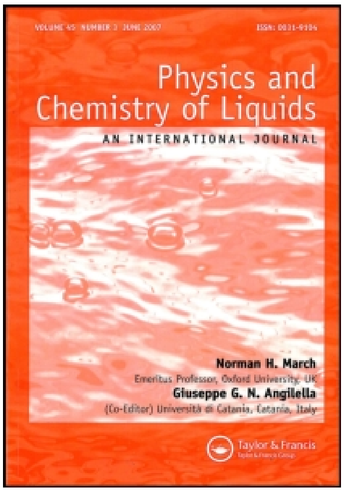

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EXCESS MOLAR VOLUMES AND VISCOSITIES FOR 1-PROPANOL AND 2-PROPANOL + METHYLACETATE SYSTEMS AT 298.15 K

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Excess molar volumes (V^E), excess viscosities (η^E) and excess energies of activation for viscous flow (ΔG^{*E}) have been obtained for the 1-propanol and 2-propanol + methylacetate systems at 298.15 K, over the whole concentration range. The results of V^E are discussed in terms of the influence of interaction between components and the Prigogine-Flory theory was used to explain the observed behavior. The predictive abilities of a few of the existing equations for mixtures viscosities have also been compared.

KEY WORDS: Excess molar volumes; excess viscosities; activation energies.

1 INTRODUCTION

Excess thermodynamic properties such as excess molar volume (V^E), excess viscosity (η^E) and excess energy of activation for viscous flow (ΔG^{*E}) have been obtained in order to explain the possible interactions between the molecules of 1-propanol (1-PR) and 2-propanol (2-PR) with methylacetate (MA) systems at 298.15 K.

Densities and viscosities at different mole fractions were measured for these two systems, in which the alcohols are polar molecules with association in their pure state and MA is a polar molecule. This work is a continuation of our studies on the thermodynamic properties of binary liquid mixtures of non-electrolytes[1,2].

2 EXPERIMENTAL SECTION

The method used in our laboratory have been described previously[1,2]. Densities (ρ) were determined with a digital densimeter AP (model DMA 45) at 298.15 K. A 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.

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Viscosities (η) of the pure components and of the mixtures were determined with a Cannon-Fenske viscosimeter calibrated with doubly distilled water and benzene. Kinetic energy corrections were applied to viscosity data. The estimated error was $\pm$ 0.005 mPa s.

The 1-PR and 2-PR Merck (puriss.) were distilled over calcium oxide and the middle fraction were collected. The MA Mallinckrodt (puriss.) was heated at reflux with acetic anhydride and then distilled over potassium carbonate. Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

3 RESULTS AND DISCUSSION

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

The excess molar volumes are calculated with the following equation:

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

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

Excess viscosities were obtained by the following equation:

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{2}$$

where the additivity law in a logarithmic form is taken for the ideal mixtures.

The excess energies of activation for viscous flow were obtained by the following equation:

$$\Delta G^{*E} = RT(\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2) \tag{3}$$

where V, V_1 and V_2 represent the molar volumes of the solutions and of the pure components.

Table 2 shows the experimental values of densities and viscosities of the two systems at 298.15 K.

Table 1 Densities and viscosities of the pure components at 298.15 K.

Substance	*$\rho \times 10^{-3}/kg\ m^{-3}$*		*$\eta/mPa\ s$*	
	Exp.	*Lit.*	*Exp.*	*Lit.*
1-propanol	0.7996	0.7995[a]	1.980	1.984[e]
2-propanol	0.7800	0.7807[b]	1.995	1.990[c]
methylacetate	0.9274	0.9273[a]	0.361	0.362[d]

[a]Ref. (3), [b]Ref. (4), [c]Ref. (5), [d]Ref. (6), [e]Ref. (7).

Table 2 Experimental values of densities and viscosities at 298.15 K.

