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LOCAL NON-RANDOMNESS AND EXCESS SECOND-ORDER THERMODYNAMIC QUANTITIES

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ABSTRACT

Systems exhibiting large H^E and G^E and within ~100 K of the UCST show a W-shape concentration dependence in C_p^E which is ascribed to two contributions: a "normal", random C_p^E of negative sign and a positive non-random C_p^E. Approaching the LCST, the W-shape should be found when the LCST is due to a large free volume difference between the components but not for an aqueous system LCST. As with C_p, other second-order quantities such as α_P and κ_T tend to infinity at T_C. It appears that a W-shape dV^E/dP would be discernible only for T less than a degree from T_C. Both random and non-random contributions to dV^E/dT have the same sign and hence the W-shape should not be found. Experimental dV^E/dT results were discussed in terms of the Flory theory. The discrepancy observed between experimental and predicted values near the UCST is associated with non-random contributions to dV^E/dT.

INTRODUCTION

Grolier and collaborators have found [1] a large number of systems where the excess heat capacity, C_p^E, has an unusual W-shape concentration dependence. This has been ascribed [2] to the presence in C_p^E of two contributions: (1) a "normal", parabolic curve of negative sign arising when polar and non-polar components are mixed, or more generally when order is destroyed during the mixing process and (2) an anomalous positive contribution associated with local non-randomness in the solution which appears towards the middle of the concentration range. A measure of non-randomness, the concentration–concentration correlation function, S_{CC} is defined by [3]

$$S_{CC} = \frac{\left(\delta^2(G/RT)^{-1}\right)}{\delta x^2}$$

and a minimum value of $S_{CC} \approx 0.7$ corresponding to $G^E \approx 800$ J mol^{-1} has been suggested [3] for the appearance of the W-shape.

Both S_{CC} and C_p tend to infinity [4] at the critical point, the former as $(T - T_C)^{-1.24}$ and the latter as $(T - T_C)^{-0.125}$. Lowering the temperature

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toward the UCST thus increases the S_{CC} and the central maximum of the W-shape. For example, in the propionitrile–cyclohexane system [5], at 40, 25 and 15 °C approaching the UCST at 13 °C, the central maximum of C_p^E at $x \approx 0.5$ is 3, 6 and 10 J K^{-1} mol^{-1}, i.e. already large at 40 °C and becoming rapidly larger as T is lowered. It is argued [5] that the W-shape is a manifestation of the critical state which continues ≈ 100 °C above T_C there being no qualitative difference between critical and non-randomness contributions to C_p^E. The excess quantity C_p^E is much more sensitive to the critical contributions than C_p of the solution itself because in C_p^E the various background contributions to C_p of the solution have been mainly eliminated through subtraction of the pure component C_p values. Although the critical contribution to C_p of the solution may be small 50–100 °C from T_C, perhaps 1–3 J K mol^{-1}, it is nevertheless discernible in C_p^E because the 'normal' contribution to C_p^E is of the same order, and is of opposite sign with a different concentration dependence [2].

Other second-order thermodynamic quantities, i.e. the thermal expansion coefficient, α_P, and the isothermal compressibility, κ_T, also tend to infinity at T_C with the same critical exponent 0.125 [6] as C_p. In the present work we consider the possibility of discerning the non-random or critical contribution in dV^E/dP and dV^E/dT after first considering C_p^E approaching the LCST rather than the UCST.

C_p^E AT THE LCST

As the UCST or LCST is approached and non-randomness is increased, H^E is reduced in magnitude causing the non-random or critical contribution to C_p^E. Approaching the LCST, where H^E is negative, the non-random contribution to $dH^E/dT = C_p^E$ is therefore positive. Two types of LCST are known: (1) in aqueous systems at low temperatures where the 'normal' C_p^E is also positive. Here the critical contribution will not appear as a W-shape, but as an enhancement and change of concentration dependence of an already positive C_p^E. This may well be discernible but only relatively close to the LCST. (2) In systems where a large difference in free volume exists between the two components, as in a polymer–solvent system or one composed of two hydrocarbons of widely different carbon number, e.g. methane + 2-methylpentane [7]. The normal C_p^E must be strongly negative and hence these systems are candidates for observation of the W-shape.

