

1165. *The Effect of Structure on Electrolyte Invasion in Ion-exchange Resins.*

By C. J. ATTRIDGE and J. R. MILLAR.

Electrolyte invasion has been measured for the sodium chloride–sodium resinate system on a series of solvent-modified styrene–divinylbenzene cation-exchange resins in bead form. The results, interpreted by the use of Glueckauf's recent theory, give a good description of the exchanger structures already independently deduced. For conventional exchangers similar interpretation of electrolyte invasion figures also indicates appreciable heterogeneity of structure, in accord with recent concepts. We conclude that the theory is generally valid for sulphonated styrene–divinylbenzene copolymers.

SYMBOLS

A, B = lowest, and highest, local counterion concentration in exchanger.

m = molal concentration of external electrolyte.

\bar{m} = local molal concentration of internal electrolyte.

$\bar{\bar{m}}$ = mean (observable) molal concentration of internal electrolyte (mequiv./g. swelling water).

M = local counterion concentration.

- C = exchange capacity (mequiv./g. dry Na^+ -form resin).
 W = water regain (g. H_2O /g. dry Na^+ -form resin).
 \bar{M} = C/W = mean (observable) counterion concentration (mequiv./g. swelling water).
 z = constant of non-uniformity in range $0 < z < 1$.
 γ_{\pm} = mean molal activity coefficient of external electrolyte.
 $\bar{\gamma}_{\pm}$ = mean molal activity coefficient of internal electrolyte.
 ϕ = volume fraction of internal solution.

INTRODUCTION

MANY workers¹⁻⁹ have pointed out that the observed electrolyte uptake of ion exchangers departs considerably from that deduced from the ideal Donnan law, which requires that the activity product, a , of the electrolyte in the aqueous phase in equilibrium with a homogeneous ion exchanger, be proportional to the activity product, \bar{a} , of the same electrolyte in the exchanger phase:

$$\bar{a} = ka \quad (1)$$

In terms of molal concentration for a 1:1 electrolyte

$$\bar{m} \cdot (M + \bar{m}) = km^2 (\gamma_{\pm} / \bar{\gamma}_{\pm})^2 \quad (2)$$

and hence if $\gamma_{\pm} / \bar{\gamma}_{\pm}$ is constant, and $M \gg \bar{m}$ (i.e., at low concentrations),

$$\bar{m} = k'm^2 \quad (3)$$

Several factors have been suggested as either contributing to or being wholly responsible for deviations from this simple power law.

(i) Experimental errors¹⁰ due to (a) incomplete separation of the internal and external phases, (b) traces of organic impurities in the exchanger phase.

(ii) Variations in the ratio, $\gamma_{\pm} / \bar{\gamma}_{\pm}$, as a consequence of electrostatic interactions between the fixed ionic sites and the invading electrolyte, resulting in an abnormal degree of ion-pairing of the latter,^{1, 2, 9} or as a consequence of variations in electrostatic potential not taken into account in arriving at equation (2).^{3, 4}

(iii) The heterogeneity of the ion-exchange matrix.^{5-8, 11}

Although the effect of (i) can be reduced to a negligible level by modifying the experimental technique and conditions,^{6, 12} the estimation of the relative contributions of (ii) and (iii) to the observed deviations is still a difficult problem. In consequence, previous workers in this field have tended to interpret results in terms of one approach and have neglected, or applied a correction for, any variations which may be due to the others. Gustafson, for example, has interpreted his recent work⁹ on polymethacrylate ion exchangers in terms of electrostatic interactions and attempted to overcome heterogeneity difficulties by arbitrarily dividing the resin into a homogeneous gel region and a "macropore" region, applying a correction to eliminate the effects of uptake in the latter. Conversely, Glueckauf and his

¹ W. C. Bauman and J. Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830.

² H. P. Gregor, F. Gutoff, and J. I. Bregman, *J. Colloid Sci.*, 1951, **6**, 323; H. P. Gregor and M. H. Gottlieb, *J. Amer. Chem. Soc.*, 1953, **75**, 3539; K. A. Kraus and G. E. Moore, *ibid.*, 1953, **75**, 1457; M. H. Gottlieb and H. P. Gregor, *ibid.*, 1954, **76**, 4639; F. Nelson and K. A. Kraus, *ibid.*, 1958, **80**, 4154; C. W. Davies and G. D. Yeoman, *Trans. Faraday Soc.*, 1953, **49**, 968; J. S. Mackie and P. Meares, *Proc. Roy. Soc.*, 1955, **A**, **232**, 485; J. Danon, *J. Phys. Chem.*, 1961, **65**, 2039.