1-PR(1) + MA(2)			*2-PR(1) + MA(2)*		
x_1	$\rho \times 10^{-3}$/kg m^{-3}	η/mPa s	x_1	$\rho \times 10^{-3}$/kg m^{-3}	η/mPa s
0.1056	0.9125	0.375	0.0988	0.9111	0.385
0.1987	0.9002	0.399	0.2003	0.8949	0.416
0.2980	0.8872	0.432	0.3227	0.8763	0.453
0.3999	0.8741	0.483	0.3967	0.8651	0.484
0.5012	0.8612	0.550	0.4976	0.8502	0.530
0.5963	0.8491	0.644	0.6660	0.8261	0.668
0.6991	0.8363	0.793	0.7895	0.8092	0.933
0.7989	0.8240	1.014	0.7978	0.8082	0.960
0.8845	0.8135	1.306	0.9011	0.7965	1.370

Each set of results were fitted with a Redlich-Kister equation of the type:

$$X^E = x_1(1 - x_1) \sum_{j=1}^{n} a_j(1 - 2x_1)^{j-1} \tag{4}$$

where a_j are the parameters obtained by a linear least squares fitting procedure. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate with n (calculated with a VAX 11/780 computer):

$$\sigma = [\sum (X^E_{\text{obs}} - X^E_{\text{cal}})^2/(n_{\text{obs}} - n)]^{1/2} \tag{5}$$

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

Figure 1 shows the experimental values of V^E, η^E and ΔG^{*E} as a function of the mole fraction of component 1. The continuous curves were calculated from Eq. (4) using the adopted values for the coefficients.

Figure 1 shows excess positive volumes over the whole concentration range. Several effects may contribute to the values of V^E, such as breaking of liquid order on mixing,

Table 3 Coefficients for Eq. (4) and standard deviation σ determined by the method of least squares.

System		a_1	a_2	a_3	a_4	a_5	a_6	σ
1-PR(1) + MA(2)	V^E	1.4911	0.0863	0,327	0.256	-	—	0.008
	η^E	−1.209	1.087	−1.057	0.998	—	—	0.01
	ΔG^{*E}	−4322	984	—	—		—	27
	G^E	2827	−48	114	100	—	—	1
2-PR(1) + MA(2)	V^E	1.8286	0.3286	2.039	−2.80	−6.66	0.198	0.02
	η^E	−1.294	1.881	−1.13	—	—	—	0.004
	ΔG^{*E}	−4662	3372	503.8	−2565	—	—	21
	G^E	2590	−1221	1349	2145	−1069	−3522	8

