

THE W-SHAPED CONCENTRATION DEPENDENCE OF C_p^E AND SOLUTION NON-RANDOMNESS: SYSTEMS APPROACHING THE UCST

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ABSTRACT

The excess heat capacity C_p^E has been measured and the concentration–concentration correlation function S_{cc} has been calculated from literature G^E and H^E values for nitroethane + cyclohexane at 35, 30, 27 and 25 °C, approaching the UCST of 23.3 °C. C_p^E has a W-shaped concentration dependence, i.e. two negative minima separated by a positive maximum which becomes progressively larger and sharper as the temperature is lowered, attaining 15 J K⁻¹ mol⁻¹ at 25 °C. The S_{cc} , a measure of solution non-randomness, has a sharp positive maximum whose temperature behaviour parallels that of C_p^E . A Flory–Huggins-theory expression for S_{cc} gives results which are qualitatively, but not quantitatively, in agreement with experimental S_{cc} values, the difference being due to an incorrect rendering of the concentration dependence of H^E approaching the UCST. 1-Nitropropane + cyclohexane at 25 °C also gives a W-shaped C_p^E with a small positive maximum of 3 J K⁻¹ mol⁻¹, consistent with a small maximum in S_{cc} , obtained from G^E , and a UCST < -70 °C. C_p^E has been measured and, lacking experimental data, S_{cc} has been calculated using the Flory–Huggins theory for propionitrile + cyclohexane at 40 °C, 25 °C, and 15 °C, approaching the UCST of 12.2 °C. The evolution of the W-shaped C_p^E and S_{cc} with decreasing T is similar to the nitroethane + cyclohexane case. The W-shape thus arises from a positive non-randomness contribution in C_p^E which increases to become infinite at the UCST, and whose behaviour is predicted qualitatively by the S_{cc} .

INTRODUCTION

The excess heat capacity C_p^E has been found to have a surprising W-shaped concentration dependence in a wide variety of systems [1]. Either two minima appear in $C_p^E(x)$ separated by a maximum, as in Fig. 3 of this paper, or there are two regions of positive $C_p^E(x)$ curvature separated by a region of negative curvature. The W-shape has been interpreted [2] as being due to the superposition of two contributions to C_p^E : (1) a ‘normal’, parabolic term of negative sign arising when polar and non-polar components are mixed, the corresponding contributions in G^E and H^E being

positive. A mixing process in which order in one of the pure components is destroyed will give similar signs; and (2) an 'anomalous' positive contribution arising from non-randomness in the solution associated with values of G^E and H^E larger than ≈ 800 and ≈ 1000 J mol⁻¹, respectively. As non-randomness must disappear towards the ends of the concentration range, contribution 2 superimposed on 1 can give the W-shape. Rubio et al. [3] suggested that a convenient measure of non-randomness is afforded by the concentration-concentration correlation function S_{cc} obtainable through light scattering or vapour pressure measurement and given by

$$S_{cc}^{-1} = \left(\frac{\partial^2(G/RT)}{\partial x_i^2} \right)_{P,T} \\ = \frac{1}{x_1 x_2} + \left(\frac{\partial^2 G^E/RT}{\partial x_i^2} \right)_{P,T} \quad (1)$$

The simple Flory-Huggins (FH) theory [3] gives

$$S_{cc}^{-1} = (1/x_1 x_2) + \left[(r-1)^2 / (x_1 + x_2 r)^2 \right] - 2\chi_1 r^2 / (x_1 + x_2 r)^3 \quad (2)$$

with $r = r_2/r_1$, the ratio of segments or molar volumes of the two components, and

$$\chi_1 = z\Delta w r_1 / kT = (a/T) + b \quad (3)$$

with Δw being the interchange free energy between segments. In eqn. (2), the first two terms are combinatorial, the first being the ideal contribution while the second non-ideal term acts to diminish S_{cc} , non-randomness and the height of the central maximum in C_p^E . The S_{cc} is increased by the negative third term in eqn. (2) which is interactional in nature. Equation (3) shows that χ_1 and S_{cc} will increase as T is decreased until $S_{cc} \rightarrow \infty$ at the UCST where the FH critical conditions are