³ F. L. Tye, *J.*, 1961, 4784.

⁴ M. G. T. Shone, *Trans. Faraday Soc.*, 1962, **58**, 472.

⁵ E. Glueckauf and R. E. Watts, *Nature*, 1961, **191**, 904.

⁶ E. Glueckauf and R. E. Watts, *Proc. Roy. Soc.*, 1962, **A**, **268**, 339.

⁷ E. Glueckauf, *Proc. Roy. Soc.*, 1962, **A**, **268**, 350.

⁸ J. M. Crabtree and E. Glueckauf, *Trans. Faraday Soc.*, 1963, **59**, 2639.

⁹ R. L. Gustafson, *J. Phys. Chem.*, 1963, **67**, 2549.

¹⁰ D. H. Freeman, *J. Phys. Chem.*, 1961, **35**, 189.

¹¹ J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *J.*, 1964, 2740.

¹² G. Scatchard and N. J. Andersen, *J. Phys. Chem.*, 1961, **65**, 1536.

co-workers,⁵⁻⁸ using a diffusion method for studying electrolyte uptake in ion-exchange membranes, have disregarded variations in $\gamma \pm / \bar{\gamma} \pm$ and used their results for a structural analysis of the exchanger, assuming a continuous distribution of M , the local concentration of counterions in the resin.

The object of the present work has been to study the uptake of a 1:1 electrolyte in sulphonated styrene-divinylbenzene exchangers in bead form and of known and well-characterised non-uniformity of structure.¹³

In view of this non-uniformity of structure it was convenient to interpret the results in terms of the Glueckauf theory, the basic features of which are outlined below. For a complete derivation readers are referred to the original paper.⁷ The mean observed electrolyte uptake has been shown to follow a power law of the form,

$$\bar{m} = k'' m^{(2-z)}, \quad (4)$$

where for a 1:1 electrolyte and a given exchanger, z is a constant in the range $0 < z < 1$, although deviations from this value may occur at extreme concentrations. The function,

$$\phi = k_0(M^{1-z} - A^{1-z})/(1-z) \quad (5)$$

has been suggested for the distribution of the local concentration M of counterions in the exchanger, where k_0 is also a constant for a given ion exchanger. The maximum local counterion concentration is given by the expression,

$$B \simeq \bar{M}(2-z)/(1-z) \quad (6)$$

provided that $B \gg A$, and k_0 is therefore given by

$$k_0 \simeq (1-z)^{2-z}/[\bar{M}(2-z)]^{1-z} \quad (7)$$

the same assumption being made.

If the experimental results are plotted as $\log \bar{m}$ against $\log m$, the gradient is $(2-z)$; from z and \bar{M} an approximate fractional distribution of the counterion within the exchanger can then be calculated.

EXPERIMENTAL AND RESULTS

Materials.—The sulphonated cross-linked polystyrene cation-exchange resins used in this work were (i) conventional materials, Zeo-Karb 225 (The Permutit Co. Ltd.), of various cross-linkings, and (ii) solvent-modified materials with matrix divinylbenzene contents from 15 to 55%, all of which were made as previously described,¹³ in toluene at a dilution of 1:2, *i.e.* at a volume fraction of monomers (F_M) of 0.33. All the exchangers used were of particle size 18—44 mesh, and in the Na^+ form. The characteristics of these resins are given in Table 1.

TABLE 1.

	Zeo-Karb 225			Solvent-modified resins ($F_M = 0.33$)						
% DVB	6.5	4.0	1.7	15	22	27	30	40	55	
\bar{C} (mequiv./g.)	4.60	4.74	4.71	4.50	4.52	4.49	3.91	3.63	3.53	
W (g./g.)	0.89	1.73	3.70	2.20	1.80	1.71	1.59	1.54	1.88	
\bar{M}	5.17	2.74	1.27	2.05	2.51	2.63	2.46	2.36	1.88	

All reagent chemicals used were AnalaR grade, and mixed-bed demineralised water was used throughout for making up the solutions and eluting the equilibrated resins.