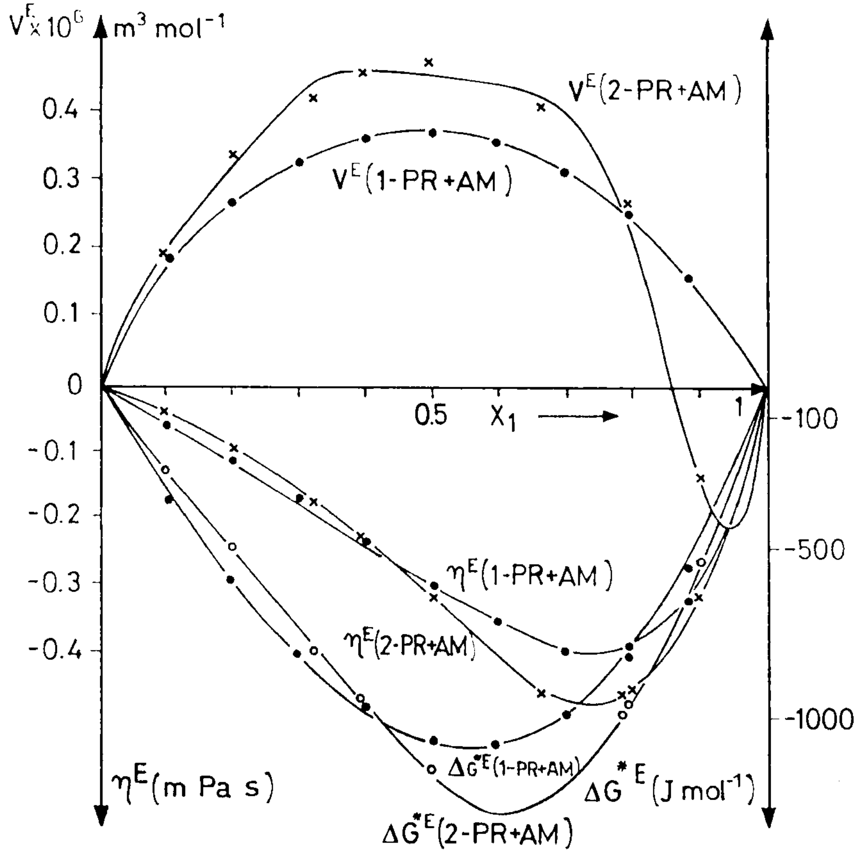

Figure 1 Excess molar volumes, excesss viscosities and excess energies of activiation for viscous flow, for the 1-propanol and 2-propanol + methylacetate system as at 298.15 K. Continuous curves were calculated from Eq. (4).

unfavorable interaction between groups, differences in molecular volumes and differences in free volumes between liquids components[8]. The first two effects produce a positive excess volume. The alcohol is an hydrogen bonded associated liquid. The addition of MA which is a polar molecule produce the disruption of the hydrogen bonded structure and gives rise to positive contribution to V^E, higher in 2-PR. The volume contraction when adding the ester at a great concentration of 2-PR could be explained as an intermolecular association between monomers of 2-PR and ester molecules at approximately $x_1 = 0.9$. We conclude that the primary contribution to the mixture effect for the systems reported here is the breakdown of the alcohol structure and consequently dispersion forces are dominant[9], with little intermolecular association between 2-PR and MA molecules.

Ortega *et al.*[10] showed that V^E values are greater when alkanes are mixed with secondary or tertiary alkanols than when mixed with primary alcohols. The selfassociation effect seem to predominate in secondary alcohol and the dipole-dipole interaction confirm the assimetry of the curve at low MA concentrations.

Generally, positive V^E corresponds to negative η^E, as in this case, which means that dispersion forces are dominant, more in the 2-PR + MA system.

According to Reed and Taylor[11] and Meyers *et al*[12], the ΔG^{*E} parameter may be considered a realible measure to detect the presence of interaction between molecules. Positive values of ΔG^{*E} can be seen in binary systems where specific interactions between molecules take place[13]. In our systems ΔG^{*E} are negative, then we conclude again that only dispersion forces are dominant.

The thermodynamic behavior of solutions has been explained using the Prigogine-Flory theory, following Awwad *et al.*[14]. The excess molar volumes V_F^E were calculated from the following equation:

$$V_F^E = \frac{(x_1 V_1^* + x_2 V_2^*)(\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2)^{7/3}(\tilde{T} - \tilde{T}_o)}{\frac{4}{3} - (\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2)} \tag{6}$$

where

$$\tilde{T}_o = \frac{(\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2)^{1/3} - 1}{(\phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2)^{4/3}} \tag{7}$$

The reduced volume is $\tilde{V}_i = V_i/V_i^*$calculated from thermal expansion coefficient (α):

$$\tilde{V}_i = [(1 + \tfrac{4}{3}\alpha_i T)/(1 + \alpha_i T)]^3 \tag{8}$$

The characteristic pressure P^* and temperature T^* are obtained from the relationship:

$$P_i^* = \alpha_i T \tilde{V}_i^2/\mathrm{k}_T \tag{9}$$

where k_T is the isothermal compresibility and $T_i^* = T_i/\tilde{T}_i$. The reduced temperature appropriate for a mixture of two components is:

$$\tilde{T} = (\phi_1 P_1^* \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2)/(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}) \tag{10}$$

where X_{12} is a constant characterizing the differences in the energy of interaction between sites on neighbouring molecules. The segment or hard-core volume fraction ϕ_1 is defined by:

$$\phi_1 = 1 - \phi_2 = x_1 V_1^*/(x_1 V_1^* + x_2 V_2^*) \tag{11}$$

The surface site fraction is:

$$\phi_2 = 1 - \phi_1 = s_2 \phi_2/(s_1 \phi_1 + s_2 \phi_2) \tag{12}$$

where s_i is the molecular surface/volume ratio for the components. The parameter X_{12} is usually done using experimental values of excess enthalpies. If $X_{12} = 0$ we obtain the Eq. (6).

