Lower Critical Solution Temperatures of Polyisobutylene plus Isomeric Alkanes

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Lower critical solution temperatures (LCST) have been obtained for polyisobutylene and some thirty isomeric pentanes, hexanes, heptanes and octanes. The LCSTs found with cyclic alkanes are about 125 deg. C higher than those with the corresponding normal alkanes. Branched isomers of the same number of carbon atoms give LCSTs which vary over some 50 deg. C. These variations in LCST are explained in terms of the differing free volumes of the solvents as shown by their different thermal expansion coefficients, and which arise from their different 'structural factors' in the Prigogine theory of solutions. The theory, with the approximation of a van der Waals liquid as recently used by Flory and collaborators, is successful in correlating the LCSTs but not in giving a quantitative prediction of the values.

THE lower critical solution temperature (LCST) in polymer solutions occurs as the temperature approaches the gas–liquid critical temperature (T_c) of the pure solvent. It is found even in mixtures of homologues of different chain length and is essentially a 'structural effect', i.e. it is due to the segments of the two component molecules being arranged in chains of different length, structure or flexibility. On the other hand, the familiar upper critical solution temperature (UCST) is associated with the segments of the components being of different chemical nature.

In the solution thermodynamics theory of Prigogine and collaborators[1] the structure of a chain-molecule affects the temperature reduction parameter $T^\star$ of the liquid. This characteristic parameter gives the reduced temperature

$$\tilde{T} = T/T^\star = c(n)\,kT/q(n)\,\epsilon^\star \tag{1}$$

The reduced temperature is a ratio of two energies. The numerator, ckT, is essentially the thermal energy of the $3c$ external degrees of motion of the chain which act to expand the liquid. On the other hand, contraction is favoured by the denominator, $q\epsilon^\star$, related to the cohesive energy of interchain contacts. Thus, a large value of $\tilde{T}$ corresponds to large values of the free volume and related quantities such as the thermal expansion coefficient (α) and compressibility (β). In the expression for $\tilde{T}$, $\epsilon^\star$ depends on the nature of the segments of the chain. However, the structural factor[1], c/q, is a characteristic of the whole chain, being essentially the number of external degrees of freedom per external contact. It decreases with increasing chain length and/or rigidity of the molecule and is therefore small for a high polymer. The LCST is associated with a large difference, τ, between the $\tilde{T}$ or $T^\star$ of the dense polymer and expanded solvent:

$$\tau = 1 - \tilde{T}_2/\tilde{T}_1 = 1 - T^\star_1/T^\star_2 \tag{2}$$

On mixing the components, changes of free volume produce a large negative volume of mixing and a large negative non-combinatorial contribution to the entropy of mixing. This latter structural effect brings about the LCST as the T_c of the solvent is approached and the free volume of the solvent increases rapidly away from that of the polymer.

The Prigogine theory has been used to correlate the LCST of a number of polymer solutions[2] including polyisobutylene (PIB) with the series of *n*-alkanes. As the solvent chain is lengthened the τ parameter decreases, and the LCST approaches the critical temperature of the solvent. In the present work, the theory is tested for a single polymer, PIB, with as solvents about thirty branched, cyclic and normal isomeric pentanes, hexanes, heptanes and octanes. The starting point of the work was the observation that the cyclic alkanes have considerably smaller coefficients of thermal expansion and hence free volumes than the corresponding normal alkanes. One thus predicts LCST closer to T_c of the solvent in the cyclic isomers.

The LCST found with the cyclic alkanes are in fact ~125 deg. higher than those for the corresponding *n*-alkanes. Furthermore the structural factor should be sensitive to branching of the alkane. The LCSTs of branched isomeric alkanes vary over ~50 deg. and can be higher or lower than the *n*-alkane value. We find that the theory is successful in correlating the LCST without invoking any difference in chemical nature of segments in the solvents. Simple models of the liquid state give qualitative predictions of the LCST.