Method.—The invasion of the Na^+ form of the exchangers by sodium chloride (a typical 1:1 electrolyte) was measured by a technique essentially that used by Bauman and Eichhorn.¹

For each sodium chloride concentration the resin (*ca.* 10 g.) and solution (*ca.* 100 ml.) were equilibrated overnight in screw-capped Polythene bottles. The resin was separated from the solution as efficiently as possible by blotting with filter paper. The imbibed sodium chloride was then eluted with demineralised water from the bulk of the resin after an aliquot had been removed for a

¹³ J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *J.*, 1963, 218.

water content determination. The concentrations of both external and eluted solutions were determined either by titration of chloride with standard silver nitrate, or, at the lower concentrations, by flame-photometric determination of the sodium ion. The method is limited, particularly for the conventional materials, by incomplete separation of the internal and external phases, and in general when the ratio $\bar{m}/m < \sim 0.1$, gives rise to anomalously high values of \bar{m} . In the solvent-modified materials, because of their higher uptake, quite low external concentrations may be used before this error becomes significant.

Fig. 1 shows the experimental results plotted as $\log \bar{m}$ against $\log m$, omitting those for the 30% and 40% F_M 0.33 divinylbenzene resins for the sake of clarity.

Fig. 2 shows the variation with external molality (m) of the water regain (W_m) expressed as a fraction of that at infinite dilution (W) for the conventional resins, and the 15% and 55% divinylbenzene solvent-modified materials. Again, for clarity, the curves for the intermediate solvent-modified materials have been omitted.

DISCUSSION

Apart from deviations at high external concentrations the plots of Fig. 1 are rectilinear

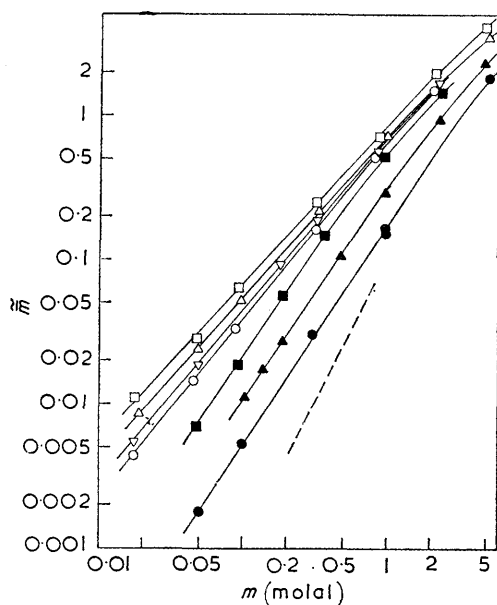


FIG. 1. Variation of mean internal molality, \bar{m} , with external molality, m , of NaCl. ● 6.5% DVB; ▲ 4.0% DVB; ■ 1.7% DVB; ○ 15% DVB; ▽ 22% DVB; △ 27% DVB; □ 55% DVB. (Open symbols—solvent-modified, F_M 0.33, materials) ----- Theoretical Donnan gradient.

and thus in agreement with the theory outlined above. These deviations are mainly due to the de-swelling of the exchangers which occurs in concentrated electrolyte solutions. This is particularly noticeable in the 1.7% and 4.0% divinylbenzene conventional materials which show appreciable de-swelling, even at $m = 0.1$ (Fig. 2).

Deviations from linearity of the ($\log \bar{m}$, $\log m$) plot at low external concentration have been predicted theoretically in two recent treatments of a non-uniform model for the exchanger. Tye³ discussed non-uniformity in terms of variation in electric potential, using as an approximation two levels of potential $\psi = \bar{\psi}$ and $\psi = 0$. His final expression was derived on the implicit assumption that the external concentration was always large in comparison with the lowest local counterion concentration (region of lowest potential) in the exchanger. This invalidates his subsequent extrapolation of the expression to $m \rightarrow 0$, which gave the result that \bar{m}/m would tend to a constant figure, leading to a decrease in the gradient of the ($\log \bar{m}$, $\log m$) plot. It is perhaps unfortunate that the experimental results at his disposal were limited in range and, at the lowest external concentrations, inaccurate; in consequence this prediction appeared more plausible than it now does. On the other hand Glueckauf⁷