$$\chi_1 = 0.5(1 + r^{-0.5})^2 \quad (4)$$

$$x_1/x_2 = r^{1.5}$$

Experimental results [3] suggest that C_p^E becomes W-shaped when S_{cc} is larger than ~ 0.7 . As T approaches the UCST, the curvature of G against x tends to zero and $S_{cc} \rightarrow \infty$ as $(T - T_c)^{-1.24}$ [4], whereas mean-field theories such as FH give an exponent of -1 . The C_p of the solution and, hence, C_p^E tend to ∞ as $(T - T_c)^{-0.125}$ [4]. In the few systems where the W-shape has been investigated at more than one temperature, it was found to be enhanced by lowering T [2]. In the present work, the temperature behaviours of C_p^E and S_{cc} are studied for T within 30° of the UCST.

EXPERIMENTAL

Heat capacity measurements were made for nitroethane + cyclohexane at 25°C, 27°C, 30°C and 35°C, for 1-nitropropane + cyclohexane at 25°C, and for propionitrile + cyclohexane at 15°C, 25°C and 40°C. A Picker flow microcalorimeter (Sodev, Sherbrooke, Que., Canada) was used together with a vibrating-cell densimeter, also from Sodev, to transform volumetric heat capacity, C_p/V , into the molar quantity. The procedures and instrumentation are described in the literature [5,6]. However, the experiments were found to be subject to a boundary effect having the following origin. The instrument measures the difference $\Delta C_p/V$ in C_p/V values between the working liquid (A) flowing through the working cell and the reference liquid (B) in the reference cell. The two cells are connected in series, the working liquid pushing the reference liquid with an interface or boundary between the two. This arrangement assures that both liquids have the same rate of flow at any moment in spite of a possible variation in flow due to irregularity of the pump. However, mixing effects at the boundary led to a somewhat different value of $\Delta C_p/V$ when A occupied the reference cell and B the working cell, i.e. when the order of passage of the liquids through the instrument was reversed [5]. The origin of the effect as described in ref. 5 apparently lies in the interdiffusion of the two liquids across the interface coupled with a large enthalpy or volume of mixing. The boundary effect may be obviated by separating the two liquids by mercury or using a membrane separator [7], giving values of $\Delta C_p/V$ which are in agreement with the average of the two $\Delta C_p/V$ values found from A \rightarrow B and B \rightarrow A procedures. However, the use of mercury or the separator (in this particular application) is extremely cumbersome and was not carried out in the C_p^E measurements. The usual determination of C_p^E through the concentration range for a 1-2 system consists of measuring C_p/V for the solution most dilute in 2 against pure 1 as reference, then using that solution as reference for the next most dilute solution, and so on in step-wise fashion until reaching pure 2. The boundary effect indicates that a discrepancy in C_p^E will exist depending on whether the experiments are performed from 1 to 2 or 2 to 1, and the experiments with mercury or a separator show that the correct C_p^E is found by averaging the two C_p^E values. In practice, ref. 6 found that for the systems tested, the discrepancy between C_p^E values was within normal experimental error, and this was confirmed for various systems in this laboratory. However, the discrepancy was not found to be negligible for nitroethane + cyclohexane where a maximum discrepancy of 0.6 J K⁻¹ mol⁻¹ occurred in the middle of the concentration range decreasing to < 0.1 J K⁻¹ mol⁻¹ when x was within 0.25 of the ends of the concentration range. The same behaviour was also found at each temperature for nitropropane + cyclohexane. On the other hand, for the propionitrile + cyclohexane system at different temperatures, there was a negligible dis-

crepancy between C_p^E values. The C_p^E points in Fig. 2 for nitroethane and nitropropane + cyclohexane are therefore averages of values obtained by measuring in the 1 to 2 and 2 to 1 directions, whereas Fig. 5 for propionitrile + cyclohexane shows unaveraged points. From repetition we find the reproducibility of C_p^E values to be $\pm 0.05 \text{ J K}^{-1} \text{ mol}^{-1}$. The possible systematic error incurred through taking the average C_p^E may be estimated from the comparison [5] of average C_p/V values with values obtained when eliminating the boundary effect through the use of mercury. The possible error would appear to be $\pm 0.06 \text{ J K}^{-1} \text{ mol}^{-1}$ for both nitroalkane systems toward the middle of the concentration range and less towards the ends. This error is absent from the propionitrile system.

