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Excess energy at constant volume at 298.15 K for alkanenitrile + alkane liquid mixtures

Ian A. McLure, Arturo Trejo*, José Luis Arriaga-Colina**
Department of Chemistry, The University, Sheffield S3 7HF, United Kingdom
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Abstract. The excess energies at constant volume for seven alkanenitrile + alkane mixtures, with propanenitrile and n-butanenitrile as the alkanenitriles and alkanes within the range pentane to tetradecane have been calculated from experimentally determined excess enthalpies and volumes of the mixtures using ideal pVT coefficients for the calculation. The results have been compared with the predictions of the Prausnitz modification of the Solubility Parameter version of the Regular Solution theory which gives a good account of the upper critical coexistence temperatures of the same mixtures using as here the limiting dilution activity coefficients of very dilute mixtures of alkanes in polar substances as the sole source of curve-fitting parameters. Despite the gross simplifications employed, the results of the calculation agree tolerably well with those from experiment. The discussion offers explanations of likely causes of the discrepancies.

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1. Introduction

The thermodynamics of binary polar + nonpolar mixtures is characterized by large positive deviations from ideality. Thus the excess Gibss functions G^E are large, and so limited liquid-liquid miscibility is common, and the excess enthalpies H^E are usually of similar magnitude, and so the excess entropies S^E are usually relatively small. In recent years well-based molecular theories have been developed for mixtures of this kind [1] and they have been successfully applied to simple mixtures such as He + HCl, Xe + HCl and HCl + HBr [2]. For mixtures of not-so simple substances the range of molecular parameters required for these more fundamental theories is rarely available and a simpler treatment must be sought. One approach of this kind that has been found of some use is the Solubility Parameter version of the Regular Solution theory of Hildebrand and Scott [3] in the form modified for polar-nonpolar mixtures by Prausnitz, Anderson, and Weimer [4,5]. This theory was originally developed to account for the activity coefficients at infinite dilution

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*Present adress: Instituto Mexicano del Petróleo, Subdirección de I.B.P. Fisicoquímica, Eje Lázaro Cárdenas No. 152, 07730 México, D.F..

**Present adress: Instituto de Estudios Avanzados, Universidad de las Américas, Apartado Postal 167, Sta. Catarina Mártir, 72820 Puebla, Pue., México.

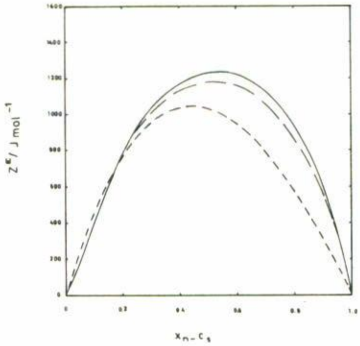

FIGURE 1. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for propanenitrile + n-pentane. Experimental values of H^E (—); experimentally derived U_V^E values (– –); calculated U_V^E values (- - -).

of a wide variety of hydrocarbons in polar solvents. Although the original form of the treatment was based on mixtures at the solvent-rich end of the composition range we have shown previously that it is reasonably successful for alkanenitrile + alkane mixtures at compositions and temperatures close to the liquid-liquid critical point [6]. Our purpose here is to report the results of testing the theory against the excess energy at constant volume at 298.15 K for seven mixtures of this kind: propanenitrile + n-pentane, n-hexane, and n-heptane and n-butanenitrile + n-hexane, n-octane, n-dodecane, and n-tetradecane.

2. Experimental excess energy at constant volume

A fundamental assumption of the Regular Solution theory is that both the excess volume V^E and the excess entropy are zero. (Henceforth all extensive quantities will be taken to refer to one mole of substance or mixture as appropriate.) For mixtures with non-zero V^E a useful way to test the theory is to compare its predictions with the so-called "excess functions at constant volume". There are numerous mixing processes for which constant-volume functions can be calculated from the experimentally-determined constant-pressure or, more exactly in most cases, constant essentially-zero pressure functions and these are discussed elsewhere [7,8]. The simplest leads to an expression for obtaining the excess Helmholtz function at constant volume A_V^E from the excess Gibbs function (at essentially zero pressure) G_p^E,

$$A_V^E = G_p^E + \frac{(V^E)^2}{2\beta_T V} \tag{1}$$

where β_T is the isothermal compressibility and V is the mixture volume, and to an expression for the excess energy at constant volume U_V^E from the excess en-

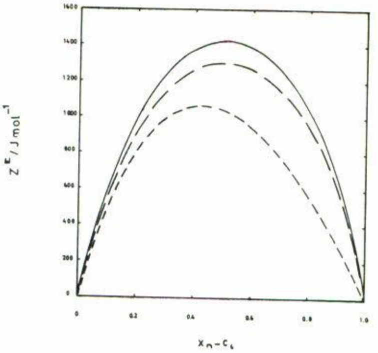

FIGURE 2. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for propanenitrile + n-hexane. Experimental values of H^E (—); experimentally derived U_V^E values (– –); calculated U_V^E (- - -) .

