qquad (3)$$

where ε^* denotes the complex dielectric permittivity of the mixture, ε^*_{al} of the *n*-hexane, ε^*_{ol} of the 1-alkanol, and x is the mole fraction of *n*-hexane.

Excess molar volumes (v^E) were calculated from densities of pure liquids and mixtures measured with an Kyoto Electronics DA-210 densimeter. The experimental technique has been previously$^{(7)}$ explained.

Mixtures were prepared by weighing with an estimated precision of $1 \cdot 10^{-4}$ in mole fraction. The densimeter was thermostated by a Hetotherm PF-CBIIe circulating-water bath to ± 0.01 K. The precision of the excess dielectric permittivity was estimated to be better than ± 0.002 and excess molar volumes better them ± 0.001 cm^3·mol^{-1}.

RESULTS AND DISCUSSION

Table 1 reports the ε' and ε'' of the measurements in terms of mole fractions for the systems investigated. In Figure 1 the ε' and ε'' are plotted against the volume fraction ϕ defined by

$$\phi = x v_{al}/(x v_{al} + (1-x) v_{ol}) \tag{4}$$

where v_{al} denotes the molar volume of the *n*-octane, and v_{ol} of the 1-alkanol, clearly showing a quasi-lineal behaviour in the ε' whilst the ε'' presents a quasi-exponential behaviour.

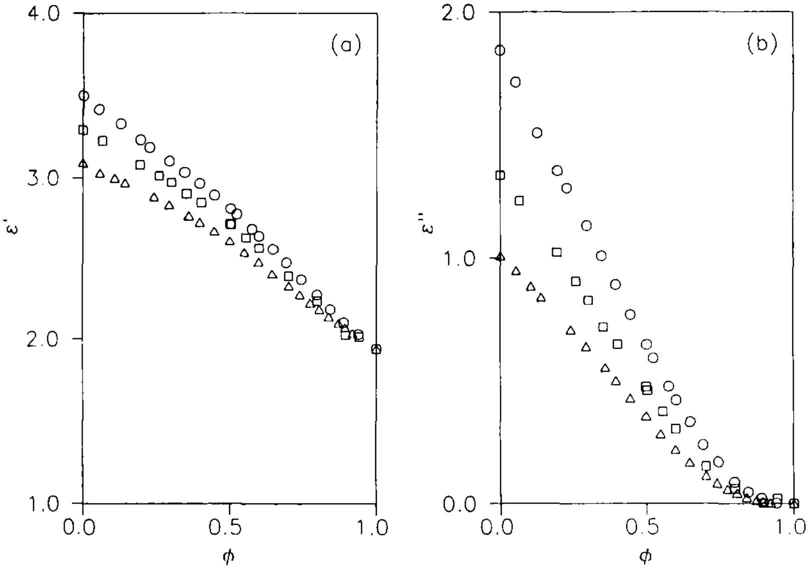

Figure 1 Experimental a) ε'; b) ε'' at 298.15 K of x $C_8H_{14} + (1-x)$ $C_nH_{2n+1}OH$ plotted against the volume fraction ϕ; ○, $n = 6$; □, $n = 7$; Δ, $n = 8$.

The experimental values of excess dielectric permittivities and excess molar volumes at 298.15 K are reported in Table 1. A function of the form:

$$Q^E = x(1-x)\sum_{i=0}^{m} A_i(2x-1)^i \qquad (5)$$

was fitted to the experimental values of the excess amounts where either $Q^E = \varepsilon^{*E}$ or $Q^E = v_m^E/(\mathrm{cm^3{\cdot}mol^{-1}})$. The coefficients A_i and the corresponding standard deviations $s(Q^E)$ given in Table 2 were calculated using the unweighted least-squares method, with the degree of the polinomial previously optimized through the application of the F-test(8).

Figures 2 and 3 show the experimental points of the ε'^E and ε''^E plotted against x as well as the curve fitted. The ε'^E and ε''^E increase when the length of the 1-alkanol increases. ε'^E is negative for the mixture with 1-hexanol and positive for the 1-heptanol and 1-octanol, whereas the ε''^E is negative for all the three systems.

