MEMBRANE SEPARATIONS IN THE LIQUID PHASE

KARL KAMMERMEYER and D. H. HAGERBAUMER
State University of Iowa, Iowa City, Iowa

Solutions can be separated in the liquid phase by means of membranes with processes utilizing osmosis, ion exchange resins incorporated in the membranes, electric potentials across membranes, and ultrafiltration. The published literature in this field is extensive. A rather comprehensive treatise on the subject of ultrafiltration was presented by Erschler(*5*), and some very interesting findings on solute retention were reported by McBain and Stuewer(*11*). The subject matter of ion exchange has been ably summarized in a recent publication by Juda, Marinsky, and Rosenberg(*9*) with an extensive bibliography. Separation of ionic from nonionic components by means of ion exclusion has been reported by Wheaton and Bauman (*14*), who also published a treatise covering nonionic separation with ion exchange resins(*15*). A recent discussion on electrochemical properties of synthetic ion exchange membranes was presented by Winger, Bodamer and Kunin(*16*). All the studies that have been reported are concerned with aqueous solutions, and in a few instances it has been stated that polar solvents other than water should be suitable.

There appears to be no published literature on the separation of homogeneous liquid mixtures of organic compounds solely by means of permeation through microporous membranes; therefore, it should be of considerable interest that experiments have been carried out which gave such separations by what might be called "fractional filtration" through a membrane having an average pore diameter of about 40×10^{-8} cm. In comparison, ultrafiltration is generally considered as taking place with pore sizes in the range of 10^{-4} cm.

The separations were accomplished with porous glass(*7, 12*), an intermediate glass state in the manufacture of Vycor-Brand glass. This material has been investigated as a medium for gas and vapor separations and was found to be an almost ideal molecular filter in such separations(*1, 6, 8*). It possesses a rather uniform pore diameter between 20 and 60 Å., with an average diameter of about 40 Å. (*4, 12*) and approximately 1.34×10^{12} pores/sq.cm.(*13*).

A publication by Nordberg(*12*) on properties of some Vycor-Brand glasses contains data on the flow of liquid water and acetone (liquid permeabilities) through porous glass. In combination with gas- and vapor-separation studies it was a logical extension of thought to conceive the possibility of separation in the liquid phase. Furthermore, work on the separation of azeotropic mixtures in the vapor phase(*6*) had shown that separation increased as the temperature of operation approached the boiling point of the mixture. Some support of the idea was also derived from publications by Manegold and Hofmann(*10*) where the contention is made that a filter which is suitable for ultrafiltration should act not only as a barrier on a go or no-go basis for molecules of different sizes, but should also exhibit partial inhibition to the movement of the larger molecules.

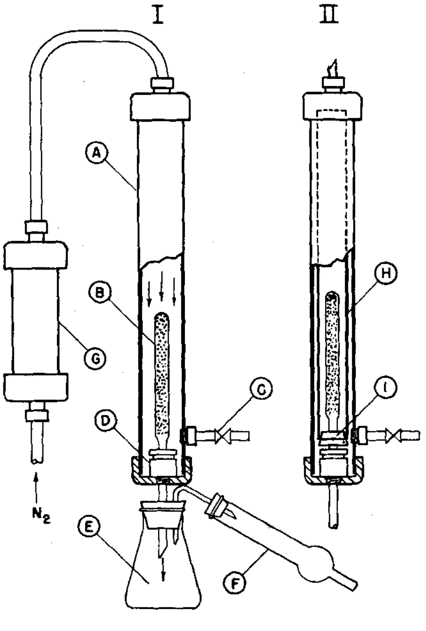

FIG. 1. SCHEMATIC DIAGRAM OF LIQUID-SEPARATION APPARATUS.

A, 1½- by 18-in.-long standard pipe; *B*, porous-glass membrane; *C*, ⅛-in. stainless steel needle valve; *D*, brass packing-gland assembly; *E*, 50-ml. collection flask; *F*, drying tube; *G*, 1½- by 10-in.-long standard pipe, silica-gel-filled gas-drying unit; *H*, 34-mm. I.D. by 16-in.-long inner glass tube; *I*, No. 7 rubber stopper.