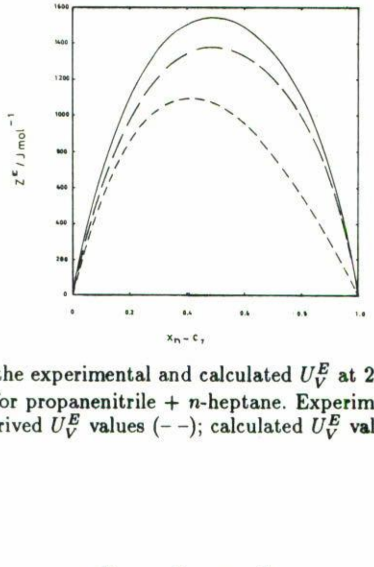

FIGURE 3. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for propanenitrile + n-heptane. Experimental values of H^E (—) ; experimentally derived U_V^E values (– –); calculated U_V^E values (- - -).

thalpy H_p^E;

$$U_V^E = H_p^E - TV^E\gamma_V, \tag{2}$$

where γ_V is the thermal pressure coefficient $(\partial p/\partial T)_V$ of the mixture. The correction in Eq. (1) is of second order and thus to a good approximation $A_V^E \sim G_p^E$. It is safe therefore, when comparing the theoretical prediction of upper critical solution temperatures against experiment, which in many ways amounts to a test of the prediction G_p^E, to ignore the difference between constant volume and constant pressure functions. For the purely energetic functions U_V^E and H_p^E, however, the difference is not negligible. Although not negligible compared to H_p^E, $TV^E\gamma_V$ is usually small enough that for an acceptable reasonably-stringent test of theory it

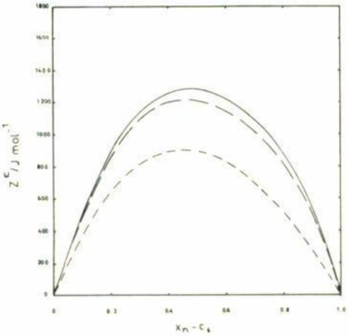

FIGURE 4. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for *n*-butanenitrile + *n*-hexane. Experimental values H^E (—); experimentally derived U_V^E values (– –); calculated U_V^E values (- - -).

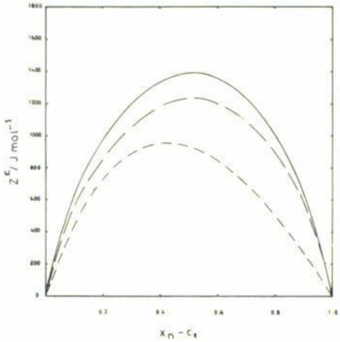

FIGURE 5. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for *n*-butanenitrile + *n*-octane. Experimental values of H^E (—); experimentally derived U_V^E values (– –); calculated U_V^E values (- - -).

is sufficient to take $T\gamma_V$ as the value for the ideal mixture instead of determining it across the entire liquid composition range for every one of the mixtures under study. This is a welcome simplification since in contrast to H^E and V^E, which can be determined by dilution calorimetry and dilatometry respectively, γ_V must be determined in a lengthy point-by-point procedure. For the ideal mixture the thermal pressure coefficient γ_V^{id} is given by

$$\gamma_V^{\mathrm{id}} = \frac{\phi_1\alpha_{p,1} + \phi_2\alpha_{p,2}}{\phi_1\beta_{p,1} + \phi_2\beta_{p,2}}, \tag{3}$$

where ϕ_i is the volume fraction of component i calculated for the ideal mixture, *i.e.* on the basis of additivity in molar volumes in the mixture, and $\alpha_{p,i}$ is the isobaric thermal expansivity of pure i. For liquids at low pressures the identity

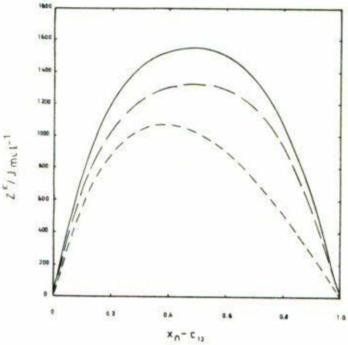

FIGURE 6. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for n-butanenitrile + n-dodecane. Experimental values of H^E (—); experimentally derived U_V^E values (– –); calculated U_V^E values (- - -).