Figure 4 shows the experimental v^E plotted against x together with the curve fitted. The excess molar volume decreases when the 1-alkanol carbon-atom number increases, showing values close to zero for the 1-heptanol + *n*-octane and 1-octanol + *n*-octane systems and essentially positive values for the system which contain 1-hexanol.

There was a difference of approximately 0.0019 found between the experimental excess molar volumes of the literature(9) and our own results, fitted with equation (5), for the 1-hexanol + *n*-octane at $x = 0.5$.

In these mixtures the behaviour of ε'^E (Fig. 5) is contrary to that of v^E (Fig. 6). This is due to the fact that when v^E decreases the number of dipoles per volume unit increases. This causes the ε'^E to increase. ε''^E (Fig. 5) increases when the length of the 1-alkanol increases and decreases when the *n*-alkane carbon-atom number increases. This behaviour is opposite to those of h^E (Fig. 7) and g^E (Fig. 8), which means a minor delay of the response of the mixture to the applied field.

Table 2 Coefficients A_i of equation (5) and standard deviations s.

	A_0	A_1	A_2	A_3	S
		x *n*-octane + $(1-x)$ 1-hexanol			
ε'^E	−0.059	−0.194	−0.419	----	0.005
ε''^E	−1.705	−0.681	−0.007	0.599	0.006
v^E	0.3033	0.5297	0.2122	0.6160	0.0013
		x *n*-octane + $(1-x)$ 1-heptanol			
ε'^E	0.197	−0.241	−0.311	----	0.005
ε''^E	−1.077	−0.769	0.200	0.416	0.008
v^E	−0.0023	0.4533	0.3413	0.7301	0.0016
		x *n*-octane + $(1-x)$ 1-octanol			
ε'^E	0.312	−0.252	−0.267	----	0.004
ε''^E	−0.673	−0.702	−0.071	0.284	0.002
v^E	−0.2662	0.4453	0.8221	0.6761	0.0011

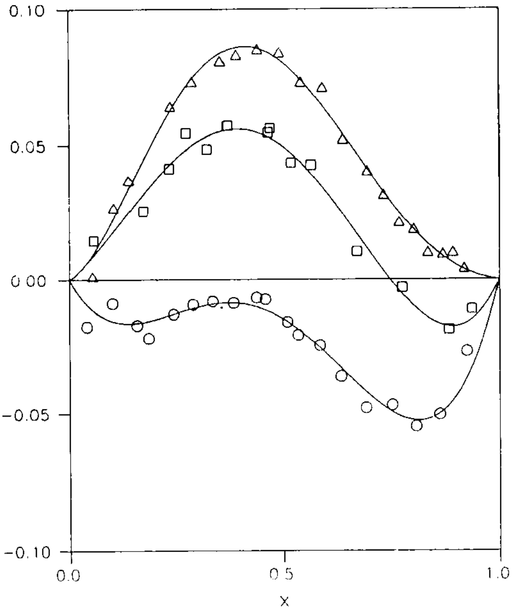

Figure 2 Experimental ε'^E at 298.15 K of x $C_8H_{14}+(1-x)$ $C_nH_{2n+1}OH$; ○, $n=6$; □, $n=7$; Δ, $n=8$. The curves have been calculated from Eq. (5).

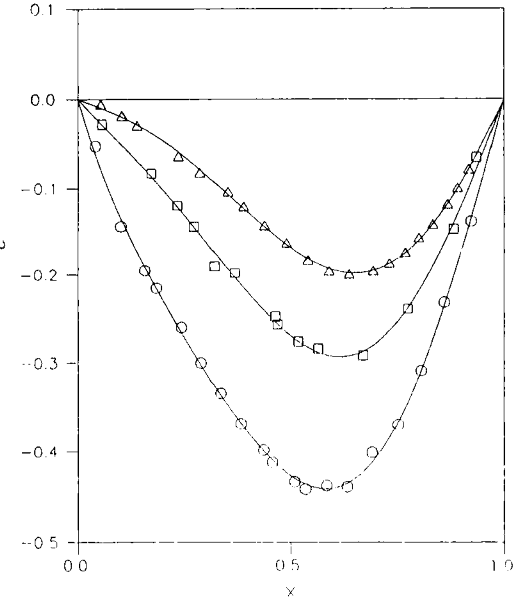

Figure 3 Experimental ε''^E at 298.15 K of x $C_7H_{14}+(1-x)$ $C_nH_{2n+1}OH$; O, $n=6$; □, $n=7$; Δ, $n=8$. The curves have been calculated from Eq. (5).