RESULTS AND DISCUSSION

Nitroethane and nitropropane + cyclohexane

S_{cc} values

Marsh and collaborators have made a thorough study of the composition dependence of G^E at 45°C for nitroethane and 1-nitropropane + cyclohexane [8] and of H^E at 25°C and 45°C for both systems [9a,b]. The smoothing equations for these data gave $G^E(x)$ at various temperatures using a linear interpolation of $H^E(x)$ between 25°C and 45°C , i.e. taking C_p^E to be independent of T . Equation (1) then gives S_{cc} as seen in Fig. 1 for 45°C , 35°C , 30°C , 27°C and 25°C , approaching the UCST for this system at 23.3°C [9a]. At each temperature, S_{cc} of the solution is much greater than $S_{cc}(\text{ideal}) = x_1x_2$, and as T approaches the UCST, S_{cc} diverges sharply. This behaviour indicates a large degree of non-randomness which attains a sharp maximum near the middle of the concentration range, and which increases as T approaches the UCST.

S_{cc} values have also been calculated using the Flory-Huggins theory, i.e. eqn. (2) with $r = 1.513$ from the molar volumes of the components at 25°C . The χ_1 parameter is found from eqn. (4) to have a value of 1.643 at the UCST, 23.3°C . Both constants a and b of eqn. (3) can be obtained using this value with the FH relation

$$H^E = aR x_1 x_2 r / (x_1 + x_2 r) \quad (5)$$

An experimental value [9a] of 1690 J mol^{-1} at 25°C was used for H^E at $x_1 = 0.50$ whence $a = 674.5 \text{ K}$ and $b = 0.632$. The values of S_{cc} at the different temperatures are shown in Fig. 2, where they are seen to have the same concentration and temperature dependences as the experimental curves of Fig. 1, but to be smaller by a factor of two, a discrepancy which can be understood as follows. The FH calculation fits χ_1 to give a zero value of $[\partial^2(G/RT)/\partial x^2]_{P,T}$ at the UCST, and then calculates values of this quan-

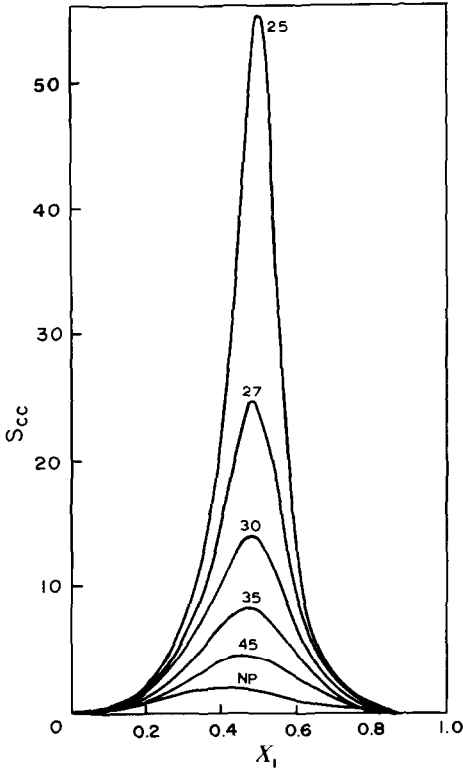


Fig. 1. The S_{cc} functions for nitroethane+cyclohexane from 45°C to 25°C, and for 1-nitropropane (NP)+cyclohexane at 25°C calculated from G^E data.