For the sake of convenience, the studies in liquid separation were then carried out with some of the same azeotropic mixtures which had been used for the vapor-phase separation study(*6*). These mixtures corresponded to constant boiling compositions at atmospheric pressure and the respective boiling points. They therefore did not represent azeotropic compositions at the temperature of liquid permeation.

EQUIPMENT AND PROCEDURE

The membrane was a porous glass cell in the form of a test tube provided with a capillary connection at the open end. One such specimen, having a wall thickness of about 1 mm., was subjected to a pressure drop of 600 lb./sq.in. (high pressure on outside) without fracture.

As the work was actually a pioneering study to establish the possibility of liquid-phase separation, the apparatus (Figure 1) was built as simply as possible. Cells I and II differ in that a floating glass liner is used in Cell II, to accommodate corrosive liquids. The area of the membrane used for the liquid-liquid separation experiments was 90.40 sq. cm. and the thickness was 1.0 ± 0.05 mm.

D. H. Hagerbaumer is with The Chemstrand Corporation, Decatur, Alabama.

TABLE 1.—SEPARATION OF ORGANIC LIQUID MIXTURES BY MEANS OF A POROUS GLASS BARRIER

Separation data and rates of permeation
(1) Average, (2) standard deviation

N_2 pressure, lb./sq. in. gauge	Rate perm. g./(sq. cm.) (min.) $\times 10^5$	Weight % *A* Perm. product	Weight % *A* Feed	Component enriched Δconcentration increase in permeated product	System *A* – *B*	Number of runs
60	(1) 5.16	44.31	43.30	*A* 1.01	EtAc*–CCl_4	10
	(2) 0.35	0.32	.....	*A* 0.10		
125	10.62	45.36	43.64	*A* 1.72	EtAc*–CCl_4	10
	0.10	0.10	0.20	*A* 0.15		
200	16.15	45.06	42.95	*A* 2.11	EtAc*–CCl_4	10
	0.47	0.06	0.06	*A* 0.18		
60	1.606	63.16	69.0	*B* 5.84	C_6H_{12}–EtOH†	5
	0.05	0.30	.....	*B* 0.27		
125	4.00	62.24	69.0	*B* 6.76	C_6H_{12}–EtOH†	5
	0.21	0.14		*B* 0.13		
200	6.57	62.4	69.0	*B* 6.6	C_6H_{12}–EtOH†	5
	0.19	0.25	.....	*B* 0.26		
60	1.465	93.49	93.54	Essentially no change *A* (−0.05)	EtOH†H_2O	5
	0.003	0.10				
125	2.84	93.41	93.54	Essentially no change *A* (−0.13)	EtOH†H_2O	5
	0.003	0.25				
200	4.48	93.25	93.54	Essentially no change *A* (−0.29)	EtOH†H_2O	5
	0.19	0.28				
60	3.87	59.25	60.40	*B* 1.15	C_6H_6–MeOH‡	5
	0.24	0.05	0.05	*B* 0.06		
125	7.74	57.95	60.56	*B* 2.61	C_6H_6–MeOH‡	5
	0.20	0.03	0.18	*B* 0.15		
200	12.57	56.28	60.11	*B* 3.83	C_6H_6–MeOH‡	5
	0.22	0.47	0.10	*B* 0.16		
60	3.15	67.00	67.4	*B* 0.4	C_6H_6–EtOH†	5
	0.06	0.25	.....	*B* 0.18		
125	6.97	67.0	67.4	*B* 0.4	C_6H_6–EtOH†	5
	0.06	0.32	.....	*B* 0.10		
200	11.29	66.6	67.4	*B* 0.8	C_6H_6–EtOH†	5
	0.16	0.05	.....	*B* 0.05		

---

*EtAc – ethyl acetate.
†EtOH – ethyl alcohol.
‡MeOH – methyl alcohol.