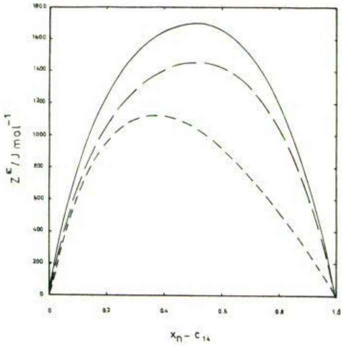

FIGURE 7. Comparison of the experimental and calculated U_V^E at 298.15 K throughout the composition range for n-butanenitrile + n-tetradecane. Experimental values H^E (—); experimentally derived U_V^E values (– –); calculates U_V^E values (- - -).

$\beta_T = \alpha_p/\gamma_V$ gives a better measure of the isothermal compressibility than is afforded by extrapolation from compressions measured at higher pressures and thus this way of evaluating β_T was employed.

The excess enthalpies were taken from Ref. [9] and the excess volumes from Ref. [10]. The densities (and hence the molar volumes and isobaric thermal expansivities) of the alkanenitriles were taken from Ref. [11] and of the alkanes from Ref. [12] and the thermal pressure coefficients of the alkenenitriles from Ref. [13] and of the alkanes from Ref. [12].

Of all the quantities needed for the calculation of constant-volume quantities only the values of V^E were not known at 298.15 K. This quantity was determined at 303.15 K to include in the range of mixtures studied the system propanenitrile + n-octane whose upper critical solution temperature lies at 300.21 K. However, it was assumed that V^E is temperature independent over this small 5 K range of temperature and so despite slight inconsistency all the calculations can be taken to refer to 298.15 K. The quantity $T\gamma_V V^E$ was fitted to expressions of the Redlich-Kister form

$$Z^E = x_1 x_2 \sum a_i (1 - 2x_2)^i. \tag{4}$$

The combination of the a_i with the Redlich-Kister coefficients for H^E given in Ref. [9] gave the coefficients for U_V^E that are listed in Table I. These in turn were used to generate the curves of the experimentally-determined U_V^E shown in Figs. 1-7. These figures also show for comparison the original H^E results.

3. Prausnitz, Anderson, and Weimer Modification of the solubility parameter version of the regular solution theory

In the Solubility Parameter version of the Regular Solution Theory the excess Helmholtz function at constant volume is given by

$$A_V^E = \phi_1 \phi_2 (x_1 V_1 + x_2 V_2)(\delta_1 - \delta_2)^2, \tag{5}$$

where x_i is the mole fraction, v_i is the molar volume, and δ_i is the solubility parameter of component i. In the Prausnitz, Anderson, and Weimer modification of the treatment for a mixture of a polar substance 1 and a nonpolar diluent 2 $(\delta_1 - \delta_2)^2$ is replaced by a sum of terms accounting for:

(a) dispersion forces $(\lambda_1 - \delta_2)^2$,

(b) the polar contribution τ_1^2 to the cohesive energy density of pure dipolar component 1, and

(c) the induction energy density $-2\Psi_{12}$ arising from inductive forces between the polar and the nonpolar molecules.

Thus A_E^V Eq. [5] for mixtures of nonpolar molecules is replaced for polar + nonpolar mixtures by

$$A_V^E = \phi_1 \phi_2 (x_1 V_1 + x_2 V_2)[(\lambda_1 - \delta_2)^2 + \tau_1^2 - 2\Psi_{12}]. \tag{6}$$

The cohesive energy density δ^2 of a liquid is given by $(-U/V)$ where U is the configurational energy, essentially equal in magnitude to the energy of vaporization of the liquid into the ideal gas state, and V is its volume.