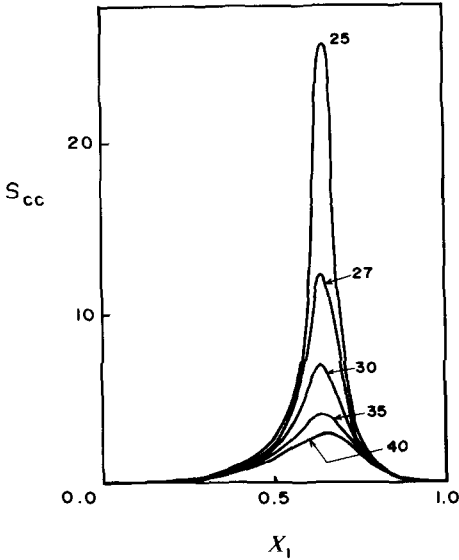


Fig. 2. The S_{cc} functions for nitroethane+cyclohexane from 40°C to 25°C calculated using the Flory-Huggins eqn. (2).

tity at high temperatures using its temperature dependence. This is $[\partial^2(H^E/RT^2)\partial x^2]_{P,T}$ and for this, FH assumes the concentration dependence given by eqn. (5), i.e. a temperature-independent value. However, it is known [10] that, in reality, with increasing non-randomness approaching the UCST, the curvature of $H^E(x)$ falls and ultimately becomes zero at the UCST. This effect is apparent in the a_2 parameter of the smoothing equations for H^E given in ref. 9a. Thus the FH theory, which ignores non-randomness, must overestimate the rate at which the curvature of G/RT against concentration departs from zero as the temperature rises from the UCST. Hence FH values of S_{cc} will be underestimated. The Guggenheim quasi-chemical approach [2] introduces non-randomness and its use brings some improvement, but with realistic values of the z parameter, the improvement is small. Nevertheless, comparison of Figs. 1 and 2 shows that in spite of its shortcomings the simple FH theory can be used to provide S_{cc} values of qualitative, if not quantitative, significance.

C_p^E values

Figure 3 shows the C_p^E curves at the same temperatures obtained through the averaging technique described in the experimental section. In each case there is a large positive maximum and two small negative minima at the ends of the concentration range, i.e. a W-shape which increases as T falls

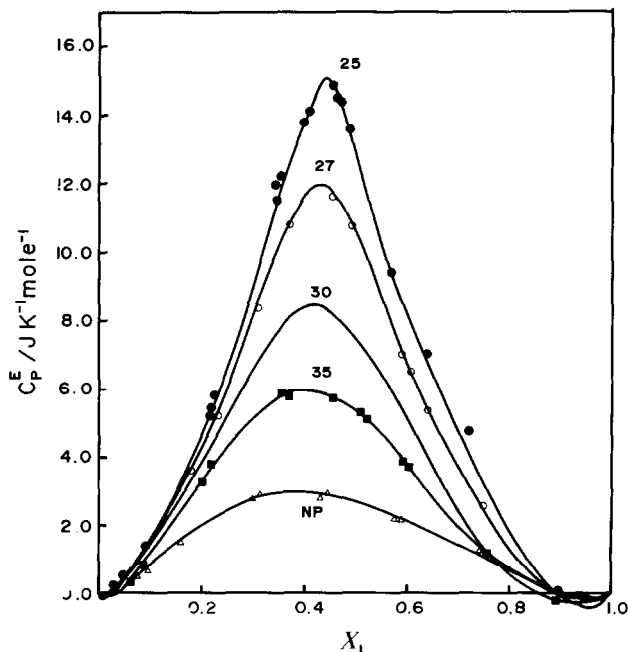


Fig. 3. C_p^E for nitroethane+cyclohexane from 35°C to 25°C and for 1-nitropropane+cyclohexane at 25°C.

toward the UCST. This behaviour, similar to that of S_{cc} is strong evidence that the W-shape arises from a positive non-randomness contribution, which increases as T decreases, superimposed on a negative, parabolic random contribution. The concentration at which S_{cc} reaches a maximum is slightly higher than that found for the C_p^E maximum, the difference probably being within experimental error for these two functions. A determination of the critical exponent for C_p approaching the UCST would appear to be a possibility. We believe, however, that the presence of the 'normal' negative contribution in C_p^E makes such a determination difficult unless T is closer to T_c than here. Values of C_p^E at 35°C may be obtained from H^E at 25 and 45°C. They have the same concentration dependence as here but, at equimolar composition, are 1 J K⁻¹ mol⁻¹ smaller. From the positive sign of $d^2 C_p^E/dT^2$, one would expect the difference between the two sets of results to be of opposite sign, a discrepancy we are unable to explain.