Before the membrane was installed, it was "normalized" in an oven at 510°C. for 12 hr. to remove adsorbed organic vapors and water vapor. This procedure was rigorously followed before each new mixture and each pure component was studied. All separation runs were made at room temperature (25° to 30°C.), which is considerably removed from the 510°C. normalizing temperature. As porous glass is normally consolidated to Vycor at much higher temperatures, the pores were assumed not to be altered during the normalizing operation.

The upstream pressure on the liquid was produced by high-pressure nitrogen from a commercial cylinder. The nitrogen was oil-pumped and was quoted by the supplier as being 99% pure, but as an added precaution to exclude moisture, it was passed through the silica-gel-filled drying unit (*G*).

The cell was completely filled by introducing the liquid to be studied through the brass fitting at the top. After a liquid of known composition was introduced, all fittings were secured and nitrogen was admitted at the desired pressure. When fresh liquid was placed in the unit, the downstream side of the membrane was flushed with about 25 cc. of product before the first run was made.

To minimize vaporization losses from flask (*E*), the glass tube leading from the flask to the drying tube (*F*) was drawn to a fine capillary. Samples of known concentration were placed in flask (*E*) by use of another stopper with only the fine capillary tube opening available to the atmosphere. Various test samples showed no detectable change in concentration after standing 2 or 3 days. When a sufficient quantity (5 to 10 cc.) of liquid permeated the membrane, the collection flask (*E*) was removed and the sample analyzed. A sample was also withdrawn from the upstream side through the needle valve (*C*).

In experiments the feed was in intimate contact with the walls of the galvanized-iron pipe. To check the possibility of any metal effect, several liquid mixtures were kept in the closed unit for at least a week. Refractive-index measurements revealed that there were no detectable effects of the pipe on feed liquids.

MATERIALS

The mixtures studied and a summary of the enrichments obtained are shown in Table 1.

All liquid mixtures were analyzed with a Zeiss Pulfrich refractometer. Refractive-index data, the method used for purifying the pure components, and the procedure for preparing the azeotropes studied have been reported in reference *6*.

RESULTS AND DISCUSSION

It has been established that certain liquids can be separated by diffusion through porous membranes. Five different liquid systems have been studied at 60, 125, and 200 lb./sq.in. gauge upstream pressure and atmospheric downstream pressure in this preliminary investigation. Separation data and rates of permeation in grams per square centimeter per minute for the five mixtures studied are presented in Figures 2 through 6.

The separation data for ethyl acetate–carbon tetrachloride show that ethyl acetate permeated the porous glass membrane faster than did carbon tetrachloride and that greater separation was obtained the higher the upstream pressure. The difference in concentration between the feed samples and permeated samples varied from 1.01 wt. % ethyl acetate at 60 lb./sq.in. gauge upstream pressure to 2.11 wt. % ethyl acetate at 200 lb./sq.in. gauge upstream pressure. The analyses were estimated to be accurate within ±0.1 wt. %.

Although an extended study was made of the rates of permeation of the ethyl acetate–carbon tetrachloride system, it was not satisfactorily determined whether the mixture permeated the membrane faster or more slowly than did ethyl acetate or whether the rates of permeation curves actually did cross as shown in Figure 2. If the mixture is faster than either pure component, then it is possible that there is decided variation in the viscosity of the mixture at various pressures, or there may be some other change in physical properties which is unaccounted for. Blocking of the pores, difference in molecular size, association and adsorption characteristics are other possibilities which should be considered. At this stage of the investigation, one can only speculate as to the reason for the decided difference between the observed rates of permeation for the mixtures compared with the pure components because of the incomplete picture of the liquid state.