$(\kappa_T V)^E = -(dV^E/dP)$

The critical contributions to C_p, κ_T and α_P of the solutions are closely related. Thus Griffiths and Wheeler [8] give for the solution in the critical region

$$(\kappa_T V)_{\mathrm{crit}} = -\left(\frac{\mathrm{d}V}{\mathrm{d}P}\right)_{\mathrm{crit}} = \frac{(C_p)_{\mathrm{crit}}}{T_C}\frac{\mathrm{d}T_C}{\mathrm{d}P} \tag{1}$$

It is assumed that the same relation holds at temperatures more removed from T_C and, correspondingly, the same equation is followed by the excess quantities. Because [6]

$$\frac{\mathrm{d}T_C}{\mathrm{d}P} = T_C\frac{(\mathrm{d}^2V/\mathrm{d}x^2)_C}{(\mathrm{d}^2H/\mathrm{d}x^2)_C} \approx T_C\frac{V^E}{H^E} \tag{2}$$

it follows that

$$(\kappa_T V)^E_{\mathrm{crit}} = -\left(\frac{\mathrm{d}V^E}{\mathrm{d}P}\right)_{\mathrm{crit}} = (C_p^E)_{\mathrm{crit}} T_C\left(\frac{V^E}{H^E}\right)^2 \tag{3}$$

The negative sign of $(\mathrm{d}V^E/\mathrm{d}P)_{\mathrm{crit}}$ is consistent with Le Chatelier's Principle or with the following argument based on the displacement of T_C by pressure. Non-randomness reduces the magnitude of V^E. Thus, if V^E is $+$ $(-)$, the critical or non-random contribution to V^E is $-$ $(+)$. From eqn. (2), the effect of pressure for V^E $+$ $(-)$ is to move T_C towards (away from) the experimental T lying above the UCST. The effect of pressure is therefore to increase (decrease) non-randomness and the magnitude of the critical contribution. Thus $(\mathrm{d}V^E/\mathrm{d}P)_{\mathrm{crit}}$ is negative for both signs of V^E. The sign of $-(\mathrm{d}V^E/\mathrm{d}P)_{\mathrm{crit}}$ is positive and could be expected to give the W-shape if the normal contribution to $-\mathrm{d}V^E/\mathrm{d}P$ were negative. The Flory theory [9] shows that this sign is attained when V^E is negative and although this sign is rarer than positive, it is found for systems which combine a component of high thermal pressure coefficient γ and low α_P with one of low γ and high α_P. Other model calculations using the Flory theory suggest that when $V^E < 0$

$$(\kappa_T V)^E = -\frac{\mathrm{d}V^E}{\mathrm{d}P} \approx 20 \times 10^{-3} V^E \text{ cm}^6 \text{ J}^{-1} \text{ mol}^{-1} \tag{4}$$

Putting $V^E \approx -1$ cm^3 mol^{-1}, $H^E \approx 1500$ J mol^{-1} and comparing eqns. (3) and (4), the value of $(C_p^E)_{\mathrm{crit}}$ which would give critical and random contributions of equal magnitude in $(\mathrm{d}V^E/\mathrm{d}P)$ is 100 J K^{-1} mol^{-1}. Such a large value of $(C_p^E)_{\mathrm{crit}}$ would only be achieved at an experimental temperature a fraction of a degree from T_C. We conclude that the W-shape in $-(\mathrm{d}V^E/\mathrm{d}P)$ cannot be as widespread a phenomenon as for C_p^E. This conclusion is consistent with previous work [10] where the Flory theory gave good predictions for $-\mathrm{d}V^E/\mathrm{d}P$ in systems where C_p^E and $\mathrm{d}V^E/\mathrm{d}T$ were sensitive to effects of structure in solution, i.e. in $\mathrm{d}V^E/\mathrm{d}P$ the 'normal' contribution is too large to allow any effects of structure to be discerned.