For the alkanes δ_2 was obtained in this way with values taken from Williamson and Scott [14] who give a useful equation for the combined quantity $V_2^2 \delta_2^2$, equal to the a of the van der Waals equation of state. For the alkanenitriles δ_1^2 was evaluated from $(\Delta H_{\text{vap}} - RT/V)$ where ΔH_{vap} is the enthalpy of vaporization and V the volume. This expression gives a good enough approximation for $(-U/V)$ if the ΔH_{vap} values refer to the temperature for which δ_1^2 is required —for large molecules ΔH_{vap} can be highly temperature dependent— and if the vapour pressure is low enough to render gas-phase nonideality negligible. Both conditions are well enough met for the alkanenitriles at 298.15 K. Following Prausnitz and Weimer [5], the overall cohesive energy density of the polar component δ_1^2 was taken as the sum of a polar and a nonpolar part, *i.e.* $\delta_1^2 = \lambda^2 + \tau^2$. The accurate enthalpies of vaporization at 298.15 K of the alkanenitriles determined by Howard and Wadso [15] were used in the calculation of δ_1^2 . The nonpolar part was evaluated according to the homomorph principle using as homomorph the hydrocarbon of similar molecular structure and nearly equal molar volume at the same reduced temperature, taken as the fraction of the gas-liquid critical temperature. Anderson [4] has constructed correlations whereby λ_1 can be calculated and from it the polar contribution τ_1^2 was evaluated by difference $\tau_1^2 = \delta_1^2 - \lambda_1^2$. The induction term was calculated by Weimer [5] from measurements of the infinite dilution activity coefficients of different classes of hydrocarbons in polar solvents. For saturate hydrocarbons he found the correlation $\Psi_{12} = 0.396\tau_1^2$ and this was adopted here. It is clear that the exact value of Ψ_{12} should be composition dependent but in the absence of other information this nicety was neglected in our calculations. The results of the calculations of U_V^E from the theory are shown in Figs. 1-7.

4. Discussion

It is clear from Figs. 1-7 that the extent of the agreement between theory and experiment is at best no more than fair. However, it is worth emphasizing that with no fitting in the theoretical treatment whatsoever on our part, although the absolute magnitude of the experimental U_V^E is not well reproduced, the theory does reproduce the relative magnitude since both the experimental U_V^E and the calculated U_V^E increase as the n-alkane chain length increases for a given n-alkanenitrile and decrease as the n-alkanenitrile chain length increases for a given alkane.

One possible cause of the quantitative discrepancy —among many that could be identified for mixtures of such complexity— is the failure of the assumption of zero excess entropy of mixing. A rough estimate of this quantity at 298.15 K is readily available from our measurements. Assuming that the excess Gibbs function be 'simple' in the sense that G^E is quadratic in mole fraction, *i.e.* $G^E = x_1x_2A$ where A is a constant at a given temperature, and that "classical" thermodynamics applies at critical solution point it can be shown [16] that at the critical endpoind CEP of a binary mixture $G^E = (R\,UCST/2)$, where *UCST* is the CEP temperature. On the further assumption that H^E is independent of temperature over the range of temperature between the *UCST* and 298.15 K (the temperature to which all our present calculations refer), the Gibbs-Helmholtz equation leads to the following approximate expression for the molar excess entropy of mixing S^E

$$S^E = \frac{H^E}{T_c} - \frac{R}{2}. \tag{7}$$

This value of S^E is essentially that for a constant-pressure process, e.i. S_p^E. The corresponding constant-volume entropy of mixing can be evaluated from

$$S_V^E = S_p^E - \gamma_V V^E. \tag{8}$$

Table II shows values of TS_p^E and TS_V^E for all our seven mixtures at 298.15 K and Table III contains the values of the properties used in their calculation. In addition for comparison, Table II also shows the values of TS_p^E for the three mixtures with propanenitrile obtained from direct vapour pressure measurements [17]. The values of the more directly-determined TS_p^E for the three propanenitrile-*n*-alkane systems were obtained from experimentally-determined G^E data at 313.15 K [17] and the H^E data [9] at 298.15 K through the use of the Gibbs-Helmholtz equation. The corresponding TS_V^E is negative for the three systems considered and decreases in magnitude as the *n*-alkane chain length increases.

All the above results indicate that, although the Solubility Parameter version of the Regular Solution theory is appropriate for predicting *UCST* [6], it gives values of G^E ($= A_V^E = U_V^E$), that are lower than the experimental value. This arises it inter alia from the fact that when using classical thermodynamics to predict *UCST* from a correct G^E function, generally implies an overprediction of the *UCST*. Thus, by using the experimental $G^E(x = 0.5)$ data in $UCST = 2G^E/R$, the *UCST* obtained are 320 K, 334 K, and 339 K for propanenitrile with *n*-pentane, *n*-hexane, and *n*-heptane, respectively. These values are about 45 K higher than the corresponding experimental data given in Table III, 278 K, 285 K, and 293 K. Yet another ignored complication is the non-quadratic dependence of the experimental G^E for the propanenitrile mixtures on mole fraction. This is clear since the coefficient of the leading term in the Redlich-Kister expressions for G^E/RT for all our mixtures exceeds 2 which is thermodynamically inconsistent with the observed stability of a single mixture liquid phase unless the coefficients of some of the higher terms are nonzero. Confirming evidence springs from the observed asymmetry of the liquid-liquid coexistence curves for some these mixtures [8].