EXPERIMENTAL AND RESULTS

Two fractions of Enjay Vistanex PIB were used, of molecular weights $3{\cdot}6 \times 10^6$ and $6{\cdot}3 \times 10^5$, determined from the intrinsic viscosities. The solvents listed in *Table 1* were Aldrich, Fisher or Baker reagent and purissimum grades and were used without further purification. The measurements of the LCST for each of the fractions were made as described previously[2], using sealed glass tubes and a turbidimetric technique to determine the temperature at which phase separation took place. The reproducibility of the LCST was ±1 deg. but the accuracy of the LCST extrapolated to infinite molecular weight is thought to be ±4 deg. The cloud-point curve was found for several systems to be flat to within 0·5 deg. from a volume fraction of one to three per cent of polymer, and for other systems a single concentration of two per cent was used. The procedure used in extrapolating the LCST for the fractions to infinite polymer molecular weight is more complicated than for the usual UCSTs. It is probably better[2] to plot the LCST rather than its reciprocal against $M^{-1/2}$. However, the two plots lead to extrapolated values within one degree as $M \to \infty$. The values found are listed for solvents in *Table 1* together with the ratios which they bear to the vapour–liquid critical temperatures of the pure solvents.

DISCUSSION

The present results for the *n*-alkanes are a few degrees different from those previously reported[2], but for *n*-octane the LCST is now found eight degrees lower than previously.

As expected, the LCST of the cyclic alkanes are much higher than for the normal isomers and are considerably closer to the T_c of the solvents. Values for cyclopentane and cyclohexane were given by Freeman and Rowlinson[3] in their first list of LCST of some 25 polymer–solvent systems. They were considerably lower than found here; this discrepancy has also been noticed by Swinton[4].

Table 1. LCST and equation of state parameters.

Substance	*LCST* (°*K*)	T_c (°*K*)	$\frac{LCST}{T_c}$	$10^3\alpha$ (*deg*$^{-1}$)	$10^4\beta$ (*atm*$^{-1}$)	$T^\star$ (°*K*)	$c_1\tau^2$
n-Pentane	344	470	0·73	1·58^{b}	2·01^{b}	4 150	0·213
2-Methylbutane	318	461	0·69	1·63^{a}	2·13^{d}	4 100	0·220
Cyclopentane	461	512	0·90	1·34^{a}	1·37^{e}	4 490	0·175
n-Hexane	402	508	0·79	1·36^{b}	1·61^{b}	4 430	0·198
2-Methylpentane	376	498	0·76	1·42^{a}	1·78^{e}	4 350	0·202
3-Methylpentane	405	505	0·80	1·37^{a}	1·67^{e}	4 420	0·193
Methylcyclopentane	478	533	0·90	1·26^{a}	1·48^{e}	4 610	0·162
Cyclohexane	516	553	0·93	1·20^{a}	1·08^{d}	4 720	0·162
n-Heptane	442	540	0·82	1·24^{b}	1·41^{b}	4·640	0·189
2-Methylhexane	426	531	0·80	1·24^{a}	1·51^{d}	4 640	0·177
3-Methylhexane	446	536	0·83	1·22^{a}	1·45^{d}	4 680	0·173
3-Ethylpentane	458	541	0·85	1·21^{a}	1·36^{d}	4 700	0·176
2,2-Dimethylpentane	404	521	0·78	1·28^{a}	1·62^{d}	4 560	0·187
2,3-Dimethylpentane	451	538	0·84	1·20^{a}	1·40^{d}	4 720	0·168
2,4-Dimethylpentane	403	520	0·78	1·30^{a}	1·60^{d}	4 530	0·198
3,3-Dimethylpentane	451	536	0·84	1·21^{a}	1·45^{d}	4 690	0·168
2,2,3-Trimethylbutane	445	532	0·84	1·23^{a}	1·52^{d}	4 660	0·168
Ethylcyclopentane	524	570	0·92	1·12^{a}	1·43^{e}	4 880	0·128
Methylcyclohexane	526	572	0·93	1·13^{a}	1·11^{d}	4 870	0·151
Cycloheptane	572	602^{g}	0·95	0·99^{c}	0·92^{c}	5 220	0·150
n-Octane	477	569	0·84	1·15^{b}	1·25^{b}	4 820	0·181
2-Methylheptane	466	561	0·83	1·15^{a}	1·35^{d}	4 820	0·167
3-Methylheptane	478	565	0·85	1·15^{a}	1·29^{d}	4 870	0·179
2,2-Dimethylhexane	454	552	0·82	1·20^{a}	1·42^{d}	4 720	0·188
2,4-Dimethylhexane	458	555	0·83	1·19^{a}	1·36^{d}	4 740	0·190
2,5-Dimethylhexane	446	552	0·81	1·21^{a}	1·43^{d}	4 690	0·195
3,4-Dimethylhexane	497	571	0·87	1·12^{a}	1·23^{d}	4 890	0·164
2,2,4-Trimethylpentane	435	544	0·80	1·20^{a}	1·50^{d}	4 720	0·180
n-Propylcyclopentane	547	604^{f}	0·91	1·04^{a}		5 080	
Cyclooctane	$\simeq$637	647^{g}	0·98	0·88^{f}	0·78^{c}	5 250	0·130
n-Decane	535	619	0·86	1·04^{b}	1·08$_{d}$	5 120	0·166
n-Dodecane	582	659	0·88	0·94^{a}	0·97^{d}	5 360	0·151