$\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$

According to the Prigogine–Flory theory [11], the random or normal V^{E} is composed of three terms: interactional, P^{*} and $\tilde{V}$ curvature. $\mathrm{D}V^{\mathrm{E}}/\mathrm{d}T$ may be considered as the sum of three corresponding terms which may be shown to be almost directly proportional to the V^{E} terms. Thus, the total $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ and V^{E} must be almost proportional, and model calculations show that

$$\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T \approx 10 \times 10^{-3} V^{\mathrm{E}} \tag{5}$$

Furthermore, the critical contribution to $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ is given by [6]

$$\left(\frac{\mathrm{d}V^{\mathrm{E}}}{\mathrm{d}T}\right)_{\mathrm{crit}} = \left(C_p^{\mathrm{E}}\right)_{\mathrm{crit}} \frac{1}{T_{\mathrm{C}}} \frac{\mathrm{d}T}{\mathrm{d}P} \approx \left(C_p^{\mathrm{E}}\right)_{\mathrm{crit}} \frac{V^{\mathrm{E}}}{H^{\mathrm{E}}} \tag{6}$$

$$\approx 5 \times 10^{-4} \left(C_p^{\mathrm{E}}\right)_{\mathrm{crit}} V^{\mathrm{E}} \tag{7}$$

Thus, approaching the UCST, both normal and critical contributions to $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ will be of the same sign, i.e. that of V^{E}, and the conditions for the occurrence of the W-shape are not met in the case of $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$. Furthermore, the critical contribution to $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ is small. From eqns. (5) and (6), this contribution becomes equal to the normal when $C_p^{\mathrm{E}} \approx 20$ J K^{-1} mol^{-1} which corresponds to the experimental temperature being only a few degrees from T_{C}. Thus although $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ near the UCST is a more sensitive indicator of non-randomness than $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}P$, its observation will still require special conditions of temperature close to T_{C}. Nevertheless, it seems worthwhile to compare Flory theory predictions with experimental values of $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ near the UCST to determine if a discrepancy between the two can be associated with a critical contribution to $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$.

Before doing this, we consider $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ approaching the two types of LCST mentioned above. Aqueous systems [12] usually exhibit negative V^{E} and positive $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ values approaching the LCST. As H^{E} is negative (or if S-shaped, $(\delta^2 H/\delta x^2)$ is positive) while $(C_p^{\mathrm{E}})_{\mathrm{crit}}$ is positive, eqn. (6) shows that $(\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T)_{\mathrm{crit}}$ is also positive. Thus both normal and critical contributions to $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ are again of the same sign as they are when approaching the UCST and the W-shape will not arise.

However, as with C_p^{E}, the second type of LCST caused by a large free volume difference between the components has V^{E} and $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$ negative while $(\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T)_{\mathrm{crit}}$ is positive. Systems approaching sufficiently close to this type of LCST should show a W-shape concentration dependence of $\mathrm{d}V^{\mathrm{E}}/\mathrm{d}T$. A possible such system is methane + 2-methylpentane where volume changes have been determined [7] approaching the LCST of 194.7 K, without however any obvious W-shape being discernible.

EXPERIMENTAL

The chemicals were from standard sources and were high purity, at least 99%. They were used without any further treatment.

Excess volumes data were obtained through density measurements using a flow densitometer from Sodev. Measurements were carried out as described in the literature [13]. V^E data were fitted to Redlich–Kister equations for each temperature. Equimolar values of V^E were then used to calculate dV^E/dT at different temperatures. The reduction parameters, $P^\star$, $V^\star$ and $T^\star$, required by the Prigogine–Flory theory were taken from the literature [14,15]. State equation parameters are given in Table 1.

V^E measurements were carried out for mixtures of: nitroethane + cyclohexane at 25, 27, 30, 35 and 50 °C; nitropropane + cyclohexane at 10 and 25 °C; propionitrile + cyC_6 at 15, 25 and 40 °C; butanone + hexadecane (n-C_{16}) at 25, 30 and 40 °C, and + 2,2,4,4,6,8,8-heptamethyl nonane (brC_{16}) at 25 and 40 °C; hexanone + n-C_{16} at 25, 30 and 40 °C; benzonitrile + n-C_6, n-C_8 at 25 and 30 °C, and + n-C_{16} at 30 and 40 °C, and brC_{16} at 40 and 50 °C; nitrobenzene + brC_{16} at 40 and 50 °C. V^E results are given as a function of concentration of component 1 in ref. 16.