Table 4 gives the parameters used to calculate V_F^E.

Table 4 Parameters for the pure liquids at 298.15 K.

Substance	*$\alpha \times 10^4$ (K^{-1})*	*$\kappa_T \times 10^7$ (kPa^{-1})*	*$V \times 10^6$ ($m^3\ mol^{-1}$)*	*$V^* \times 10^6$*	*$P^* \times 10^6$ ($J\ mol^{-1}$)*	*T^* (K)*	$\tilde{V}$	$\tilde{T}$
1-propanol	9.56^a	10.76^b	75.16	60.68	435	5364	1.2386	0.0556
2-propanol	10.94^a	11.41^c	76.98	60.77	392	4984	1.2667	0.0598
methylacetate	14.27^a	9.57^a	79.88	60.09	785	4379	1.3292	0.0681

^{a}Ref. (21), ^{b}Ref. (22), ^{c}Calculated with the following equation: (unpublished data)

$$\log \kappa_T = 7.971 - 0.414\gamma + 0.0086\gamma^2$$

where γ is the surface tension = 21.24 mN m^{-1}.

The values of V^E obtained with this theory for equimolecular solutions of the two systems are shown in Table 5. The obtained values are greater than the experimental ones.

On the other hand, desviations from ideality may be quantitatively related to thermodynamic properties of mixtures through two semiempirical theories of liquid viscosity, namely the absolute rate and free volume. According to Bloomfield and Dewan[15] (BD) scheme, η/η_{id} is evaluated by:

$$\ln \eta/\eta_{id} = \alpha \ln \eta_{fv} + \beta \ln \eta_{ar} \tag{13}$$

where η_{fv} and η_{ar} represents the deviations from ideal behavior calculated by the free volume and absolute rate reaction theories respectively, and α and β are weighting coefficients usually are made equal to 1. Both contributions are respectively given by:

$$\ln \eta_{fv} = \frac{1}{\tilde{V} - 1} - \frac{x_1}{\tilde{V}_1 - 1} - \frac{x_2}{\tilde{V}_2 - 1} \tag{14}$$

$$\ln \eta_{ar} = -G^R/RT \tag{15}$$

where G^R is the residual energy of mixing, calculated with the following expression:

$$G^R = G^E + \mathrm{RT}\left[x_1 \ln\left(\frac{x_1}{\phi_1}\right) + x_2 \ln\left(\frac{x_2}{\phi_2}\right)\right] \tag{16}$$

Table 5 Summarized calculations of V^E at $x_1 = 0.5$ using Eq. (6).

System	*$V^E \times 10^6/m^3\ mol^{-1}$*	
	Exp.	*Calc.*
1-PR(1) + MA(2)	0.368	0.611
2-PR(1) + MA(2)	0.479	0.543