(a) Computed from density data of the American Petroleum Institute, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*. Carnegie Press: Pittsburgh, 1953

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(e) Measured using an ultracentrifuge technique

(f) Estimated by extrapolation from data on other cyclic alkanes with alkyl side-chains

(g) Measured

The values for the branched isomers are widely spread on both sides of the *n*-alkane LCST. The four dimethylpentane isomers are remarkable in that two have LCST fifty degrees different from those of the other pair. As with the cyclic alkanes, a high value of the LCST/T_c ratio (and of the LCST itself) is correlated with a low value of α and a high value of T_c both of which indicate a low solvent free volume and hence greater similarity between the solvent and the polymer. We shall return to this simple correlation after discussing a correlation based on the Prigogine theory.

Theory

The Prigogine corresponding states approach has been used to give a theory[5] of the LCST in chain-molecule mixtures including its relation to the critical line in P, T, composition space and the effect of pressure on the LCST. It is predicted that for a solution of a polymer of very high M, a lower critical solution point must occur below T_c of the solvent and at a low polymer volume fraction. This is approximately that given by the Flory–Huggins theory for the usual upper critical solution point, viz.

$$\phi_2 = (1 + r^{1/2})^{-1} \tag{3}$$

Here r may be taken as the ratio of the molar volumes of the components. At the LCST the χ_1 parameter in the chemical potential of the solvent attains a critical value. According to the Flory–Huggins approximation for the combinatorial entropy of mixing, this is

$$\chi_1 = \tfrac{1}{2}(1 + r^{-1/2})^2 \tag{4}$$

At the low concentration of equation (3) the pressure and temperature dependent χ_1 can be related to reduced thermodynamic quantities (indicated by tilde) *of the pure solvent*

$$\frac{\chi_1(P,T)}{c_1} = \frac{-\tilde{U}(\tilde{P},\tilde{T})}{\tilde{T}}\nu^2 + \frac{\tilde{C}_p(\tilde{P},\tilde{T})}{2}\left(\tau + \frac{\tilde{\beta}\tilde{P}}{\tilde{\alpha}\tilde{T}}\,\pi\right)^2 \tag{5}$$

The parameter c_1 of the solvent may be found from the reduction parameter $S^\star$ for the entropy of the solvent, i.e.

$$Rc_1 = S^\star = P^\star V^\star / T^\star \tag{6}$$

The parameters ν, π and τ all indicate differences in molecular characteristics of the two components. The parameter ν^2 characterizes differences in force fields and segment sizes between the polymer and solvent molecules. The first term of equation (5) is the usual χ_1 term and is associated with the relative weakness of interaction between segments of chains of different chemical species. Following ref. 2 this contribution will be provisionally ignored for the present systems of chemically similar molecules at high temperatures.

The second term of equation (5) is the contribution arising from the free volume difference between the liquids. The parameter τ is defined by equation (2) while the parameter π is similarly related to differences of the pressure reduction parameters $P^\star$, i.e.

$$\pi = P_1^\star / P_2^\star - 1 \tag{7}$$

In the present case, the pressure is the saturation pressure of the solvent and hence is small. The term $(\tilde{\beta}\tilde{P}/\tilde{\alpha}\tilde{T})\,\pi$ is therefore negligible compared with τ and may be dropped. Equation (5) then becomes

$$\chi_1(P,T)/c_1 = \tilde{C}_p(\tilde{P},\tilde{T})\,\tau^2/2 \tag{8}$$

The function $\tilde{C}_p$ is of importance since it is its increase with rise of temperature which brings about the LCST. Since $\tilde{C}_p$ tends to infinity as the gas–liquid critical point of the solvent is approached it is more convenient to deal with its reciprocal. Combining equations (4) and (8), the reduced