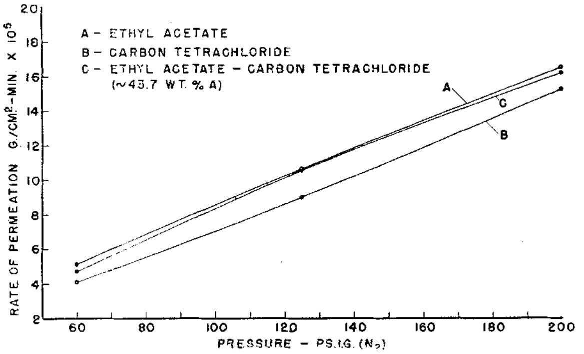

FIG. 2. ETHYL ACETATE–CARBON TETRACHLORIDE RATES OF PERMEATION THROUGH POROUS GLASS AT VARIOUS PRESSURES.

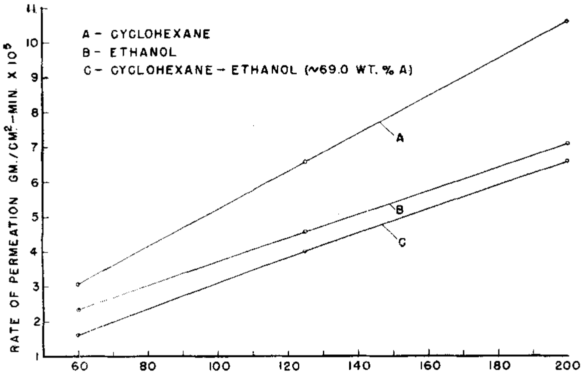

FIG. 3. CYCLOHEXANE-ETHANOL RATES OF PERMEATION THROUGH POROUS GLASS AT VARIOUS PRESSURES.

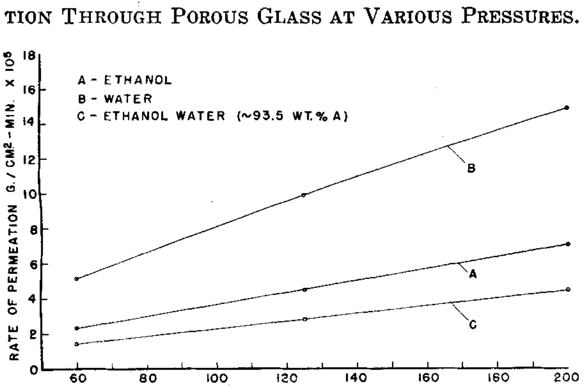

FIG. 4. ETHANOL-WATER RATES OF PERMEATION THROUGH POROUS GLASS AT VARIOUS PRESSURES.

The separation data for the cyclohexane-ethanol system show that ethanol permeates porous glass considerably faster than does cyclohexane. The effect of upstream pressure on separation is somewhat inconclusive when the data for individual runs are compared; however, in general it appears that better separation is obtained at the higher upstream pressures. About the same average degree of separation was obtained at 125 and 200 lb./sq.in. gauge upstream pressure. The analyses were estimated to be accurate within ±0.2 wt. %. The rates of permeation for the cyclohexane-ethanol system and the pure components are presented in Figure 3. It was interesting to observe that the mixture passed through the membrane more slowly than did either of the pure components, but still the degree of separation was quite large.

The separation results for the ethanol-water system presented were somewhat disappointing, for no separation was detected which was considered reliable. Of course, it may be significant that the feed was so rich in ethanol that some separation was obtained but escaped detection because of analysis limitations. Analysis of the ethanol-water system refractometrically was estimated to be within ±0.5 wt. %. Although no separation was reported for this system, it is believed that a more refined method of analysis may reveal separation even though it is quite concentrated in ethanol. The rates of permeation for ethanol-water and the pure components are shown in Figure 4. Comparison of Figures 3, 4, and 5 revealed that ethanol-water, cyclohexane-ethanol, and the benzene-methanol systems were analogous in that all the mixtures permeated the membrane at slower rates than did the pure components.