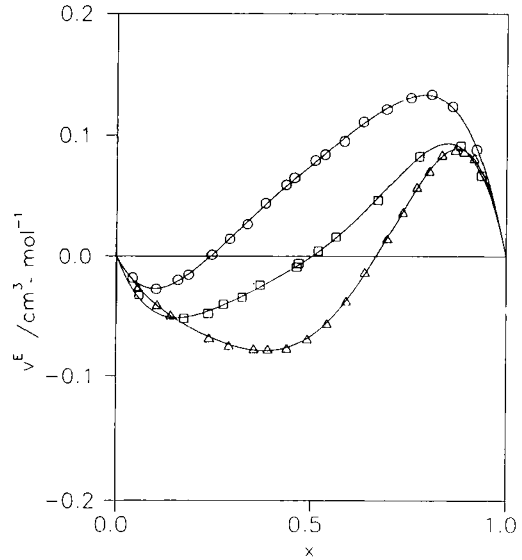

Figure 4 Experimental v^E at 298.15 K of x $C_8H_{14}+(1-x)$ $C_nH_{2n+1}OH$; ○, $n=6$; □, $n=7$; Δ, $n=8$. The curves have been calculated from Eq. (5).

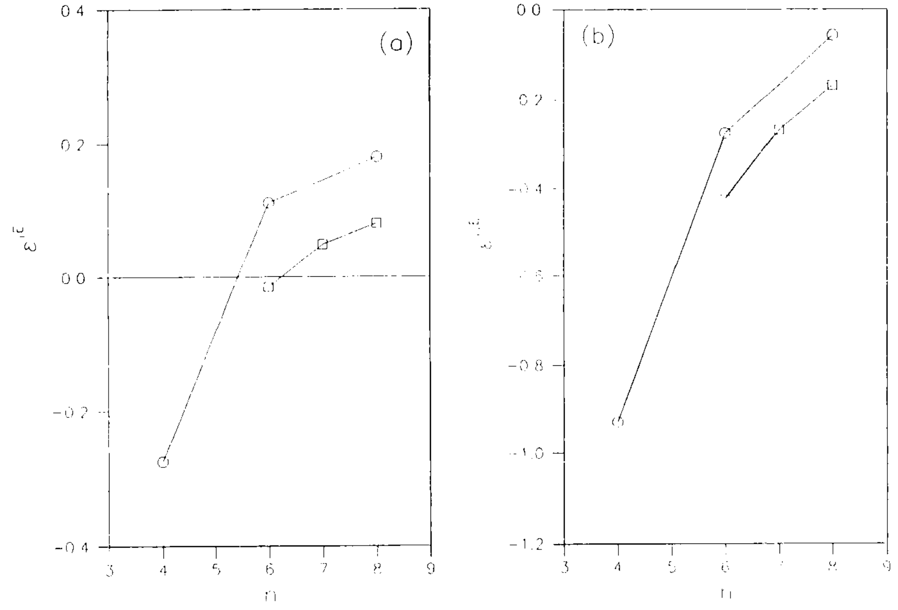

Figure 5 Experimental a) ε'^E and b) ε''^E at 298.15 K of 0.5 $C_mH_{2m+2}+0.5C_nH_{2n+1}$ OH; ○, $m=6^{(1)}$; □ $m=8$, this work.