LCST occurring at a reduced pressure P for a polymer of infinite M must obey the relation

$$\tilde{C}_p^{-1}(\tilde{P},\tilde{T}) = c_1\tau^2 \tag{9}$$

van der Waals expression for $\tilde{C}_p$

Prigogine suggested the use of a simple smoothed potential cell model to predict reduced thermodynamic functions such as $\tilde{C}_p$. Flory and collaborators have used[6] in conjunction with this a van der Waals dependence of the configurational energy of the liquid on the volume, i.e.

$$\tilde{U} = -\tilde{V}^{-1} \tag{10}$$

The equation of state is then essentially the Hirschfelder–Eyring equation of state, which in reduced form is

$$\tilde{P}\,\tilde{V}/\tilde{T} = (1-\tilde{V}^{-1/3}) - (\tilde{V}\tilde{T})^{-1} \tag{11}$$

With this model one has[5]

$$\tilde{C}_p^{-1}(\tilde{P},\tilde{T}) = \{1-\tfrac{2}{3}\tilde{V}^{-1/3}\} - 2\,(1-\tilde{V}^{-1/3})/(\tilde{P}\tilde{V}^2+1) \tag{12}$$

Equation (12) used in (8) gives an expression for $\chi_1(P,T)$. If $P=0$, one obtains the same expression for χ_1 as equation (26) of Flory, Orwoll and Vrij[6] except for the inclusion of end-effects in their equation.

Determination of c_1 and τ^2

Equation (11) leads to expressions for three equation of state quantities at zero pressure: the molar volume, α and β (cf. ref. 6). Experimental values of these quantities can then be used to give respectively the three reduction parameters $V^\star$, $T^\star$ and $P^\star$, and the parameter c_1 may be obtained for the solvents using equation (4). Values of α and β at 20°C are listed in *Table 1* for the solvents. Using $\alpha = 5{\cdot}56 \times 10^{-4}\ \text{deg}^{-1}$ for PIB[7] at 20°C, $T^\star = 7\,533$ deg. for the polymer. This value and those of $T_1^\star$ for the solvents give the τ values for the systems, and ultimately $c_1\tau^2$ as listed in *Table 1*.

The precision of $c_1\tau^2$ depends on that of α and β for the solvents. The order of magnitude of possible error in α and β was taken as one per cent which leads to a possible lack of precision of ± 5 per cent in $c_1\tau^2$. The absolute validity of the $c_1\tau^2$ values depends on the validity of the model. For instance, the assumption of another energy/volume dependence different from that of a van der Waals liquid [equation (10)] gives other values of the reduction parameters. It seems, however, that the relative magnitudes are largely preserved so that the correlation of data will be independent of the model chosen. A procedure such as that used previously[2] which assumes no model but only the law of corresponding states could have been adopted, but is certainly less convenient in practice. We will see below that the simple theory outlined above allows an intercomparison of LCST values for the systems. It does not, however, give accurate *a priori* predictions of the LCST.

The gas–liquid critical temperature and $T^{\star}$

According to the reduced equation of state, equation (11), the gas–liquid critical temperature takes place at a single value of the reduced temperature, $\tilde{T}_c$, which is[5] 0·1187 for this particular model. Thus,

$$T_c = 0{\cdot}1187 T^{\star} \qquad (13)$$

and the vapour–liquid critical point of a pure liquid is proportional to its temperature reduction parameter. In *Figure 1* we plot T_c against $T^{\star}$ and notice that equation (13) is in fact fulfilled to a considerable degree. Using equation (13), $T/T_c = \tilde{T}/0{\cdot}1187$ and the ratio of the LCST to T_c may be taken as a measure of the reduced LCST.