concluded that, as $m \rightarrow 0$, the volume fraction in which $M < m$ will decrease rapidly and the gradient of the $(\log \bar{m}, \log m)$ plot will thus tend to increase until it is approximately equal to the theoretical value of 2. Working with radiotracers at very low external concentration he was able to demonstrate the beginnings of such an effect. The essential difference in the Glueckauf approach is that even in the largest pores, the electrical potential never becomes zero, and there is a lower limit A to the distribution $\phi(M)$ of counterion concentrations. This is illustrated diagrammatically in Fig. 3.

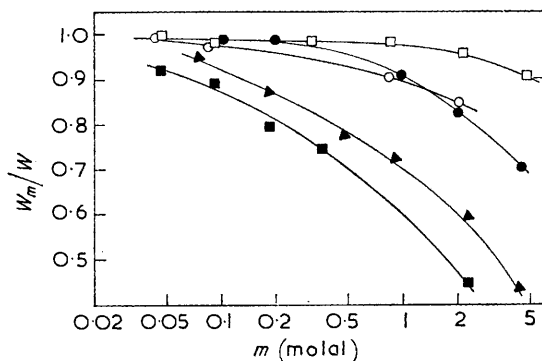


FIG. 2. Fractional decrease in water regain with increasing external electrolyte concentration. (Symbols as for Fig. 1.)

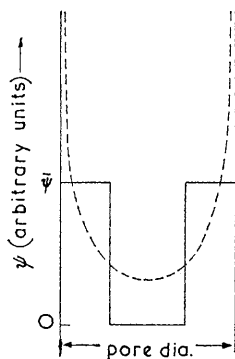


FIG. 3. Models for variation of electrostatic potential across a pore.

———— Tye, - - - - - Glueckauf.

No tendency for \bar{m}/m to level off at a constant value is apparent in Fig. 1 even for the most macroporous of the solvent-modified materials. Although forms of distribution $\phi(M)$ which could give rise to a small decrease in gradient at concentrations around 10^{-2} molal are conceivable, we believe that any such effects so far reported on conventional materials have been due to errors (i) (a) and (b). In the present work it is possible that these errors have masked the beginnings of an increase in gradient at the lowest m values for the solvent-modified materials, but unlikely since little or no effect would be expected above 10^{-3} molal.

By using the values of z deduced from the gradients in Fig. 1, approximate values of B and k_0 (see Table 2) have been calculated by equations (6) and (7), respectively.

TABLE 2.

% DVB	Zeo-Karb 225			Solvent-modified resins ($F_M = 0.33$)					
	6.5	4.0	1.7	15	22	27	30	40	55
z	0.485	0.495	0.500	0.740	0.790	0.855	0.870	0.895	0.900
k_0	0.127	0.175	0.256	0.143	0.120	0.093	0.088	0.075	0.074
B	15.2	8.2	3.81	9.95	14.5	20.8	21.4	24.8	21.2

The significance of these structural parameters can be seen by considering the solvent-modified materials. These have already been shown¹³ to have heterogeneous structures,

becoming increasingly more non-uniform as the divinylbenzene content increases, until over about 27% divinylbenzene they are markedly macroporous. Similar conclusions were drawn from a study of the kinetics of exchange of H^+ with large organic ions in similar resins.¹⁴ In the extreme case, pores and channels with dimensions well over 1000 Å have been illustrated in electron micrographs of the unswollen hydrocarbon matrix, implying even larger pores in the sulphonated and water-swollen exchanger. On the other hand, as the divinylbenzene content is increased at a constant volume fraction of monomers, there is an increase in the cross-linking and entanglement of the tightest parts of the structure of the resins which is demonstrated by their ion-exchange equilibria.¹¹ The maximum local counterion concentrations, B , given in Table 2 reach a limit for the series of about 25 molal. Since there is little indication of a successive increase in B and the ion exchange capacities tend to decrease over the range 27% to 55% divinylbenzene, it appears likely that this limit is due to incomplete sulphonation in regions beyond a given degree of local cross-linking rather than to a common maximum degree of local cross-linking of the parent matrices.