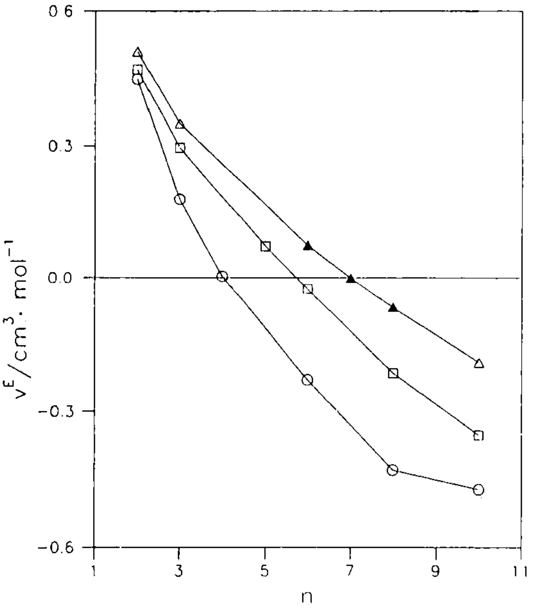

Figure 6 v^E at 298.15 K of 0.5 C_mH_{2m+2} + 0.5 $C_nH_{2n+1}OH$; ○, literature(1,10–13) $m = 6$; □, literature(9,14,15) $m = 7$; ▲ experimental $m = 8$ Δ, literature(9,10,16,17) $m = 8$.

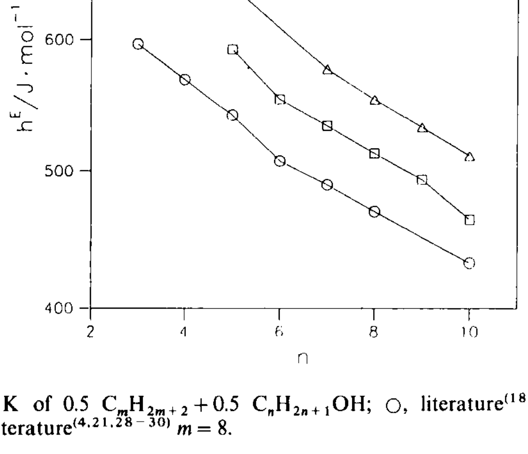

Figure 7 h^E at 298.15 K of 0.5 C_mH_{2m+2} + 0.5 $C_nH_{2n+1}OH$; ○, literature(18–24) $m = 6$; □, literature(4,24–29) $m = 7$; Δ, literature(4,21,28–30) $m = 8$.

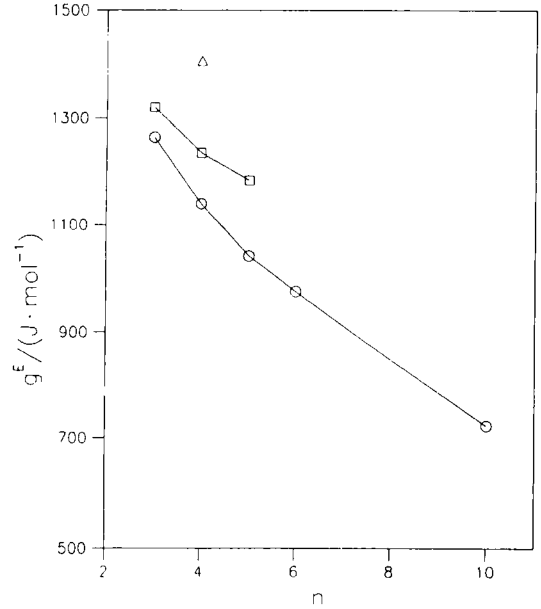

Figure 8 g^E at 298.15 K of 0.5 C_mH_{2m+2} + 0.5 $C_nH_{2n+1}OH$; O, literature(31–36) $m = 6$; □, literature(16,37,38) $m = 7$; Δ, literature(39) $m = 8$.