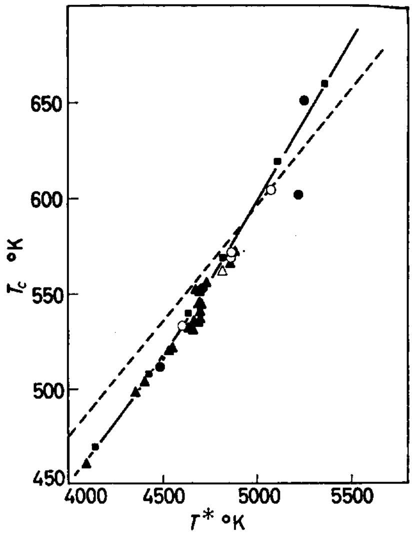

Figure 1—Plot of the critical temperatures of alkane solvents against $T^{\star}$ obtained at 20°C: normal alkanes (■), branched alkanes (▲), alkyl cycloalkanes (○), cyclic alkanes (●). The full line is drawn through the *n*-alkane points, and the broken line according to equation (13)

Effect of pressure on the LCST

The effect of pressure on the LCST of the polyethylene–pentane[8] and polyisobutylene–isopentane[9] systems has been found to be ~0·5 deg./atm. Since most of the present LCST occur under equilibrium vapour pressures of about 5 atm the LCST at zero pressure would be within a few degrees of the value obtained. For the purpose of interpretation the difference could be ignored and the pressure set equal to zero in equation (12). It is, however, possible to take the pressure effect into account. We have plotted the reduced equilibrium vapour pressure as a function of reduced temperature for a number of the solvents used here, and find to a high order of approximation a single curve of $\tilde{P}$ against $\tilde{T}$. Thus $\tilde{C}_p^{-1}(\tilde{P},\tilde{T})$ may be considered as a function of the single variable $\tilde{T}$. *Figure 2* shows $\tilde{C}_p^{-1}(\tilde{T})$ from equations (12) and (11) using the above empirical relation of $\tilde{P}$ to $\tilde{T}$. It is plotted against $\tilde{T}/0{\cdot}1187 = T/T_c$.

Correlation of the LCST through equation (9)

Figure 2 also shows $c_1\tau^2$ for the systems plotted against the LCST$/T_c$ ratio. If the corresponding states approach and equation (9) are correct, a single curve for all the systems should result, giving a representation of $\tilde{C}_p^{-1}$ against T/T_c. Except possibly for the cyclic alkanes, the correlation is satisfactory, particularly in view of the ±5 per cent precision estimated for the $c_1\tau^2$ values. About 100 deg. of the ~125 deg. difference between the LCSTs of the cyclic and normal alkanes has been explained by the theory in terms of the lower $c_1\tau^2$ values for the cyclic alkanes. The cyclic alkane points remain higher than the others, by ~0·04 T_c corresponding to 25 deg. The explanation of this discrepancy cannot lie in a difference of force fields between these solvents and the segments of the polymer. Although such a difference may in fact exist, it would raise the predicted χ_1 value and would therefore lower the predicted LCST.

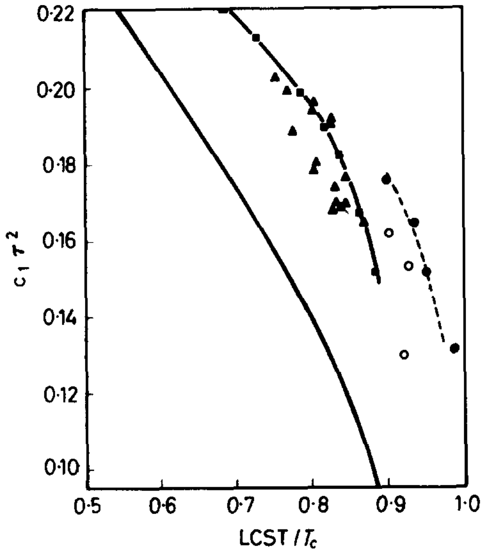

Figure 2—Correlation of LCST values: $c_1\tau^2$ against the LCST$/T_c$ ratios: normal alkanes (■), branched alkanes (▲), alkyl cycloalkanes (○), cyclic alkanes (●). The full line is drawn through the *n*-alkane points, the broken line through cyclic alkane points. The full line to the left is drawn from equation (12) using the smoothed potential cell model and the Flory assumption of van der Waals dependence of the energy on volume

The values of $c_1\tau^2$ for the normal alkanes are consistently higher than for the branched isomers. This means that the LCST$/T_c$ ratio for the normal alkanes should be lower than for the branched. However, in fact there is no general tendency of this sort with the result that the points for the *n*-alkanes lie slightly above those for most of the branched solvents.