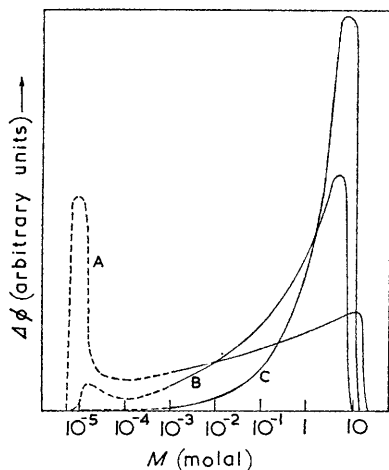


FIG. 4. Calculated volume fraction-counterion concentration distributions.

A, 55% DVB } solvent-modified resins
 B, 15% DVB }
 C, 6.5% DVB Zeo-Karb 225

In Fig. 4 are shown distributions of local counterion concentration in terms of $\Delta\phi$ [the increase in volume fraction ϕ for constant increments in $\log M$, calculated from equation (5)] for the 15% and 55% divinylbenzene solvent-modified resins and the 6.5% divinylbenzene Zeo-Karb 225. To facilitate comparison the histograms have been drawn as continuous curves, and a single arbitrary value of A has been taken. This value ($\sim 10^{-5}$ molal) in a system of cylindrical pores would be associated with a pore diameter of ~ 5000 Å, which corresponds roughly to the largest pores observed in electron micrographs of the 55% divinylbenzene resin. The true value of A differs for each distribution, and since experimental results have not been obtained below $\bar{m} \sim 10^{-3}$ the shapes of the distributions below this point are hypothetical and are shown as dotted curves. They are nevertheless reasonable, since values of $A > 10^{-3}$ are ruled out by the rectilinearity of the curves of Fig. 1, while those less than 10^{-6} (corresponding to pores $> 20,000$ Å in diameter) are unrealistic.

Fig. 4 illustrates well the effect on structure of solvent-modification already deduced from earlier studies.^{11,13,14} The solvent-modified resins, especially the 55% divinylbenzene material, are shown to have much of their internal solution volume contained in large pores. The conventional Zeo-Karb 225, on the other hand, appears comparatively uniform, and, despite its lower divinylbenzene content, more highly cross-linked. As effectively the top end of the distribution is stationary, it is not surprising that the variation in the uniformity of the distribution should parallel the results of these earlier studies, whose parameters were

¹⁴ J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, *J.*, 1963, 2779.

only characteristic of porosity. To illustrate the significance of this approach in terms of porosity, a single parameter for each exchanger, the porosity factor p , may be introduced where p is the fraction of the internal solution volume for which the local counterion concentration is less than a given value M_p . From the theory given above:

$$p = [\bar{M}(1-z)/M(2-z)]^{(1-z)} \quad (8)$$

Fig. 5 shows the values of p calculated from this expression for the modified materials, plotted as a function of divinylbenzene content for $M_p = 10^{-2}$ and 10^{-3} . Although the exact

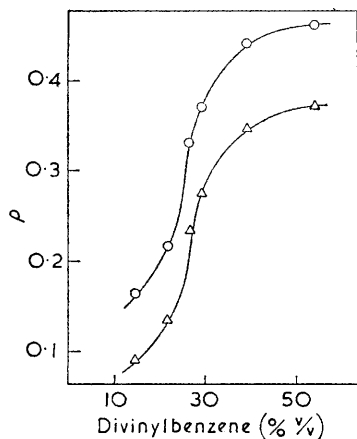


FIG. 5. Variation of porosity factor, p , with percentage divinylbenzene content for the solvent-modified exchangers.

$$\bigcirc, M_p = 10^{-3} \quad \triangle, M_p = 10^{-2}$$

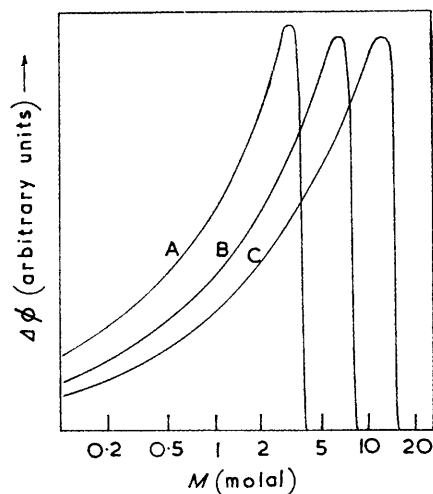


FIG. 6. Calculated volume fraction-counterion concentration distributions for conventional resins.