The accuracy of the V^E measurement depends on the system studied, i.e. it is greater for the nitriles or nitro compounds than for the ketones, for instance, but in any case it is estimated as being not less than ± 0.01 cm³ mol⁻¹ for V^E and not less than $\pm 1 \times 10^{-3}$ cm³ K⁻¹ mol⁻¹ for dV^E/dT.

TABLE 1

Equation of state quantities for pure components at 25 °C

Component	$P^\star$ (J cm^{-3})	$10^3\ \alpha$ (K^{-1})	ρ (g cm^{-3})	s (Å^{-1})
Acetone	589.6	1.42	0.78502	0.85
2-Butanone	582	1.29	0.7999	0.89
Propionitrile	675	1.119	0.9953	1.0
Nitroethane	682	1.117	1.0446	1.07
Nitropropane	675	1.119	0.9953	1.0
Benzonitrile	728	0.884	1.00053	1.0
Nitrobenzene	710.67	0.825	1.1977	1.04
n-Hexane (n-C_6)	423	1.384	0.6554	1.04
n-Octane (n-C_8)	439	1.165	0.6983	0.99
n-Hexadecane (n-C_{16})	463	0.884	0.7699	0.90
2,2,4,4,6,8,8-Heptamethyl-nonane (brC_{16})	399	0.872	0.7856	0.77
Cyclohexane (cyC_6)	530	1.217	0.7739	0.93

RESULTS AND DISCUSSION

Tables 2–4 give, for the different systems studied, the experimental temperature for dV^E/dT, the equimolar values of experimental and theoretical dV^E/dT, the values of V^E measured at 25°C and values of the interaction parameter (X_{12}) fitted to V^E.

An attempt has been made to evaluate the critical part of dV^E/dT. As the Flory theory has successfully predicted dV^E/dT for mixtures of alkanes where the components are believed to be randomly mixed, taking then the predicted value to be approximately the random contribution, the dis-

TABLE 2

Thermodynamic quantities for ketones in normal and branched alkanes

System	UCST (°C)	T (°C)	V^E (cm^3 mol^{-1})	$10^3 dV^E/dT$ (cm^3 K^{-1} mol^{-1}) Exp.	$10^3 dV^E/dT$ [a] (cm^3 K^{-1} mol^{-1}) Theor.	X_{12} (J cm^{-3})
Acetone +						
n-C$_6$	−39	20	1.025	10.5	9.7	45.2
n-C$_{16}$	13	20	1.255	12.6	8.2	55.9
brC$_{16}$	5	17.5	1.155	17.0	6.98	32.5
2-Butanone +						
n-C$_{16}$	< m.p.	32.5	1.08	5.0	4.9	35.0
brC$_{16}$	< m.p.	32.5	0.85	5.54	4.1	12.9
3-Hexanone +						
n-C$_{16}$	< m.p.	32.5	0.79	2.7		

[a] With X_{12} fitted to V^E.

TABLE 3

Thermodynamic quantities for propionitrile, nitroethane, nitropropane + cyclohexane

System	UCST (°C)	T (°C)	V^E (cm^3 mol^{-1})	$10^3 dV^E/dT$ (cm^3 K^{-1} mol^{-1}) Exp.	$10^3 dV^E/dT$ [a] (cm^3 K^{-1} mol^{-1}) Theor.	X_{12} (J cm^{-3})
Propionitrile +						
cyC$_6$	12.2	20	0.70	5.0	6.13	50
Nitroethane +						
cyC$_6$	23	26	0.8	10	6.53	73.0
		37.5		4.0		
Nitropropane +						
cyC$_6$	< m.p.	20	0.72	3.67	5.63	57.0

[a] With X_{12} fitted to V^E.