The S_{cc} and C_p^E for nitropropane + cyclohexane at 25°C are also shown in Figs. 1 and 3. The S_{cc} was obtained from G^E and H^E data from refs. 8 and 9b, as described above. The C_p^E was again obtained using the averaging procedure. The smaller values of S_{cc} and C_p^E for this system are consistent with the smaller values of G^E and H^E , i.e. 1160 and 1507 J mol⁻¹, and a much lower value of the UCST, i.e. < -70°C, all of which reflects the smaller fraction of the nitropropane molecule which is of NO₂ character. Nevertheless, it is remarkable that even at 100°C from the UCST, the non-randomness is still sufficient to produce a W-shape, S_{cc} still being above the value of 0.7 suggested as a threshold for the appearance of the W-shape [3].

Propionitrile + cyclohexane

Figures 4 and 5 show S_{cc} and C_p^E values for propionitrile + cyclohexane at temperatures approaching the UCST, estimated to lie at 12.2°C [11]. The concentration dependence of G^E in the literature did not seem to be sufficiently well established to give accurate values of S_{cc} . In order to obtain a qualitative view of S_{cc} , FH theory and eqn. (2) were used, fitting constants a and b of eqn. (3) to the UCST and to a 25°C value of $H^E = 1350$ J mol⁻¹ at the critical concentration of $x_1 = 0.665$, estimated from the H^E for propionitrile + methylcyclohexane and + *n*-hexane [12]. The results in Fig. 3 presumably constitute lower limits which, however, should be qualitatively correct. Figure 5 shows the values of C_p^E at the three temperatures. The boundary effect was negligible for this system and the figure shows the points obtained by proceeding from propionitrile to cyclohexane and vice versa. The W-shape again occurs here, increasing in amplitude as the UCST is approached. In fact the values are very similar to those in Fig. 2 for nitroethane + cyclohexane approaching its UCST. Again, the S_{cc} behaviour is similar to that of C_p^E and similar to that found for the nitroethane + cyclohexane system.

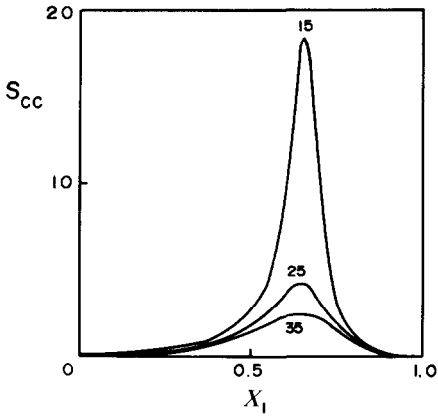


Fig. 4. The S_{cc} function for propionitrile + cyclohexane at 35°C, 25°C and 15°C calculated using the Flory-Huggins eqn. (2).