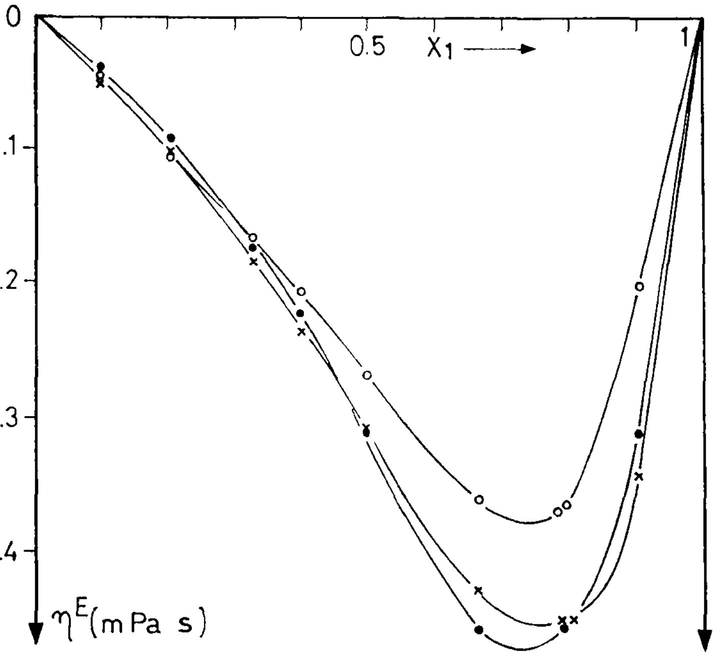

Figure 2 Excess viscosities for the 1-propanol (1) + methylacetate (2) system at 298.15 K. Experimental results ....; Bloomfield and Dewan results o o o o; Teja and Rice results x x x x .

In the BD scheme, the relationships between η_{fv} and η_{ar} and the excess thermodynamic theory of liquid mixtures were proposed by Flory and coworkers[16,17].

Molar excess free Gibbs energies (G^E) were calculated for these systems (see Table 3)[18].

The reduced volume is related to V^E by:

$$\tilde{V} = \frac{V^E}{x_1 V_1^* + x_2 V_2^*} + \phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2 \tag{17}$$

Similar treatment was given by Celda *et al.*[19].

Figures 2 and 3 show η^E from Prigogine-Flory theory, following BD, together with experimental results for comparison.

Finally, we applied Teja and Rice[20] corresponding states method to calculation viscosities of mixtures. These authors proposed the relation:

$$\ln(\eta\xi) = \ln(\eta\xi)^{(r_1)} + \frac{\omega - \omega^{(r_1)}}{\omega^{(r_2)} - \omega^{(r_1)}}\left[\ln(\eta\xi)^{(r_1)} - \ln(\eta\xi)^{(r_2)}\right] \tag{18}$$

where r_1 and r_2 refers to the properties of two reference fluids (in this case, the pure components) and ω is the acentric factor.

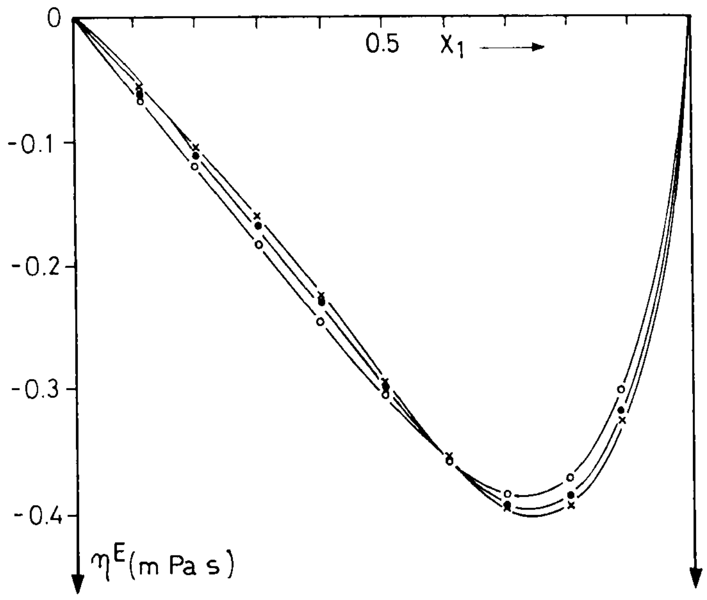

Figure 3 Excess viscosities for the 2-propanol (1) + methylacetate (2) system at 298.15 K. Experimental results ....; Bloomfield and Dewan results o o o o; Teja and Rice results x x x x .

For mixtures, the pseudo properties T_{cm}, V_{cm} and ω_m of an hypothetical equivalent substance replacing the pure fluids are define as:

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{19}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{20}$$

$$\omega_m = \sum_i x_i \omega_i \tag{21}$$

$$\mathrm{M}_m = \sum_i x_i M_i \tag{22}$$

$$T_{cij} V_{cij} = \psi_{ij} (T_{cii} V_{cii} T_{cjj} V_{cjj})^{1/2} \tag{23}$$

$$V_{cij} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \tag{24}$$

where ψ_{ij} is a binary interaction coefficient which must be evaluated from experimental data. The values of ξ from Eq. (18) is obtained as:

$$\xi = V_c^{2/3}/(T_c M)^{1/2} \tag{25}$$

The two reference fluids contributions should be at the same reduced temperature of the mixtures. Using values of η from literature and our own values we calculate constants A and B from the equation:

$$\ln(\eta\xi) = A + B/T_R \tag{26}$$

Table 6 Parameters of the pure components at 298.15 K.