$$\left. \begin{array}{l} \text{A, 1.7\% DVB} \\ \text{B, 4.0\% DVB} \\ \text{C, 6.5\% DVB} \end{array} \right\} \text{Zeo-Karb 225}$$

shape varies slightly with the value of M_p used, both curves indicate a large relative increase in porosity over the range 25–30% divinylbenzene, in excellent agreement with other independent criteria of porosity previously reported.¹³ The two M_p values illustrated correspond (again on the cylindrical pore model) to pore diameters of ~ 170 and ~ 540 Å, respectively. Current usage¹⁵ would place the arbitrary division between “microporosity” and “macroporosity” at some figure intermediate between these two values, and using an appropriate value of M_p a relative scale of macroporosity has been established for a wide range of ion exchangers.¹⁶

¹⁵ M. M. Dubinin, *Quart. Rev.*, 1955, **9**, 101.

¹⁶ C. J. Attridge and J. R. Millar, unpublished results.

For the conventional materials, application of the Glueckauf theory leads to the approximate relative distributions shown in Fig. 6. Here, the B values increase with increasing divinylbenzene content more rapidly than in the solvent-modified resins and the effect generally is to shift the entire distribution to higher M values. In comparison with the solvent-modified materials the distributions are much more uniform but they still show appreciable fractions of pore space even in the 6.5% divinylbenzene materials where the electrical potential is quite low. The rapidly decreasing swelling and electrolyte invasion which occur as the divinylbenzene content is increased beyond about 10% preclude conclusive demonstration by the present experimental method of a further decrease in the z values, but there is a suggestion that these do not decrease to zero, *i.e.*, the cross-linked polystyrene sulphonate materials all show appreciable non-uniformity of structure. The comment by Gordon¹⁷ that differences of as little as 0.1 in counterion molality should be detectable in such resins by proton magnetic resonance methods referred to inter-particle heterogeneity; it has, however, erroneously been taken by Gustafson⁹ as evidence against the existence of a distribution of local counterion molalities in the resin phase. More recently, Dinius, Emerson, and Choppin¹⁸ have confirmed that the proton magnetic resonance spectra of conventional sulphonated cross-linked polystyrene resins are consistent with the Glueckauf model, and that differences in local counterion molality in the resin phase would not be detectable by current techniques.

The nearest approach to a uniform ion-exchange matrix for which the Glueckauf treatment predicts a zero value of z are the sodium zeolites. So far the only information available^{19, 20} covers a very small range indeed of external solution molarity, but over this range the slope agrees quite closely with the theoretical. Any deviation in this system would indicate an appreciable contribution from effects other than physical heterogeneity of the ion-exchanger matrix. In view of the good agreement of the structures deduced by the Glueckauf theory and those already established for the solvent-modified exchangers we conclude that his approach is generally valid for ion exchangers of the cross-linked polystyrene sulphonate type. While for such highly porous structures as the 27% to 55% divinylbenzene series a two-region model of the type suggested by Tye or Gustafson might well be a reasonable approximation, for conventional exchangers a continuous distribution of local counterion concentrations appears to be the most probable physical explanation of the observed deviations from the predictions of the ideal Donnan law.

We acknowledge helpful and constructive criticism of the manuscript by Dr. E. Glueckauf and also thank Dr. R. E. Kressman and Dr. J. A. Kitchener for their interest in, and advice on, its preparation.

RESEARCH LABORATORY, THE PERMUTIT CO. LTD.,
PONTYCLUN, GLAMORGAN.

[Received, August 7th, 1964.]

¹⁷ J. E. Gordon, *J. Phys. Chem.*, 1962, **66**, 1150.

¹⁸ R. H. Dinius, M. T. Emerson, and G. R. Choppin, *J. Phys. Chem.*, 1963, **67**, 1178.

¹⁹ R. M. Barrer and W. M. Meier, *J.*, 1958, 299.

²⁰ R. M. Barrer and A. J. Walker, *Trans. Faraday Soc.*, 1964, **60**, 171.