The separation results for the benzene-methanol system show that methanol permeates porous glass faster than does benzene. Furthermore, the degree of separation was noted to more than triple when the upstream pressure increased from 60 to 200 lb./sq.in. gauge. The accuracy of the analyses was established to be within ±0.2 wt. %. The rates of permeation for the benzene-methanol system and the pure components are presented in Figure 5. Unlike those for the other systems studied, the rates of permeation of the pure components

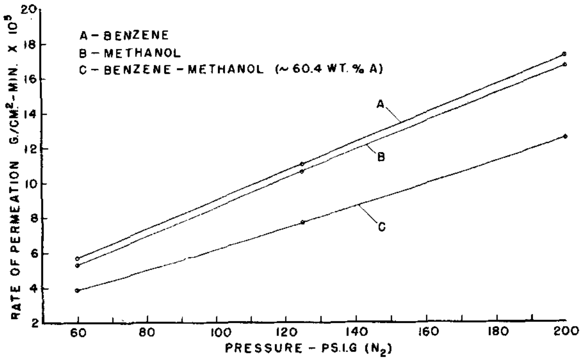

FIG. 5. BENZENE-METHANOL RATES OF PERMEATION THROUGH POROUS GLASS AT VARIOUS PRESSURES.

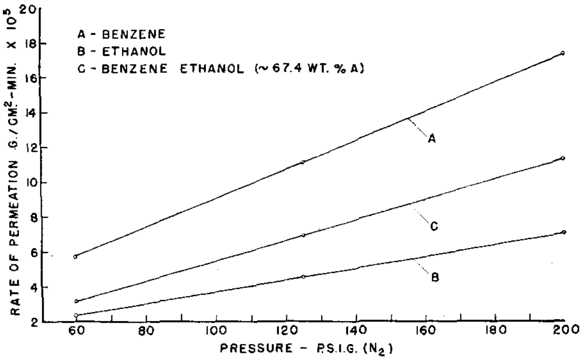

FIG. 6. BENZENE-ETHANOL RATES OF PERMEATION THROUGH POROUS GLASS AT VARIOUS PRESSURES.

were found to be very close to each other, and the curve for the mixture was relatively far removed from that for the pure components.

The separation results for the benzene-ethanol system indicate that ethanol permeates the membrane faster than benzene. It cannot be stated with any degree of confidence that increased upstream pressure results in an increase in the degree of separation for this system; however, when the data for 200 lb./sq.in. gauge upstream pressure are compared with the separation results at the lower upstream pressure, one might speculate that the degree of separation tends to be enhanced at higher upstream pressures. The analyses were estimated to be accurate within ±0.2 wt. %. The rates of permeation for the benezene-ethanol system were also unlike the other systems studied (except possibly the ethyl acetate–carbon tetrachloride system) because the curve for the rates of permeation of the mixture fell between the curves for the pure components. The decided contrast between the curves for the rates of permeation shown in Figure 5 and 6 for the benzene-methanol and benzene-ethanol systems, respectively, is rather perplexing. Benzene is common to both systems; however, the addition of a methylene group to the alcohol certainly appears to alter the permeation characteristics of the two systems. Then again, it should be recalled that methanol is the border compound between the alcohols and a seemingly unpredictable compound, water.

The rates-of-permeation curve for water (Figure 4) was the only curve which deviated from a linear form. Actually, it is believed that the rates of permeation for water may be found to fall on a straight line. Water was the only pure liquid which was found difficult to collect because it would not drain from the Vycor capillary tube on the membrane. Consequently, the validity of the water rates is somewhat questionable.

It is interesting to compare the direction of the liquid-liquid separation data with the azeotropic vapor separation data reported in reference *6* and to speculate on a possible explanation of the separation mechanism. Table 2 shows the direction of separation together with compilations of some physical properties which might be considered as having a bearing on the process.