Substance	T_c/K	$V_c \times 10^6/m^3$	ω	M	T_R	$\eta/mPa\ s$	ξ
1-propanol	536.7[a]	219[a]	0.623[a]	60.094	0.5554	1.980	0.20231
2-propanol	508.3[a]	220[a]	0.665[a]	60.094[a]	0.5866	1.995	0.20852
methylacetate	506.8[a]	228[a]	0.324[a]	74.080[a]	0.5883	0.361	0.19261

[a] Ref. (5).

Next, values of $(\eta\xi)^{(r_1)}$ and $(\eta\xi)^{(r_2)}$ at the same T_R of the mixture were calculated with $\psi = 0.876$.

Table 6 gives the parameters used to calculate viscosities and Figures 2 and 3 show the Teja-Rice (TR) values for η^E. This last theory gives better results than the BD scheme.

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References

1. J. L. Zurita, M. L. G. de Soria, M. A. Postigo and M. Katz, *J. Sol. Chem.*, **16**, 163 (1987).
2. M. L. G. de Soria, J. L. Zurita, M. A. Postigo and M. Katz, *Thermochimica Acta*, **130**, 249 (1988).
3. I. Nagata, T. Ohta and S. Nakagawa, *J. Chem. Eng. Japan*, **9**, 276 (1976).
4. G. N. Eduijee and A. P. Boyes, *J. Chem. Eng. Data*, **25**, 249 (1980).
5. R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd. Ed., McGraw-Hill Book Co. New York (1977).
6. A. Weissberger, *Technique of Organic Chemistry*, Vol. VII *Organic Solvents*, 2nd ed. Interscience Publ., New York (1955).
7. A. D'Aprano, I. D. Donato, F. Caponetti and V. Agrigento, *J. Sol. Chem.*, **11**, 793 (1979).
8. M. G. Prolongo, R. M. Masegosa, H. I. Fuentes and A. Horta, *J. Phys. Chem.*, **88**, 2163 (1984).
9. J. R. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).
10. J. Ortega, M. I. Paz Andrade y E. Rodriguez, *J. Chem. Eng. Data*, **31**, 336 (1986).
11. T. M. Reed and T. E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959).
12. R. Meyer, M. Meyer, J. Metzer and A. Peneloux, *J. Chem. Phys.*, **62**, 405 (1971).
13. R. Palepu, J. Oliver and B. Mackinnon, *Can. J. Chem.*, **63**, 1024 (1985).
14. A. M. Awwad and M. A. Salman, *Fluid Phase Equilibria*, **31**, 105 (1986).
15. V. A. Bloomfield and R. K. Dewan, *J. Phys. Chem.*, **75**, 3113 (1971).
16. P. J. Flory, R. A. Orwoll and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 and 3515 (1964).
17. A. Abe and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1838 (1965).
18. G. C. Pedrosa, J. A. Salas, F. Davolio and M. Katz, *Actas I° Simposio Latinoamericano sobre Propiedades de los Fluidos y Equilibrio de Fases para el Diseño de Procesos Químicos*, Concepción, Chile (1987).
19. B. Celda, R. Gavara, R. Tejero and J. E. Figueruelo, *J. Chem. Eng. Data*, **20**, 77 (1981).
20. A. S. Teja and P. Rice, *Ind. Eng. Chem. Fundamental*, **20**, 77 (1981).
21. N. A. Lange, *Handbook of Chemistry*, 9th ed. Handbook Publ. Inc. Sandusky, Ohio (1956).
22. M. L. Rey, E. Aicart, G. Tardajos and J. M. Diaz Peña, *J. Chem. Soc, Faraday Trans.* **2**, 80, 437 (1984).