References

1. T. P. Iglesias, J. L. Legido, L. Romani, M. I. Paz Andrade, *Phys. Chem. Liq.*, **35**, 135 (1993).
2. J. Fernández, J. L. Legido, M. I. Paz Andrade, L. Pías, J. Ortega, *Fluid Phase Equilibria*, **55**, 293 (1990).
3. J. Peleteiro, E. Carballo, J. L. Legido, L. Romani, M. López, M. I. Paz Andrade, *Thermochimica Acta*, **1**, 207, (1992).
4. A. Amigo, J. L. Legido, R. Bravo, M. I. Paz Andrade, *J. Chem. Thermodyn.* **22**, 1059 (1990).
5. J. A. Riddick, W. B. Bunger, T. K. Sakano, Organic Solvents *Techniques of Chemistry*. Wiley, New York (1986).
6. T. E. Daubert, R. P. Danner, Data Compilations *Tables of Properties of Pure Compounds. AIChE*, New York (1985).
7. M. T. Lorenzana, J. L. Legido, E. Jiménez, J. Fernández, L. Pías, J. Ortega, M. I. Paz Andrade, *J. Chem. Thermodyn.* **21**, 1017 (1989).
8. P. Bevington, Data Reduction and Error Analysis for the *Physical Sciences*. McGraw-Hill, New York. (1969).
9. A. J. Treszcanowicz, G. C. Benson, *J. Chem. Thermodyn.* **12**, 173 (1980).
10 M. Ruel, *An. Quim.* **69**, 821 (1973).
11. A. Heintz, B. Smchmittecker, D. Warner. *J. Chem. Eng. Data.* **31**, 487 (1986).
12. C. Berro, M. Rogalski, A. Peneloux, *J. Chem. Eng. Data.* **27**, 352 (1982).
13. D. Wagner, A. Heintz, *J. Chem Eng. Data.* **31**, 483 (1986).
14. A. J. Treszcanowicz, G. C. Benson, *J. Chem. Thermodyn.* **9**, 1189 (1977).
15. A. J. Treszcanowicz, G.C. Benson, *J. Chem. Thermodyn.* **10**, 967 (1978).
16. C. Berro, A. Peneloux, *J. Chem. Eng. Data.* **29**, 206 (1984).
17. A. J. Treszcanowicz, O. Kiyohara, G. C. Benson, *J. Chem. Thermodyn.* **13**, 253 (1981).
18. I. Brow, W. Fock, F. Smith, *Aust. J. Chem.* **17**, 1106 (1964).
19. F. Kimura, G. C. Benson, *J. Chem. Eng. Data.* **26**, 317 (1981).

20. F. Vaseley, V. Dohnal, M. Prchal, *Collect. Czech. Chem. Commun.* **47**, 1045 (1982).
21. T. H. Nguyen, G. A. Ratcliff, *J. Chem. Eng. Data.* **20**, 252 (1975).
22. F. Sarmiento, M. I. Paz Andrade, J. Fernandez, R. Bravo, M. Pintos, *J. Chem. Eng. Data.* **30**, 321 (1985).
23. T. T. Lai, T. H. Doan-Nguyen, J. H. Vera, G. A. Ratcliff, Can. *J. Chem. Eng.* **56**, 358, (1978).
24. M. K. Kumaran, G. C. Benson, *J. Chem. Thermodyn.* **16**, 175 (1984).
25. H. C. Van Ness, M. M. Abbott, *Int. DATA Ser. Select. Data Mixtures, Ser. A.* **1**, (1976).
26. S. E. Hamam, M. K. Kumaran, G. C. Benson, *J. Chem. Thermodyn.* **16**, 1013 (1984).
27. L. Nuñez, E. Isorna, M. I. Paz Andrade, Acta Cient. Compostelana **13**, 3 (1976).
28. A. Amigo, J. L. Legido, R. Bravo, M. I. Paz Andrade, *J. Chem. Thermodyn.* **21**, 1207 (1989).
29. A. Amigo, J. L. Legido, R. Bravo, M.I. Paz Andrade, *J. Chem. Thermodyn.* **22**, 633 (1990).
30. V. Ragaini, R. Santi, S. Carra, *Lincei-Rend. Sc. Fis. Mat. Nat.* **45**, 540 (1968).
31. S. Ch. Hwang, R. L. Robinson, *J. Chem. Eng. Data.* **22**, 319 (1977).
32. I. Brow, W. Fock, F. Smith, *J. Chem. Thermodyn.* **1**, 273 (1969).
33. C. Berro, M. Rogalski, A. Peneloux, *Fluid Phase Equilibria.* **8**, 352 (1982).
34. S. A. Wieczorek, J. Stecki *J. Chem. Thermodyn.* **10**, 177 (1978).
35. S.G. Sayegh, G. A. Ratcliff, *J. Chem. Eng. Data.* **21**, 71 (1976).
36. S. A. Wieczorek, *J. Chem. Thermodyn.* **11**, 239 (1979).
37. J. Sipowska, S. Wieczorek, *J. Chem. Thermodyn.* **12**, 459 (1980).
38. I. Máchová, J. Linek, I. Wichterle, *Fluid Phase Equilibria.* **41**, 257 (1988).
39. P. Gieryez, J. Gregorowicz, S. Malanowski, *J. Chem. Thermodyn.* **20**, 385 (1988).