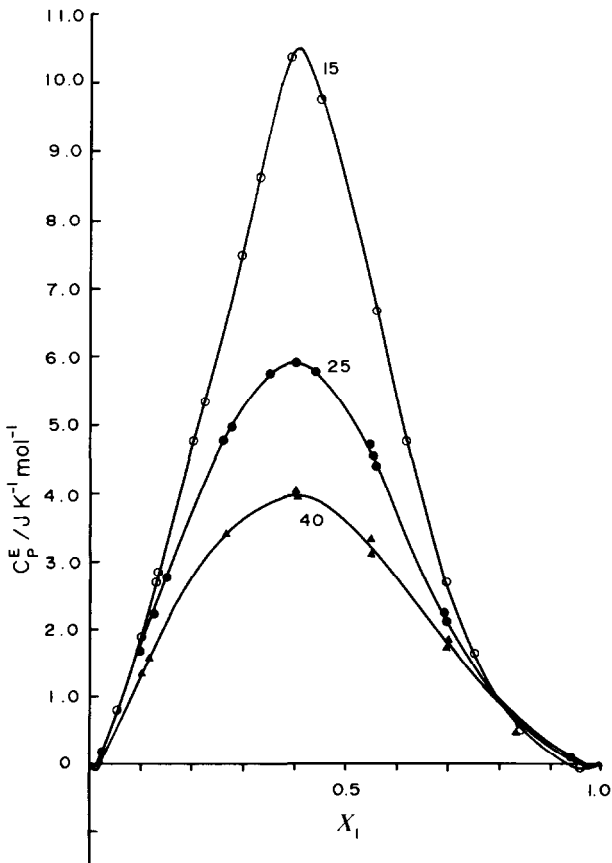


Fig. 5. C_p^E for propionitrile + cyclohexane at 40°C, 25°C and 15°C.

The three systems discussed contain strongly polar molecules. However, the non-polar system perfluoroheptane + 2,2,4-trimethylpentane at 30 °C also has a W-shaped C_p^E [13] which is similar to those for nitroethane + cyclohexane at 25 °C and propionitrile + cyclohexane at 15 °C. A positive maximum of 16 J K⁻¹ mol⁻¹ occurs associated with a UCST at 23 °C and a large positive H^E (2100 J mol⁻¹) and G^E (1360 J mol⁻¹). The S_{cc} at 30 °C calculated using $G^E(x)$ values [14] is similar to those found for the previous systems with a large maximum of 29 [13]. We may conclude that the W-shaped C_p^E is caused by the non-randomness contribution which increases as the UCST is approached, and that experimental or calculated values of S_{cc} are helpful measures of this non-randomness. The Flory–Huggins theory for S_{cc} was shown in ref. 3 to predict the concentration at which the W-shape appears for systems having components of different molecular size. The present work shows that the FH S_{cc} , although not in quantitative agreement with experimental values, is a predictor of the height of the central maximum C_p^E at temperatures approaching the UCST.

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REFERENCES

- 1 M. Pintos, R. Bravo Baluja, M.I. Paz Andrade, J. Roux-Desgranges and J.P.E. Grolier, *Can. J. Chem.*, 66 (1988) 1179; and refs. therein.
- 2 M.-E. Saint Victor and D. Patterson, *Fluid Phase Equilibrium*, 35 (1987) 237.
- 3 R.G. Rubio, M. Caceres, R.M. Masegosa, L. Andreoli-Ball, M. Costas, and D. Patterson, *Ber. Bunsenges. Phys. Chem.*, 93 (1989), 48; L. Andreoli-Ball, M. Costas, D. Patterson, R.G. Rubio, M. Caceres, and R.M. Masegosa, *Ber. Bunsenges. Phys. Chem.*, 93 (1989) 882.
- 4 J.S. Rowlinson and F.L. Swinton, *Liquids and Liquids Mixtures*, Butterworths, London, 3rd edn., 1982.
- 5 J.L. Fortier, G.C. Benson and P. Picker, *J. Chem. Thermodyn.*, 8 (1976) 289.
- 6 J.L. Fortier and G.C. Benson, *J. Chem. Thermodyn.*, 8 (1976) 411.
- 7 J.P.E. Grolier and A. Inglese, *Can. J. Chem.*, 54 (1976) 1952.
- 8 K.N. Marsh, H.T. French, and H.P. Rogers, *J. Chem. Thermodyn.*, 11 (1979), 89.
- 9 a) K.N. Marsh, *J. Chem. Thermodyn.*, 17 (1985) 600.
b) K.N. Marsh, W.A. Allan, and A.E. Richards, *J. Chem. Thermodyn.*, 16 (1984) 1107.
- 10 W.J. Gaw and R.L. Scott, *J. Chem. Thermodyn.*, 3 (1971) 335.
- 11 A.W. Francis, *Critical Solution Temperatures*, Advances in Chemistry Series, Am. Chem. Soc. Washington, 1961.
- 12 J.J. Christensen, R.W. Hanks, and R.M. Izatt, *Handbook of Heats of Mixing*, Wiley, New York, 1982.
- 13 M.-E. Saint Victor, Ph.D. Thesis, McGill University, Montreal, 1988.
- 14 A.G. Williamson and R.L. Scott, *J. Phys. Chem.*, 65 (1961) 275.