The possibilities of interpretation of the results are numerous, particularly so as the data are so few in number. The only two properties which line up consistently with the direction of enrichment are molecular weight and dipole moment. It happens, however, that all the binary systems which were investigated in a quantitative manner contained a more polar component which also had the lower molecular weight. Thus this agreement may be entirely coincidental; nevertheless, it is possible that a more highly polar compound might more easily permeate a siliceous membrane, which certainly possesses some polarity itself, than would a compound of lower polarity. Although the less polar compound probably would not be retarded, it might not be able to pass the polar network of the membrane so easily as a highly polar compound. If the qualitative separation results for the system acetone–methyl alcohol are given some consideration, then the only property which corresponds to the direction of separation is the dipole moment. As a matter of fact, the latter system is one where the higher molecular weight compound also possesses the greater dipole moment.

It is well known that in liquid-solid interface systems there may be competition between the solvent and the solute molecules for the surface of the adsorbent, that the relative extent of adsorption may depend on a number of variables including polarity and hydrogen-bonding ability, and that solubility as well as many other physical properties of either the adsorbent or the adsorptive can have a major

TABLE 2.—SEPARATION IN LIQUID PHASE AND RELATED PROPERTIES

	Component enriched		Component having					
System	In liquid phase	In vapor phase	Lower mol. wt.	Higher dipole moment	Lower viscosity	Smaller collision diameter	Greater surface tension	Lower critical temp.
CCl_4 – EtAc	EtAc	EtAc	EtAc	EtAc	EtAc	CCl_4	CCl_4	EtAc
C_6H_{12} – EtOH	EtOH	C_6H_{12}	EtOH	EtOH	C_6H_{12}	EtOH	C_6H_{12}	EtOH
EtOH – H_2O	H_2O	EtOH	H_2O	H_2O	H_2O	H_2O	H_2O	EtOH
C_6H_6 – MeOH	MeOH	C_6H_6	MeOH	MeOH	MeOH	MeOH	C_6H_6	MeOH
C_6H_6 – EtOH	EtOH	C_6H_6	EtOH	EtOH	C_6H_6	EtOH	C_6H_6	EtOH
*Me_2CO–MeOH	Me_2CO	Me_2CO	MeOH	Me_2CO	Me_2CO	MeOH	Me_2CO	Me_2CO

*Qualitative separation results only.

effect(*2*). Considering the relative complexity of a permeation process, in which a liquid mixture passes over and in part through an active capillary system, such as a barrier, and where the components of the mixture may differ radically in their properties, it is not surprising that an explanation of the mechanism of the process is not readily available. A promising attack of the problem, not involving an adsorption mechanism, has been suggested by Drickamer(*3*). This is by way of the thermodynamic pressure effect, a phenomenon which so far has received little attention because a pressure gradient normally is dissipated into turbulence. In the small pores of the porous glass barrier, however, this may not be the case, and the pressure effect, through the pressure gradient, may be the cause of the observed separations.

It is not known whether the barrier adsorbed any components selectively, although this possibility does, of course, exist. However, about 25 cc. of permeated liquid was always collected before any runs were made. In addition, as much as 160 cc. was collected during a series of runs (CCl_4-EtAc) without any definite trend in concentration changes being shown for ten runs. In view of these facts it is believed that selective adsorption, if at all present, did not have any pronounced effect on the process.

Any strict evaluation of the experimental data must first of all take into account that the work was of a pioneering nature. The data are valid, but they should at this time be considered semiquantitative rather than strictly quantitative. The fact has been established that separation in the liquid phase by means of a microporous membrane is possible. In addition, the results give a very good indication of the magnitude of the attainable separation and of the approximate rates for the particular membrane and the range of pressures which were employed.

LIMITATIONS AND EXTENSIONS OF FINDINGS

It is readily apparent that the study was concerned mainly with the question of whether liquid mixtures could be separated by permeation through a microporous membrane. Consequently, the experimental apparatus and the procedure were as simple as possible, the installation of a continuous flow system not being warranted. Although the actual system was really a batch type, involving concentration changes in the residual liquid, the proportion of permeated product liquid to the bulk of the residual liquid was so small that the separation data are still valid. As a matter of fact, depletion in the residual liquid takes place in the faster permeating component therefore, the concentration changes are based on a higher concentration of the faster component than should actually have been present in the unpermeated liquid, and the reported results are for this reason on the conservative side.