The curve of $\tilde{C}_p^{-1}(T) = c_1\tau^2$ found from the experimental LCST differs from that drawn from equation (12) in *Figure 2*. Correspondingly, using the known $c_1\tau^2$ values, the theoretical $\tilde{C}_p^{-1}(T)$ curve would predict values of the LCST which would be too low. For instance, for *n*-pentane,

$$c_1\tau^2 = 0{\cdot}215$$

and the predicted LCST would be 268°K instead of the observed 344°K, corresponding to values of χ_1 predicted to be too large. A discrepancy of the same sign is found by Eichinger and Flory[7] in their calculation of χ_1 for PIB–n-pentane at room temperature. They also assume end-effects, i.e. that the fields of force around the ends of the n-alkanes are different from those around middle segments; this produces an additional contribution to χ_1. If end-effects were to be invoked here, a further decrease of the predicted LCST would occur.

The $c_1\tau^2$ values used here were obtained from equation of state data at 20°C. It is known, however, that the reduction of parameters do vary with temperature showing an inadequacy of the theoretical equation of state. It was therefore possible that better agreement between theory and experiment could have been obtained by determining $c_1\tau^2$ at higher temperatures nearer the LCST. To test this we have calculated $c_1\tau^2$ for PIB–n-hexane using data of refs. 6 and 7 at temperatures from 20° to 150°C. There is a decrease of this quantity, as required, but only of the order of 20 per cent between these temperatures. It is thus insufficient to bring the experimental points in *Figure 2* into agreement with the line predicted from equation (12).

We conclude that the variations of the LCST amongst the systems may be completely ascribed to the differing free volumes of the isomeric solvents resulting from different structural factors. Furthermore, the Prigogine theory with the assumption of a van der Waals energy/volume dependence is adequate to give reduction parameters to correlate the data but it cannot predict absolute values of the LCST.

Correlation of LCST with T_c

According to the above treatment, the temperature interval between the LCST and T_c depends on $c_1\tau^2$ or largely on τ^2. This parameter is associated with the difference between the free volumes of the components, as

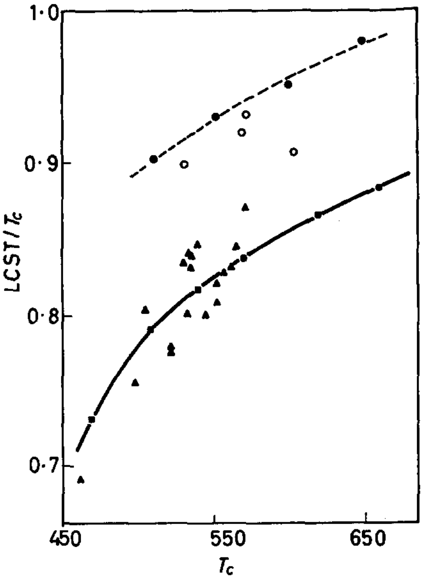

Figure 3—Correlation of LCST/T_c of the solvents: normal alkanes (■), branched alkanes (▲), alkyl cycloalkanes (○), cyclic alkanes (●)

characterized by their values of α or T_c. Hence in the present case with a single polymer for all the systems, a correlation should exist between the LCST/T_c and α or T_c of the solvents. The correlation with T_c is presented in *Figure 3*. It seems less successful than that with $c_1\tau^2$. This indicates that although c_1 varies little between alkanes, it plays a significant role in the correlation.

Methane–alkane systems

Davenport and Rowlinson[10] have obtained the LCST for, amongst others, systems containing methane and five of the alkanes used here. In three other cases where the same alkanes were used as in the present work, the LCST is obscured below the quadruple point at which crystallization takes place and which thus constitutes an upper limit for the value of the LCST. The $T^\star$ parameters for the alkanes lie between the values of this parameter for methane and polyisobutylene. Thus a low value of the LCST for a PIB plus alkane system should correlate with a high value for the methane plus alkane system. A relation of this type is in fact found.

We are grateful to the National Research Council of Canada for their support, and to the Province of Quebec for a France–Quebec Scholarship to J.-M. B.

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(*Received June 1968*)

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