TABLE 4

Thermodynamic quantities for benzonitrile and nitrobenzene in several alkanes

System	UCST (°C)	T (°C)	V^E (cm^3 mol^{-1})	$10^3\,dV^E/dT$ (cm^3 K^{-1} mol^{-1}) Exp.	$10^3\,dV^E/dT$ [a] (cm^3 K^{-1} mol^{-1}) Theor.	X_{12} (J cm^{-3})
Benzonitrile +						
n-C_6		27.5	−0.775	−15.0	−8.44	44.5
n-C_8		27.5	−0.310	−1.1	−3.16	32.4
n-C_{16}		35	0.265	5.0	2.9	23.4
brC_{16}		45	0.435	10.15	1.76	11.2
Nitrobenzene +						
n-C_6	20.3	23	−0.99	−17.0	−10.5	45.5
brC_{16}		45	0.07	−6.2	0.65	16.7

[a] With X_{12} fitted to V^E.

crepancy between experimental and predicted values for each system will give the sign of the critical or non-random dV^E/dT and a crude approximation of its magnitude. It is observed in the tables that this difference is temperature dependent for almost all systems and increases faster as T is closer to the critical point. At any temperature farther than a few degrees from T_C, this difference vanishes, and the theory correctly predicts the results. Contrary to C_p^E, where the effect of the critical state is still discernible $\approx 100\,°C$ from T_C, the effect of the critical state on dV^E/dT is perceptible only within a few degrees of T_C.

Mixtures of acetone + normal or branched alkanes and nitroethane, and propionitrile + cyC_6 all satisfy eqn. (5) and the critical dV^E/dT shows the same sign as V^E. It decreases rapidly with increase of T and vanishes, leading to good agreement with the Flory theory prediction. Mixtures of butanone and hexanone with normal and brC_{16}, and nitropropane + cyC_6 are all far from their UCST and the results all agree with the theoretical predictions.

Benzonitrile was mixed with different alkanes ($n = 6$, 8, 10, 16, brC_{16}). V^E has been observed to be positive, negative or S-shaped [17]. dV^E/dT takes the sign of V^E in each case. The calculated non-random dV^E/dT also shows the same sign as V^E. Thereby, it can be concluded that the non-random contribution may be either positive or negative. The critical dV^E/dT calculated for the n-C_6 mixture is negative and large; it is ≈ 0 for n-C_8 and positive for n-C_{16} and brC_{16}. brC_{16} mixtures exhibit a large discrepancy between experimental and theoretical values, as expected because of the proximity of the UCST, while surprisingly n-C_{16} mixtures show good agreement with Flory theory predictions, even though the system is near the UCST. The existence of correlation of molecular orientations (CMO) in alkane liquids such as n-C_{16} has been suggested by Tancrede et al. [18].

CMO during mixing is manifested by a negative contribution to dV^E/dT [19]. It can then be suggested that dV^E/dT for benzonitrile + n-C_{16} contains a negative contribution caused by the destruction of CMO in n-C_{16} and that could probably counterbalance the positive contribution coming from non-randomness in solution. Hence the observed value of dV^E/dT should only reflect the random or 'normal' contribution which is well-predicted by Flory's theory. However, it has been shown [19] that orientational order decreases with branching of alkane molecules, leading to an absence of any CMO in the highly branched hexadecane ($br C_{16}$). The large critical or non-random part should then be responsible for this large discrepancy between experimental and theoretical values of dV^E/dT.

C_p^E and V^E values of nitrobenzene mixtures [17] reveal similar results with benzonitrile and a similar conclusion can be reached for dV^E/dT results. However, with reference to mixtures containing cyclohexane (Table 3), one should note that despite the proximity of the UCST, no discrepancy has been observed between experimental and theoretical values of dV^E/dT for propionitrile + cyC_6 systems and Flory's theory agrees well at all temperatures studied. Furthermore, C_p^E for these systems shows a large and positive W-shape [5] even at $T \approx 40\,°C$ away from UCST.

The W-shape concentration dependence is definitely a more general phenomenon for C_p^E than it is for dV^E/dT. However, if approaching the UCST the W-shape dV^E/dT seems to be an extremely rare phenomenon, its observation should be possible for certain systems (large free volume difference) as T approaches the LCST, because in those particular cases, the 'normal' and the critical contributions to dV^E/dT are expected to be of opposite signs.

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