Probably the most serious limitation of the present study was the fact that only one type of membrane was investigated. Undoubtedly other types of membranes will work. Of particular interest will be porous metal membranes, which should have a much less adsorptive character than a siliceous membrane. Likewise, combination-type membranes, which might contain hydrophilic or hydrophobic components, will be of great interest. Furthermore, the question of whether more bulky molecules can be separated by membranes having correspondingly larger pore sizes is of paramount importance.

All these problems are now being investigated. In addition, the use of higher pressures and elevated temperatures is contemplated. Some specific applications which are under consideration are the study of desalting of saline waters, waste-water purification, and separation of salt melts and of liquefied compound mixtures.

Only a very limited amount of work was done with separation of ionic compounds in aqueous solution, but it can be stated that sufficient evidence was obtained to permit the conclusion that the process may work with ionic mixtures.

CONCLUSIONS

It has been established that separations in the liquid phase can be accomplished by straightforward pressure permeation through microporous membranes. The reported results indicate what may be expected of such a process.

Industrial applications will largely depend on the rates of permeation which can ultimately be obtained. While the process suffers from the basic disadvantage of all membrane processes, that is, inherently low rates, it is entirely possible that the use of high pressures combined with membrane-development studies will result in favorable economic possibilities. A definite advantage is in the saving of thermal costs over processes which require vaporization. Future work has to some extent already been indicated. The most pressing need will be for studies of operating factors, investigation of available membranes, and improvement of promising membranes.

ACKNOWLEDGMENT

This study was sponsored by the United States Atomic Energy Commission and the support of the work is gratefully acknowledged, as is the generosity of the Corning Glass Works in supplying many of the porous glass membranes. The authors are greatly indebted to Dr. D. W. Brubaker of The Chemstrand Corporation, who participated in this work and whose suggestions contributed materially to the success of the study.

LITERATURE CITED

1. Brubaker, D. W., and Karl Kammermeyer, "*Proceedings of 1953 Conference on Nuclear Engineering*." Univ. Calif., Berkeley (Sept. 9-11, 1953).
2. Cassidy, H. G., in "Technique of Organic Chemistry," vol. 5, A. Weissberger, ed., Interscience Publishers, Inc., New York (1951).
3. Drickamer, H. G., Univ. Illinois, private communication.
4. Emmett, P. H., and M. Cines, *J. Phys. & Colloid Chem.*, **51**, 1248-62 (1947).
5. Erschler, B., *Kolloid-Z* **68**, 289-98 (1934).
6. Hagerbaumer, D. H., and Karl Kammermeyer, *Chem. Eng. Progr. Symposium Series No. 10*, **50**, 25-44 (1954).
7. Hood, H. P., and M. E. Nordberg, U. S. Patent 2,106,744 (1938).
8. Huckins, H. E., and Karl Kammermeyer, *Chem. Eng. Progr.*, **49**, 180-4, 294-8 (1953).
9. Juda, W., J. A. Marinsky, and N. W. Rosenberg, *Ann. Rev. Phys. Chem.*, 4, 373-98 (1953).
10. Manegold, E., and R. Hofmann, *Kolloid-Z.*, 51, 220-30, 308-15 (1930); 52, 19-24 (1930).
11. McBain, J. W., and R. F. Stuewer, *J. Phys. Chem.*, **40**, 1157-68 (1936).
12. Nordberg, M. E., *J. Am. Ceram. Soc.*, 27, 299-305 (1944).
13. Schwertz, F. A., *loc. cit.*, **32**, 390 (1949).
14. Wheaton, R. M., and W. C. Bauman, *Ann. N. Y. Acad. Sci.*, **57**, 159 (1953).
15. ———, *Ind.Eng. Chem.*, 45, 228-33 (1953).
16. Winger, A. G., G. W. Bodamer, and R. Kunin, *J. Electrochem. Soc.*, **100**, 178-84 (1953).