Furthermore, since TS_V^E, no matter how determined, does not exactly equal zero, the Regular Solution theory should not be expected to reproduce accurately the observed U_V^E behaviour for the systems considered.

Finally, it should be pointed out that the Prausnitz modification alters the term in Eq. (6) containing the solubility parameters of the pure substances reduces to essentially the polar terms, the purely dispersion term going close to zero. As a consequence, thus the final numerical values depend greatly on Weimer's value for Ψ_{12}. A change in this by 5% for the propanenitrile + *n*-alkanes and 7% for the *n*-butanenitrile + *n*-alkanes would bring the theory and experiment into agreement although no useful purpose would result from the manoeuvre.

a_0	a_1	a_2	a_3	a_4	a_5
		propanenitrile + n-pentane			
4732	−295	1375	710	−387	−2965
		propanenitrile + n-hexane			
5223	31	1370	−423	1038	−646
		propanenitrile + n-heptane			
5534	231	1359	−931	1306	
		n-butanenitrile + n-hexane			
4839	661	1122	−1240	24	
		n-butanenitrile + n-octane			
4951	−209	691	−2	2292	
		n-butanenitrile + n-dodecane			
5307	110	2652	1020	−781	240
		n-butanenitrile + n-tetradecane			
5837	−208	1749	871	817	

TABLE I. Coefficients a_i/J mole^{-1} for Eq. (4) corresponding to the fitting of U_V^E.

System	TS_p^E	TS_p^E (direct)	TS_V^E	TS^{Ev} (direct)
propanenitrile + n-pentane	88.9	−94	33.9	−149
propanenitrile + n-hexane	256.4	+40	132.5	−84
propanenitrile + n-octane	336.1	+137	173.4	−26
n-butanenitrile + n-hexane	323.0	—	253.3	—
n-butanenitrile + n-octane	374.4	—	219.4	—
n-butanenitrile + n-dodecane	388.1	—	167.2	—
n-butanenitrile + n-tetradecane	468.3	—	231.9	—

TABLE II . Values of TS_p^E and TS_V^E at 298.15 K and equimolar composition derived from the observed $UCST$ along with the more directly-determined values obtained from measured G^E data TS_V^E and TS_V^E. All the values are quoted in J/mole^{-1}.

System	$\frac{H^E}{\text{J mol}^{-1}}$	$\frac{G^E}{\text{J mol}^{-1}}$	$\frac{V^E}{\text{cm}^3\text{mol}^{-1}}$	$\frac{\gamma_V}{\text{MPa K}^{-1}}$	$\frac{UCEP}{\text{K}}$
propanenitrile + n-pentane	1237	1331	0.194	0.950	277.5
propanenitrile + n-hexane	1428	1388	0.440	0.945	284.7
propanenitrile + n-octane	1546	1442	0.566	0.965	292.6
n-butanenitrile + n-hexane	1280		0.240	0.976	244.2
n-butanenitrile + n-octane	1397		0.518	1.00	258*
n-butanenitrile + n-dodecane	1554		0.697	1.063	284.7
n-butanenitrile + n-tetradecane	1702		0.746	1.062	297.2

*Interpolated value

TABLE III. Values of the mixture properties used in the calculation of TS_p^E and TS_V^E. The molar excess quantities are given at equimolar compositions, and γ_V was obtained assuming ideality on a volume-fraction basis.

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Resumen. Se calculan las energías de exceso a volumen constante para siete mezclas de alcanonitrilo + alcano normal con propanonitrilo y *n*-butanonitrilo como los alcanonitrilos y *n*-pentano, *n*-hexano, *n*-heptano, *n*-octano, *n*-dodecano y *n*-tetradecano como los alcanos normales a partir de datos experimentales de la entalpía y volumen de exceso de los sistemas binarios y de datos PVT. Los resultados se comparan con las predicciones obtenidas de la Teoría de Soluciones Regulares en su versión del Parámetro de Solubilidad, la cual proporciona una buena descripción de las temperaturas de solubilidad de los sistemas binarios. Los resultados de la teoría concuerdan razonablemente con los valores derivados del experimento.